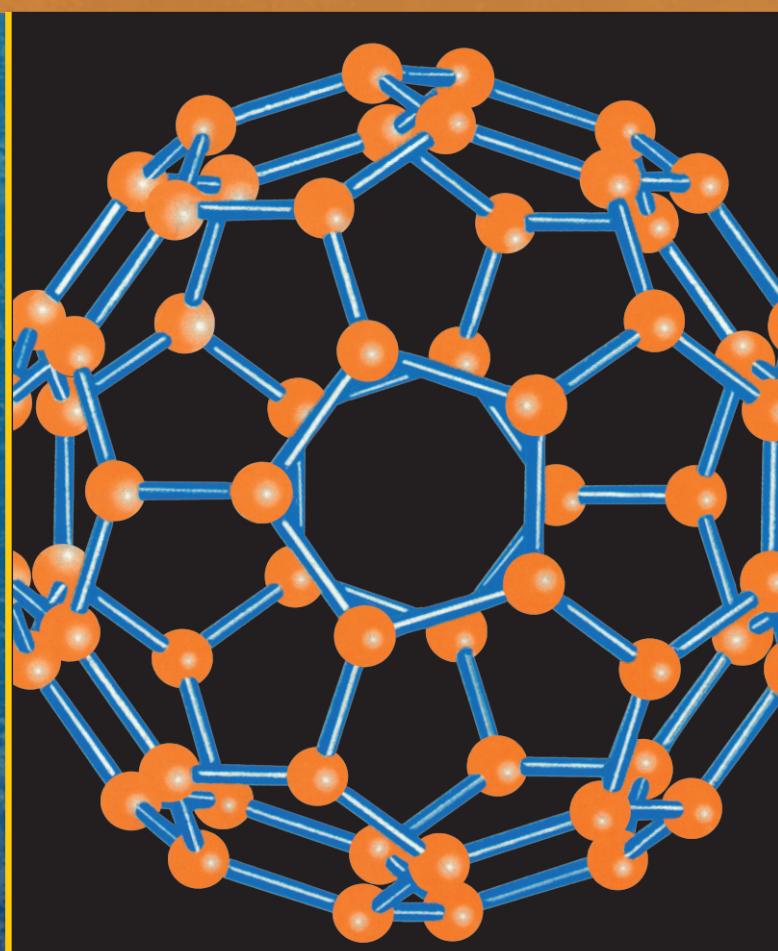


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J. D. LEE
CONCISE
INORGANIC
CHEMISTRY
FOR JEE (MAIN & ADVANCED)

FOURTH EDITION



SUDARSAN GUHA

J.D. Lee
Concise
Inorganic Chemistry
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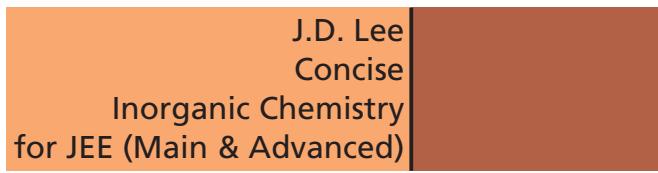


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Concise
Inorganic Chemistry
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Adapted by
Sudarsan Guha

WILEY



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Preface

Concise Inorganic Chemistry by J.D. Lee is a book widely used by students preparing for JEE as the most comprehensive and authentic text for understanding Inorganic Chemistry. The purpose of adaptation of this book is to provide a complete textbook of Inorganic Chemistry that covers the entire syllabus of JEE (Main and Advanced) in proper sequence of topics and provides in-depth explanation of topics. The use of book should give confidence to the students to apply their knowledge to problem-solving and attempting JEE.

In this new (fourth) edition, major changes have been made in the Chapter 8: Hydrogen, where the concept of hydrogen bonding is now explained with specific examples relevant to JEE. Chapter 9: The *s*-Block Elements has been made more concise with more focus on topics required from JEE perspective. Major changes have been made in Chapter 10: The *p*-Block Elements. It is now divided into six separate parts as Group 13, Group 14, Group 15, Group 16, Group 17 and Group 18 Elements. Each part is followed by a separate set of exercises for that particular group. Miscellaneous questions based on multiple concepts have been placed at the end of the chapter. Apart from this new questions have been included in the exercises at the end of most of the chapters.

I would like to acknowledge my students for their intellectual doubts and my colleagues for their valuable arguments in various aspects of the subject. This enhanced my understanding of the subject and helped me to teach better. I am especially indebted to my college Belur Ram Krishna Mission, Calcutta University for teaching me 'How to read and learn chemistry?' and Bansal classes where I have got the opportunity to apply my knowledge and teach chemistry. I am thankful to my promise to make this book as 'only one book for Inorganic Chemistry' engineering aspirants.

For the future also, any suggestions for the improvement of this book are welcome by the author.

Sudarsan Guha

M. Tech. (IIT-Kanpur)

Note to the Student

The Joint Entrance Examination (JEE) comprises the Main and Advanced examinations, which are essential stepping stones for all engineering aspirants. The JEE Main is focused primarily on evaluating the conceptual strength of the students. The JEE Advanced would further judge the ability of top performers in JEE Main to extend the conceptual strength to application-based problem solving. For complete preparation of these prestigious examinations, a book that is rich in conceptual strength and enriched with problem-solving tools and assessment would serve as a one-stop solution!

Concise Inorganic Chemistry by J.D. Lee has been the definitive text for learning Inorganic Chemistry since its first edition appeared about 45 years ago. The book captures the fundamentals of the subject in a simple and logical framework of factual knowledge. The description is long enough to cover the essentials, yet short enough to be interesting. Its unparalleled approach to teaching Inorganic Chemistry is the reason why it is probably the most favoured resource for an IIT aspirant like you today.

In collaboration with experts in JEE (Main & Advanced) coaching, the fifth edition of the original book has now been adapted to give you the best book available in Inorganic Chemistry for preparing for the toughest engineering entrance exam in India. This adaptation offers the dual advantage of unmatched explanation of concepts as developed by “Master teacher” and appropriate applications of the concepts to problem solving as developed by an expert in this area.

Let's walk through some of the special book features that will help you in your efforts to take the JEE (Main & Advanced) with confidence.

A. STRUCTURE OF THE BOOK

1. Structure of an Atom
2. Periodic Table and Periodic Properties
3. Chemical Bonding
4. Hydrolysis
5. Coordination Compounds
6. Metallurgy
7. Qualitative Salt Analysis
8. Hydrogen and its Hydrides
9. The *s*-Block Elements and their compounds
10. The *p*-Block Elements and their Compounds
11. The *d*-Block Elements and their Compounds
12. The *f*-Block Elements and their Compounds

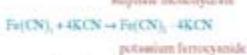
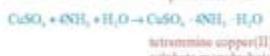
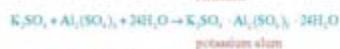
The original book has been reorganized in a manner to provide more structured approach as per the JEE (Main & Advanced) syllabus requirement. The progression is from basic concepts such as Structure of an Atom, Periodic Table and Periodic Properties and Chemical Bonding to practical aspects of Metallurgy and Qualitative Salt Analysis. This is followed by description on Hydrogen and its compounds and some compounds and properties of *s*-, *p*-, *d*- and *f*-block elements.

B. PEDAGOGY

Coordination Compounds

5.1 | DOUBLE SALTS AND COORDINATION COMPOUNDS

Addition compounds are formed when stoichiometric amounts of two or more stable compounds join together. For example:

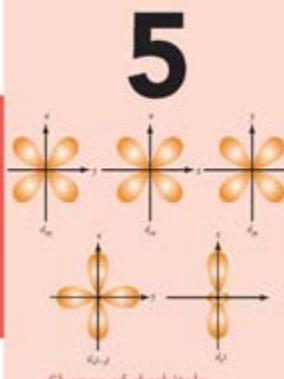


Addition compounds are of two types:

1. Those which lose their identity in solution (double salts)
2. Those which retain their identity in solution (complexes)

When crystals of carnallite are dissolved in water, the solution shows the properties of K^+ , Mg^{2+} and Cl^- ions. In a similar way, a solution of potassium alum shows the properties of K^+ , Al^{3+} and SO_4^{2-} ions. These are both examples of double salts which exist only in the crystalline state.

Where the other two examples of coordination compounds dissolve they do not form simple ions = Cu^{2+} , or Fe^{2+} and CN^- – but instead their complex ions remain intact. Thus the cuproammonium ion $[Cu(H_2O)_6(NH_3)_6]^{2+}$ and the



Shapes of d orbitals.

Contents

- 5.1 Double Salts and Coordination Compounds
- 5.2 Werner's Work
- 5.3 More Recent Methods of Studying Complexes
- 5.4 Classification of Ligands
- 5.5 Effective Atomic Numbers
- 5.6 Shapes of d Orbitals
- 5.7 Bonding in Transition Metal Complexes
- 5.8 Valence Bond Theory
- 5.9 Crystal Field Theory
- 5.10 Effect of Crystal Field Splitting
- 5.11 Tetragonal Distortion of Octahedral Complexes (Jahn-Teller Distortion)
- 5.12 Square Planar Arrangements
- 5.13 Tetrahedral Complexes
- 5.14 Magnetism
- 5.15 Extension of the Crystal Field Theory to Allow for Some Covacency
- 5.16 Nomenclature of Coordination Compounds
- 5.17 Isomerism

CHAPTER OPENER

Each chapter starts with an opening vignette related to the topic, and listing of contents of that chapter. This gives you an overview of the chapter and helps to identify the extent of coverage.

CONCEPT EXPLANATION

Concepts are explained in a manner easy to read and understand. They are descriptive to the extent required and provide reasons for the structure, properties and reactions of compounds. Many fascinating applications of inorganic compounds are also explained.

Ligands which cause only a small degree of crystal field splitting are termed weak field ligands. Ligands which cause a large splitting are called strong field ligands. Most Δ values are in the range 7000 cm^{-1} to $30,000\text{ cm}^{-1}$. The common ligands can be arranged in ascending order of crystal field splitting Δ . The order remains practically constant for different metals, and this series is called the spectrochemical series.

Spectrochemical series

weak field ligands

$I^- < Br^- < S^2- < Cl^- < NO_3^- < F^- < OH^- < EtOH < \text{oxalate} < H_2O < \text{EDTA} < (\text{NH}_3 \text{ and pyridine}) < \text{ethylenediamine} < \text{dipyridyl} < o\text{-phenanthroline} < \text{NO}_2^- < \text{CN}^- < \text{CO}$

strong field ligands

The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effects of σ and π -bonding. The halides are in the order expected from electrostatic effects. In other cases we must consider covalent bonding to explain the order. A pattern of increasing σ donation is followed:

$\text{halide donors} < \text{O donors} < \text{N donors} < \text{C donors}$

The crystal field splitting produced by the strong field CN^- ligand is about double that for weak field ligands like the halide ions. This is attributed to π bonding in which the metal donates electrons from a filled t_{2g}

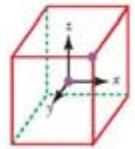
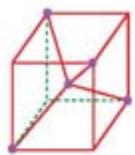
FIGURES

Figure 5.19 Relation of a tetrahedron to a cube.

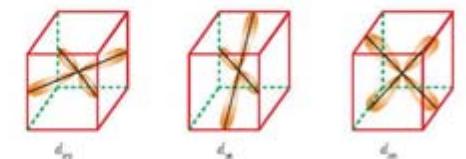
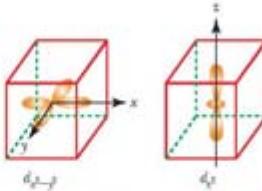


Figure 5.20 Orientation of d orbitals relative to a cube.

The text is sprinkled with multiple figures which present two-dimensional representations of compounds and their structures. This visual representation enhances understanding and helps the student visualize what a molecule may look like.

TABLES

A large number of tables capture data on structure, properties and other such parameters. The tabular representation supports comparative study of properties and draws out changing trends in them. The trends of various properties of elements along the periodic table are also amply illustrated.

Table 5.5 Effective atomic numbers of some metals in complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN
Cr	24	$[\text{Cr}(\text{CO})_6]$	0	12	36
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12	36
Fe	26	$[\text{Fe}(\text{CO})_6]$	0	10	36
Co	27	$[\text{Co}(\text{NH}_3)_6]^{2+}$	3	12	36
Ni	28	$[\text{Ni}(\text{CO})_6]$	0	8	36
Cu	29	$[\text{Cu}(\text{CN})_4]^{2-}$	1	8	36
Pd	46	$[\text{Pd}(\text{NH}_3)_4]^{2+}$	4	12	54 (Xe)
Pt	78	$[\text{Pt}(\text{Cl})_6]^{4-}$	4	12	86 (Rn)
Fe	26	$[\text{Fe}(\text{CN})_6]^{3-}$	3	12	35
Ni	28	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2	12	38
Pd	46	$[\text{Pd}(\text{Cl})_6]^{2-}$	2	8	52
Pt	78	$[\text{Pt}(\text{NH}_3)_6]^{2-}$	2	8	84
Ti	22	$[\text{Ti}(\sigma-\text{C}_5\text{H}_5)_2(\pi-\text{C}_5\text{H}_5)]^0$	4	16	34
Fe	26	$[\text{Fe}(\pi-\text{C}_5\text{H}_5)]^0$	2	12	36
Fe	26	$[\text{Fe}(\text{CO})_5(\text{NO})]^{2-}$	0	10	36
Co	27	$[\text{Co}(\text{CO})_6]^{3-}$	-1	8	36
V	23	$[\text{V}(\text{CO})_6]^{3-}$	-1	12	36

C. ASSESSMENT – AS PER JEE (MAIN & ADVANCED) PATTERN

Application of concepts to problem solving is the core of JEE (Main & Advanced), so it is important to test our understanding of concepts. For the test to be effective, the assessment technique should be comprehensive and in the context of this book, also in resonance with the JEE Main and JEE Advanced paper pattern. Each part of the assessment should be modeled on the actual paper pattern because unless the student practices the JEE way, he/she will not be sufficiently equipped to take the examination. Keeping this in mind, the assessment has been divided into:

SINGLE CORRECT CHOICE TYPE QUESTIONS

These are the regular multiple choice questions with four choices provided. Only one among the four choices will be the correct answer.

SINGLE CORRECT CHOICE TYPE QUESTIONS

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. Which of the following bidentate ligand(s) has similar donor atoms?
 (A) py (B) bn
 (C) en (D) gly^-

2. Consider the formation of the following metal carbonyl complex.
 $\text{Ni} + 4\text{CO} \rightarrow [\text{Ni}(\text{CO})_4]$
 surface (7)
 monocrystalline

Select the correct statement(s) about compound Y.
 (A) Compound Y has no counter ion.
 (B) Four monodentate uninegative ligands are connected with central metal ion.
 (C) This compound produces two ions in its aqueous

(D) None of these.

9. Which of the following types of isomerism is/are possible for the compound $[\text{Co}(\text{Cl})(\text{en})_2(\text{NH}_2 - \text{C}_6\text{H}_4 - \text{Me})\text{Cl}_2]$?
 (A) Geometrical isomerism
 (B) Linkage isomerism
 (C) Optical isomerism
 (D) Ligand isomerism

10. Which of the following pairs of compounds has the same EAN value but does not obey Sidgwick EAN rule?
 (A) $\text{Fe}(\text{CO})_5, \text{Ni}(\text{CO})_4$
 (B) $[\text{Fe}(\text{NH}_3)_6]^{2+}, [\text{Cr}(\text{C}_2\text{O}_4)_6]^{4-}$

These are multiple choice questions with four choices provided. One or more of the four choices provided may be correct.

COMPREHENSION TYPE QUESTIONS

Comprehension-type questions consist of a small passage, followed by three/four multiple choice questions based on it. The questions are of single correct answer type (with some exceptions).

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1–2

Isomers in coordination chemistry include many types. In structural isomers hydrate or solvent isomers, ionization isomers and coordination isomers have same overall formula but have different ligands attached to the central atom or ion.

The terms linkage isomerism or ambidentate isomerism are used for cases of bonding through different atoms of the same ligand.

1. Which of the following is not correctly matched against indicated isomerism?
 (A) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}][\text{Br}_3]$: Ionization isomerism
 (B) $[\text{Rh}(\text{PPh}_3)_3(\text{CO})(\text{NCS})_2]$: Linkage isomerism
 (C) $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$: Coordination isomerism
 (D) $[\text{Zn}(\text{gly})_4]$ tetrahedral : Geometrical isomerism

2. Ma_bb_c complex has two geometrical forms: facial and
 (A) $[\text{Fe}(\text{NH}_3)_4(\text{H}_2\text{O})_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$, tetrahedral.
 (C) $[\text{Ni}(\text{NH}_3)_4][\text{NO}_3] \cdot 2\text{H}_2\text{O}$; square planar.
 (D) $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2][\text{NO}_3]_2$; octahedral.

5. Which of the following statements are true for the second complex?
 (A) It has the EAN value of 36.
 (B) It can show optical isomerism.

2. *Ma,b*, complex has two geometrical forms: facial and

ASSERTION-REASONING TYPE QUESTIONS |

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
- (C) If Statement I is true but Statement II is false.
- (D) If Statement I is false but Statement II is true.

1. Statement I: Only *cis* $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ reacts with oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) to form $[\text{PtCl}_2(\text{ox})]^2-$ not the *trans*

2. Statement I: Under the strong field ligand only, the degeneracy of the *d*-orbital is lost.

Statement II: After splitting of the *d*-orbitals also, Hund's rule is not violated anywhere.

3. Statement I: NO is $3e^-$ -donor.

Statement II: The antibonding electron of NO is very much susceptible to donate a part from its lone pair.

4. Statement I: Dithiooxalate is bidentate ambidentate ligand.

Statement II: At a time either two S atoms or two O atoms act as donor atoms.

These questions check the analytical and reasoning skills of the students. Two statements are provided – Statement I and Statement II. The student is expected to verify if (A) both statements are true and if both are true, verify if statement I follows from statement II; (B) both statements are true and if both are true, verify if statement II is not the correct reasoning for statement I; (C), (D) which of the statements is untrue.

INTEGER ANSWER TYPE QUESTIONS |

The questions in this section are numerical problems for which no choices are provided. The students are required to find the exact answers to numerical problems which can be one-digit or two-digit numerals.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

- 1.** Find the number of diamagnetic complexes which show geometrical isomerism.
 $[\text{NiF}_6]^{4-}$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{CoF}_6(\text{H}_2\text{O})]$,
 $[\text{Fe}(\text{en})_3\text{Cl}_3]\text{Cl}$, $[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$
- 2.** Find the number of complexes in which stability constant value is greater than the stability constant value

6. The number of stereoisomers, optically active isomers and geometrical isomers for the complex $[\text{Co}(\text{en})(\text{pn})(\text{NO}_2)_2]^+$ is _____ + _____ and _____ respectively.

7. If CFSE increases by 30% and 40% respectively for Co^{2+} to Rh^{3+} and for Rh^{3+} to Ir^{4+} , then the total increase in CFSE for Ir^{4+} with respect to Co^{2+} is _____ %.

MATRIX-MATCH TYPE QUESTIONS |

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D),

while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

- 1.** Match the processes with their respective characteristics.

Column-I	Column-II
(A) $[\text{CoCl}_4]^{2-} \rightarrow [\text{Co}(\text{en})_3\text{Cl}_2]$	(P) Change in number of geometrical isomers
(B) $[\text{Fe}(\text{EDTA})]^{12-} \rightarrow [\text{Fe}(\text{en})]^{12-}$	(Q) Change in number of stereoisomers

Column I

Column II

(C) $[\text{M}(\text{AB})_2]^{2+}$	(R) The number of geometrical isomers is four.
(D) $[\text{Ma}_2\text{b}_2\text{cd}]^{2+}$	(S) The number of optically active isomers is four.

These questions are the regular “Match the Following” variety. Two columns each containing 4 subdivisions or first column with four subdivisions and second column with more subdivisions are given and the student should match elements of column I to that of column II. There can be one or more matches.

D. USE OF SI UNITS

SI units for energy are used throughout this edition, thus making a comparison of thermodynamic properties easier. Ionization energies are quoted in kJ mol^{-1} , rather than ionization potentials in eV. Older data from other sources use eV and may be converted into SI units (1 kcal = 4.184 kJ, and 1 eV = $23.06 \times 4.184 \text{ kJ mol}^{-1}$).

Meters are strictly the SI units for distance, and bond lengths are sometimes quoted in nanometers (1 mm = 10^{-9} m). However Ångström units Å (10^{-10} m) are a permitted unit of length, and are widely used by crystallographers because they give a convenient range of numbers for bond lengths. Most bonds are between 1 and 2 Å (0.1 to 0.2 nm). Ångström units are used throughout for bond lengths.

The positions of absorption peaks in spectra are quoted in wave numbers cm^{-1} , because instruments are calibrated in these units. It must be remembered that these are not SI units, and should be multiplied by 100 to give SI units of m^{-1} , or multiplied by 11.96 to give J mol^{-1} .

The SI units of density are kg m^{-3} , making the density of water 1000 kg m^{-3} . This convention is not widely accepted, so the older units of g cm^{-3} are retained so water has a density of 1 g cm^{-3} .

In the section on magnetism both SI units and Debye units are given, and the relation between the two is explained. For inorganic chemists who simply want to find the number of unpaired electron spins in a transition metal ion, Debye units are much more convenient.

E. NOMENCLATURE FOLLOWED IN THE PERIODIC TABLE

For a long time chemists have arranged the elements in groups within the periodic table in order to relate the electronic structures of the elements to their properties, and to simplify learning. There have been several methods of naming the groups.

A number of well known books name the main groups and the transition elements as A and B subgroups, which dates back to the older Mendeleev periodic table of more than half a century ago. Its disadvantages are that it may over emphasize slight similarities between the A and B subgroups, and there are a large number of elements in Group VIII.

In earlier versions of this book the *s*-block and the *p*-block were numbered as Groups I to VII and 0, depending on the number of electrons in the outer shell of the atoms, and the transition elements were dealt with as triads of elements and named as the top element in each group of three.

The IUPAC has recommended that the main groups and the transition metals should be numbered from 1 to 18. This system has gained acceptance, and has now been adopted throughout this book.

I	II									III	IV	V	VI	VII	0
IA	IIA	IIIB	IVB	VB	VIB	VIIIB	<...VIIIB...>	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H															
Li	Be									B	C	N	O	F	He
Na	Mg									Al	Si	P	S	Cl	Ne
K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni	Cu	Zn	Ga	Ge	As	Se	Br	Ar
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru Rh Pd	Ag	Cd	In	Sn	Sb	Te	I	Kr
Cs	Ba	La	Hf	Ta	W	Re	Os Ir Pt	Au	Hg	Tl	Pb	Bi	Po	At	Xe
1	2	3	4	5	6	7	8 9 10	11	12	13	14	15	16	17	18

F. APPENDICES

Appendix A	Abundance of the elements in the Earth's crust
Appendix B	Melting points of the elements
Appendix C	Boiling points of the elements
Appendix D	Densities of solid and liquid elements
Appendix E	Electronic structures of the elements
Appendix F	Some average single bond energies and some double and triple bond energies
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Appendix H	Atomic weights based on $^{12}\text{C} = 12.000$
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Structure of an Atom

1.1 | ATOMS

An atom is the smallest entity of an element which retains all of its properties. It consists of several stable and unstable fundamental particles. The examples of stable particles are neutron, proton and electron and those of unstable particles are meson, positron, neutrino, antineutrino and antiproton. The fundamental stable particles are of interest to us here. The characteristics of the stable fundamental particles that make up the atom are listed in Table 1.1.

All atoms consist of a central nucleus surrounded by one or more electrons in orbitals. The nucleus always contains protons and all nuclei heavier than hydrogen contain neutrons too (Figure 1.1).

The protons and neutrons together make up most of the mass of an atom. Both protons and neutrons are particles of unit mass, but a proton has one positive charge and a neutron is electrically neutral (i.e. carries no charge).

An atom is represented as ${}_Z^A X$, where A is the mass number (i.e. $n + p$) and Z is the atomic number (i.e. p or e).

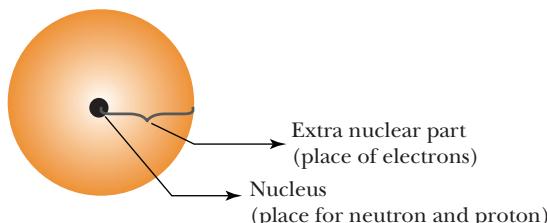
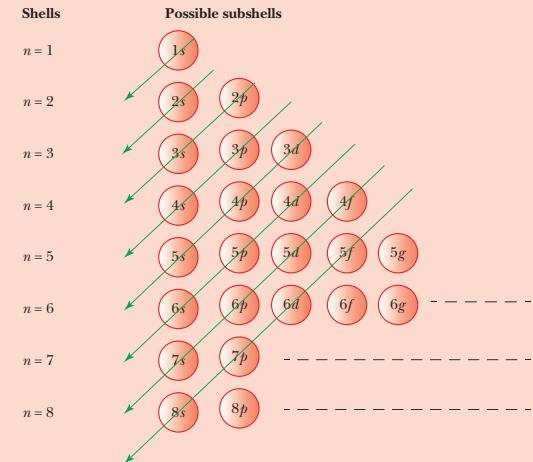


Figure 1.1 Structure of an atom.



Sequence of filling of energy levels.

Contents

- 1.1** Atoms
- 1.2** Some Important Definitions
- 1.3** Electronic Configuration of an Atom

Table 1.1 Characteristics of fundamental particles of an atom

Name of particle	Discovery	Mass	Nature of charge	Amount of charge	Radius	Presence in the atom
Electron (e) ($_{-1}e^0$)	J.J. Thomson, 1897	0.000548 amu or 9.12×10^{-28} g or 9.12×10^{-31} kg (1/1837 th of H atom)	Negatively charged	-1.602×10^{-19} C or -4.8×10^{-10} esu	—	Outside the nucleus of an atom
Proton (p) ($_{1}H^1$)	E. Rutherford, 1911	1.0076 amu or 1.6725×10^{-24} g or 1.6725×10^{-27} kg	Positively charged	$+1.602 \times 10^{-19}$ C or $+4.8 \times 10^{-10}$ esu	1.2×10^{-12} cm	Inside the nucleus of an atom
Neutron (n) ($_{0}n^1$)	J. Chadwick, 1932	1.0089 amu or 1.675×10^{-24} g or 1.675×10^{-24} kg	Neutral	0	1.2×10^{-12} cm	Inside the nucleus of an atom

1.2 | SOME IMPORTANT DEFINITIONS

Some important definitions related to atomic structure of atoms are described as follows:

1. Isotopes: Elements having the same atomic number but different mass number are known as isotopes. For example,

- a. $_{1}H^1$, $_{1}D^2$ and $_{1}T^3$
- b. $_{8}O^{16}$, $_{8}O^{18}$
- c. $_{6}C^{12}$, $_{6}C^{14}$
- d. $_{17}Cl^{35}$, $_{17}Cl^{37}$

2. Isobars: Elements having the same mass number but different atomic number are known as isobars. For example,

- a. $_{18}Ar^{40}$ and $_{20}Ca^{40}$
- b. $_{6}C^{14}$ and $_{7}N^{14}$

3. Isotones: Elements having the same number of neutrons are known as isotones. For example,

- a. $_{12}Mg^{24}$ and $_{11}Na^{23}$
- b. $_{9}F^{19}$ and $_{8}O^{18}$
- c. $_{6}C^{14}$ and $_{8}O^{16}$
- d. $_{15}P^{31}$ and $_{16}S^{32}$

4. Isodiaphers: Elements having the same value of isotopic excess are known as isodiaphers, where isotopic excess = $(A - 2Z)$. For example,

- a. $_{15}P^{31}$, $_{17}Cl^{35}$, $_{11}Na^{23}$, $_{3}Li^7$, $_{13}Al^{27}$, $_{19}K^{39}$, $_{9}F^{19}$, all have isotopic excess of $(A - 2Z) = 1$.
- b. $_{6}C^{14}$, $_{8}O^{18}$, $_{1}T^3$, $_{24}Cr^{50}$, all have isotopic excess of $(A - 2Z) = 2$.

- c. $^{17}\text{Cl}^{37}$ and $^{21}\text{Sc}^{45}$, both have isotopic excess of $(A - 2Z) = 3$.
 d. $^{24}\text{Cr}^{52}$ and $^{26}\text{Fe}^{56}$, both have isotopic excess of $(A - 2Z) = 4$.

5. Isoelectronic species: The species having the same number of electrons are known as isoelectronic species. (It may be an atom, ion or a molecule.) For example,

- a. C^{4-} , N^{3-} , O^{2-} , F^- , Ne , Na^+ , Mg^{2+} , Al^{3+}
 b. Si^{4-} , P^{3-} , S^{2-} , Cl^- , Ar , K^+ , Ca^{2+} , Sc^{3+}
 c. H_2S , HCl , Ar , SH^-
 d. NH_2^- , NH_3 , CH_4 , H_2O , OH^- , NH_4^+ , OH^- , NH^{2-}
 e. $[\text{Ni}(\text{CO})_4]$, $[\text{Co}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Fe}(\text{CO})_2(\text{NO})_2]$
 f. CO_3^{2-} , NO_3^- , BO_3^{3-}
 g. SiO_4^{4-} , PO_4^{3-} , SO_4^{2-} , ClO_4^-

Now-a-days the definition of isoelectronic species is also observed to extend to include the species having the same number of valence shell electrons (described later in the section on Classification of elements as *s*, *p*, *d* and *f*-block elements). For example, the following species can also be considered isoelectronic because they have the same number of valence shell electrons:

- a. ClO_4^- , BrO_4^- , IO_4^-
 b. PO_4^{3-} , AsO_4^{3-} , SbO_4^{3-}
 c. SO_4^{2-} , SeO_4^{2-} , TeO_4^{2-}
 d. NOCl , NO_2^- , NOBr
 e. NO_2Cl , NO_2Br , NO_3^-

6. Isosters: Species that are isoelectronic as well as consist of the same number of atoms are known as isosters. For example,

- a. CH_4 , NH_4^+
 b. CO_3^{2-} , NO_3^- , BO_3^{3-}
 c. NH_2^- , H_2O
 d. SiO_4^{4-} , PO_4^{3-} , SO_4^{2-} , ClO_4^-

1.3 | ELECTRONIC CONFIGURATION OF AN ATOM

To define the position of an electron in an atom, the following terms need to be defined:

- 1. Orbital:** It is defined as the space occupied by the electrons around the nucleus of an atom where the probability of finding an electron is the maximum.
- 2. Quantum numbers:** These are the parameters required to characterize an orbital or an electron. There are four different quantum numbers which are named as follows:
 - Principal quantum number (denoted by n)
 - Azimuthal quantum number (denoted by l)
 - Magnetic quantum number (denoted by m or m_l)
 - Spin quantum number (denoted by s or m_s).

An orbital can be described by the first three quantum numbers, that is, n , l and m , while the description of an electron requires all four quantum numbers, that is, n , l , m and s .

Quantum numbers

The characteristic features of the four quantum numbers are described as follows:

1. Principal quantum number (n): This quantum number indicates the distance of an electron from the nucleus. It can have values of 1, 2, 3, 4 ... up to ∞ . As the value of n increases, the distance of the electron/orbital from the nucleus increases as well as the energy of the electron increases.

Principal quantum numbers having different values of n are also considered as different energy shells which are represented as follows:

n	1	2	3	4	5	6	7	$\dots\infty$
Energy shells	K	L	M	N	O	P	Q	

2. Azimuthal quantum number (l): This quantum number indicates the shape of an orbital (not of electron) and can have values from 0 to $(n-1)$ for a particular value of n . For example, for $n = 5$, the values of l are 0, 1, 2, 3, 4.

Each value of l indicates the sub-energy level or subshell within the particular shell or energy level, which are denoted as follows:

l	0	1	2	3	4
Subshell or sub-energy level	s	p	d	f	g

Note: The notations for the sub-energy levels come from the spectroscopic terms that were used to describe the atomic spectra and have the following full form:

$s \rightarrow$ sharp	$f \rightarrow$ fundamental
$p \rightarrow$ principal	$g \rightarrow$ generalized
$d \rightarrow$ diffused	

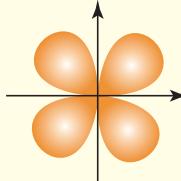
These subshells have different shapes which are depicted in Table 1.2.

Table 1.2 The shapes of subshells

Subshell	Shape	Description
s -orbital		Spherically symmetrical
p -orbital		Dumbbell shaped

(Continued)

Table 1.2 (Continued)

Subshell	Shape	Description
d -orbital		Double dumbbell shaped

Note:

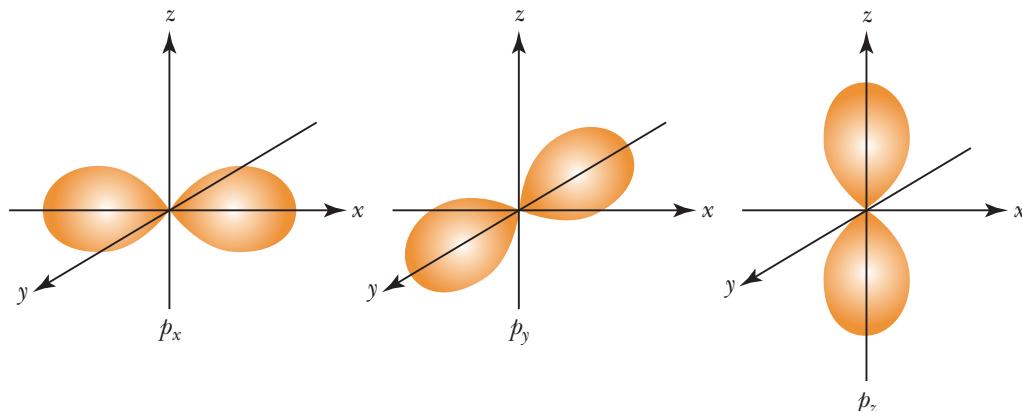
- (i) f and g subshells are of complicated shape and beyond the scope of syllabus.
- (ii) These shapes of subshells are not experimentally observed as these are the 3D – plots of solution of Schrödinger wave equation which is not part of the syllabus for JEE.

3. Magnetic quantum number (m or m_l): This quantum number indicates the possible orientations of an orbital in space. The value of m for a particular value of l varies from $+l$ to $-l$ including zero. For example,

Value of l (for $n = 4$)	Possible values of m	Total possible values
0	0	1
1	+1, 0, -1	3
2	-2, -1, 0, +1, +2	5
3	-3, -2, -1, 0, +1, +2, +3	7

The different values of m for a particular value of l gives the possible orientations of the corresponding orbital in space. Each possible orientation is considered as a particular orbital.

- a. s -subshell consists of one orbital that is known as s -orbital.
- b. p -subshell consists of three orbitals that are known as p_x , p_y and p_z orbitals which are lying along the respective axis (Figure 1.2).

**Figure 1.2** Orientation of three p -orbitals.

- c. d -subshell consists of five orbitals that are known as d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} which are shown in Figure 1.3.

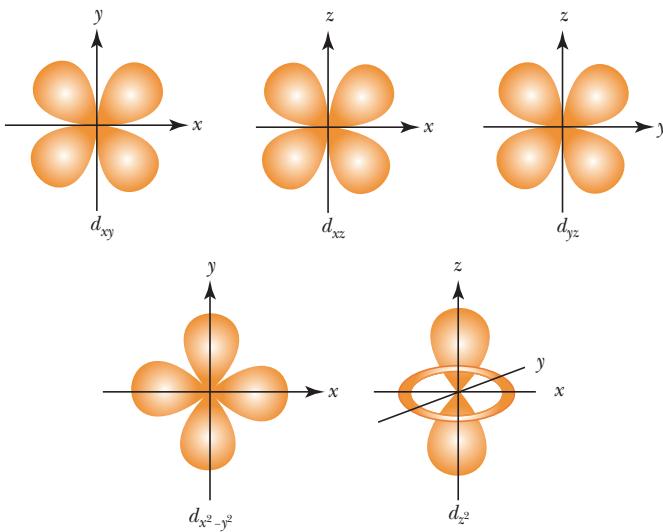


Figure 1.3 Orientation of five d -orbitals.

Note:

- (i) d_{xy} , d_{yz} , d_{xz} orbitals are known as non-axial d -orbitals because the lobes of the orbitals are not available along the axis.
- (ii) $d_{x^2-y^2}$ and d_{z^2} are known as axial d -orbitals because the lobes of orbitals are along the axis.

4. **Spin Quantum Number (s or m_s):** It is the quantum number which is required to describe an electron only (not the orbital) and it characterizes the spin of an electron. An electron is not only moving around the nucleus but also spinning about its own axis. It may spin either clockwise or anticlockwise.

- a. The possible values of spin quantum number are $+1/2$ and $-1/2$, but it is not fixed, that is, if the value of s is $+1/2$ for clockwise spinning, then the value of s is $-1/2$ for anticlockwise and vice-versa. Also, the electrons present in parallel spin must have the same spin value, for example, or

$$\text{or } s = -1/2 \quad -1/2 \quad -1/2$$

$$\text{or } s = +1/2 \quad +1/2 \quad +1/2$$



Aufbau principle

The electrons are filled up in the empty orbitals of an atom from the lowest energy orbital to the higher energy orbital. The energy sequence of empty orbitals is given in Figure 1.4, in which the energy of the subshells increases along the directions of arrow.

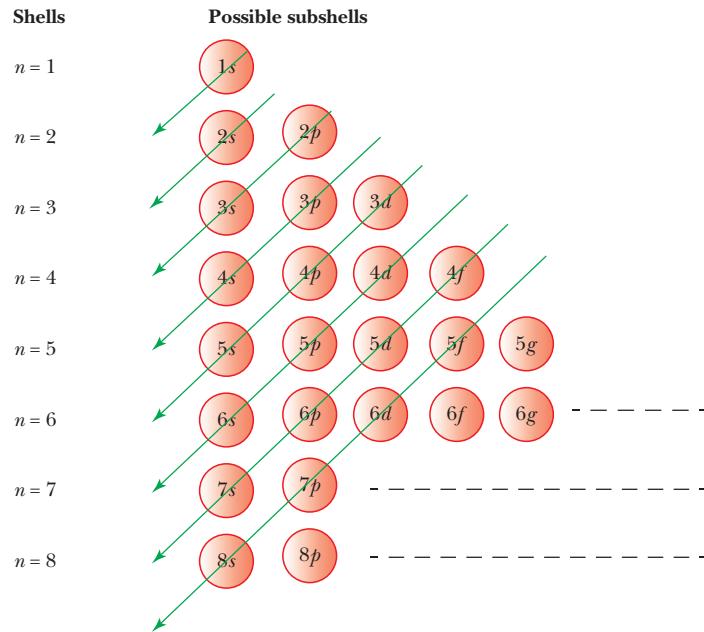


Figure 1.4 Sequence of filling of energy levels.

Alternatively, the above energy sequence or the energy comparison between any two subshells can be established very easily on the basis of $(n + l)$ rule which is stated as follows:

1. Smaller the value of $(n + l)$ for a particular subshell smaller will be its energy.
2. If for two subshell, the $(n + l)$ value is the same then the subshell having higher value of n will have higher energy. For example,

$$\text{for } 3d \Rightarrow n+l = 3+2 = 5 \quad \text{and for } 4p \Rightarrow n+l = 4+1 = 5 \quad \text{same}$$

Between the two, $4p$ has higher energy as compared to that of $3d$.

Let us compare the energy of the following subshells according to $(n + l)$ rule:

$5p, 4s, 4d, 3d, 4f, 6s$

Based on the $(n + l)$ rule, we have

Subshell	$(n + l)$
$5p$	$5 + 1 = 6$
$4s$	$4 + 0 = 4$
$4d$	$4 + 2 = 6$
$3d$	$3 + 2 = 5$
$4f$	$4 + 3 = 7$
$6s$	$6 + 0 = 6$

Hence the energy order will be: $4f > 6s > 5p > 4d > 3d$

Pauli exclusion principle

We have seen that three quantum numbers n , l and m are needed to define an orbital. Each orbital may hold up to two electrons, provided they have opposite spins. Thus, an extra quantum number is required to define the spin of an electron in an orbital. Thus four quantum numbers are needed to define the energy of an electron in an atom.

The Pauli's exclusion principle states that *no two electrons in one atom can have the same values of all four quantum numbers or an orbital in a subshell can accommodate a maximum of two electrons of opposite spin.*

Based on the above rule, the number of electrons which can be accommodated in each main energy level can be calculated by permuting the quantum numbers, as shown in Table 1.3.

Table 1.3 Maximum number of electrons in a shell

Shell number n (Principal quantum number)	Possible values of l (designated subshell)	Possible values of m (Magnetic quantum number)	Possible number of orbitals in a subshell	Possible number of orbitals in a shell	Maximum number of electrons present in a shell
1	0($1s$)	0	1	1	2
2	0($2s$)	0	1	4	8
	1($2p$)	+1 0 -1	3		
3	0($3s$)	0	1	9	18
	1($3p$)	+1 0 -1	3		
	2($3d$)	+2 +1 0 -1 -2	5		
4	0($4s$)	0	1	16	32
	1($4p$)	+1 0 -1	3		
	2($4d$)	+2 +1 0 -1 -2	5		

(Continued)

Table 1.3 (Continued)

Shell number <i>n</i> (Principal quantum number)	Possible values of <i>l</i> (designated subshell)	Possible values of <i>m</i> (Magnetic quantum number)	Possible number of orbitals in a subshell	Possible number of orbitals in a shell	Maximum number of electrons present in a shell
	3(4 <i>f</i>)	+3 +2 +1 0 -1 -2 -3	7		

So on...

Note:

- (i) The number of orbitals present in a subshell is $(2l + 1)$.
- (ii) The total number of electrons present in a subshell is $2(2l + 1)$.
- (iii) Total number of orbitals present in a shell is n^2 .
- (iv) Total number of electron present in a shell is $2n^2$.

Based on the above rules, let us find the number of subshell, orbitals and maximum number of electrons that can be accommodated in *R* shell.

Shell	K	L	M	N	O	P	Q	R
<i>n</i> =	1	2	3	4	5	6	7	8

Hence, for R shell, *n* = 8.

The number of subshell = 8 (i.e. 0, 1, 2, 3, 4, 5, 6, 7).

The number of orbitals in this shell = $8^2 = 64$.

The maximum number of electrons that can be accommodated in this shell = $2n^2 = 2 \times 64 = 128$.

Hund's rule

According to this rule, the degenerate orbitals (i.e. orbitals having same energy) will be filled by one electron each having same spin and then only pairing of electrons will take place. Alternatively, the filling up of electron in the degenerate orbitals will take place in such a way that the multiplicity (*M*) value will be maximum where *M* is defined as follows:

$$M = 2|S| + 1$$

where *S* = total spin value of all electrons in degenerate orbitals.

For example, consider the nitrogen atom; the electronic distribution is shown as follows:

${}^7\text{N} :$	$1s^2$	$2s^2$	$2p^3$	$M = 2 S + 1$
				(correct)
				(wrong)
				(correct)
				(wrong)

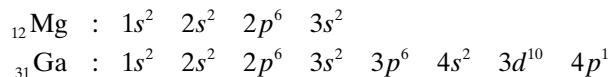
$S = 1/2 + 1/2 + 1/2 = 3/2 \quad M = 4$

$S = +1/2 - 1/2 - 1/2 = -1/2 \quad M = 2$

$S = -1/2 - 1/2 - 1/2 = -3/2 \quad M = 4$

$S = +1/2 - 1/2 + 1/2 = 1/2 \quad M = 2$

Using all the above discussed rules, that is, Aufbau principle, Pauli's exclusion principle and Hund's rule, the electronic configuration of different elements can be written. For example,



The electronic configuration of all the known elements is given in Table 1.4.

Table 1.4 Electronic configurations of elements

Element	Atomic number (Z)	Subshells																
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d
H	1	1																
He	2	2																
Li	3	2	1															
Be	4	2	2															
B	5	2	2	1														
C	6	2	2	2														
N	7	2	2	3														
O	8	2	2	4														
F	9	2	2	5														
Ne	10	2	2	6														
Na	11	2	2	6	1													
Mg	12	2	2	6	2													
Al	13	2	2	6	2	1												
Si	14	2	2	6	2	2												
P	15	2	2	6	2	3												
S	16	2	2	6	2	4												
Cl	17	2	2	6	2	5												
Ar	18	2	2	6	2	6												
K	19	2	2	6	2	6	1											
Ca	20	2	2	6	2	6	2											
Sc	21	2	2	6	2	6	1	2										
Ti	22	2	2	6	2	6	2	2										
V	23	2	2	6	2	6	3	2										
Cr*	24	2	2	6	2	6	5	1										
Mn	25	2	2	6	2	6	5	2										
Fe	26	2	2	6	2	6	6	2										
Co	27	2	2	6	2	6	7	2										
Ni	28	2	2	6	2	6	8	2										
Cu*	29	2	2	6	2	6	10	1										
Zn	30	2	2	6	2	6	10	2										
Ga	31	2	2	6	2	6	10	2	1									
Ge	32	2	2	6	2	6	10	2	2									
As	33	2	2	6	2	6	10	2	3									
Se	34	2	2	6	2	6	10	2	4									

(Continued)

Element	Atomic number (Z)	Subshells																
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d
Br	35	2	2	6	2	6	10	2	5									
Kr	36	2	2	6	2	6	10	2	6									
Rb	37	2	2	6	2	6	10	2	6								1	
Sr	38	2	2	6	2	6	10	2	6								2	
Y	39	2	2	6	2	6	10	2	6	1							2	
Zr	40	2	2	6	2	6	10	2	6	2							2	
Nb*	41	2	2	6	2	6	10	2	6	4							1	
Mo*	42	2	2	6	2	6	10	2	6	5							1	
Tc	43	2	2	6	2	6	10	2	6	5							2	
Ru*	44	2	2	6	2	6	10	2	6	7							1	
Rh*	45	2	2	6	2	6	10	2	6	8							1	
Pd*	46	2	2	6	2	6	10	2	6	10							0	
Ag*	47	2	2	6	2	6	10	2	6	10							1	
Cd	48	2	2	6	2	6	10	2	6	10							2	
In	49	2	2	6	2	6	10	2	6	10							2	1
Sn	50	2	2	6	2	6	10	2	6	10							2	2
Sb	51	2	2	6	2	6	10	2	6	10							2	3
Te	52	2	2	6	2	6	10	2	6	10							2	4
I	53	2	2	6	2	6	10	2	6	10							2	5
Xe	54	2	2	6	2	6	10	2	6	10							2	6
Cs	55	2	2	6	2	6	10	2	6	10							2	6
Ba	56	2	2	6	2	6	10	2	6	10							2	
La*	57	2	2	6	2	6	10	2	6	10							2	
Ce*	58	2	2	6	2	6	10	2	6	10	2						2	
Pr	59	2	2	6	2	6	10	2	6	10	3						2	
Nd	60	2	2	6	2	6	10	2	6	10	4						2	
Pm	61	2	2	6	2	6	10	2	6	10	5						2	
Sm	62	2	2	6	2	6	10	2	6	10	6						2	
Eu	63	2	2	6	2	6	10	2	6	10	7						2	
Gd*	64	2	2	6	2	6	10	2	6	10	7	2					1	
Tb	65	2	2	6	2	6	10	2	6	10	9	2					2	
Dy	66	2	2	6	2	6	10	2	6	10	10	2					2	
Ho	67	2	2	6	2	6	10	2	6	10	11	2					2	
Er	68	2	2	6	2	6	10	2	6	10	12	2					2	
Tm	69	2	2	6	2	6	10	2	6	10	13	2					2	
Yb	70	2	2	6	2	6	10	2	6	10	14	2					2	
Lu	71	2	2	6	2	6	10	2	6	10	14	2					2	
Hf	72	2	2	6	2	6	10	2	6	10	14	2					2	
Ta	73	2	2	6	2	6	10	2	6	10	14	2					3	
W	74	2	2	6	2	6	10	2	6	10	14	2					4	
Rc	75	2	2	6	2	6	10	2	6	10	14	2					5	

(Continued)

Element	Atomic number (Z)	Subshells																
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6	2			
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7	2			
Pt*	78	2	2	6	2	6	10	2	6	10	14	2	6	9	1			
Au*	79	2	2	6	2	6	10	2	6	10	14	2	6	10	1			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10	2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10	2	1		
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10	2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10	2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10	2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2	
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	2
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2	2
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	2
Es	99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2
Lr	103	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1
Rf	104	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	2
Db	105	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	3
Sg	106	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	4
Bh	107	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	5
Hs	108	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	6
Mt	109	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	7
Ds	110	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	8
Rg**	111	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	10

The (*) marked elements are those for which the Aufbau principle is not strictly followed. Elements beyond the (**) marked element are also known. The elements with atomic numbers 112, 114 and 116 have been discovered and assigned official IUPAC names copernicium, fleuorium and livermorium, respectively. The elements with atomic numbers 113, 115, 117 and 118 are yet to be discovered.

Stability of half-filled and fully-filled shells

Some of the exceptions in the elements, for which the electronic configuration does not follow the Aufbau principle, are:

$_{29}\text{Cu}$	${} : [\text{Ar}]4s^13d^{10}$	$_{44}\text{Ru}$	${} : [\text{Kr}]5s^14d^7$
$_{47}\text{Ag}$	${} : [\text{Kr}]5s^14d^9$	$_{45}\text{Rh}$	${} : [\text{Kr}]5s^14d^8$
$_{79}\text{Au}$	${} : [\text{Xe}]4f^{14}6s^15d^{10}$	$_{46}\text{Pd}$	${} : [\text{Kr}]5s^04d^{10}$
$_{24}\text{Cr}$	${} : [\text{Ar}]4s^13d^5$	$_{78}\text{Pt}$	${} : [\text{Xe}]6s^14f^{14}5d^9$
$_{42}\text{Mo}$	${} : [\text{Kr}]5s^14d^5$	$_{57}\text{La}$	${} : [\text{Xe}]6s^25d^14f^0$
$_{41}\text{Nb}$	${} : [\text{Kr}]5s^14d^4$	$_{89}\text{Ac}$	${} : [\text{Rn}]7s^26d^14f^0$
		$_{90}\text{Th}$	${} : [\text{Rn}]7s^26d^25f^0$

Several above violations of Aufbau principle can be explained on the basis of achieving either half-filled or fully-filled configurations of a subshell which are relatively more stable. The extra stability of half-filled and fully-filled configurations can be attributed to the following reasons:

1. The symmetry leads the stability (as the rule of nature).
2. The exchange energy is more for half-filled and fully-filled electronic configuration. For example, consider the electronic configuration shown in Figure 1.5, in which the possible exchange of positions of electrons is depicted.

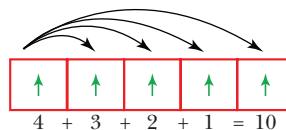


Figure 1.5 Possible exchanges of positions.

After exchanging the position between any two electrons, it gives the same configuration. During this exchange of position of electrons, some amount of energy is released which is known as exchange energy. More number of exchanges causes release of more energy.

For the above case (i.e. d^5 configuration), the total number of possible exchanges is ten. Similarly for d^{10} configuration, the total number of possible exchanges will be $(10 + 10) = 20$, (only two electron of same spin are allowed to exchange their position). Hence, ten exchanges are possible for five electrons having $+1/2$ spin and another ten exchanges are possible for five electrons having $-1/2$ spin. Hence fully-filled configuration is more stable as compared to half-filled configuration.

Electronic configuration of ions

(Recommended for study after covering Chapter 2)

1. For an anion:

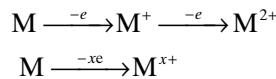


If the atomic number of an atom A is Z, then total number of electrons in A^- is $(Z + 1)$ and in A^{2-} is $(Z + 2)$. Hence, to arrive at the electronic configuration, count the total number of electrons in the anion and fill them in the empty orbital available in that element. For example, consider N^{3-} :

Total number of electrons = $7 + 3 = 10$.

The electronic configuration is: $1s^2 2s^2 2p^6$.

2. For cation:

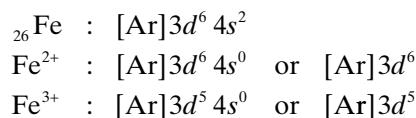


Hence, the total number of electrons in M^{x+} is $= Z - x$ where Z is the atomic number of M .

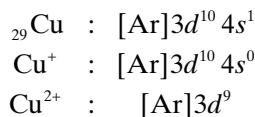
Then write the electronic configuration as usual if M is an element of s -block or p -block.

But if M is an element of d -block or f -block, then write the electronic configuration of the respective element M first and then remove the x number of electrons from ns , then from $(n-1)d$ and then from $(n-2)f$ orbital gradually. For example, consider Fe and Cu ions for d -block elements.

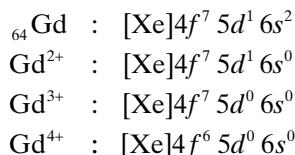
(i)



(ii)



Similarly for f -block elements, consider the example of Gd.



Following the Hund's rule, after obtaining the electronic configuration, the number of unpaired electrons (if any) can be calculated for any element or ion. From the number of unpaired electrons, it can further be predicted if the species is paramagnetic or diamagnetic. If we assume that the magnetic moment arises entirely from unpaired electron spins, then the spin only magnetic moment value can be calculated using the following formula:

$$\text{Spin only magnetic moment } (\mu_s) = \sqrt{n(n+2)} \text{ BM}$$

where n is the number of unpaired electrons present in the species. Spin only magnetic moment is also referred to as magnetic momentm for convenience sake.

- Paramagnetic:** The substance consisting of unpaired electron(s) (either one or more) is known as paramagnetic and it is attracted by the magnetic field. Paramagnetic substances are coloured in general.
- Diamagnetic:** The substance consisting of no unpaired electron is known as diamagnetic and it is repelled by the magnetic field. Diamagnetic substances are generally colourless.

Let us predict the magnetic behaviour of ions based on their electronic configurations. For example, consider Mn^{2+} , the electronic configuration is:



The electronic configuration shows the presence of five unpaired electrons, hence it is paramagnetic and the magnetic moment (μ_s) is

$$\begin{aligned} \mu_s &= \sqrt{5(5+2)} \text{ BM} \\ &= \sqrt{35} \text{ B.M} = 5.92 \text{ BM} \end{aligned}$$

Nodal planes of different orbitals

Nodal plane is defined as the plane, passing through nucleus, at which the probability of finding electrons present in that orbital is zero. The possible nodal for different subshells are listed as follows:

1. The number of nodal plane for s -orbital is zero.
2. The number of nodal plane for p -orbital is one.
 - a. xy -plane is the nodal plane for p_z -orbital.
 - b. xz -plane is the nodal plane for p_y -orbital.
 - c. yz -plane is the nodal plane for p_x -orbital.
3. The number of nodal planes for d -orbital is two.
 - a. xz -plane and yz -plane are the nodal planes for d_{xy} orbital.
 - b. xz -plane and xy -plane are the nodal planes for d_{yz} orbital.
 - c. yz -plane and xy -planes are the nodal planes for d_{xz} orbital.
 - d. For $d_{x^2-y^2}$ orbital, planes perpendicular to xy -plane and inclined by 45° angle with x and y -axis are the nodal planes.
 - e. For d_z^2 orbital, there are no nodal planes but there are two nodal conical surfaces available.

Slater's rule

In 1930, it was suggested by J. C. Slater that any one electron in an atom is attracted by all protons in the nucleus and repelled by other electrons present in the same shell or inner shell (Figure 1.6). He established a simple relation for determining the net attraction on an electron, which is given by:

$$Z_{\text{eff}} = Z - \sigma$$

where Z_{eff} is the effective nuclear charge on that specified electron; Z is the atomic number and σ is the shielding constant or screening constant which is the measure of net repulsion on that electron caused by other electrons in the same shell and inner shells.

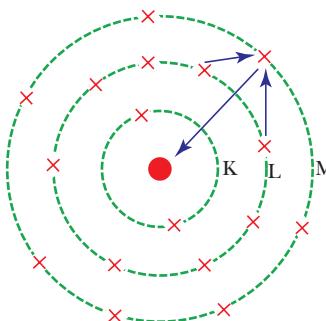


Figure 1.6 Attractive and repulsive forces experienced by electrons in an atom.

The value of the screening constant (σ) can be calculated by the following rules:

1. Write the electronic configuration of an atom as follows:

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f)...

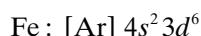
Note that only the presentation will be in the above format but the number of electrons in a subshell will be as in the electronic configuration obtained in accordance with Aufbau principle, Hund's rule and Pauli exclusion principle.

2. For electrons present in s or p -subshell:
 - a. The electrons present on the right side of the group made by () of the electron for which σ is to be calculated, have no contribution to the value of σ .

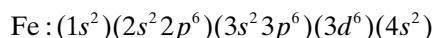
- b. Other electrons present in the same shell number will have the contribution of 0.35 each (except for the electrons in 1s subshell, that contribute 0.3).
 - c. Electrons present in the $(n-1)$ th shell will have the contribution of 0.85 each.
 - d. Electrons present in the $(n-2)$ th shell onward will have the contribution of 1.0 each.
3. For electrons present in the *d* or *f* subshell.
- a. Same as for electron present in *s* or *p*-subshell.
 - b. The other electrons present in the same group [i.e. within ()], will have the contribution of 0.35 each.
 - c. Rest of the electrons left of this group will have the contribution of 1.0 each.

Based on the above rules, we can now calculate the Z_{eff} for an electron in various subshells. Some examples are as follows:

1. Z_{eff} for electrons in 4s and 3d subshells of Fe. The electron configuration is



According to Slater's rules, it needs to be written as :



For 4s-electron,

$$\sigma = 10 \times 1 + 14 \times 0.85 + 1 \times 0.35 = 22.25 \quad (\text{Follow the rules from the right of the expression}). \text{ Substituting, we get,}$$

$$Z_{\text{eff}} = 26 - 22.25 = 3.75$$

For 3d-electron,

$$\sigma = 18 \times 1.0 + 5 \times 0.35 = 19.75$$

(Note that two electrons in 4s-subshell have no contribution as per the rule.) Substituting, we get,

$$Z_{\text{eff}} = 26 - 19.75 = 6.25$$

Using Slater's rule, it can be understood that the 3d electrons are more strongly attracted by its nucleus as compared to 4s electrons. Hence, though the electrons are filled first in the 4s-subshell, yet removal of electron takes place from 4s subshell first followed by the removal of electron of 3d subshell for first transition series element, and it can be generalized for all transition element, that is, the removal of electron will take place *ns* subshell first and then from $(n-1)d$ subshell.

2. Z_{eff} for electrons in 4s and 3d subshells of Sc.

The electronic configuration as per Slater's rule can be written as Sc: $(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^1)(4s^2 4p) \dots$

For 4s electron,

$$\begin{aligned} \sigma &= 10 \times 1.0 + 9 \times 0.85 + 1 \times 0.35 = 18 \\ \Rightarrow Z_{\text{eff}} &= 21 - 18 = 3.0 \end{aligned}$$

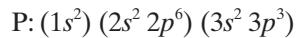
For 3d electron,

$$\begin{aligned} \sigma &= 18 \times 1.0 = 18 \\ \Rightarrow Z_{\text{eff}} &= 21 - 18 = 3.0 \end{aligned}$$

Here, Z_{eff} for both 4s and 3d subshells are the same and it does not conclude that the removal of electron will take place from 4s subshell first. More accurate method is developed by Clementi and Raimondi which suggests that Z_{eff} of 4s subshell is less than that of 3d subshell. (But this method involves some more rigorous calculations that are out of syllabus of JEE.)

3. Z_{eff} for electrons in 3s and 3p subshells of P atom.

Electronic configuration according to Slater's rule is



For electron present in $3s$ subshell:

$$\sigma = 2 \times 1 + 8 \times 0.85 + 4 \times 0.35 = 10.2$$

$$Z_{\text{eff}} = 15 - 10.2 = 4.8$$

For electron present in $3p$ subshell:

$$\sigma = 2 \times 1 + 8 \times 0.85 + 4 \times 0.35 = 10.2$$

$$Z_{\text{eff}} = 15 - 10.2 = 4.8$$

Hence, Z_{eff} is the same for an electron in the same group though the subshells are different.

Periodic variation of Z_{eff} values

(Recommended for reading after studying Chapter 2)

- 1. In a period:** Z_{eff} increases from left to right in a period. For example,

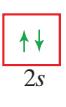
Li	Be	B	C	N	O	F	Ne
1.3	1.95	2.60	3.25	3.90	4.55	5.20	5.85

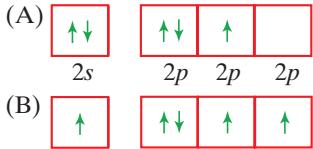
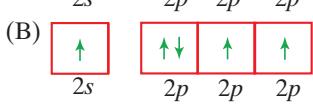
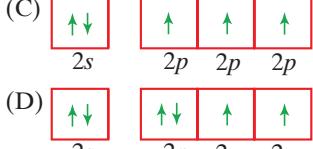
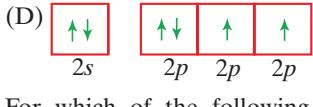
- 2. In a group:** In the Z_{eff} values calculated using Slater's rule, there is slight increase observed in a group. However, when calculated according to Clementi and Raimondi method, a more accurate steady increase in Z_{eff} values was observed down a group for all groups. For example,

H	Li	Na	K	Rb	Cs
Z_{eff} (by Slater):	1.0	1.3	2.2	2.2	2.2
Z_{eff} (by Clementi and Raimondi):	1.0	1.279	2.507	3.495	

SINGLE CORRECT CHOICE TYPE QUESTIONS

- The electrons, identified by quantum number n and l :
 - (I) $n = 3; l = 0$
 - (II) $n = 5; l = 2$
 - (III) $n = 2; l = 1$
 - (IV) $n = 4; l = 3$
 can be placed in order of increasing energy from the lowest to highest as:
 - (A) III < I < IV < II
 - (B) I < III < IV < II
 - (C) II < III < IV < I
 - (D) II < IV < I < III
- An electron has a spin quantum number $+1/2$ and magnetic quantum number -1 . It cannot be present in:
 - (A) d -orbital
 - (B) f -orbital
 - (C) p -orbital
 - (D) s -orbital
- Consider the following electronic configuration

			
2s	2p _x	2p _y	2p _z

 If one electron is added into the given electronic arrangement, then upcoming electron will have:
 - (A) Similar spin with that of electron of $2p_z$.
 - (B) Similar value of magnetic quantum number with that of $2p_x$.
- The orbital diagram in which the Aufbau principle is violated
 - (A) 
 - (B) 
 - (C) 
 - (D) 
- For which of the following orbitals, the electron finding probability is zero, if we move along the z -axis?
 - (A) $2p_x$
 - (B) $2p_y$
 - (C) $2p_z$
 - (D) $3d$

- (I) p_x
 (II) p_y
 (III) d_{z^2}
 (IV) $d_{x^2-y^2}$
 (A) I and II
 (B) III
 (C) I, II and IV
 (D) I, II and III

7. The degeneracy of H-atom in a shell is 9. The value of principal quantum number (n) for the shell is

- (A) 3
 (B) 9
 (C) 1
 (D) None of these

8. Process I $X(g) \xrightarrow{+3e^-} X^{3-}(g)$

Process II $X(g) \xrightarrow{-3e^-} X^{3+}(g)$

Which of the following is not changed during both the processes?

- (A) Total number of protons
 (B) Number of neutrons
 (C) Both (A) and (B)
 (D) Total number of electrons

9. Find the maximum number of electrons that can be filled in P shell.

- (A) 6
 (B) 2
 (C) 72
 (D) 50

10. In a hypothetical atom, the number of electrons in shell and subshell are x and y , respectively, where each electron has three possible spin states represented as $s = +1/2, -1/2$ and 0.

Then the value of $x + y$ is

- (A) $2n^2 + 4l + 2$
 (B) $3n^2 + 3l + 1$
 (C) $3n^2 + 6l + 3$
 (D) $6n^2 + 3l + 3$

11. The correct order of spin multiplicity of various ions of manganese including its neutral state is

- (A) $Mn^{7+} > Mn^{6+} > Mn^{4+} > Mn^{2+} > Mn$
 (B) $Mn > Mn^{2+} > Mn^{4+} > Mn^{6+} > Mn^{7+}$
 (C) $Mn^{7+} < Mn^{6+} < Mn^{4+} < Mn^{2+} = Mn$
 (D) All have equal spin multiplicity

12. Match the electronic configuration with the rule that it is violating.

Column-I **Column-II**

- (S) Aufbau's and Hund's rule

Column-II

(4)		
	2s	2p

Code:

P	Q	R	S
(A) 1	2	3	4
(B) 3	4	2	1
(C) 2	4	1	3
(D) 2	1	4	3

13. In which block will copper be placed if the Aufbau principle is not followed and the filling of electron takes place in the following sequence, $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f \dots$?

- (A) s
 (B) p
 (C) d
 (D) f

14. Which of the following is correct about Z_{eff} for an element?

- (A) Z_{eff} is same for (ns, np) electron.
 (B) Z_{eff} is same for (nd, nf) electron.
 (C) σ is not same for (ns, np) electron.
 (D) σ is same for (nd, nf) electron.

15. The number of possible orientations of d orbitals in space is

- (A) 2
 (B) 3
 (C) 4
 (D) 5

16. Spin only magnetic moment of dipositive ion of Mn is:

- (A) 0
 (B) $\sqrt{8}$ BM
 (C) $\sqrt{24}$ BM
 (D) $\sqrt{35}$ BM

17. The zero probability of finding the electron in $d_{x^2-y^2}$ orbital is

- (A) on two opposite side of nucleus along x -axis.
 (B) in the nucleus
 (C) same on all the sides around the nucleus.
 (D) None of these

18. If Z_{eff} of F ($Z = 9$) is X and Z_{eff} of Li ($Z = 3$) is Y then find the value of $|X - Y|$

- (A) 4.90
 (B) 3.90
 (C) 2.90
 (D) 1.90

19. Which electronic configuration does not follow the Aufbau rule?

- (A) $1s^2, 2s^2, 2p^6$
 (B) $1s^2, 2s^2, 2p^4, 3s^2$
 (C) $1s^2$
 (D) $1s^2, 2s^2, 2p^6, 3s^3$

Column-I

- (P) Only Aufbau's principle

Column-II

(1)		
	2s	2p

- (Q) Only Pauli's exclusion principle

(2)		
	2s	2p

- (R) Only Hund's rule

(3)		
	2s	2p

- 20.** Which of the following may have same set of quantum numbers?
- (A) Last electron of Sc and last electron of Fe.
 (B) Unpaired electron of C and entered electron in C^- .
 (C) Last electron of Sc and last electron of Y.
 (D) Unpaired electron in $2p$ orbital of N and unpaired electron in $2p$ orbital of B.
- 21.** Which out of Co (II) salts and Cd (II) salts, is attracted or repelled by the magnetic field?
- (A) Co (II) salts are attracted and Cd (II) salts are repelled.
 (B) Co (II) salts are repelled and Cd (II) salts are attracted.
 (C) Co (II) salts are attracted, while Cd (II) salts are not affected by the magnetic field.
 (D) Both Co (II) and Cd (II) salts are repelled.
- 22.** An electron present in which of the following orbitals has the minimum value for $(n + l + m + s)$? Consider the minimum possible value for m and s (where ever applicable).
- (A) $3p$
 (B) $5p$
 (C) $4d$
 (D) $5s$
- 23.** Choose the correct statement among the following:
- (A) Number of orbitals in n^{th} shell is n^2 .
 (B) Number of orbitals in a subshell is $(2l - 1)$.
 (C) Number of subshells in n^{th} shell is $(n - 1)$.
 (D) Number of electrons in an orbital of a subshell is $2(2l + 1)$.
- 24.** In boron atom shielding of the last electron is due to
- (A) electrons of K shell only.
 (B) all the electrons of K and L shells.
 (C) two electrons of $1s$ and $2s$ each.
 (D) all the electrons of L shell only.
- 25.** Which of the following statements is correct?
- (A) Total number of electrons in a subshell is $2l + 1$.
 (B) p_z , $d_{x^2-y^2}$ and d_{z^2} orbitals are non-axial.
 (C) Only s orbital has directional orientation while p_z , d and f orbitals have non-directional properties.
 (D) Spin multiplicity of nitrogen atom is 4.
- 26.** Imagine a Universe in which the four quantum numbers can have the same possible value as in our Universe except that the magnetic quantum number (m) can have integral values from 0 to $\pm (l + 1)$. Find the electronic configuration of atomic number 20.
- (A) $1s^6 2s^6 2p^8$
 (B) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
 (C) $1s^4 2s^4 2p^6 3s^4 3p^2$
 (D) $1s^2 1p^6 2s^2 1d^{10}$
- 27.** The subshells which are filled just before and just after the filling of $5p$ subshell are respectively:
- (A) $5s, 5d$
 (B) $4d, 6s$
 (C) $4d, 4f$
 (D) $6s, 4f$
- 28.** Which of following species has the magnetic moment value of 3.87 BM ?
- (A) Fe^{3+}
 (B) Cr^{2+}
 (C) Co^{2+}
 (D) Au^{3+}
- 29.** Give the correct order of initials **True (T)** or **False (F)** for following statements.
- (I) Number of electrons having $l = 0$ is 10 in Pd.
 (II) The value of Z_{eff} for $3d$ electron of Cr and $3d$ electron of Mn is same as number of electron in d sub shell of Cr and Mn are the same.
 (III) Multiplicity of Fe is equal to that of Ni^{2+} .
 (IV) Value of l/n for last electron of element having atomic number 57 is 0.4,
- (A) T T T T
 (B) F T T T
 (C) T F T F
 (D) F F F T
- 30.** According to Slater rule, the set of elements that show incorrect order of Z_{eff} are:
- (A) Al > Mg
 (B) Na > Li
 (C) K > Na
 (D) None of these
- 31.** The magnetic moment and nature for isolated gaseous ion Au^{3+} is
- (A) zero and diamagnetic.
 (B) 2.82 BM and diamagnetic.
 (C) 2.82 BM and paramagnetic.
 (D) None of these.
- 32.** The correct set of quantum numbers for the last electron of Na^+ is
- (A) $3, 0, 0, -\frac{1}{2}$
 (B) $3, 1, 0, +\frac{1}{2}$
 (C) $3, 1, 1, +\frac{1}{2}$
 (D) $2, 1, 0, -\frac{1}{2}$
- 33.** Select the correct statement for Ne.
- (A) It is not isoelectronic with H_2O
 (B) Its last electron enters in S orbital
 (C) The value of m must be zero for the last electron.
 (D) The value of l must be 1 for the last electron.

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

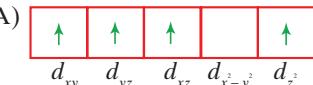
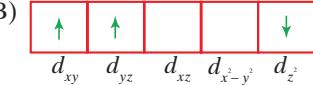
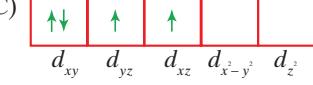
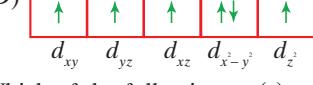
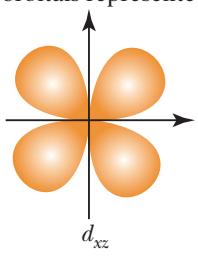
1. Hund's rule is violated in which of the following electronic configurations?
- (A) 
 d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}
- (B) 
 d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}
- (C) 
 d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}
- (D) 
 d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}
2. Which of the following set(s) consist of only isoelectronic species?
- (A) N^3- , O^3- , Ne , Na^+
(B) NO_3^- , SiO_4^{4-} , CO_3^{2-}
(C) Hg^{2+} , Pb^{4+}
(D) H , He^+ , Li^{2+} , Be^{3+}
3. If two subshells have equal value of $(n+l)$ and one of them has $n=4$, $l=3$, while second subshell has dumbbell shape. Then which of the following statement is/are correct?
- (A) Second subshell has value of $n=6$.
(B) Second subshell has one nodal plane.
(C) Second subshell is d -subshell.
(D) First subshell is f -subshell.
4. Select the correct statement(s) among the following.
- (A) The maximum value of principal quantum number is 7.
(B) For $n=2$, there may be four subshells and these may contain a maximum of 8 electrons.
(C) M shell can accommodate a maximum of 18 electrons.
(D) The energy of $5p$ -orbitals is more than that of $4d$ -orbitals.
5. Which of the following statements are not true for d_{xy} orbital?
- (A) It is double dumbbell shaped.
(B) The lobes lie in between x -and z -axes.
(C) P_z orbital is perpendicular to d_{xy} orbital.
(D) The lobes of P_x orbital are collinear with those of d_{xy} orbital.
6. Which are the orbitals represented in Figure 1.7?
- 
7. Which of the following orbitals are represented by $n=4$ and $l=1$?
- (A) $4p_y$
(B) $4p_x$
(C) $4d_{xy}$
(D) $4d_{x^2-y^2}$
8. Which of the following electronic configurations are incorrect for a d^6 system for an isolated gaseous ion?
- (A) 
 d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}
- (B) 
 d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}
- (C) 
 d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}
- (D) 
 d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}
9. Using the Slater's rule, choose the correct statements among the following.
- (A) Value of σ (shielding constant) for d -electrons of penultimate shell of Sc, Y, La are equal.
(B) Z_{eff} for d -electrons of penultimate shell of Sc, Y, La are equal.
(C) Value of σ increases by a factor of 0.3 in the first period from left to right.
(D) Value of Z_{eff} increases by a factor of 0.35 in the second period from left to right.
10. Which of the following quantum numbers may be the same for an electron present in $3p$ and $5p$ orbitals?
- (A) Principal quantum number
(B) Azimuthal quantum number
(C) Magnetic quantum number
(D) Spin quantum number
11. Choose the correct options from the following:
- (A) Cr and S have the same number of valence shell electrons.
(B) Cr and S have different number of unpaired electrons in their ground state.
(C) Cr and S are the elements of the same period.
(D) In the long form of the periodic table, the Group number of Cr and S is 6 and 16, respectively.
12. Which of the following set of quantum numbers are valid for electrons of ground state electronic configuration of elements having atomic number upto 25.

Figure 1.7 Multiple correct choice type question 2.

n l m s
(A) 3 2 0 $+\frac{1}{2}$

n l m s
(B) 4 0 0 $+\frac{1}{2}$

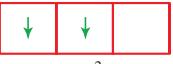
n l m s
(C) 4 1 0 $-\frac{1}{2}$

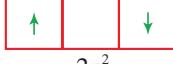
n l m s
(D) 2 2 +1 $+\frac{1}{2}$

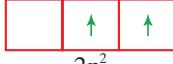
13. Select the incorrect statements among the following.

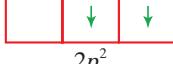
- (A) In $d_{x^2-y^2}$ orbital, two nodal planes are present in xz - and yz -plane.
 (B) d_{xy} and $d_{x^2-y^2}$ have one common nodal plane.
 (C) One $4d$ orbital contains only two electrons of the same spin.
 (D) One $3d$ orbital contains a total of 10 electrons.

14. Which of the following can be a stable ground state electronic configuration (only valence shell) of carbon atom?

(A)  
 $2s^2$ $2p^2$

(B)  
 $2s^2$ $2p^2$

(C)  
 $2s^2$ $2p^2$

(D)  
 $2s^2$ $2p^2$

15. Which of the following species is isoelectronic with Ne?

- (A) H_2O
 (B) C^{4-}
 (C) Na^+
 (D) NH_2^-

16. Choose the correct option regarding energy of empty orbitals.

n l m s
(I) 4 0 0 $+\frac{1}{2}$

(II) 3 2 0 $-\frac{1}{2}$

(III) 3 1 1 $+\frac{1}{2}$

(IV) 3 0 0 $-\frac{1}{2}$

- (A) I > IV
 (B) II > I
 (C) II > III
 (D) I = III

17. Which of the following may represent the possible quantum numbers for the last electron of Ga?

(A) 3, 1, +1, $+\frac{1}{2}$

(B) 4, 0, +1, $+\frac{1}{2}$

(C) 4, 1, 0, $-\frac{1}{2}$

(D) 4, 1, +1, $+\frac{1}{2}$

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1–2

Nodal plane of an orbital is the region around the nucleus where probability of finding electrons of that orbital is zero. Number of nodal planes of an orbital = l .

- 1.** Nodal plane of s -orbital is
 (A) xy -plane (B) yz -plane
 (C) xz -plane (D) None of these
- 2.** Which of the following contains at least one common nodal plane?
 (A) p_x and d_{xz} (B) d_{xy} and $d_{x^2-y^2}$
 (C) $d_{x^2-y^2}$ and d_{z^2} (D) p_z and d_z

Passage 2: For Questions 3–4

In a hypothetical system, all the known concepts of shell, subshell, orbitals, etc., exist in the same way as in our system except that the $(n + l)$ rule is modified to $(n - l)$ rule for deciding the subshell energy. In case of equal value of $(n - l)$, the higher value of n gives the higher energy.

- 3.** In this hypothetical system S ($Z = 16$) will be a
 (A) p -block element (B) s -block element
 (C) d -block element (D) f -block element

- (A) 25
 - (B) 26
 - (C) 27
 - (D) 28

Passage 3: For Questions 5–6

The effective nuclear charge (Z_{eff}) takes into account the interelectronic repulsion in multielectron atoms. Slater's rule helps us in evaluating Z_{eff} for various species. Apply Slater's rules to answer the following questions.

11. The element is isoelectronic with which of the following species?

- (A) Fe^-
 - (B) Ni^+
 - (C) Cu^{2+}
 - (D) All of these

12. The number of unpaired electrons in the divalent cation of the element in isolated gaseous state is

 - (A) 0
 - (B) 3
 - (C) 4
 - (D) 1

Passage 6: For Questions 13–15

Three quantum numbers are required to define an orbital while four quantum numbers are required to describe an electron.

13. Which of the following statement is correct?

 - (A) The quantum numbers of the electron in H atom are exactly identical with that of one electron of He atom.
 - (B) The maxima of the radial distribution of s orbital decreases as the principal quantum number increases.
 - (C) According to Pauli's exclusion principle, the lower energetic orbital will be filled first.
 - (D) The N atom has the electronic configuration of $1s^2 2s^2 2p^3$ which is represented as



14. $(n + l)$ is maximum and minimum for which of the following orbitals: $6s$, $5p$, $6d$, $4d$, $2p$, $3s$, $2s$?

- (A) 6f and 1s
 - (B) 6d and 2s
 - (C) 5p and 3s
 - (D) 6s and 2p

15. Which of the following statements is correct for H atom?

- (A) H atom can be placed both in Group 1 and Group 18.
 - (B) H atom can be placed both in Group 1 and Group 17.
 - (C) H atom produces smallest anion in reality.
 - (D) $2s, 2p, 3s$ orbitals are not available in H atom.

Passage 5: For Questions 10–12

The general electronic configuration of outer most and penultimate shell is given as $(n-1)s^2(n-1)p^6(n-1)d^x\ ns^2$. Then for an element with $n=4$ and $x=7$

10. The number of protons present in the divalent cation of the element of above configuration is

Passage 7: For Questions 16–18

The electronic configuration of an element is written as follows: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

16. On removal of one electron, the electronic configuration will become
 (A) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
 (B) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^1$
 (C) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s$
 (D) None of these.
17. The screening constant value for an electron in $3s$ is identical with that of an electron present in
 (A) $3p$ orbital.
 (B) $3d$ orbital.
 (C) $4s$ orbital.
 (D) $4p$ orbital.
18. Which of the following statements is incorrect?
 (A) In calculation of σ value (shielding constant) for an electron in $4s$ orbital, the contribution of $1s$ electron is 0.3.
 (B) In calculation of σ value for an electron in $3d$ orbital, the contribution of $4s$ electron is zero.
 (C) In calculation of σ value for an electron in $3d$ orbital, the contribution of electron present in $3p$ orbital is 1.0.
 (D) In calculation of σ value for an electron in $4s$ orbital, the contribution of electron present in $3p$ orbital is 0.85.

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
 (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
 (C) If Statement I is true but Statement II is false.
 (D) If Statement I is false but Statement II is true.

1. **Statement I:** Each f -block series contains 14 elements.

Statement II: The f orbitals can have seven possible orientations in space and can accommodate maximum of 14 electrons in the f -subshell.

2. **Statement I:** The $3p$ orbitals are higher in energy as compared to $3s$ orbital.

Statement II: $(n+l)$ for $3p$ orbitals is lower than that of $3d$ orbitals.

3. **Statement I:** Cu^+ is repelled by magnetic field.

Statement II: All electrons are paired up in Cu^+ ion.

4. **Statement I:** The fully filled configuration is more stable as compared to half-filled configuration.

Statement II: More exchange energy causes greater stability.

5. **Statement I:** Mn can show maximum oxidation state of +7.

Statement II: Total number of valence shell electrons present in Mn is 5.

6. **Statement I:** The p_x, p_y, p_z orbitals are called degenerate orbitals.

Statement II: p_x, p_y , and p_z orbitals have almost the same energy.

7. **Statement I:** Pairing of electrons in degenerate orbitals decreases the energy of the system.

Statement II: Spinning directions of the two paired electrons are different.

8. **Statement I:** The electronic configuration for d^5 system is wrongly represented as



Statement II: Hund's rule is violated in the above representation.

9. **Statement I:** In writing the electronic configuration of an atom, the $5s$ orbital will be filled before $4p$ orbital.

Statement II: The $(n+l)$ values for $5s$ orbital and $4p$ orbital are identical.

INTEGER ANSWER TYPE QUESTIONS

1. Among the given elements, number of species which are isodiaphers of each other are _____.
 $_{92}^{238}U, {}_{88}^{230}Ra, {}_{89}^{232}Ac, {}_{90}^{234}Th$
2. Total number of orbitals that are to be filled completely before entering into the $6s$ subshell for filling of electrons is _____.
 (Add the digits till you get single digit answer.)
3. Find the maximum value of $n+l+m$ for the last electron present in an element which belongs to fifth period and group number 15.
4. Find the total number of elements out of the given elements which will need two more electrons to achieve 8 electrons in the outermost shell.
 Na, C, N, P, F, O
5. If unknown element X has Z_{eff} value of 3.5 and only two electrons of valence shell contribute towards sigma (σ) calculation, then what is the atomic number of element? (Consider elements up to atomic number 20.)
 (Add the digits till you get single digit answer.)
6. Find the total number of possible exchanges for d^4 configuration in an element.

7. If Z_{eff} of Mg is 2.85, then what will be the value of y for magnesium, where $y = \frac{(\sigma + 0.85)}{2}$?
8. How many elements amongst the following have at least 4 electrons in p -subshells?
B, N, Al, Si, P, Cl
9. If Aufbau's rule is not followed and electron filling is done shell after shell, then number of unpaired electrons present in copper will be _____.
10. The first excited state of Cl^- ion will have degeneracy of _____.
11. Maximum number of degenerate orbitals in M shell of Li^{2+} is _____.
12. Number of groups incorrectly mentioned according to their relationship given in brackets is _____.
(A) ${}_{\text{8}}^{16}\text{O}$, ${}_{\text{8}}^{17}\text{O}$, (isotopes)
(B) CaO , KF (isosteres)
(C) ${}_{\text{7}}^{15}\text{N}$, ${}_{\text{9}}^{19}\text{F}$, (isobars)
(D) Na^+ , Mg^{2+} , Al^{3+} (isoelectronic)
(E) ${}_{\text{1}}^{3}\text{H}$, ${}_{\text{2}}^{4}\text{He}$, (isodispersers)
(F) H_2O , NH_3 (isosteres)
(G) ${}_{\text{19}}^{40}\text{K}$, ${}_{\text{20}}^{40}\text{Ca}$ (isobars)
(H) ${}_{\text{19}}^{39}\text{K}$, ${}_{\text{20}}^{40}\text{Ca}$ (isotones)
13. The number of chemical species among the following which can produce spin magnetic moment greater than zero is _____.
 Sc^{3+} , V^{3+} , Cr^{6+} , Mn^{2+} , Zn , Pd , Ag^+ , Cu^{2+} , Hg , Cu^+ , Cu^{3+}
14. The ratio of unpaired electrons present in d orbitals of Co^{2+} and Cr^{3+} is _____.
15. In Mn, the maximum number of electrons having $m_s = +\frac{1}{2}$ is _____.
16. In Mn, the minimum number of electrons having $m_s = -\frac{1}{2}$ is _____.
17. In the following species, the number of them having same magnetic moment value is _____.
 Fe^{3+} , Co^{3+} , Ni^{2+} , Mn^{3+} , Cu^+ , Zn^{2+} , Cd^{2+} , Cu^{2+} , Ag^+ .
18. The total value of m for all electrons in N atom is _____.
19. Find maximum number of electrons in Al for which $\frac{l \times m}{n} = 0$. (Atomic number of Al = 13).
20. Find total number of orbitals in S atom, for which $|m| \leq 1$ and which contains at least one electron. (Atomic number of S = 16).
21. Find total number of orbitals in which electron density is observed along any of the axis (x , y or z).
 $s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}$
22. Calculate maximum number of electrons in ${}_{25}\text{Mn}$ which have $n = 3, m = 0$ and $s = +1/2$.
23. Find the maximum number of electrons in Cr atom which have $m = -1$ and $s = +1/2$ but $n \neq 2$.
24. Find the number of electrons having $(n \times l + m) = 3$ for Kr atom (Atomic number = 36)
25. The shielding constant for the last electron in Sc is _____.
26. The Z_{eff} on the last electron in Sc is _____.
27. The number of species among the following, having magnetic moment value of 2.84 BM is _____.
 Fe^{2+} , Cr , Cr^{3-} , Ti^{2+} , Mn^{2+} , V^{3+}
28. The number of electrons for Cd^{2+} that have the value of azimuthal quantum number $l = 1$ is _____.
29. The number of electrons present in the Br^- ion that have the value of magnetic quantum number $m = +1$ is _____.
30. The Z_{eff} on the last electron of Zr^{3+} ion is _____.
31. The Z_{eff} on the electron present in $5d$ orbital of Gd (atomic number = 64) is _____.

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as **(A)**, **(B)**, **(C)** and **(D)**, while those in Column II are labelled as **(P)**, **(Q)**, **(R)**, **(S)** and **(T)**. Any given statement in Column I can have correct matching with one or more statements in Column II.

1. Match the orbitals with their spatial arrangement.

Column-I Column-II

- (A) p_z (P) xy plane is the nodal plane.
(B) d_{xz} (Q) yz plane is the nodal plane.
(C) d_{yz} (R) xz plane is the nodal plane.

- (D) d_{xy} (S) Has a common nodal plane with p_x
(T) Has a common nodal plane with d_{xy}

2. Match the shell with the property.

Column-I Column-II

- (A) K (P) Maximum number of electrons present is 18.
(B) L (Q) If the shell is fully occupied, some electrons must have value of $m = 0$.
(C) M (R) There are no electrons with l value of 2, if the shell is fully occupied.
(D) N (S) p subshell is present.

3. Match the electronic configuration with the nature/property of the element.

Column-I	Column-II
(A) $[\text{Ar}] 3d^{10} 4s^2 4p^6 5s^1$	(P) p -block element.
(B) $[\text{Ne}] 3s^2 3p^6 4s^2 3d^6$	(Q) Zero group element.
(C) $1s^2 2s^2 2p^6 3s^2 3p^6$	(R) d -block element.
(D) $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^3$	(S) 4th period element.
	(T) Paramagnetic element.

4. Match the ion with the property.

Column-I	Column-II
(A) Fe^{2+}	(P) Set of quantum number for the last electron $n = 2, l = 1, m = 1, s = +\frac{1}{2}$
(B) Mn^{4+}	(Q) Magnetic moment (μ) = Zero.
(C) Zn^{2+}	(R) Spin multiplicity (SM) = 4
(D) Na^+	(S) Paramagnetic

ANSWERS

Single Correct Choice Type Questions

- | | | | | |
|--------|---------|---------|---------|---------|
| 1. (A) | 8. (C) | 15. (D) | 22. (A) | 29. (D) |
| 2. (D) | 9. (C) | 16. (D) | 23. (A) | 30. (C) |
| 3. (D) | 10. (C) | 17. (B) | 24. (C) | 31. (C) |
| 4. (B) | 11. (C) | 18. (B) | 25. (D) | 32. (D) |
| 5. (B) | 12. (C) | 19. (B) | 26. (A) | 33. (D) |
| 6. (C) | 13. (A) | 20. (D) | 27. (B) | |
| 7. (A) | 14. (A) | 21. (A) | 28. (C) | |

Multiple Correct Choice Type Questions

- | | | | | |
|------------------|------------------|-------------------|------------------------|--------------|
| 1. (B), (C) | 5. (B), (D) | 9. (B), (C) | 13. (A), (B), (C), (D) | 17. (C), (D) |
| 2. (A), (C), (D) | 6. (A), (C), (D) | 10. (B), (C), (D) | 14. (A), (C), (D) | |
| 3. (A), (B), (D) | 7. (A), (B) | 11. (A), (B), (D) | 15. (A), (B), (D) | |
| 4. (C), (D) | 8. (C), (D) | 12. (A), (B) | 16. (A), (B), (C) | |

Comprehension Type Questions

- | | | | | |
|--------|--------|---------|---------|---------|
| 1. (D) | 5. (D) | 9. (A) | 13. (A) | 17. (A) |
| 2. (A) | 6. (D) | 10. (C) | 14. (B) | 18. (A) |
| 3. (C) | 7. (B) | 11. (D) | 15. (B) | |
| 4. (D) | 8. (C) | 12. (B) | 16. (B) | |

Assertion-Reasoning Type Questions

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (A) | 3. (A) | 5. (C) | 7. (D) | 9. (D) |
| 2. (B) | 4. (A) | 6. (C) | 8. (A) | |

Integer Answer Type Questions

- | | | | | |
|------|------|------|------|-------|
| 1. 4 | 3. 7 | 5. 4 | 7. 5 | 9. 1 |
| 2. 9 | 4. 1 | 6. 6 | 8. 4 | 10. 5 |

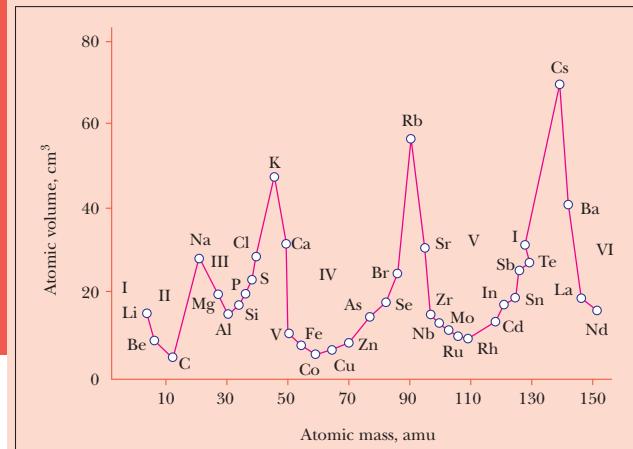
- | | | | | |
|---------------|---------------|---------------|---------------|--------------|
| 11. 9 | 16. 10 | 21. 6 | 26. 3 | 31. 3 |
| 12. 3 | 17. 4 | 22. 3 | 27. 2 | |
| 13. 4 | 18. 0 | 23. 2 | 28. 18 | |
| 14. 1 | 19. 9 | 24. 6 | 29. 8 | |
| 15. 15 | 20. 9 | 25. 18 | 30. 4 | |

Matrix-Match Type Questions

- | | |
|---|--|
| 1. (A) → (P)
(B) → (P), (Q), (S), (T)
(C) → (P), (R), (T)
(D) → (Q), (R), (S) | 3. (A) → (T)
(B) → (R), (S), (T)
(C) → (P), (Q)
(D) → (P), (T) |
| 2. (A) → (Q), (R)
(B) → (Q), (R), (S)
(C) → (P), (Q), (S)
(D) → (Q), (S) | 4. (A) → (S)
(B) → (R), (S)
(C) → (Q)
(D) → (P), (Q) |

2

Periodic Table and Periodic Properties



2.1 | PERIODIC TABLE

Historically, elements with similar or related properties were grouped together into family of elements. For example, lithium, sodium and potassium formed the family of active metals whereas copper, silver and gold formed the family of noble metals. Based on the systematic relationships among the elements, a chart known as periodic table evolved that reflected systematic trends in physical and chemical properties of elements. **Periodic table** is the arrangement of elements in a tabular form on the basis of their properties that facilitates the systematic study of properties of elements.

Genesis of periodic classification

The early attempts at classification of elements were based on the experimental observation on the limited number of elements that were known at that time.

Dobereiner's triad

In 1829, German chemist Dobereiner was able to identify several groups of three elements that showed similarity in physical and chemical properties. He observed that in the set of three elements having similar properties (called triads), the atomic weight of the middle element is the arithmetic mean of the atomic weights of other two elements. Some examples of Dobereiner's triads are as follows:

Lother Meyer's curve.

Contents

- 2.1 Periodic Table
- 2.2 Classification Of Elements Based On Electronic Configuration
- 2.3 Periodic Trends In Properties

	Element	At. weight	Mean weight of first and last element
(i)	Li	7	
	Na	23	$\frac{7+39}{2} = 23$
(ii)	K	39	
	Ca	40	
(iii)	Sr	88	$\frac{40+137}{2} = 88.5$
	Ba	137	
(iv)	Cl	35.5	
	Br	80	$\frac{35.5+127}{2} = 81.25$
	I	127	
	S	32	
	Se	79	$\frac{32+127.6}{2} = 79.8$
	Te	127.6	

Only few such triads were available at that time and day by day as many more elements were discovered, the rule could no longer be generalized.

Newland's octave law

An English chemist Alexander Newlands made the next attempt at classification of elements. He arranged the 56 elements known then in increasing order of their atomic weight and observed that, “the properties of every eighth element are similar to that of first one”. He compared this relationship to the first octave in music with eight notes and called it Newlands’ law of octaves. The elements were arranged as follows:

Sa	Re	Ga	Ma	Pa	Dha	Ni	Sa
Li	Be	B	C	N	O	F	Na
Na	Mg	Al	Si	P	S	Cl	K
K	Ca						

The limitations of this classification of elements were that:

- (i) The inert gases were not discovered till then.
- (ii) Beyond Ca, this repetition was not observed.

Lother Meyer's curve

Lother Meyer plotted the atomic volume versus atomic mass, where the atomic volume is defined as follows:

$$\text{Atomic volume} = \frac{\text{Gram atomic mass of an element}}{\text{Density (in g/ml)}}$$

The curve obtained is referred to as Lother Meyer's curve and is shown in Figure 2.1.

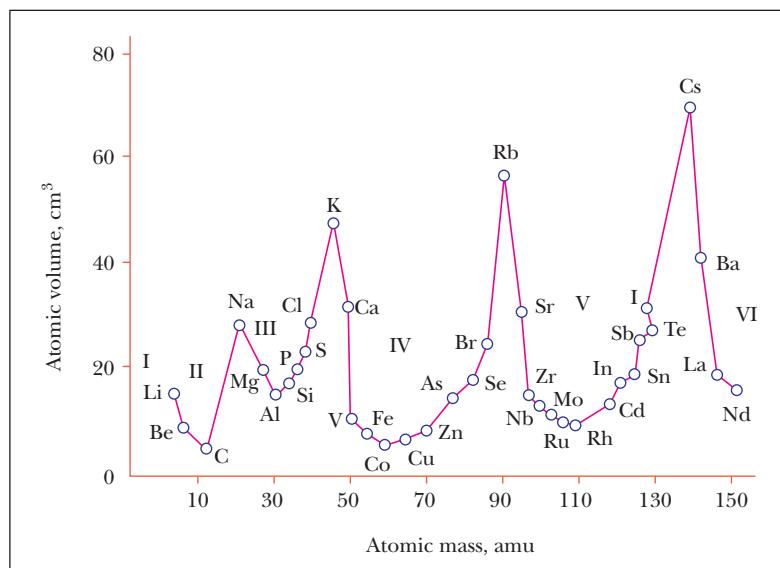


Figure 2.1 Lother Meyer's curve.

From this plot, he observed that:

1. The elements having similar properties are in the same position of the curve. For example,
 - a. Alkali metals (Li, Na, K, Rb, Cs) are at the peaks of the curve.
 - b. Alkaline earth metals (Be, Mg, Ca, Sr, Ba) are at the descending part of the curve.
 - c. Halogens (F, Cl, Br, I) are at the ascending part of the curve.
 - d. Most of the transition elements are lying in the broad minimas of the curve.
2. The atomic volume of the elements changes periodically in a period, it initially decreases and then increases with broad minimas.
3. The atomic volume increases in a group, that is, in elements that exhibit similar properties.
4. Many other physical properties of the elements also change in a periodic manner like melting point, boiling point, density, thermal expansion coefficient, etc.

Based on these observations, he proposed that the physical properties of elements are periodic functions of their atomic weights and this formed the basis of Mendeleev's periodic table, which was also presented around the same time.

Mendeleev's periodic table

The earliest version of the current form of periodic table was presented simultaneously by Dmitri Mendeleev of Russia and Lothar Meyer of Germany. Both the scientists arranged the elements in order of increasing atomic weights and observed that elements with similar properties (in families) appeared at regular intervals.

Mendeleev's periodic law stated that *the physical and chemical properties of elements are the periodic function of their atomic weights*.

In 1871, Mendeleev published a short periodic table which:

1. Consisted of only 63 elements. Inert gases were not included as these were not discovered at that time.
2. These elements were arranged in seven horizontal rows called as periods and eight vertical columns called as groups.
3. Some vacant sites were specified for undiscovered elements and their properties predicted. These were found true and verified when these elements were discovered later.

In the periodic table, so constructed, the elements in the same families (e.g., lithium, sodium, potassium) were arranged in vertical columns designated as Groups I, II, III, IV, V, VI, VII, VIII. The horizontal rows were referred to as series.

Mendeleev's periodic table was later modified after the discovery of inert gases and several other elements. The inert gases were placed in new Group 0. Each long period was divided into two series, named as *odd* and *even* depending on the serial number. The first seven elements formed the even series and the last seven elements formed the odd series (not including the inert gases). The vertical Groups I to VII were further divided into two subgroups A and B to accommodate elements with difference in properties. The elements of even series in the long periods were placed in subgroup A while the elements of odd series were placed in the B subgroup. The Group 0 was not split further and in Group VIII three sets containing three elements each were placed.

Table 2.1 Modern version of Mendeleev's short periodic table

Group \ Period	0	I		II		III		IV		V		VI		VII		VIII		
		A	B	A	B	A	B	A	B	A	B	A	B	A	B			
1	He 2	H 1																
2	Ne 10	Li 3	Be 4			B 5		C 6		N 7		O 8		F 9				
3	Ar 18	Na 11	Mg 12			Al 13		Si 14		P 15		S 16		Cl 17				
4		K 19	Ca 20	Sc 21		Ti 22		V 23		Cr 24		Mn 25		Fe 26	Co 27	Ni 28		
	Kr 36		Cu 29	Zn 30		Ga 31		Ge 32		As 33		Se 34		Br 35				
5		Rb 37		Sr 38	Y 39	Zr 40		Nb 41		Mo 42		Tc 43		Ru 44	Rh 45	Pd 46		
	Xe 54		Ag 47	Cd 48		In 49		Sn 50		Sb 51		Te 52		I 53				
6		Cs 55	Ba 56	La* 57-71	Hf 72	Ta 73		W 74		Re 75				Os 76	Ir 77	Pt 78		
	Rn 86		Au 79	Hg 80	Tl 81	Pb 82		Bi 83		Po 84		At 85						
7		Fr 87	Ra 88	Ac** 85-103														
The Rare Earths																		
*Lanthanide series (6th period)			Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71		
**Actinide series (7th period)			Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103		

The designation of the subgroups A and B given here is quite arbitrary and the new designation is given in the long form Periodic table as per the latest Convention.

Important characteristics of modern version of Mendeleev's short periodic table are listed as follows:

I. Horizontal rows or Periods

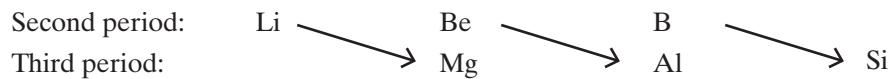
- First period consists of 2 elements and is known as very short period.
- Second period consists of 8 elements and is known as first short period.
- Third period consists of 8 elements and is known as second short period.
- Fourth period consists of 18 elements and is known as first long period.
- Fifth period consists of 18 elements and is known as second long period.
- Sixth period consists of 32 elements and is known as very long period.
- Seventh period is an incomplete period.

II. Vertical columns or Groups

1. Group IA elements are called as alkali metals (expect H).
2. Group IIA elements are called as alkaline earth metals.
3. Group VB elements are called as pnicogens.
4. Group VIIB elements are called as chalcogens.
5. Group VIIIB elements are called as halogens.
6. Group 0 elements are called as inert gases.

III. Other features

1. Lanthanides or Lanthanoids or Rare earths: These include elements from Ce (58) to Lu (71). The word earths refer to the oxides and in fact elements are found in nature first in the form of their oxides. Hence they are called as rare earths. The name sometimes confuses to suggest that their availability may be rare which is not correct. Rather, they occur widely in nature and usually together.
2. Actinides or Actinoids: These include elements from Th (90) to Lr (103).
3. Coinage metals: These include Cu, Ag and Au. These metals were once used as currency.
4. Noble metals: These include Ag, Au, Pt and Hg. They are so called because of their very low reactivity.
5. Transuranium metals: Elements beyond U (92) are known as transuranium metals.
6. The elements of third period are called as bridging elements because the concept of subgroups A and B starts after this period. Also, these elements maintain some similarities in properties with both subgroups A and B elements.
7. Diagonal relationship: There are three set of elements, that is, (Li, Mg), (Be, Al) and (B, Si), which, though, placed in different groups, show some similarities in their properties. This kind of similarity in properties is known as diagonal relationship and is attributed to their similar sizes.



The **merits** of Mendeleev's periodic table are listed as follows:

1. The study of properties of elements became more systematic and easier.
2. There are several vacant positions from which the guidance of discovery of new elements was found. The rectification of atomic weights was done for several elements. For example, Be and Al show similarities in their properties, so it was considered that the valency of Be is 3 like Al. Hence the atomic weight of Be

$$\begin{aligned}
 &= \text{Equivalent weight} \times \text{valency} \\
 &= 4.5 (\text{experimentally determined}) \times 3 = 13.5
 \end{aligned}$$

But no suitable position was found for Be according to its calculated atomic weight. But actually the valency of Be is 2 according to group number and its atomic weight is rectified ($4.5 \times 2 = 9$).

3. Similarly the atomic weight rectification is also done for indium.

The **demerits** of Mendeleev's periodic table are given as follows:

1. Some of the elements are wrongly placed though their atomic weights are larger compared to the next one. For example,

$$\begin{array}{lll}
 \text{(i) Ar : 40} & \text{(ii) Te : 127.6} & \text{(iii) Co : 58.9} \\
 \text{K : 39} & \text{I : 126.9} & \text{Ni : 58.6}
 \end{array}$$

2. Though the isotopes have different mass yet they don't have any different (significant) position in the periodic table.
3. Subgroup elements do not have sufficient similarities in their properties yet they are placed in the same group.
4. The position of hydrogen is uncertain (either in Group I A or VII B).
5. The rare earth elements ($4f$ and $5f$ series) are all placed in Group III A and they do not have any separate position in the table.
6. The classification of metals and non-metals is not done in this table.
7. In Group VIII, three elements are placed together.

Moseley's work

In 1913, Moseley performed an experiment in which he bombarded high speed electrons on different metal surfaces and obtained X-rays. He observed that there existed a systematic mathematical relationship between the wavelengths of the X-rays produced and the atomic numbers of the elements. This came to be known as Moseley's law and is expressed as:

$$\sqrt{\nu} \propto Z$$

where ν is the frequency of X-rays and Z is the atomic number of elements. The plot of $\sqrt{\nu}$ vs. Z is a straight line (Figure 2.2)

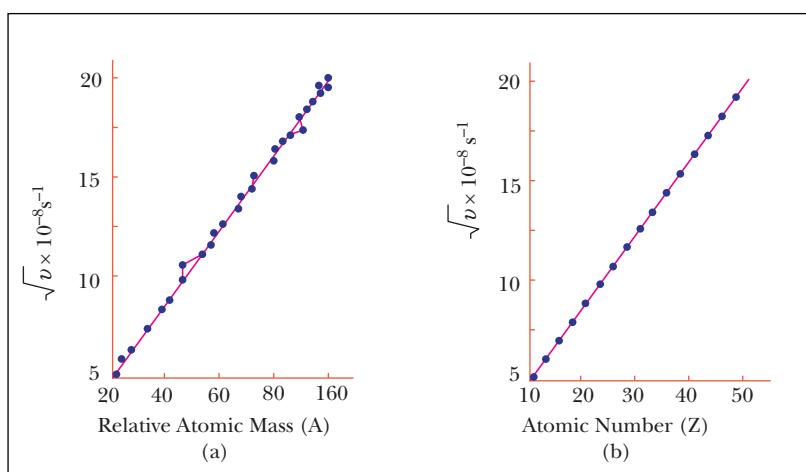


Figure 2.2 Plots obtained in Moseley's experiments.

Moseley's experiment showed that the proper sequence criterion for the periodic arrangement of atoms was not atomic weight but atomic number. The cause of similarity of properties was the repetition of the outer shell electronic configuration at regular intervals. This observation formed the basis of the modern periodic table.

Modern periodic law

According to the modern periodic law, the physical and chemical properties of the elements are the periodic functions of their atomic number. The long form of periodic table based upon the modern periodic law is depicted in Figure 2.3. Note that the arrangement of A and B subgroups is different from that in the modified form of Mendeleev's periodic table. The left and right corners of the table are assigned as subgroups A and the middle of the periodic table is assigned as subgroups B.

		s-Block (ns)										d-Block, ($n-1$) d							p-Block (np) (nonmetals)							
Group	Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	•						
		IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIIIB				IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	••					
1 (1s)	H 1			Transition metals (d-block)														H 1	He [†] 2							
2 (2s, 2p)	Li 3	Be 4															B 5	C 6	N 7	O 8	F 9	Ne 10				
3 (3s, 3p)	Na 11	Mg 12															Al 13	Si 14	P 15	S 16	Cl 17	Ar 18				
4 (4s, 3d, 4p)	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36								
5 (5s, 4d, 5p)	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54								
6 (6s, 4f, 5d, 6p)	Cs 55	Ba 56	La [*] 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86								
7 (7s, 5f, 6d, 7p)	Fr 87	Ra 88	Ac ^{**} 89	Unq 104 (Rf)	Unq 105 (Db)	Unq 106 (Sg)	Unq 107 (Bh)	Unq 108 (Hs)	Unq 109 (Mt)	Unq 110	Unq 111	Unq 112														

• New convention
•• Earlier convention

The Rate Earths, ($n-2$) f

f-block	*Lanthanides series(f1) Period: 6			Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
	**Actinide series(f5) Period: 7			Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

Post transition metals

Figure 2.3 The long form of modern periodic table and its segments.

Note: In some of the books, just to read easily, the groups are arranged as I A to VII A and then I B to VIII B from left to right. The naming of groups as A and B is of no significance as such and it is only the group number that is important, which is identical in both the arrangements.

2.2 | CLASSIFICATION OF ELEMENTS BASED ON ELECTRONIC CONFIGURATION

We have learnt that the assignment of all the electrons in an atom into specific shells or orbitals (s, p, d, f) is known as the element's electronic configuration. The elements can be arranged in the long form of the periodic table based on the electronic configuration and classified as s , p , d and f -block elements.

- 1. s-block elements:** If the last electron enters into s -orbital, the elements are called as s -block elements. The general valence (outermost) shell electronic configuration is given by ns^{1-2}
 - Alkali metals: $[IG] ns^1$
 - Alkaline earth metals: $[IG] ns^2$
where IG represents the inert gas core.
- 2. p-block elements:** If the last electron enters into the p -orbital, the elements are called as p -block elements. The general valence shell electronic configuration is $ns^2 np^{1-6}$. The p -block elements are placed in Group number III A to VIII A (13 to 18).
 - Valence shell electrons for s -block elements is equal to the number of electrons in the s orbital having the highest principal quantum number.
 - Valence shell electrons for p -block elements are equal to the number of electrons in the s and p orbitals having highest principal quantum number.

- c. The total number of valence shell electrons is equal to its group number according to *A* and *B* convention.
 - d. $\text{He}^+(ns^2)$ is excluded from *p*-block in terms of electronic configuration and it is better to consider it as *s*-block element. But according to its chemical behavior it is justified to place it in the Group 0, that is, Group 18.
3. ***d*-block elements:** If the last electron enters into *d* orbital, the elements are called as *d*-block elements (except Thorium). The general valence shell electronic configuration is:

$$ns^{0-2}(n-1)d^{1-10}$$

or $ns^{1-2}(n-1)d^{1-10}$ (except for palladium)

Total valence shell electrons of *d*-block elements = Total number of electrons in the outermost shell (*ns* orbital) and penultimate shell [$(n-1)$ *d* orbitals]. For example,

In Co : [Ar] $4s^2 3d^7 : 2 + 7 = 9$, the maximum number of electrons that can be lost is 9 though it is not yet observed.

In Fe : [Ar] $4s^2 3d^6 : 2 + 6 = 8$, the maximum number of electrons that can be lost is 8. It is also not yet observed but in case of Ru and Os this situation is observed in compounds RuO_4 and OsO_4

4. ***f*-block elements:** If the last electron of the elements enters into *f*-orbital, they are considered as *f*-block elements. The general valence shell electronic configuration is:

$$ns^2(n-1)d^{0-1}(n-2)f^{1-14}$$

Total valence shell electrons = Electrons present in *ns*, $(n-1)$ *d* and $(n-2)$ *f* orbitals or subshells.

Prediction of period and group number of an element from its electronic configuration

1. **For the period:** The highest principal quantum number available in the electronic configuration is the period number of that element (except in the case of Pd).
2. **For the group number:**
 - a. For *s*-block elements: Total number of valence shell electrons is the group number of it.
 - b. For *p*-block element: $(\text{Total number of valence shell electron} + 10) = \text{Group number of it.}$
 - c. For *d*-block element: Total number of valence shell electrons is the group number.
 - d. For *f*-block element: All elements are placed in the Group III or Group III B.

Neil Bohr's classification

According to Neil Bohr's classification, the elements in the periodic table can be classified as:

1. **Inert elements:** These include noble (inert) gases, He to Rn.
2. **Normal or Representative elements:** These are elements which involve outer shells consisting solely of *s*- and *p*-electrons (except inert gases).
3. **Transition elements (*d*-block) elements:** These are defined as 'elements having vacant or partially vacant *d*-orbital in their ground state or stable oxidation state'. (Nowadays Zn, Cd, Hg are not considered as transition elements, they are simply known as *d*-block elements.)
4. **Inner transition elements (*f*-block) elements:** These include two series of elements from atomic numbers

58(Ce) to 71 (Lu) and 90 (Th) to 103 (Lr)

Naming of super heavy elements

In 1977, IUPAC recommended a method of naming the super heavy elements from their atomic number. The digits of atomic number of an element are expressed serially using the following numerical roots:

0 = <i>nil</i>	4 = <i>quad</i>	8 = <i>oct</i>
1 = <i>un</i>	5 = <i>pent</i>	9 = <i>enn</i>
2 = <i>bi</i>	6 = <i>hex</i>	
3 = <i>tri</i>	7 = <i>sept</i>	

Then successive roots are put together and the name is ended with *ium*. When some letters are repeated, then the following precedence is to be adopted:

$$tri + ium = trium, \quad enn + nil = ennil$$

Some illustrations for naming these are given as follows:

Atomic number	Numerical roots	Name	Symbol
101	<i>un+nil+un</i>	<i>Unnilunium</i>	<i>Unu</i>
105	<i>un+nil+pent</i>	<i>Unnilpentium</i>	<i>Unp</i>
111	<i>un+un+un</i>	<i>Unununium</i>	<i>Uuu</i>
212	<i>bi+un+bi</i>	<i>Biunbium</i>	<i>Bub</i>

2.3 | PERIODIC TRENDS IN PROPERTIES

The trends that occur in the characteristic properties of the elements in the periodic table allow us to accurately predict the properties and reactions of these elements.

Atomic radius

The radius of the atom is the distance from the nucleus to the outermost electron or up to point at which the probability of finding of electron is the maximum. Since the atoms are not available in the atomic state in most of the cases, three kinds of atomic radii are measured for any atom and these are covalent radius, van der Waals radius and metallic radius. The three types of radii are discussed as follows.

Covalent radius

The covalent radius of an element represents the contribution of that element to the length of a bond that is predominantly covalent. For example, the covalent radius of any element A is taken to be one half of the internuclear distance in the homonuclear diatomic molecule A_2 as shown in Figure 2.4.

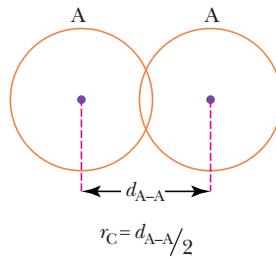


Figure 2.4 Covalent radius of homonuclear diatomic molecule.

The covalent radius is given by

$$r_C = \frac{d_{A-A}}{2}$$

where d_{A-A} is the internuclear distance between the two same atoms when they are covalently bonded.

When two different atoms are covalently bonded then the equation given by Schomaker and Stevenson is used to obtain the covalent radius (Figure 2.5).

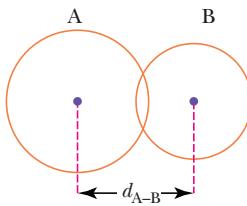


Figure 2.5 Covalent radius of heteronuclear diatomic molecule.

The covalent radius, when r_A and r_B are expressed in Å is given by

$$d_{A-B} = r_A + r_B - 0.09\Delta\chi$$

where,

d_{A-B} = Internuclear distance between A and B

$$r_A = \text{covalent radius of A} = \frac{d_{A-A}}{2}$$

$$r_B = \text{covalent radius of B} = \frac{d_{B-B}}{2}$$

$\Delta\chi$ = Difference in electronegativity between A and B

0.09 Å = a constant

When r_A and r_B are expressed in picometers, then the equation is given by

$$d_{A-B} = r_A + r_B - 9\Delta\chi$$

where $1\text{\AA} = 10^{-10}\text{m}$ and $1\text{picometer} = 10^{-12}\text{m} \Rightarrow 1\text{\AA} = 10^2 \text{ picometer}$.

In the later stage, the above equation was modified by Pauling and Stevenson as

$$d_{A-B} = r_A + r_B - |C_A\chi_A - C_B\chi_B|$$

C_A and C_B are constants for two different atoms and χ_A and χ_B are the electronegativities of A and B.

Metallic radius

For metals the metallic radius is defined as half of the internuclear distance separating two adjacent metal atoms in a metallic lattice (Figure 2.6).

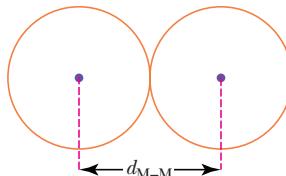


Figure 2.6 Metallic radius

Metallic radius is given by

$$r_M = \frac{d_{M-M}}{2}$$

where d_{M-M} is the internuclear distance between two metal atoms in their metallic lattice.

van der Waals radius

The sum of the van der Waals radii of two atoms is the shortest distance between two immediately adjacent atoms (either of same or different elements) in the structure of the solid compound in which they are not bonded to each other (Figure 2.7).

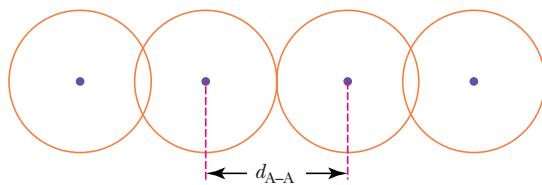


Figure 2.7 van der Waals radius

The van der Waals radius is given by

$$r_v = \frac{d_{A-A}}{2}$$

If any particular element can provide all three kinds of radius then

$$r_v > r_M > r_C$$

Otherwise, generally van der Waals radius > covalent radius.

Note: The radii of the inert gas elements is generally expressed in terms of only van der Waals' radii because most of these gases (other than xenon and krypton) do not form chemical compounds. In the compounds of xenon and krypton with oxygen and fluorine, the radii are expressed in terms of covalent radii.

Periodic variation of atomic radii

1. Variation in a period: In representative (*s*- and *p*- block) elements, there is a general decrease of atomic radius in a period because the effective nuclear charge (Z_{eff}) increases across a row. If all are van der Waals radii, then



For covalent radii

$$\underbrace{\text{Ne}}_{\substack{\text{van der} \\ \text{Waals} \\ \text{radius}}} > \underbrace{\text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}}_{\text{Covalent radius}}$$

For *d*-block elements, the variation of atomic radii in a period is depicted in Figure 2.8. The atomic radius initially decreases, then remains constant and finally increase again. The values of the radii of *d*-block elements and trends in the sizes are discussed further in chapter 11.

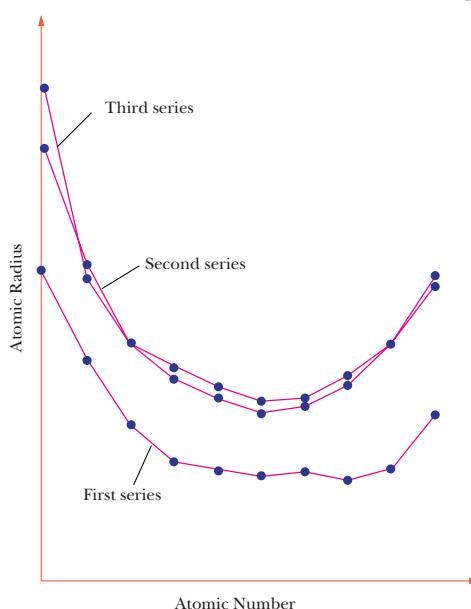
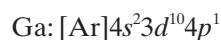


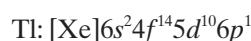
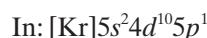
Figure 2.8 Variation of atomic radii of *d*-block elements in a period.

2. Variation in a group: For representative (*s*- and *p*- block) elements, the atomic radii increases down the group. This is due to successive use of orbitals with principal quantum number (*n*) one higher than the last. Some exceptions to this are:

a. The radius of gallium is expected to be greater than that of aluminium but $r_{\text{Al}} \approx r_{\text{Ga}}$. This behavior can be explained on the basis of electronic configuration for the two elements and the poor shielding effect of *d*-electrons.



b. Similarly, the radius of thallium is expected to be greater than that of indium but $r_{\text{In}} \approx r_{\text{Tl}}$. This is explained on the basis of electronic configuration and poor shielding of *d* and *f* electrons



For *d*-block elements, the trend in atomic radii is: $r_{3d \text{ series}} < r_{4d \text{ series}} \approx r_{5d \text{ series}}$

This is because the radius increases as the shell number increases. The radius of elements of *4d*- series is about the same as elements of *5d* series. This is due to the lanthanoid contraction that causes increase in Z_{eff} value due to poor shielding of fourteen *f* electrons. The exception to this behaviour is : $\text{Sc} < \text{Y} < \text{La}$. This is because there is no *4f* electron in the electronic configuration of La.

For *f*-block elements, in lanthanoids, the variation of atomic radii with increasing atomic number is presented in the graph depicted in Figure 2.9. The effective nuclear charge increases along the period so the atomic radius for the elements decreases. The exceptions to the trend are Eu and Yb and the explanation for this is discussed in Chapter 12.

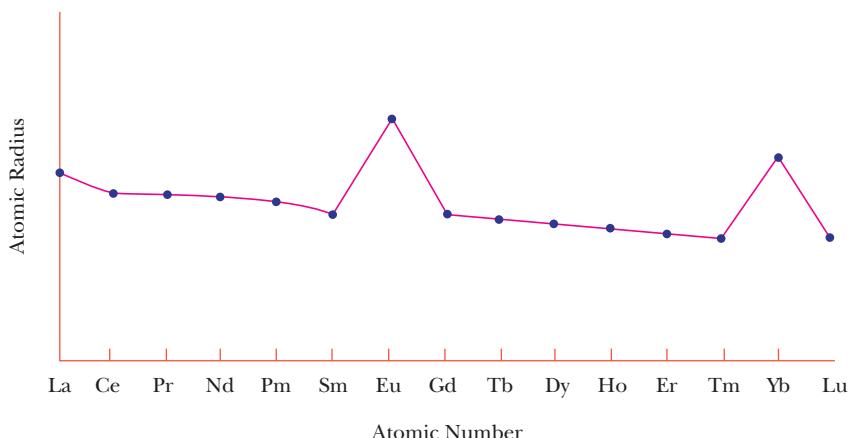


Figure 2.9 Variation in atomic radii with increase in atomic number for lanthanoids.

For actinoids, there is a smooth decrease in atomic radius from Th to Lr.

Ionic radius

When a positive ion is formed, the number of positive charges on the nucleus exceeds the number of electrons and effective nuclear charge is increased, resulting in the remaining electrons being attracted more strongly by the nucleus. Thus a positive ion is always smaller than the corresponding atom and more the electrons removed smaller is the ion.

When a negative ion is formed, one or more electrons are added to an atom and the effective nuclear charge is reduced. The electron cloud expands and the size of negative ion is more than that of the atom (Figure 2.10).

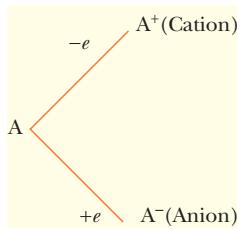


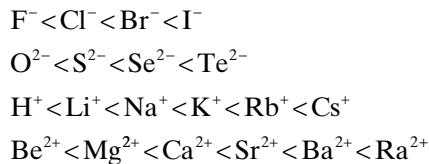
Figure 2.10 Formation of positive and negative ions from an atom.

Thus the order of radius is:



Ionic radius depends upon following factors:

1. If the shell number increases the ionic radius increases. Therefore, in a group, the ionic radius increases. For example,



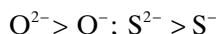
2. The trend in the radius of ions is:

- a. If the charge of cation increases, the ionic radius decreases. For example,

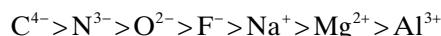


The smallest cation is H^+ .

- b. If the charge of anion increases, the ionic radius increases. For example,



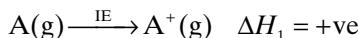
3. For isoelectronic species, as the number of protons increases the radius of ion decreases.



Note: The smallest anion is F^- and not H^- (ionic radius 208 pm). The radius order of anions is $F^- < Cl^- < Br^- < H^- < I^-$. The exception in the size of H^- is because this is the only anion with e/p ratio = 2.

Ionization energy

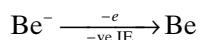
Ionization energy (IE) is the energy required to remove an electron from an isolated gaseous atom in its ground state.



It is measured in eV atom⁻¹ or kJ mol⁻¹.

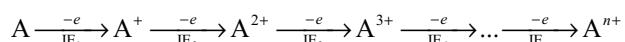
Some characteristic features of ionization energy are listed as follows:

1. The ionization energy for an atom is always positive and for an ion may be negative.



2. Successive ionization energy always increases for any species because the e/p ratio gradually decreases.

Thus,



$$IE_1 < IE_2 < IE_3 < IE_4 < \dots < IE_n$$

Note that:

$$IE_1 \text{ of } A^+ = IE_2 \text{ of } A, IE_1 \text{ of } A^{2+} = IE_2 \text{ of } A^+ = IE_3 \text{ of } A$$

3. Observing the sudden jump of successive IE values we can predict the number of valence shell electrons of the corresponding atom. For example,

Element	IE ₁	IE ₂	IE ₃	IE ₄	IE ₅	No. of valence electrons
Na	5.139	47.28	71.68	98.91		1
Ge	11.26	26.38	47.44	77.41	392.07	4
Al	5.98	18.22	28.44	119.4		3

*Ionization energy is expressed in eV/atom⁻¹.

Sodium achieves stable configuration of neon after losing one electron. Germanium achieves stable configuration of [Ar]3d¹⁰ after losing four electrons and aluminium loses three electrons to achieve stable configuration of neon. Hence, they do not show tendency to lose any more electrons and sudden jump in the values of IE are observed.

Ionization energy **depends upon** the following factors:

1. It decreases when shell number or the radius increases.
2. It increases when Z_{eff} increases.
3. It decreases when σ (shielding constant) increases.
4. It is more for half-filled and fully-filled electronic configurations.
5. It also depends upon the orbitals from which the electron is removed. If the principal quantum number is the same, then the energy required for removal of electrons from different orbitals shows the following order: $s > p > d > f$.

Periodic variations in ionization energy

The trends in ionization energy of elements in the periodic table are discussed as follows:

1. For representative (s- and p- block) elements:

- a. *In a period:* The Z_{eff} increases in a period, hence IE increases. The observed overall values for periods show the following order:

$$\begin{array}{l} \text{Irregular trend: } \left. \begin{array}{l} \text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne} \\ \text{Na} < \text{Al} < \text{Mg} < \text{Si} < \text{S} < \text{P} < \text{Cl} < \text{Ar} \\ \text{K} < \text{Ga} < \text{Ca} < \text{Ge} < \text{Se} < \text{As} < \text{Br} < \text{Kr} \end{array} \right\} \\ \text{Regular trend: } \left. \begin{array}{l} \text{Rb} < \text{Sr} < \text{In} < \text{Sn} < \text{Sb} < \text{Te} < \text{I} < \text{Xe} \\ \text{Cs} < \text{Ba} < \text{Tl} < \text{Pb} < \text{Bi} < \text{Po} < \text{At} < \text{Rn} \end{array} \right\} \end{array}$$

Some exceptions to the trend are:

(i) $\text{Be} > \text{B} \quad \text{Mg} > \text{Al} \quad \text{Ca} > \text{Ga}$

Be, Mg and Ca have fully-filled ns^2 orbitals and hence higher IE values, while B, Al and Ga attain fully-filled ns^2 configuration on losing one electron.

(ii) $\text{N} > \text{O} \quad \text{P} > \text{S} \quad \text{As} > \text{Se}$

N, P and As have half-filled electronic configuration and hence higher IE values, while O, S and Se achieve half-filled configuration on loss of one electron.

(iii) a. IE_2 of Group I A $>$ IE_2 of Group II A elements

b. IE_2 of Group V A $>$ IE_2 of Group VI A elements

- b. *In a group:* The IE generally decreases down a group. Some exceptions to the trend are:

(i) $\text{Al}_{5.98 \text{ eV}} \approx \text{Ga}_{5.99 \text{ eV}}$ (due to poor shielding of ten d electrons in Ga)

(ii) $\text{In}_{5.78 \text{ eV}} < \text{Tl}_{6.01 \text{ eV}}$ (due to lanthanoid contraction)

Hence, the overall order for the group is

$\text{B} > \text{Tl} > \text{Ga} \geq \text{Al} > \text{In}$

- c. $\text{Sn}_{7.344 \text{ eV}} < \text{Pb}_{7.416 \text{ eV}}$ (due to lanthanoid contraction in Pb)

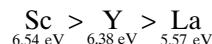
The overall order for its group elements is:



2. For *d*-block elements:

In a period: There is slight increase due to increase in Z_{eff} values along the period but it is not prominent. But there is a sudden jump from copper to zinc, silver to cadmium and gold to mercury because of full-filled configurations.

In a group: IE_1 of $3d$ series $\approx \text{IE}_1$ of $4d$ series while IE_1 of $4d$ series $< \text{IE}_1$ of $5d$ series due to lanthanide contraction. The exception to the trend is:



Note that lanthanide contraction is not observed in case of lanthanum.

Applications of ionization energy

1. Low ionization energy of an element indicates that metallic or electropositive character is more.
2. High ionization energy of an element indicates that element is either an inert gas or halogen.
3. Low ionization energy of an element means reactivity of the element is more by means of loss of electron.
4. Low ionization energy of an element means that its reducing power is high. For example, for alkali metals the reducing power order is



The exception of lithium atom is due to its high hydration energy and this will be discussed on Chapter 9.

5. If the difference in ionization energy, that is, $\Delta(\text{IE}_2 - \text{IE}_1)$ is greater than 16 eV atom^{-1} , then the $(+1)$ oxidation state is stable. For example, for Na, $\Delta(\text{IE}_2 - \text{IE}_1) \approx 41 \text{ eV atom}^{-1} \Rightarrow \text{Na}^+$ is more stable.
6. If value of $\Delta(\text{IE}_2 - \text{IE}_1)$ is less than 11 eV atom^{-1} then the $(+2)$ oxidation state is stable. For example, for Mg, value of $\Delta(\text{IE}_2 - \text{IE}_1) \approx 7 \text{ eV atom}^{-1} \Rightarrow \text{Mg}^{2+}$ is more stable.

Electron affinity

Electron affinity is the energy released when one mole of electron is added to one mole of an element in its isolated gaseous state (ground state).



It is represented as EA and its unit is eV atom^{-1} or kJ mol^{-1} or kcal mol^{-1} . It is also known as electron gain enthalpy and represented as ΔH_{eg} .

According to the *old convention*, for an element A



The negative sign indicates that energy is released. For those cases in which energy is absorbed the EA value considered as zero.

According to the *new convention*, ΔH_{eg} may be negative or positive depending upon the circumstance and



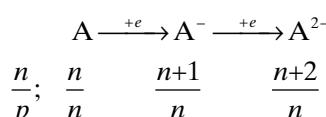
While at any other temperature T,

$$\Delta H_{\text{eg}} = -EA - \frac{5}{2}RT$$

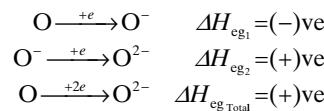
Hence, it is better to consider $\Delta H_{\text{eg}} \approx -EA$.

Note:

- (i) $EA_1 > EA_2$, that is for an element, the electron affinity for the first electron is greater than that of the second electron.

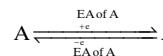


(ii) Successive electron affinity always decreases. For example,



(iii) ΔH_{eg_2} for all elements is positive.

(iv) The electron affinity and ionization energy are related as



It is clear that

$$|\text{EA of } A| = |\text{IE of } A^-|$$

Accordingly,

$$|\text{EA of } A^+| = |\text{IE of } A|$$

$$|\text{EA of } A^{2+}| = |\text{IE of } A^+|$$

... and so on

Periodic trends of electron affinity

For representative (s- and p-block) elements:

- a.** *In a group:* There is decrease of electron affinity in general but for p-block elements only the EA_1 of second period element is less than EA_1 of third period element.

Second period		Third period
B	<	Al
C	<	Si
N	<	P
O	<	S
F	<	Cl

The third period elements have larger size and vacant 3d orbitals, which can accommodate incoming electron easily.

- b.** *In a period:* The electron affinity increases from left to right as Z_{eff} increases (except inert gases) in a period. Some exceptions to the trend are:

- (i)** EA of alkali metals > EA of alkaline earth metals, depicted as follows:

Alkali metals	Alkaline earth metals
$ns^1 \xrightarrow{+e} ns^2$	$ns^2 \xrightarrow{+e} ns^2 np^1$
Fully-filled electronic configuration is achieved	Fully-filled electronic configuration is disturbed
ΔH_{eg} is (-)ve	ΔH_{eg} is (+)ve

- (ii)** EA of C > EA of N. Similarly,

$$\begin{array}{l} \text{EA of Si} > \text{EA of P} \\ \text{EA of Ge} > \text{EA of As} \\ \text{EA of Sn} > \text{EA of Sb} \\ \text{EA of Pb} < \text{EA of Bi} \end{array}$$

- (iii)** EA of Group IA > EA of Group IIIA

$$\begin{array}{l} \text{EA of Li} > \text{EA of B} \\ \text{EA of Na} > \text{EA of Al} \\ \text{EA of K} > \text{EA of Ga} \\ \text{EA of Rb} > \text{EA of In} \\ \text{EA of Cs} > \text{EA of Th} \end{array}$$

On addition of an electron, the elements C, Si, Ge and Sn achieve half-filled electronic configuration while in case of N, P, As and Sb do not have the tendency to gain electron and thus lose their half-filled configuration.

Electron affinity **depends** upon a number of factors, that include:

1. It decreases when radius increases.
2. It increases when Z_{eff} increases.
3. It decreases when σ increases.
4. EA of half-filled and full-filled electronic configuration is less.
5. EA order for addition of electron in different orbitals having the same principal quantum number is $s > p > d > f$

Note: Some general observations are listed as follows.

1. ΔH_{eg_1} is negative for most of the elements.
2. ΔH_{eg_1} is positive for:
 - a. inert gas elements.
 - b. alkaline earth metals (Be and Mg only).
 - c. for N only

Electronegativity

In 1931, Pauling defined electronegativity of an atom as the tendency of the atom to attract electrons (bond pair) towards itself when combined in a compound. It is a unitless and dimensionless quantity.

Electronegativity **depends** upon the following factors:

1. It decreases when radius increases.
2. It increases when Z_{eff} increases.
3. It decreases when σ (shielding constant) increases.
4. It increases when the oxidation state of an element increases.
5. It increases as much the percentage of s character in hybrid orbital increases. For example,

Carbon compound	Hybridization	Electronegativity value
\ / -C - C - / \	sp^3	2.5
\ / C = C / \	sp^2	2.75
-C ≡ C -	sp	3.25

If two atoms have similar electronegativities, that is similar tendencies to attract electrons, the bond between them is largely covalent. But when the difference between the electronegativities is large, the bond has high degree of polar character. Some important approaches for obtaining values of electronegativity are discussed as follows:

1. **Pauling scale:** This scale is based upon energy calculation and the expression is

$$\chi_A \sim \chi_B = 0.102\sqrt{\Delta_{A-B}} \quad (\text{when energies are expressed in kJ mol}^{-1})$$

$$\text{or } \chi_A \sim \chi_B = 0.208\sqrt{\Delta_{A-B}} \quad (\text{when energies are expressed in kcal mol}^{-1})$$

where χ_A is electronegativity of A, χ_B is electronegativity of B;

Δ_{A-B} is the resonance energy of bond A – B = $|E_{A-B}$ (observed) – E_{A-B} (theoretical)|

$$E_{A-B} \text{ (theoretical)} = \sqrt{E_{A-A} \times E_{B-B}}$$

The values of electronegativity in Pauling scale for different elements are given as follows:

F	O	Cl	N	Br	I	S	C	P	H	B	Si
4	3.5	3.16	3.04	2.85	2.55	2.58	2.5	2.18	2.1	2.04	1.8

2. Mulliken scale: Mulliken suggested an alternate approach to electronegativity based on the ionization energy and electron affinity of the element. In this scale, the electronegativity is given by the relation

$$\chi_M = \frac{IE + EA}{2}$$

where IE and EA are expressed in eV atom⁻¹. Thus electronegativity is the average of ionization energy and electron affinity. The values of electronegativity are about 2.8 times larger than the Pauling values. Thus the relationship more in use is

$$\chi_P = \frac{\chi_M}{2.8}$$

More accurately

$$\chi_P = 0.336\chi_M - 0.2$$

3. Allred Rochow scale: Allred defined electronegativity as the attractive force between nucleus and an electron at a distance equal to covalent radius. In this scale, the electronegativity is given by

$$\chi_{AR} = \frac{0.359 Z_{eff}}{r^2}$$

where r is the covalent radius in Å and Z_{eff} is the effective nuclear charge on the incoming electron or peripheral electron. The following equation gives the correlation of χ_{AR} with χ_P

$$\chi_P = \chi_{AR} + 0.744$$

Periodic variations of electronegativity

1. In a period, the electronegativity increases from left to right as Z_{eff} increases.
2. In a group, the electronegativity decreases in general.

Some important points related to electronegativity are listed as follows:

1. Fluorine has the highest electronegativity in the periodic table, that is, 4.
2. Caesium is having lowest electronegativity in the periodic table, that is, 0.7(excluding the radioactive element Fr).
3. Alkali metals have the lowest electronegativity in their respective period.
4. Halogens have the highest electronegativity in their respective period.
5. Electronegativity of inert gases is zero.

Applications of Electronegativity

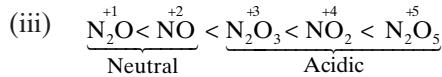
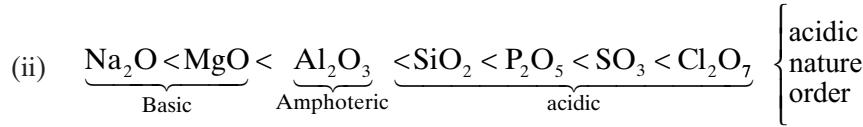
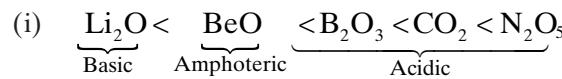
Some applications of electronegativity are listed as follows:

1. Percentage ionic character in a bond can be calculated using Haney-Smith equation:

$$\% \text{ ionic character} = 16|\Delta\chi| + 3.5(\Delta\chi)^2$$

where $\Delta\chi$ is the difference in electronegativity between the two atoms.

2. The acidic and basic properties of metal oxides can be predicted. As $\Delta\chi$ increases, the acidic strength of oxides of different elements decreases. For example,



In aqueous medium, the acidic oxides lead to formation of acids HNO_2 and HNO_3 .



acidic nature order

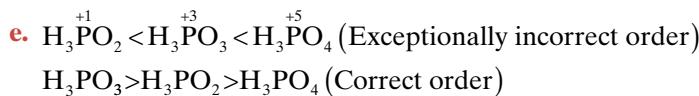
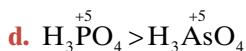
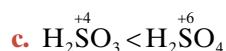
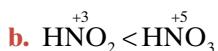
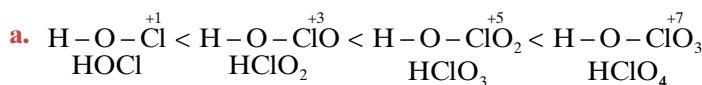
Note: Some important points to note are as follows:

- a. Most of the metallic oxides are basic in nature except ZnO , Al_2O_3 , PbO , PbO_2 , SnO , SnO_2 , BeO , which are amphoteric in nature.
- b. In general alkali metal and alkaline earth metal oxides are more basic compared to oxides of d -block elements.
- c. For those oxides which are basic or acidic or amphoteric, the corresponding hydroxides are also of similar nature.

Basic oxide	Basic hydroxide	Acidic oxide	Acidic hydroxide	Amphoteric oxide	Amphoteric hydroxide
Na_2O	NaOH	SiO_2	$\text{Si}(\text{OH})_4$	Al_2O_3	$\text{Al}(\text{OH})_3$
MgO	$\text{Mg}(\text{OH})_2$	B_2O_3	$\text{B}(\text{OH})_3$	ZnO	$\text{Zn}(\text{OH})_2$
MnO	$\text{Mn}(\text{OH})_2$	N_2O_5	HNO_3	BeO	$\text{Be}(\text{OH})_2$
CuO	$\text{Cu}(\text{OH})_2$				

- d. Amphoteric substance is one which reacts with both acid as well as base. Neutral substance does not react with acid as well as base and when passed through water keeps it neutral.

3. The strength of oxyacids can be predicted easily, provided the number of OH group attached to central atom remains the same. Some examples are:

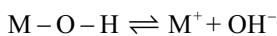


Note: The oxidation state is the formal charge developed by a particular atom by shifting the bond pair towards more electronegative atom completely. For example



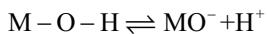
4. M–O–H like compound will act as acid or as base can be predicted very easily.

a. Acts as a base when



$$|\chi_O - \chi_M| > |\chi_O - \chi_H|$$

b. Acts as an acid when



$$|\chi_O - \chi_H| > |\chi_O - \chi_M|$$

Some example are:

(i) Cs–O–H is a base because

$$\chi_O - \chi_{Cs} = 3.5 - 0.7 = 2.8$$

while

$$\chi_O - \chi_H = 3.5 - 2.1 = 1.4$$

(ii) Cl–O–H is an acid because

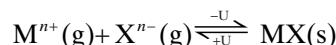
$$\chi_O - \chi_{Cl} = 3.5 - 3.16 = 0.34$$

while

$$\chi_O - \chi_H = 3.5 - 2.1 = 1.4$$

Lattice Energy

Lattice energy is the characteristic of ionic compounds. It is the energy released to form one mole of ionic compound (in solid form) from their respective isolated gaseous ions.



The mathematical relation for lattice energy is as follows:

$$\text{Lattice energy} = \int_{\infty}^r \frac{kq_1q_2dr}{r^2} = -\frac{kq_1q_2}{r}$$

The order for lattice energy is:



where X = F, Cl, Br, I

Similarly,

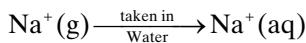


and

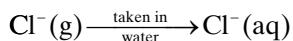


Hydration Energy

Hydration energy is the energy released when an isolated gaseous ion gets hydrated and it is measured in terms of kJ mol^{-1} or kJ ion^{-1} . The hydration process can be depicted as follows:



$$\Delta H_{\text{hydration}}(\text{cation}) = (-)\text{ve}$$



$$\Delta H_{\text{hydration}}(\text{anion}) = (-)\text{ve}$$

$$\text{Total hydration energy} = \Delta H_{\text{hydration}}(\text{cation}) + \Delta H_{\text{hydration}}(\text{anion})$$

Hydrated radius: It is the distance from the nucleus of a particular ion to that particular point up to which the associated water molecules are immobile due to its attraction (Figure 2.12).

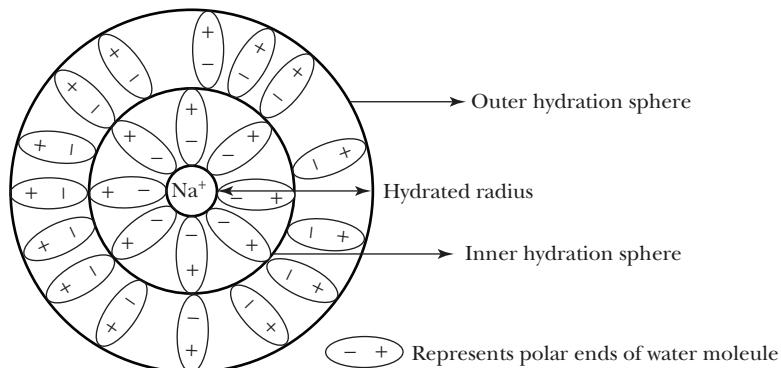
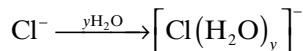
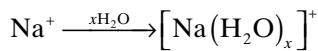


Figure 2.12 Hydrated Na^+ ion

Hydration number: It is the number of water molecules associated to a particular ion when it is hydrated. For example,



x : Hydration number for Na^+

y : Hydration number for Cl^-

Hydration energy, hydrated radius and hydration number of a particular ion depends upon the charge per unit area. Hence their order is the same for the following cations in the given examples:

- (i) $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq}) > \text{K}^+(\text{aq}) > \text{Rb}^+(\text{aq}) > \text{Cs}^+(\text{aq})$
- (ii) $\text{Be}^{2+}(\text{aq}) > \text{Mg}^{2+}(\text{aq}) > \text{Ca}^{2+}(\text{aq}) > \text{Sr}^{2+}(\text{aq}) > \text{Ba}^{2+}(\text{aq})$
- (iii) $\text{F}^-(\text{aq}) > \text{Cl}^-(\text{aq}) > \text{Br}^-(\text{aq}) > \text{I}^-(\text{aq})$
- (iv) $\text{Fe}^{2+}(\text{aq}) < \text{Fe}^{3+}(\text{aq})$

Ionic Mobility

Ionic mobility is defined as the ability of an ion to move in an aqueous solution. Larger the hydrated radius, lesser is the ionic mobility, that is,

$$\text{Ionic mobility} \propto \frac{1}{\text{Hydrated radius of ion}}$$

Thus, the order of ionic mobility is in the reverse order of the hydrated radius order, for example

- (i) $\text{Li}^+(\text{aq}) < \text{Na}^+(\text{aq}) < \text{K}^+(\text{aq}) < \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$
- (ii) $\text{Be}^{2+}(\text{aq}) < \text{Mg}^{2+}(\text{aq}) < \text{Ca}^{2+}(\text{aq}) < \text{Sr}^{2+}(\text{aq}) < \text{Ba}^{2+}(\text{aq})$
- (iii) $\text{F}^-(\text{aq}) < \text{Cl}^-(\text{aq}) < \text{Br}^-(\text{aq}) < \text{I}^-(\text{aq})$
- (iv) $\text{Na}^+(\text{aq}) > \text{Mg}^{2+}(\text{aq}) > \text{Al}^{3+}(\text{aq})$

SINGLE CORRECT CHOICE TYPE QUESTIONS

1. From the given information of element M

$$M \rightarrow M^{3+} + 3e^- \quad \Delta H = x \text{ kJ/mole}$$

$$\text{IE}_1(M) = y \text{ kJ/mole}$$

$$\text{IE}_1(M^{2+}) = z \text{ kJ/mole}$$

The value of $\text{IE}_2(M)$ will be

(A) $(x + y + z) \text{ kJ/mole}$

(B) $(x - y - z) \text{ kJ/mole}$

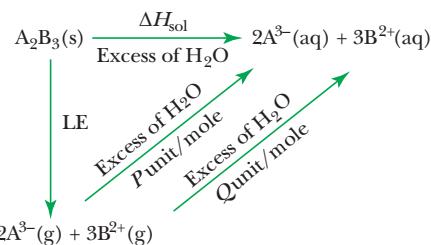
(C) $(x - y + z) \text{ kJ/mole}$

(D) $z - (x + y) \text{ kJ/mole}$

2. In the given cycle, if P and Q are the magnitude of hydration energies ($\Delta H_{\text{hydration}}$) per mole for A^{3+} (g) and B^{2-} (g) ions, respectively. Then the value of

$$\left(P + \frac{3}{2}Q \right)$$

(Consider only magnitude of $\Delta H_{\text{hydration}}$ and LE is the lattice energy of ionic compound.)



(A) $\frac{\Delta H_{\text{sol}} - \text{LE}}{2}$

(B) $\frac{3}{2}(\Delta H_{\text{sol}} - \text{LE})$

(C) $\Delta H_{\text{sol}} - \text{LE}$

(D) $\Delta H_{\text{sol}} + \text{LE}$

3. Two elements have set of quantum numbers of their last filled subshell of valence shell as follows:

$$X \rightarrow n = 4; l = 1$$

$$Y \rightarrow n = 5; l = 2$$

Then which statement is incorrect?

(A) Element Y has greater atomic number than atomic number of element X.

(B) Element X has 10 electrons in d subshell.

- (C) Element X is not a transition element.

- (D) Atomic size of element Y is equal to the atomic size of element X.

4. Which of the following elements have electron affinity greater than S?

(A) O

(B) Se

(C) Te

(D) None of these

5. Among O, O^+ , O^{2+} and O^2- , the species having most positive and most negative value of ΔH_{eg} are, respectively

(A) O^+ and O

(B) O^{2+} and O^{2-}

(C) O and O^{2-}

(D) O^{2-} and O^{2+}

6. Select the correct order for the property given in brackets.

(A) $\text{F}^+(\text{g}) < \text{Cl}^+(\text{g})$: (EA order)

(B) $\text{F}(\text{g}) < \text{Cl}(\text{g})$: (ΔH_{eg} order)

(C) $\text{O}(\text{g}) > \text{S}(\text{g})$: (ΔH_{eg} order)

(D) $\text{S}^{2-}(\text{g}) < \text{Cl}^-(\text{g})$: (IE order)

7. For electronic configuration

$ns^2 (n-2) f^{1-14} (n-1)d^{0-1}$, if $n = 7$, then the element belongs to

(A) Lanthanoids

(B) Actinoids

(C) Inner transition elements

(D) Both (B) and (C)

8. The valence shell of the element X contains 2 electrons in $5s$ subshell. Below that shell, element X has a partially filled $4d$ subshell, then what type of element is X?

(A) Alkali metal

(B) Alkaline earth metal

(C) Chalcogen

(D) None of these

9. Give the correct letter T for true and F for false for the following statements.

(I) For Mn, the order of energy is $3s = 3p = 3d$ for shell number 3.

(II) 32 elements are present in fifth period of long form periodic table.

(III) For Zr^{2+} ion, $\mu_m = \sqrt{8}$ BM

(IV) General valence shell electronic configuration for *f*-block elements is $(n-2)f^{1-14}(n-1)d^{10}ns^2$.

- (A) TTFT
 (B) TFTT
 (C) FFTF
 (D) FTTF

10. Match the elements with their corresponding IE_1 .

Column-I	Column-II
(P) N	(1) +800
(Q) O	(2) +900
(R) Be	(3) +1300
(S) B	(4) +1400

Code:

	P	Q	R	S
(A)	2	3	1	4
(B)	1	2	3	4
(C)	4	3	2	1
(D)	1	4	2	3

11. Match the elements of given atomic number with their properties.

Column-I	Column-II
(P) (11)	(1) IE is maximum
(Q) (19)	(2) $Z_{eff} = 2.2$ (on last electron)
(R) (37)	(3) Size largest
(S) (55)	(4) Position is next to Kr

Code:

	P	Q	R	S
(A)	1	1, 2	1, 2	3, 4
(B)	1, 2	2, 4	2, 4	2, 3
(C)	1, 2	2	2, 4	2, 3
(D)	2, 3	2	2, 4	2, 3

12. Match the species with their respective ionic size.

Column-I	Column-II
(P) Mg^{2+}	(1) 1.19 \AA
(Q) O^{2-}	(2) 0.72 \AA
(R) Na^+	(3) 1.16 \AA
(S) F^-	(4) 1.26 \AA

Code:

	P	Q	R	S
(A)	3	1	2	4
(B)	2	4	1	3
(C)	2	4	3	1
(D)	4	2	3	1

13. Match the electronic configuration with their respective ΔH_{eg} (kJ/mole)/value.

Column-I	Column-II
(P) $1s^2, 2s^2, 2p^6$	(1) -328
(Q) $1s^2, 2s^2, 2p^4$	(2) -122
(R) $1s^2, 2s^2, 2p^2$	(3) -141
(S) $1s^2, 2s^2, 2p^5$	(4) +116

Code:

	P	Q	R	S
(A)	3	1	2	4
(B)	2	4	1	2
(C)	2	4	3	1
(D)	4	3	2	1

14. Match the atoms/ions with their corresponding electron affinity. (eV/atom).

Column-I	Column-II
(P) F	(1) 3.4
(Q) F^-	(2) 17.4
(R) Cl	(3) 13
(S) Cl^+	(4) 3.6

Code:

	P	Q	R	S
(A)	1	3	4	2
(B)	2	1	3	4
(C)	1	2	4	3
(D)	3	1	2	4

15. Which of the following species has the highest electronegativity?

- (A) C (*sp* hybridized)
 (B) N (*sp*² hybridized)
 (C) N (*sp* hybridized)
 (D) C (*sp*³ hybridized)

16. Choose the correct order of ionic radius for the following species.

- (A) $Cl^- > I^- > Te^{2-} > Ar^+$
 (B) $Te^{2-} > I^- > Cl^- > Ar^+$
 (C) $I^- > Te^{2-} > Cl^- > Ar^+$
 (D) $I^- > Cl^- > Ar^+ > Te^{2-}$

17. Choose the correct order of radius for the following species.

- (A) $Na^+ < Na < Na^-$
 (B) $Na^- > Na^+ > Na$
 (C) $Na < Na^- < Na^+$
 (D) $Na > Na^+ > Na^-$

- 18.** Choose the correct order of ionization energy for the following species.
- (A) Sc > La > Y
 (B) Sc > Y ≈ La
 (C) Sc > Y > La
 (D) Sc < Y > La
- 19.** The electronegativities of two elements A and B are χ_A and χ_B respectively and the relationship between them is given by
- $$|\chi_A - \chi_B| = 0.102\sqrt{\Delta_{A-B}}$$
- where Δ_{A-B} is the resonance energy expressed in kJ mol^{-1} . If Δ_{A-B} is zero, then which of the following statements is true?
- (A) $\chi_A > \chi_B$
 (B) $\chi_A < \chi_B$
 (C) $\chi_A = \chi_B$
 (D) Cannot be predicted.
- 20.** Choose the incorrect order for acidic strength.
- (A) $\text{CO}_2 > \text{CO}$
 (B) $\text{SO}_2 < \text{SO}_3$
 (C) $\text{HClO}_2 > \text{HOCl}$
 (D) $\text{SiO}_2 > \text{CO}_2$
- 21.** Which of the following processes is endothermic?
- (A) $\text{S} \rightarrow \text{S}^-$
 (B) $\text{S}^- \rightarrow \text{S}^{2-}$
 (C) $\text{Na} \rightarrow \text{Na}^-$
 (D) $\text{P} \rightarrow \text{P}^-$
- 22.** Which of the following processes is exothermic?
- (A) $\text{N}^- \rightarrow \text{N}$
 (B) $\text{N} \rightarrow \text{N}^+$
 (C) $\text{N} \rightarrow \text{N}^-$
 (D) $\text{N}^+ \rightarrow \text{N}^{2+}$
- 23.** Which of the following statements is incorrect?
- (A) With the decrease in electronegativity in a group the metallic character increases.
 (B) Smaller ionization energy value indicates that electropositive character is more.
 (C) Electronegativity does not depend upon $Z_{\text{effective}}$.
 (D) Successive ionization energies always increase for an element.
- 24.** Write the period number, group number and block of the element having atomic number 42.
- (A) 5, 5, *d*
 (B) 5, 6, *d*
 (C) 5, 2, *d*
 (D) 5, 15, *p*
- 25.** The atomic numbers of two elements A and B are 17 and 20 respectively. The formula of an ionic compound made by A and B is (where the cation is conventionally written first)
- (A) AB
 (B) A_2B
 (C) AB_2
 (D) BA_2
- 26.** The successive ionization energies (IE) for an element A are as follows
- $$\text{A} \xrightarrow{\text{IE}_1} \text{A}^+ \xrightarrow{\text{IE}_2} \text{A}^{2+} \xrightarrow{\text{IE}_3} \text{A}^{3+} \rightarrow \dots$$
- If the IE_1 and IE_3 values are 27 kJ mol^{-1} and 51 kJ mol^{-1} respectively, then the value of IE_2 is _____ kJ mol^{-1} .
- (A) 21
 (B) 33
 (C) 59
 (D) 63
- 27.** Consider three hypothetical ionic compounds AB, A_2B and A_2B_3 where in all the compounds B is in -2 oxidation state and A has a variable oxidation state. What is the correct order of lattice energy of these compounds?
- (A) $\text{A}_2\text{B} > \text{AB} > \text{A}_2\text{B}_3$
 (B) $\text{A}_2\text{B}_3 > \text{AB} > \text{A}_2\text{B}$
 (C) $\text{AB} > \text{A}_2\text{B} > \text{A}_2\text{B}_3$
 (D) $\text{A}_2\text{B}_3 > \text{A}_2\text{B} > \text{AB}$
- 28.** Choose the correct order of the property given below:
- (A) $\text{N}^{3-} < \text{O}^{2-}$: Ionic radius
 (B) N > O: First ionization energy
 (C) N > O: Second ionization energy
 (D) N > O: Electron affinity order
- 29.** The ionization energies for B, Tl and In are x , y and z kcal mol^{-1} respectively. Choose the correct relationship between them.
- (A) $z > x \approx y$
 (B) $x > y > z$
 (C) $x > y > z$
 (D) $x < y > z$
- 30.** The smallest size cation and anion that can exist are respectively
- (A) H^+ and H^-
 (B) H^+ and F^-
 (C) Li^+ and F^-
 (D) Li^+ and H^-
- 31.** If the atomic number of an inert gas element is Z , then an element with which of the following atomic numbers will have the highest electronegativity according to Pauling scale?

- (A) $Z - 2$
(B) $Z + 1$
(C) $Z + 1$
(D) $Z + 2$

32. For an element the successive ionisation energy values (in eV atom⁻¹) are given below 12.32, 26.84, 44.56, 65.73, 203.9, 251.12, 308.4. The element that satisfies the above values is
(A) Si
(B) Ca
(C) Al
(D) S

33. What is the atomic number of the element which belongs to fifth period and Group 16?
(A) 50
(B) 34
(C) 52
(D) 53

34. Which of the following valence shell electronic configuration is correct for *d*-block elements?
(A) ns^2np^{1-6}
(B) ns^{1-2}
(C) $ns^{0-2}(n-1)d^{1-10}$
(D) None of these.

35. Identify the block to which an element with electronic configuration: [Kr]4d¹⁰4f⁴5s²5p⁶5d¹6s² belongs to
(A) *s*-block
(B) *p*-block
(C) *d*-block
(D) *f*-block

36. Find the electronic configuration of the element that is placed just below the element with atomic number 25 in the same group.
(A) 1s²2s²2p⁶3s²3p⁶4s²3d⁵
(B) 1s²2s²2p⁶3s²3p⁶4s²3d¹⁰4p⁶5s²4d⁵
(C) 1s²2s²2p⁶3s²3p⁶4s¹3d⁶
(D) 1s²2s²2p⁶3s²3p⁶4s²3d¹⁰4p⁶5s¹4d⁵

37. If an element X forms the highest oxide of the formula XO_3 , then it belongs to Group
(A) 14
(B) 15
(C) 16
(D) 17

38. The group number for the inner transition element is
(A) 3
(B) 6
(C) 4
(D) 8

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. Choose the correct statement among the following.

 - $IE_1(\text{Na}) < IE_1(\text{Mg})$
 - $IE_3(\text{Mg}) > IE_3(\text{Al})$
 - $IE_1(\text{Al}) < IE_1(\text{Mg})$
 - $IE_2(\text{N}) > IE_2(\text{O})$

2. If electronegativity of elements P, Q, R and S are respectively 0.8, 1.2, 1.8 and 2.5, then choose the hydroxides which are basic in nature.

(A) POH	(B) QOH
(C) ROH	(D) SOH

3. Which of the following ions have radius greater than F^- ?

(A) H^-	(B) Cl^-
(C) Br^-	(D) I^-

4. Consider two cations X and Y which have 8 and 18 electrons respectively in their outermost shell (both belong to 3d-series). Select the correct statement among the following.

 - Cation X and Y both have 8 electrons in their penultimate shell.
 - Difference between total number of electrons of X and Y is 10.
 - Cation Y may be of element Ni.
 - Cation X may be of element Sc.

5. An element has maximum values of quantum numbers as

Maximum value of $n = 4$,
 Maximum value of $l = 2$,
 Maximum value of $m = +2$,
 Maximum value of $s = +1/2$
 (Subshells having at least one electron are considered only.) Then select the incorrect statements.

 - Element belongs to 5d series.
 - Element must belong to p-block.
 - Element must have at least 4 electrons in d-subshell.
 - Element belongs to fourth period.

6. If two elements of p-block have difference of group number = 4, then difference of their valence shell electrons will not be

(A) 2	(B) 3
(C) 4	(D) 6

7. Which of the following is/are correct order of ionization energy?

 - $\text{Ag} > \text{Cu} > \text{Au}$
 - $\text{Sc} > \text{Y} > \text{La}$
 - $\text{Pd} < \text{Pt} < \text{Ni}$
 - $\text{Al} \leq \text{Ga} < \text{B}$

8. Which of the following elements have electron affinity greater than O?
- (A) F (B) S
(C) Se (D) Cl
9. An element with atomic number 48 ($Z = 48$) of the periodic table will
- (A) belong to p -block.
(B) be placed in group number 12.
(C) be called a transition element.
(D) have twenty electrons with $l = 2$.
10. Identify the correct statements among the following.
- (A) IE_{Zn} ($Z = 30$) $< IE_{Ga}$ ($Z = 31$).
(B) The Mulliken's scale of electronegativity = $(EA + IE)/2$, where EA and IE can be expressed in any energy unit.
(C) On Pauling's scale, electronegativity of F is maximum.
(D) $\chi_{Cs} < \chi_K$ (where χ is the electronegativity).
11. In which period or group of periodic table (long form) transition elements are not present?
- (A) Third group (B) Third period
(C) Twelfth group (D) Thirteenth group
12. Choose the correct ionization energy order for the given species:
- (A) $O > S > S^- > O^-$
(B) $F > F^- > Cl^- > Cl$
(C) $O > O^- > S^- > S$
(D) $F > Cl > Cl^- > F^-$
13. Which of the following statements are correct?
- (A) The electron affinity of Si is greater than that of C.
(B) BeO is amphoteric while B_2O_3 is acidic.
(C) The ionization energy of Tl is less than that of Al.
(D) The ionization energy of elements of Cu-group is less than that of the respective elements of Zn-group.
14. Choose the incorrect statements from the following:
- (A) Ionization energy of atom may be negative.
(B) Ionization energy of an ion may be negative.
(C) Ionization energy is inversely proportional to radius.
- (D) Electron present in p orbital is in need of less energy for its removal as compared to electron present in d orbital having the same principal quantum number.
15. Among the elements with the following atomic numbers, which are d -block elements?
- (A) 29 (B) 81
(C) 46 (D) 58
16. In which of the following processes the energy is being absorbed?
- (A) $Na(g) \rightarrow Na^-(g)$
(B) $Na^+ \rightarrow Na^+(aq)$
(C) $A^+(g) + B^-(g) \rightarrow AB(s)$
(D) $N(g) \rightarrow N^+(g)$
17. The formation of the oxide ion $O^{2-}(g)$ requires first an exothermic and then an endothermic step as shown below:
- $$O(g) + e^- \rightarrow O^-(g); \Delta H^\circ = -142 \text{ kJ mol}^{-1}$$
- $$O^-(g) + e^- \rightarrow O^{2-}(g); \Delta H^\circ = +844 \text{ kJ mol}^{-1}$$
- Which is not the cause of the above fact?
- (A) Oxygen is more electronegative.
(B) Oxygen has high electron affinity.
(C) O^- ion has comparatively larger size than oxygen atom.
(D) O^- ion will tend to resist the addition of electron.
18. IE_1 of an element is lower than that of IE_2 because
- (A) it is difficult to remove an electron from cation compared to from the same element.
(B) the ionisation process is endothermic.
(C) the size of cation is smaller than its atom.
(D) all of the above.
19. In which of the following statements is the correct order with respect to the given property?:
- (A) $Fe^{3+}(aq) > Fe^{2+}(aq)$: Ionic mobility order.
(B) $Br^-(aq) < Cl^-(aq) < F^-(aq)$: Hydrated radius order.
(C) $SbH_3 > AsH_3 > PH_3$: M – H bond polarity order.
(D) $S > C > H > B$: Electronegativity order.

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1– 2

Along the period, atomic/ionic radius and metallic character generally decreases, while IE, EN and nonmetallic character and oxidizing power increases.

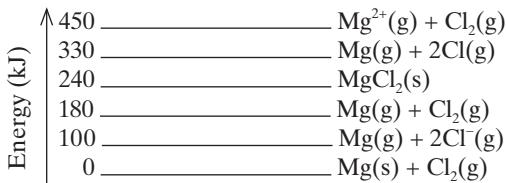
1. If the value of electron gain enthalpy (ΔH_{eg}) of 4 elements are given below, then the element which may behave as strongest oxidizing agent is

Element	ΔH_{eg}
P	-153 kJ/mole
Q	-90 kJ/mole
R	86 kJ/mole
S	-209 kJ/mole
(A) Q	(B) P
(C) S	(D) R

2. If the ionic radius of M^+ and X^- are about 135 and 209 pm respectively, then the expected values of atomic radius of M and X may be respectively (in pm) (M and X are metal and non-metal, respectively of same period.)
- (A) 180, 90
(B) 135, 209
(C) 90, 180
(D) same radius which is average of 135 and 209 pm.

Passage 2: For Questions 3–4

Born Haber cycle is used to calculate enthalpy of formation of ionic compounds. It is based on Hess's law which states that enthalpy of reaction does not depend upon the method followed by the reaction. Energy of some systems is given below:



Using the given data, answer the following questions.

3. The enthalpy of formation (in kJ) of $\text{MgCl}_2(\text{s})$ is
 (A) 510 (B) 320
 (C) 180 (D) 240
4. Electron affinity (in kJ/mole) of chlorine is
 (A) 170 (B) 115
 (C) 230 (D) 105

Passage 3: For Questions 5–6

X, Y and Z are three consecutive elements. X on addition of one electron and Y on addition of two electrons become isoelectronic with element Z.

5. Element Y will have following property:
 (A) Atomic number of Y is higher than atomic number of Z.
 (B) Atomic number of Y is higher than atomic number of X.
 (C) Element Y is placed in periodic table at left side of element X if both are in same period.
 (D) None of these
6. Select correct statement:
 (A) Difference between atomic number of X and Y is 3.
 (B) Difference between total number of protons of X and Y is 2.
 (C) Both (A) and (B).
 (D) Difference between atomic number of X and Z is 1.

Passage 4: For Questions 7–8

Electronegativity is the property of a bonded atom. The tendency of an atom to attract the shared pair of electrons towards itself is called electronegativity. Different scales of electronegativity have been proposed by different scientists, some of them being Pauling's scale, Mulliken's scale and Allred Rochow scale.

The ionization potential of two atoms A and B are 14 eV/atom and 10.8 eV/atom respectively and their electron affinities are 8.4 eV/atom and 6 eV/atom respectively.

With respect to the above given information answer the following questions.

7. If atoms A and B form a covalent bond, then what is the percent covalent character in the bond?
 (A) 19.5 (B) 50
 (C) 80.5 (D) 25
8. If A is an atom of the periodic table, then the value of $(n+1)$ for the unpaired electron in A is
 (A) 4 (B) 2
 (C) 1 (D) 3

Passage 5: For Questions 9–11

Isoelectronic species have the same number of electrons. This property is not only restricted to atoms but also observed in molecules and ions.

9. Choose the correct order of radius.
 (A) $\text{O}^{2-} > \text{F}^-$
 (B) $\text{Al}^{3+} < \text{Na}^+$
 (C) $\text{Na}^+ < \text{N}^{3-}$
 (D) All of these
10. Which of the following statements is correct for the following isoelectronic series?
 $\text{S}^{2-}, \text{Cl}^-, \text{K}^+, \text{Ca}^{2+}$

- (A) The size of the ions initially increases then decreases.
 (B) The first ionization energy decreases from left to right.
 (C) The first ionization energy increases from left to right.
 (D) None of these
11. Which of the following sets of isoelectronic species does not have the same shape?
 (A) H_2S and HCl
 (B) NO_3^- and CO_3^{2-}
 (C) ClO_4^- and SO_4^{2-}
 (D) NO_2^+ and CO_2

Passage 6: For Questions 12–14

The electronegativities of four elements A, B, C, D are 4, 3.17, 0.7 and 2.85 respectively and the electronegativities of hydrogen (H) and oxygen (O) atoms are 2.1 and 3.5 respectively.

12. Which of the following bonds is most polar?
 (A) B–C (B) A–D
 (C) B–D (D) C–D
13. Which of the following bonds is least polar?
 (A) O–H (B) O–C
 (C) A–C (D) H–D
14. Which of the following compounds does not act as acid?
 (A) $\text{H} - \text{O} - \text{A}$ (B) $\text{H} - \text{O} - \text{B}$
 (C) $\text{H} - \text{O} - \text{C}$ (D) $\text{H} - \text{O} - \text{D}$

Passage 7: For Questions 15–17

The electron affinity is an inherent property of the atom and it depends upon several factors.

15. The correct electron affinity order is
 (A) $\text{F} > \text{Cl}$
 (B) $\text{Cl} > \text{F}$
 (C) $\text{S} < \text{P}$
 (D) $\text{N} > \text{O}$

16. Which of the following is an incorrect statement?
 (A) The first ionization energy of A^- is equal to the electron affinity of A.
 (B) The second electron affinity is always greater than the first electron affinity for an element.
 (C) The process $O \rightarrow O^{2-}$ is endothermic
 (D) The process $Li \rightarrow Li^+$ is endothermic.
17. Which of the following reactions would not proceed in the forward direction spontaneously?
 (A) $Xe + He^+ \rightarrow Xe^+ + He$
 (B) $Si + Cl^+ \rightarrow Si^+ + Cl$
 (C) $F^- + I \rightarrow F + I^-$
 (D) $Be^- + B \rightarrow B^- + Be$

Passage 8: For Questions 18–19

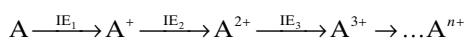
Ionization potential is the minimum amount of energy needed to remove the outermost electron from the gaseous isolated atom. Its unit is $eV \text{ atom}^{-1}$ or kJ mol^{-1} . Successive ionization energy is the amount of energy needed to remove electron successively from a gaseous ion, it may be termed as IE_2 , IE_3 ,.... The difference in the values of IE_1 , IE_2 ,... helps to determine electronic configuration of the elements.

Element	IE_1	IE_2	IE_3 (kcal/mol)
P	497	947	1500
Q	98	735	1100
R	176	347	1850
S	296	530	2050

18. Which of the element (X) can make MX type compound (where X is the halogen and M is alkali metal)?
 (A) P (B) Q
 (C) R (D) S
19. The order of ionic mobility in aqueous solution of the following ions will be
 (A) $R_{(aq)}^{2+} > S_{(aq)}^{2+}$
 (B) $S_{(aq)}^{2+} > R_{(aq)}^{2+}$
 (C) $S_{(aq)}^{2+} = R_{(aq)}^{2+}$
 (D) cannot be correlated.

Passage 9: For Questions 20–21

Successive ionisation energies of an element is represented as follows



20. Which of the following statement is correct?
 (A) In some of the elements IE_2 values may be negative.
 (B) IE_1 of A^{3+} = IE_2 of A^+ .

- (C) Successive electron affinity of A^{n+} is gradually decreasing.
 (D) None of these is correct.
21. If A has the electronic configuration of $1s^2 2s^2 2p^3$, then which of the following statement is correct?
 (A) IE_1 of A is negative.
 (B) IE_1 of A is less than that of A^- .
 (C) $IE_2 = IE_3$ for above element.
 (D) All of the above statements are correct.

Passage 10: for Questions 22–24

Ionization energy is always positive for an element and successive ionization energies always gradually increase.

22. The successive ionization energy for an element is given below in mJ/mole.

0.7865, 1.5771, 3.2316, 4.3555, 16.091, 19.785, 23.786, 29252

Predict the number of valence shell electrons in the given element.

- (A) 1
 (B) 2
 (C) 3
 (D) 4

23. For an element having only one valence shell electron, which of the following difference will have the maximum value.

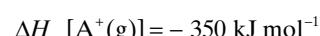
- (A) $IE_2 - IE_1$
 (B) $IE_3 - IE_2$
 (C) $IE_3 - IE_1$
 (D) cannot be predicted

24. Choose the incorrect ionization energy order

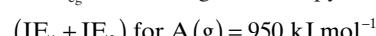
- (A) Al > Ga
 (B) Ti > In
 (C) Pb > Sn
 (D) Y < Sc

Passage 11: For Questions 25–27

Given the following information



where ΔH_{eg} is electron gain enthalpy.



25. The value of ΔH_{eg} of $A^{2+}(g)$ in kJ mol^{-1} is
 (A) +600 (B) -600 (C) -500 (D) +500
26. The value of IE_1 of A^- in kJ mol^{-1} is
 (A) +450 (B) +350 (C) +600 (D) +250
27. The $\Delta H_{hydration}$ of $A^{2+}(g)$ in kJ mol^{-1} is
 (A) +250 (B) -350 (C) -250 (D) -300

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
- (C) If Statement I is true but Statement II is false.
- (D) If Statement I is false but Statement II is true.

1. Statement I: Acetylene forms salts with metals like Ca and Ba more easily as compared to C_2H_4 .

Statement II: The polarity of C–H bond in C_2H_2 is more than that in C_2H_4 .

2. Statement I: Tl^{3+} has higher electronegativity as compared to Tl^+ .

Statement II: The oxidation state of Tl in TlI_3 is not +3.

3. Statement I: $CH_3I + OH^- \rightarrow CH_3OH + I^-$ and $CF_3I + OH^- \rightarrow CF_3OH + I^-$

Statement II: Both these reactions are nucleophilic substitution reactions.

4. Statement I: The size H^- is greater than that of F^- .

Statement II: The e/p ratio in H^- is 2 while that in F^- is $10/9$.

5. Statement I: The inner transition elements are placed in Group 3 B.

Statement II: The most stable oxidation state in case of the inner transition elements is +3.

6. Statement I: The actinide contraction is more as compared to the lanthanide contraction.

Statement II: 5f electrons have much lower shielding effect as compared to 4f electrons because 5f orbitals are more diffused than 4f orbitals.

7. Statement I: For elements in the lanthanide series, the atomic radius decreases gradually from left to right with the exception of Eu ($Z = 63$) and Yb ($Z = 70$).

Statement II: Only two electrons are involved in the metallic bonding of Eu and Yb and three electrons are involved in case of other elements of the lanthanide series.

8. Statement I: The ionization energy of Na^{2+} is less than that of Na^+ .

Statement II: Na^+ has an inert gas configuration.

9. Statement I: The electron affinity of P is less than that of Si.

Statement II: Z_{eff} increases in a period from left to right.

10. Statement I: The acidic strength of H–O–X decreases from $X = Cl$ to $X = I$.

Statement II: The electronegativity decreases from Cl to I.

11. Statement I: H^- is a stronger reducing agent as compared to H atom.

Statement II: The electronic configuration of H and H^- is $1s^1$ and $1s^2$, respectively.

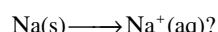
INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. How many of the following options are incorrect in accordance with the mentioned properties?

- (I) IP_1 of ion $M^{2+} > EA1$ of M^{3+} .
(IP = ionization potential, and EA = electron affinity)
- (II) $S > Se > Te > O$ (order of EA)
- (III) $Li < Be < B < C$ (order of electronegativity)
- (IV) $Mn^{4+} < Mg^{2+} < Na < F^-$ (order of ionic size)
- (V) $Li^+ > Na^+ < K^+$ (order of hydrated size)
- (VI) $NaCl > MgCl_2 > AlCl_3$ (order of lattice energy)

2. How many of the following energies are involved in the transformation of



3. Which of the following elements form amphoteric oxides?

Be, B, Al, Ga, Sn, Zn, Ge, Cu, Mn

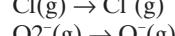
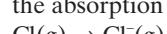
4. Calculate the ionization energy (in eV/atom) of fluorine if its electronegativity on Pauling's scale is 4 and its electron gain enthalpy is -3.4 eV/atom.
(Add the digits till you get single digit answer.)

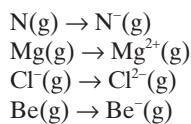
5. Successive ionization energies data (in eV/atom) of an element of second period is

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
120	133	167	719	797	850

Find the group number of element according to long form periodic table (1 – 18 convention)

6. How many of the following reactions proceed with the absorption of energy?



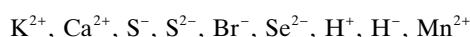


7. The number of elements among the following, which have lower electronegativity than oxygen atom, based on Pauling scale, is _____.

F, Cl, Br, I, H, S, P, K, Ca

8. The first four successive ionization energies for an element are 6.113, 11.871, 50.908 and 67.01 (in eV) respectively. The number of valence shell electrons is _____.

9. The number of species among the following, having inert gas configuration is _____.



10. The number of elements among the following atomic numbers that are *p* block elements is _____.
- 83, 79, 42, 64, 37, 54, 34

11. The difference in the electronegativity of two atoms, when the percentage ionic character is 19.5%, is _____.

12. Bond length of A–A bond is 124 pm and bond length of B–B bond is 174 pm. The bond length (in pm) of A–B bond in AB molecule if percent ionic character of A–B bond is 19.5% is _____.

13. The number of pairs, in which electron affinity of the second element is more than that of the first element is _____.

(F, Cl) (C, N) (O, N) (F, Ne) (B, C), (O, S)

14. The number of species having higher first ionization energy than Ca from the following is _____.

Ga, Ge, Br, Se, Kr, As, K

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the processes with the characteristic changes.

Column I	Column II
(A) $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$	(P) Exothermic in nature
(B) $\text{F} \rightarrow \text{F}^-$	(Q) Endothermic in nature
(C) $\text{H} \rightarrow \text{H}^-$	(R) Becomes diamagnetic
(D) $\text{N}^+ \rightarrow \text{N}^-$	(S) The magnetic moment undergoes a change

2. Match the properties with the parameters that they are dependent on.

Column I	Column II
(A) Electron affinity	(P) Radius
(B) Ionization potential	(Q) Z_{eff}

Column I	Column II
(C) Electronegativity	(R) Half-filled or fully filled configuration
	(S) Screening constant

3. Match the ionic species with their characteristics.

Column I	Column II
(A) Mn^{2+}	(P) Has the highest ionization energy
(B) Mn^{4+}	(Q) Has the highest ionic radius
(C) Mn^{3+}	(R) Has the highest magnetic moment
(D) Mn^{7+}	(S) Paramagnetic
	(T) Diamagnetic

4. Match the elements with their properties.

Column I	Column II
(A) K	(P) One electron in the <i>s</i> orbital of valence shell
(B) Cu	(Q) Transition element
(C) La	(R) One unpaired electron
(D) Au	(S) Member of the 4th period

ANSWERS

Single Correct Choice Type Questions

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (B) | 3. (D) | 5. (D) | 7. (D) | 9. (C) |
| 2. (A) | 4. (D) | 6. (B) | 8. (D) | 10. (C) |

- | | | | | |
|----------------|----------------|----------------|----------------|----------------|
| 11. (C) | 17. (A) | 23. (C) | 29. (B) | 35. (D) |
| 12. (C) | 18. (C) | 24. (B) | 30. (B) | 36. (B) |
| 13. (D) | 19. (C) | 25. (D) | 31. (B) | 37. (C) |
| 14. (C) | 20. (D) | 26. (B) | 32. (A) | 38. (A) |
| 15. (C) | 21. (B) | 27. (B) | 33. (C) | |
| 16. (B) | 22. (A) | 28. (B) | 34. (C) | |

Multiple Correct Choice Type Questions

- | | | | | |
|------------------------------|------------------------------|--------------------------|--------------------------|--------------------------|
| 1. (A), (B), (C), (D) | 5. (A), (B), (C) | 9. (B), (D) | 13. (A), (B), (D) | 17. (A), (B), (C) |
| 2. (A), (B), (C) | 6. (A), (B), (D) | 10. (C), (D) | 14. (A), (D) | 18. (A), (C) |
| 3. (A), (B), (C), (D) | 7. (B), (D) | 11. (B), (C), (D) | 15. (A), (C) | 19. (B), (C), (D) |
| 4. (A), (B), (D) | 8. (A), (B), (C), (D) | 12. (A), (D) | 16. (A), (B), (C) | |

Comprehension Type Questions

- | | | | | |
|---------------|----------------|----------------|----------------|----------------|
| 1. (C) | 7. (C) | 13. (D) | 19. (A) | 25. (B) |
| 2. (A) | 8. (D) | 14. (C) | 20. (A) | 26. (A) |
| 3. (D) | 9. (D) | 15. (B) | 21. (A) | 27. (C) |
| 4. (B) | 10. (C) | 16. (B) | 22. (D) | |
| 5. (C) | 11. (A) | 17. (C) | 23. (C) | |
| 6. (D) | 12. (A) | 18. (A) | 24. (A) | |

Assertion–Reasoning Type Questions

- | | | | | |
|---------------|---------------|---------------|----------------|--|
| 1. (A) | 4. (A) | 7. (A) | 10. (A) | |
| 2. (B) | 5. (A) | 8. (D) | 11. (B) | |
| 3. (D) | 6. (A) | 9. (B) | | |

Integer Answer Type Questions

- | | | | | |
|-------------|--------------|-------------|--------------|--------------|
| 1. 2 | 4. 19 | 7. 8 | 10. 3 | 13. 3 |
| 2. 3 | 5. 13 | 8. 2 | 11. 1 | 14. 5 |
| 3. 6 | 6. 4 | 9. 5 | 12. 5 | |

Matrix–Match Type Questions

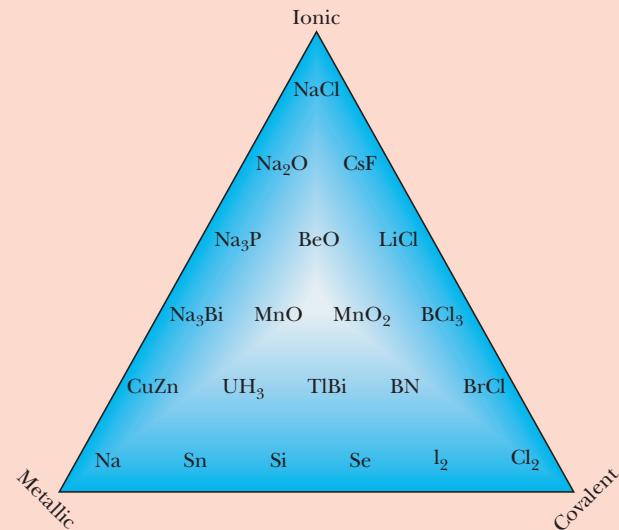
- | | |
|--|--|
| 1. (A) → (Q), (S)
(B) → (P), (R), (S)
(C) → (P), (R), (S)
(D) → (P) | 3. (A) → (Q), (R), (S)
(B) → (S)
(C) → (S)
(D) → (P), (T) |
| 2. (A) → (P), (Q), (R), (S)
(B) → (P), (Q), (R), (S)
(C) → (P), (Q), (R), (S) | 4. (A) → (P), (R), (S)
(B) → (P), (Q), (R), (S)
(C) → (Q), (R)
(D) → (P), (Q), (R) |

3

Chemical Bonding

Contents

- 3.1 Attainment of a Stable Configuration
- 3.2 Types of Bonds
- 3.3 Transitions between the Main Types of Bonding
- 3.4 The Covalent Bond
- 3.5 Valence Bond Theory
- 3.6 Valence Shell Electron Pair Repulsion (VSEPR) Theory
- 3.7 The Extent of *d* Orbital Participation in Molecular Bonding
- 3.8 Types of Covalent Bonds (Sigma (σ) and Pi (π) Bonds)
- 3.9 Molecular Orbital Method
- 3.10 LCAO Method
- 3.11 Rules for Linear Combination of Atomic Orbitals
- 3.12 Examples of Molecular Orbital Treatment for Homonuclear Diatomic Molecules
- 3.13 Examples of Molecular Orbital Treatment for Heteronuclear Diatomic Molecules
- 3.14 Dipole Moment
- 3.15 The Ionic Bond
- 3.16 Close Packing
- 3.17 Ionic Compounds of the type AX (ZnS , $NaCl$, $CsCl$)
- 3.18 Ionic Compounds of the Type AX_2 (CaF_2 , TiO_2 , SiO_2)



The three types of chemical bonds—ionic, covalent, and metallic—form a 2D plane.

- 3.19 Layer Structures (CdI_2 , $CdCl_2$, $[NiAs]$)
- 3.20 Lattice Energy
- 3.21 Stoichiometric Defects
- 3.22 Nonstoichiometric Defects
- 3.23 Born–Haber Cycle
- 3.24 Polarizing Power and Polarizability – Fajans' Rules
- 3.25 Melting Point of Ionic Compounds
- 3.26 Solubility of Ionic Compounds
- 3.27 Electrical Conductivity and Colour
- 3.28 Acidic Nature of Oxides
- 3.29 Thermal Stability of Ionic Compounds
- 3.30 Weak Forces
- 3.31 Interactions between Ions and Covalent Molecules
- 3.32 The Metallic Bond
- 3.33 Theories of Bonding in Metals
- 3.34 Conductors, Insulators and Semiconductors

3.1 | ATTAINMENT OF A STABLE CONFIGURATION

How do atoms combine to form molecules and why do atoms form bonds? A molecule will only be formed if it is more stable, and has a lower energy, than the individual atoms.

To understand what is happening in terms of electronic structure, consider first the Group 18 elements. These comprise the noble gases, helium, neon, argon, krypton, xenon and radon, which are noteworthy for their chemical inertness. Atoms of the noble gases do not normally react with any other atoms, and their molecules are monatomic, i.e. contain only one atom. The lack of reactivity is because the atoms already have a low energy, and it cannot be lowered further by forming compounds. The low energy of the noble gases is associated with their having a complete outer shell of electrons. This is often called a *noble gas structure*, and it is an exceptionally stable arrangement of electrons.

Normally only electrons in the outermost shell of an atom are involved in forming bonds, and by forming bonds each atom acquires a stable electron configuration. The most stable electronic arrangement is a noble gas structure, and many molecules have this arrangement. However, less stable arrangements than this are commonly attained by transition elements.

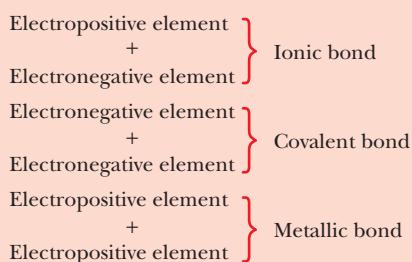
3.2 | TYPES OF BONDS

Atoms may attain a stable electronic configuration in three different ways: by losing electrons, by gaining electrons, or by sharing electrons.

Elements may be divided into:

1. Electropositive elements, whose atoms give up one or more electrons fairly readily.
2. Electronegative elements, which will accept electrons.
3. Elements which have little tendency to lose or gain electrons.

Three different types of bond may be formed, depending on the electropositive or electronegative character of the atoms involved.



Ionic bonding involves the complete transfer of one or more electrons from one atom to another. Covalent bonding involves the sharing of a pair of electrons between two atoms, and in metallic bonding the valency electrons are free to move throughout the whole crystal.

These types of bonds are idealized or extreme representations, and though one type generally predominates, in most substances the bond type is somewhere between these extreme forms. For example, lithium chloride is considered to be an ionic compound, but it is soluble in alcohol, which suggests that it also possesses a small amount of covalent character. If the three extreme bond types are placed at the corners of a triangle, then compounds with bonds predominantly of one type will be represented as points near the corners. Compounds with bonds intermediate between two types will occur along an edge of the triangle, whilst compounds with bonds showing some characteristics of all three types are shown as points inside the triangle (Figure 3.1).

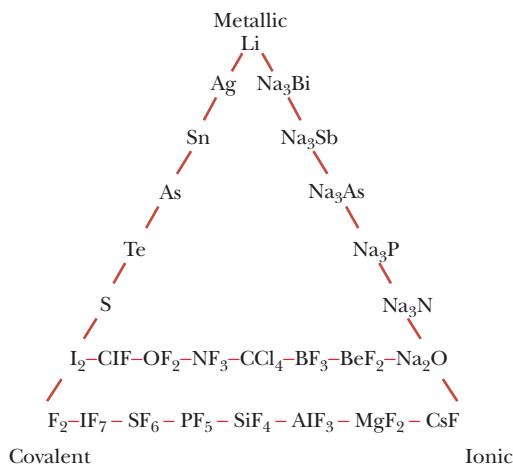


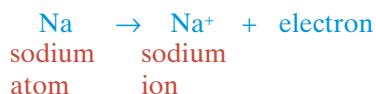
Figure 3.1 Triangle illustrating the transitions between ionic, covalent and metallic bonding.
(Reproduced from *Chemical Constitution*, by J.A.A. Ketelaar, Elsevier.)

3.3 | TRANSITIONS BETWEEN THE MAIN TYPES OF BONDING

Few bonds are purely ionic, covalent or metallic. Most are intermediate between the three main types, and show some properties of at least two, and sometimes of all three types.

Ionic bonds

Ionic bonds are formed when electropositive elements react with electronegative elements. Consider the ionic compound sodium chloride. A sodium atom has the electronic configuration $1s^2 2s^2 2p^6 3s^1$. The first and second shells of electrons are full, but the third shell contains only one electron. When this atom reacts it will do so in such a way that it attains a stable electron configuration. The noble gases have a stable electron arrangement and the nearest noble gas to sodium is neon, whose configuration is $1s^2 2s^2 2p^6$. If the sodium atom can lose one electron from its outer shell, it will attain this configuration and in doing so the sodium acquires a net charge of +1 and is called a sodium ion Na^+ . The positive charge arises because the nucleus contains 11 protons, each with a positive charge, but there are now only 10 electrons. Sodium atoms tend to lose an electron in this way when they are supplied with energy, and so sodium is an electropositive element:

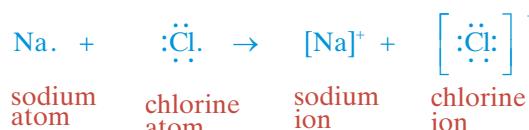


Chlorine atoms have the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^5$. They are only one electron short of the stable noble gas configuration of argon $1s^2 2s^2 2p^6 3s^2 3p^6$, and when chlorine atoms react, they gain an electron. Thus chlorine is an electronegative element.

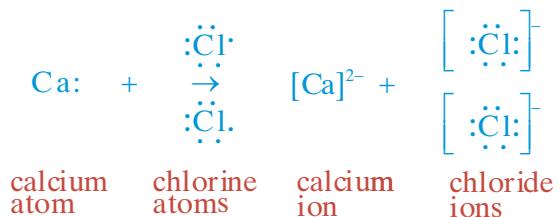


Through gaining an electron, an electrically neutral chlorine atom becomes a chloride ion with a net charge of -1.

When sodium and chlorine react together, the outer electron of the sodium atoms is transferred to the chlorine atoms to produce sodium ions Na^+ and chloride ions Cl^- . Electrostatic attraction between the positive and negative ions holds the ions together in a crystal lattice. The process is energetically favourable as both sorts of atoms attain the stable noble gas configuration, and sodium chloride $Na^+ Cl^-$ is formed readily. This may be illustrated diagrammatically in a Lewis diagram showing the outer electrons as dots:



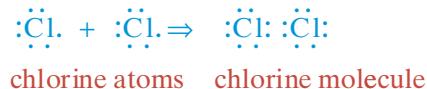
The formation of calcium chloride CaCl_2 may be considered in a similar way. Ca atoms have two electrons in their outer shell. Ca is an electropositive element, so each Ca atom loses two electrons to two Cl atoms, forming a calcium ion Ca^{2+} and two chloride ions Cl^- . Showing the outer electrons only, this may be represented as follows:



Covalent bonds

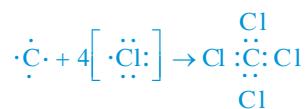
When two electronegative atoms react together, both atoms have a tendency to gain electrons, but neither atom has any tendency to lose electrons. In such cases the atoms share electrons so as to attain a noble gas configuration.

First consider diagrammatically how two chlorine atoms Cl react to form a chlorine molecule Cl_2 (only the outer electrons are shown in the following diagrams):



Each chlorine atom gives a share of one of its electrons to the other atom. A pair of electrons is shared equally between both atoms, and each atom now has eight electrons in its outer shell (a stable octet) – the noble gas structure of argon. In this electron dot picture (Lewis structure), the shared electron pair is shown as two dots between the atoms Cl : Cl. In the valence bond representation, these dots are replaced by a line, which represents a bond Cl—Cl.

In a similar way a molecule of tetrachloromethane CCl_4 is made up of one carbon and four chlorine atoms:



The carbon atom is four electrons short of the noble gas structure, so it forms four bonds, and the chlorine atoms are one electron short, so they each form one bond. By sharing electrons in this way, both the carbon and all four chlorine atoms attain a noble gas structure. It must be emphasized that although it is possible to build up molecules in this way in order to understand their electronic structures, it does not follow that the atoms will react together directly. In this case, carbon and chlorine do not react directly, and tetrachloromethane is made by indirect reactions.

A molecule of ammonia NH_3 is made up of one nitrogen and three hydrogen atoms:



The nitrogen atom is three electrons short of a noble gas structure, and the hydrogen atoms are one electron short of a noble gas structure. Nitrogen forms three bonds, and the hydrogen atoms one bond each, so all four atoms attain a stable configuration. One pair of electrons on the N atom is not involved in bond formation, and this is called a *lone pair* of electrons.

Other examples of covalent bonds include water (with two covalent bonds and two lone pairs of electrons), and hydrogen fluoride (one covalent bond and three lone pairs):



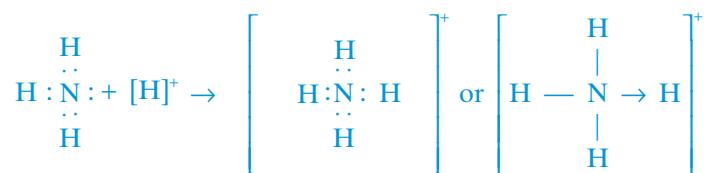
Oxidation numbers

The oxidation number of an element in a covalent compound is calculated by assigning shared electrons to the more electronegative element, and then counting the theoretical charge left on each atom. (Electronegativity is described in Chapter 2.) An alternative approach is to break up (theoretically) the molecule by removing all the atoms as ions, and counting the charge left on the central atom. It must be emphasized that molecules are not really broken, nor electrons really moved. For example, in H_2O , removal of two H^+ leaves a charge of -2 on the oxygen atom, so the oxidation state of O in H_2O is $(-II)$. Similarly in H_2S the oxidation state of S is $(-II)$; in F_2O the oxidation state of O is $(+II)$; in SF_4 the oxidation state of S is $(+IV)$; whilst in SF_6 the oxidation state of S is $(+VI)$. The concept of oxidation numbers works equally well with ionic compounds, and in CrCl_3 , the Cr atom has an oxidation state of $(+III)$ and it forms Cr^{3+} ions. Similarly in CrCl_2 , Cr has the oxidation state $(+II)$, and exists as Cr^{2+} ions.

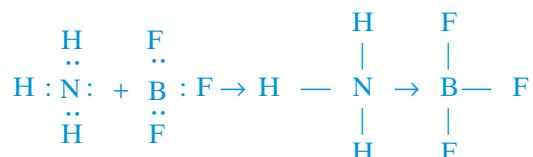
Coordinate bonds

A covalent bond results from the sharing of a pair of electrons between two atoms, where each atom contributes one electron to the bond. It is also possible to have an electron pair bond where both electrons originate from one atom and none from the other. Such bonds are called coordinate bonds or dative bonds. Since, in coordinate bonds, two electrons are shared by two atoms, they differ from normal covalent bonds only in the way they are formed, and once formed they are identical to normal covalent bonds.

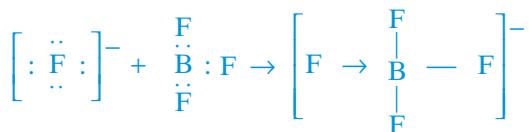
Even though the ammonia molecule has a stable electron configuration, it can react with a hydrogen ion H^+ by donating a share in the lone pair of electrons, forming the ammonium ion NH_4^+ :



Covalent bonds are usually shown as straight lines joining the two atoms, and coordinate bonds as arrows indicating which atom is donating the electrons. Similarly ammonia may donate its lone pair to boron trifluoride, and by this means the boron atom attains a share in eight electrons:



In a similar way, a molecule of BF_3 can form a coordinate bond by accepting a share in a lone pair from a F^- ion.

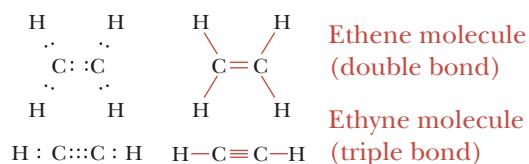


There are many other examples, including:



Double and triple bonds

Sometimes more than two electrons are shared between a pair of atoms. If four electrons are shared, then there are two bonds, and this arrangement is called a double bond. If six electrons are shared then there are three bonds, and this is called a triple bond:



Metallic bonds and metallic structures

Metals are made up of positive ions packed together, usually in one of the three following arrangements:

1. Cubic close-packed (also called face-centred cubic).
2. Hexagonal close-packed.
3. Body-centred cubic.

Negatively charged electrons hold the ions together. The number of positive and negative charges is exactly balanced, as the electrons originated from the neutral metal atoms. The outstanding feature of metals is their extremely high electrical conductivity and thermal conductivity, both of which are because of the mobility of these electrons through the lattice.

3.4 | THE COVALENT BOND

There are several different theories which explain the electronic structures and shapes of known molecules, and attempt to predict the shape of molecules whose structures are so far unknown. Each theory has its own virtues and shortcomings. None is rigorous. Theories change in the light of new knowledge and fashion. If we knew or could prove what a bond was, we would not need theories, which by definition cannot be proved. The value of a theory lies more in its usefulness than in its truth. Being able to predict the shape of a molecule is important. In many cases all the theories give the correct answer.

The Lewis theory

The octet rule

The Lewis theory was the first explanation of a covalent bond in terms of electrons that was generally accepted. If two electrons are shared between two atoms, this constitutes a bond and binds the atoms together. For many light atoms a stable arrangement is attained when the atom is surrounded by eight electrons. This octet can be made up from some electrons which are ‘totally owned’ and some electrons which are ‘shared’. Thus atoms continue to form bonds until they have made up an octet

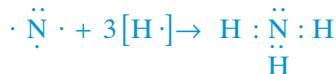
of electrons. This is called the ‘octet rule’. The octet rule explains the observed valencies in a large number of cases. There are exceptions to the octet rule; for example, hydrogen is stable with only two electrons. Other exceptions are discussed later. A chlorine atom has seven electrons in its outer shell, so by sharing one electron with another chlorine atom both atoms attain an octet and form a chlorine molecule Cl_2 .



A carbon atom has four electrons in its outer shell, and by sharing all four electrons and forming four bonds it attains octet status in CCl_4 .



In a similar way, a nitrogen atom has five outer electrons, and in NH_3 it shares three of these, forming three bonds and thus attaining an octet. Hydrogen has only one electron, and by sharing it attains a stable arrangement of two electrons.



In a similar way an atom of oxygen attains an octet by sharing two electrons in H_2O and an atom of fluorine attains an octet by sharing one electron in HF .



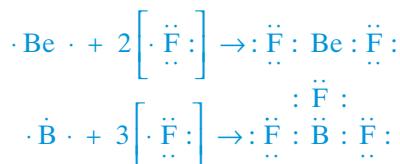
Double bonds are explained by sharing four electrons between two atoms, and triple bonds by sharing six electrons.



Exceptions to the octet rule

The octet rule is broken in a significant number of cases:

- For example, for atoms such as Be and B which have less than four outer electrons. Even if all the outer electrons are used to form bonds an octet cannot be attained.



- The octet rule is also broken where atoms have an extra energy level which is close in energy to the p level, and may accept electrons and be used for bonding. PF_3 obeys the octet rule, but PF_5 does not. PF_5 has ten outer electrons, and uses one $3s$, three $3p$ and one $3d$ orbitals. Any compound with more than four covalent bonds must break the octet rule, and these violations become increasingly common in elements after the first two periods of eight elements in the periodic table.
- The octet rule does not work in molecules which have an odd number of electrons, such as NO and ClO_2 , nor does it explain why O_2 is paramagnetic and has two unpaired electrons.

Despite these exceptions, the octet rule is surprisingly reliable and did a great deal to explain the number of bonds formed in simple cases. However, it gives no indication of the shape adopted by the molecule.

Sidgwick–Powell theory

In 1940 Sidgwick and Powell reviewed the structures of molecules then known. They suggested that for molecules and ions that contain only single bonds, the approximate shape can be predicted from the number of electron pairs in the outer or valence shell of the central atom (Table 3.1). The outer shell contains one or more bond pairs of electrons, but it may also contain unshared pairs of electrons (lone pairs). Bond pairs and lone pairs were taken as equivalent, since all electron pairs take up some space, and they repel each other. Repulsion is minimized if the electron pairs are orientated in space as far apart as possible. Based on this theory, the following molecular shapes were suggested depending on number of electron/lone pairs in the valence shell.

1. If there are two pairs of electrons in the valence shell of the central atom, the orbitals containing them will be oriented at 180° to each other. It follows that if these orbitals overlap with orbitals from other atoms to form bonds, then the molecule formed will be linear.
2. If there are three electron pairs on the central atom, they will be at 120° to each other, giving a plane triangular structure.
3. For four electron pairs the angle is $109^\circ 28'$, and the shape is tetrahedral.
4. For five pairs, the shape is a trigonal bipyramidal.
5. For six pairs the angles are 90° and the shape is octahedral.

Table 3.1 Molecular shapes predicted by Sidgwick–Powell theory

Number of electron pairs in outer shell	Shape of molecule	Bond angles
2	linear	 180°
3	plane triangle	 120°
4	tetrahedron	 $109^\circ 28'$
5	trigonal bipyramidal	 120° and 90°
6	octahedron	 90°
7	pentagonal bipyramidal	 72° and 90°

3.5 | VALENCE BOND THEORY

What is the essence of hybridization?

Initially it was considered that unpaired electrons in the valence shell of an atom and only the pure atomic orbitals are involved in the bond formation, except when coordinate covalent bonds are formed. This can explain the formation of molecules like H_2 , HX (where $\text{X} = \text{F, Cl, Br, I}$), X_2 , H_2O , NH_3 , etc. However, the formation of BeH_2 , BH_3 and CH_4 (like compounds) cannot be explained, since Be has no unpaired electron in its ground state, and B and C also have 1 and 2 unpaired electrons respectively. The valence bond theory was modified to explain the formation of such compounds. It was suggested that in all such cases, a pair of electrons gets unpaired and one of the electrons is excited to the next available vacant orbital of slightly higher energy. The driving force for this process is the energy released in the bond formation by unpaired electrons. Accordingly, the number of unpaired electrons in Be, B, and C is 2, 3, and 4 respectively.



Hence Be, B, C can show covalency of 2, 3 and 4 respectively. Apart from this, the existence of PF_5 , SF_6 , IF_7 , XeF_2 , XeF_4 , XeF_6 can also be well explained by this theory.

If purely atomic orbitals were involved in bonding, then in the formation of methane molecule the three C–H bonds will be formed by the p – s overlap and the fourth C–H bond will be formed by the s – s overlap. Since the s – s overlap may take place from any direction, there is no certainty of the location of the fourth H atom. Hence, the following two observations are expected

1. All $\widehat{\text{HCH}}$ angles are not certain.
2. Three C–H bonds formed by the p – s overlap are stronger than the one C–H bond formed by the s – s overlap (see Section 3.8).

But in reality, this is not observed, instead we observe that

1. All $\widehat{\text{HCH}}$ bond angles are identical with a value of $109^\circ 28'$.
2. All C–H bond lengths and strengths are identical.

So to explain the above observations, the theory of hybridization was introduced. **Hybridization** can be defined as the mixing of pure atomic orbitals of comparable energy.

Features of hybrid orbitals

1. The number of hybrid orbitals of equal energy formed is same as the number of atomic orbitals that are mixed. All the hybrid orbitals formed have identical characteristics. For example, one s orbital and three p orbitals are mixed to form four sp^3 hybrid orbitals, which are of equal energy; and each sp^3 hybrid orbital has 25% s character and 75% p character. For different hybridizations possible of s , p and d orbitals, the percentages of s , p and d characters are given in Table 3.2.
2. The shape of each hybrid orbital is such that one lobe is small and the other lobe is large (Figure 3.2).
3. As the % s character increases in a hybrid orbital, the hybrid orbital becomes bulkier and shorter. On the other hand as the % p or % d character increases, the orbital becomes longer and thinner (Figure 3.3).
4. As the % s character increases, the energy of the hybrid orbital decreases and as the % p or % d character increases, the energy of the hybrid orbital increases.
5. The s , p and d orbitals involved in the different types of hybridization are as follows:

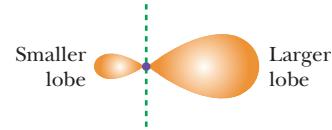


Figure 3.2 Shape of hybrid orbital.

Table 3.2 Percentage of s , p , d characters in various hybridized orbitals

Hybridization type	% s	% p	% d
sp	50	50	–
sp^2	33.33	66.67	–
sp^3	25	75	–
sp^3d	20	60	20
sp^3d^2	~16.5	50	~33
sp^3d^3	~14	~43	~43

sp : $s + \text{any } p \text{ orbital.}$
 sp^2 : $s + \text{any two } p \text{ orbitals.}$
 sp^3 : $s + p_x + p_y + p_z$
 sp^3d : $s + p_x + p_y + p_z + d_{z^2}$ [Trigonal bipyramidal geometry]
 sp^3d : $s + p_x + p_y + p_z + d_{x^2-y^2}$ [Square pyramidal geometry]
 dsp^2 : $(n-1)d_{x^2-y^2} + ns + np_x + np_y$
 sp^3d^2 : $ns + np_x + np_y + np_z + nd_{x^2-y^2} + nd_{z^2}$
 d^2sp^3 : $(n-1)d_{x^2-y^2} + (n-1)d_{z^2} + ns + np_x + np_y + np_z$
 sp^3d^3 : $ns + np_x + np_y + nd_{x^2-y^2} + nd_{xy} + np_z + nd_{z^2}$
 d^3s : $(n-1)d_{xy} + (n-1)d_{xz} + (n-1)d_{yz} + ns$ [Tetrahedral geometry]

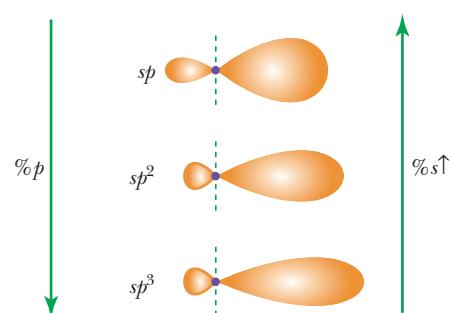


Figure 3.3 Shape of hybrid orbitals with increasing p character.

Calculation of steric number

For molecule/species having only **one central atom**, the steps involved are:

1. Calculate n , which is equal to number of total valence shell electrons of all atoms + number of negative charges (if any) – number of positive charges (if any).

Note: (a) It is considered that valence shell electrons for H atom is seven (just to make calculation easier).

(b) The value of n cannot be odd.

2. Divide n by 8, which results in $Q + R$ (if any)

where Q = number of σ bond pairs,

R = number of unshared electrons on the central atom.

Hence,

$\frac{R}{2}$ \Rightarrow number of lone pairs of electrons on the central atom.

Note: This is only a mathematical trick to obtain steric number in a simple manner.

3. Obtain **steric number** (S.N.) of the molecule, which is the number of atoms bonded to the central atom of a molecule plus the number of lone pairs on the central atom.

Therefore,

$$\text{S.N.} = \left(Q + \frac{R}{2} \right)$$

This number is used to determine shapes of the molecules. Hints about the structure of molecules can be obtained from S.N. as shown in Table 3.3.

Table 3.3 Relation between steric number, hybridization and geometry of molecules

Steric number	Hybridization	Orientation of the hybrid orbital in space or electronic geometry around the central atom	Angles between hybrid orbitals
2	sp	Linear	180°
3	sp^2	Trigonal planar	120°

(continued)

Table 3.3 (continued)

Steric number	Hybridization	Orientation of the hybrid orbital in space or electronic geometry around the central atom	Angles between hybrid orbitals
4	sp^3	Tetrahedral (Td)	109°28'
5	sp^3d	Trigonal bipyramidal (TBP)	Axial (a) and equatorial (e) : 90° e and e : 120° a and a : 180°
6	sp^3d^2	Octahedral (Oh)	Between two adjacent orbitals : 90° Between two opposite orbitals : 180°
7	sp^3d^3	Pentagonal bipyramidal (PBP)	a and a : 180° a and e : 90° e and e : 72°

3.6 | VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

This theory was developed by Gillespie in 1957 to improve the Sidgwick–Powell theory to predict and explain molecular shapes and bond angles more exactly. This theory may be summarized in the following points:

1. Electron pairs tend to minimize repulsions and these are in the order—lone pair–lone pair > lone pair–bond pair > bond pair–bond pair. (Here bond pair refers to a single bond.) Shapes of the molecules depend upon repulsions between bond pair and lone pair electrons.
2. The double bond is in need of more space as compared to the single bond. The repulsion order in relation to the bonds is as follows:
double bond – double bond > double bond – single bond > single bond – single bond.
3. Keeping the central atom (having lone pair) same, if the electronegativity of the surrounding atom increases, the bond angle will decrease provided no other factors like size and back bonding play any role.
4. Keeping the surrounding atoms same, if the electronegativity of the central atom (having the lone pair) increases, the bond angle increases.
5. Sometimes the lone pair may be transferred from filled shell of an atom to unfilled shell of the adjacent bonded atom. This phenomenon of transferring electron is known as ‘back bonding’.

The use of VSEPR theory in explaining the shapes of the molecules is discussed below.

Effect of lone pair

1. If the lone pair(s) is (are) absent, the shape of the molecule is identical with the electronic geometry of the central atom as shown in Table 3.3.

2. If the lone pair(s) is (are) present, the bond angles get distorted and the shape of the molecule can be visualized from the three-dimensional figure obtained after placing the bond pairs and lone pair(s) in a manner such that the repulsion between them is minimised. (The location of the lone pair will not be considered in the shape determination because electrons are not visible.)

Shapes of the species undergoing different hybridizations:

1. For sp hybridization

The steric number is 2.

The possible values of $Q + \frac{R}{2}$ are

$2 + 0 \Rightarrow$ Linear geometry, e.g. BeH_2 , BeCl_2 , BH_2^+ , NO_2^+ .

or $1 + 1 \Rightarrow$ Linear geometry, e.g. CO .

2. For sp^2 hybridization

The steric number is 3.

The possible values of $Q + \frac{R}{2}$ are

$3 + 0 \Rightarrow$ Trigonal planar geometry, e.g. BX_3 , AlCl_3 , AlBr_3 , CH_3^+ , CO_3^{2-} , NO_3^- , etc.

or $2 + 1 \Rightarrow$ Bent / V-shaped / Angular geometry, e.g. NO_2^- , SnCl_2 , SO_2 , etc.

3. For sp^3 hybridization

The steric number is 4.

The possible values of $Q + \frac{R}{2}$ are

$4 + 0 \Rightarrow$ Tetrahedral geometry, e.g. BH_4^- , NF_4^+ , NH_4^+ , SiF_4 , PH_4^+ , etc.

or $3 + 1 \Rightarrow$ Pyramidal geometry, e.g. NH_3 , SnCl_3^- , SO_3^{2-} , SeO_3^{2-} , etc.

or $2 + 2 \Rightarrow$ Angular / V-shaped / Bent geometry, e.g. H_2O , Cl_2O , NH_2^- , etc.

Note: More the number of lone pairs, lesser will be the bond angle. Hence the bond angles of CH_4 , NH_3 and H_2O are $109^\circ 28'$, 107 and $104^\circ 5'$ respectively.

4. For $sp^3\text{d}$ hybridization

The steric number is 5.

The possible values of $Q + \frac{R}{2}$ are

$5 + 0 \Rightarrow$ TBP geometry, e.g. PCl_5 , PF_5 , SbF_5 , PCl_2F_3 , PCl_3F_2 , XeO_3F_2 , etc.

or $4 + 1 \Rightarrow$ See-saw geometry, e.g. SF_4 , SF_2Cl_2 , XeO_2F_2 ,

or $3 + 2 \Rightarrow$ T-shaped geometry, e.g. ClF_3 , XeF_3^+ , BrF_3 , XeOF_2 , etc.

or $2 + 3 \Rightarrow$ Linear geometry, e.g. XeF_2 , ICl_2^- , $[\text{I}(\text{CN})_2]^-$, etc.

The relative location of the bond pair and the lone pair is decided by **Bent's rule**, which states that the more electronegative atom prefers to stay in the orbital having less s character, while the lone pair prefers to stay in the orbital having more s character. Alternatively, it may be stated as follows. For TBP geometry, the more electronegative atom prefers to stay in the axial position, while the lone pair prefers to stay in the equatorial position.

The above statement is explained through the following concepts:

- It is suggested that $sp^3d = sp^2 + pd$, i.e. all five hybrid orbitals in sp^3d hybridization are not equal, and the concept of unequal hybridization (kind of failure of hybridization theory) starts here. So the equatorial set of orbitals is made of sp^2 hybrid orbitals, while the axial set is made of pd hybrid orbitals. It is also supported by the fact that in PCl_5 , $d_{\text{P-Cl}}(a)$ is greater than $d_{\text{P-Cl}}(e)$.
- The order of energy required to remove an electron from a particular orbital having the same principal quantum number is $s > p > d > f$. This follows the order of proximity of orbitals to the nucleus. We know that the more electronegative atom attracts the bond pair towards itself, and this

kind of withdrawing of electrons will be easiest when the attached orbital of it from the central atom consists of minimum or nil *s* character. Hence, the more electronegative atom prefers the orbitals having less *s* character or axial position in the TBP geometry.

Again, the bond pair is attracted by two atoms, while the lone pair is attracted by only one atom. Hence, the lone pair will try to come closer to the nucleus and only the *s* orbital can do so easily. Hence, the lone pair prefers the orbital having more *s* character or the equatorial position in TBP geometry.

Based on the above explanation, the structures of some molecules with sp^3d hybridization are shown in Figure 3.4.

Note: The effect of the lone pair on bond angles makes them bent, see-saw and T-shaped.

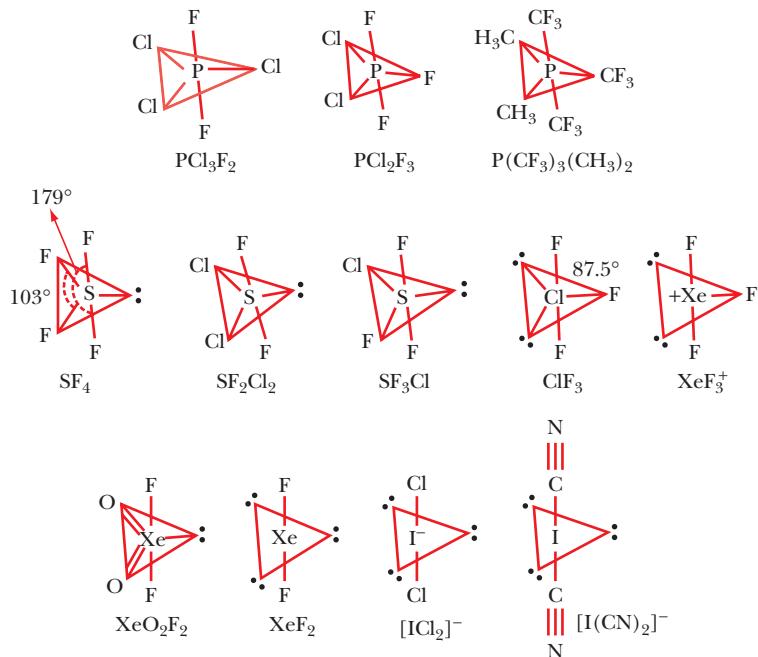


Figure 3.4 Geometry of some molecules with sp^3d hybridization.

5. For sp^3d^2 hybridization

The steric number is 6.

The possible values of $Q + \frac{R}{2}$ are

$6 + 0 \Rightarrow$ Octahedral geometry, e.g. SF_6 , $TeCl_6$, XeO_6^{4-} , XeO_2F_4 , etc.

or $5 + 1 \Rightarrow$ Square pyramidal geometry, e.g. IF_5 , XeF_5^+ , $XeOF_4$, etc.

or $4 + 2 \Rightarrow$ Square planar geometry, e.g. XeF_4 , $[ICl_4]^-$, etc.

Structures of some molecules with sp^3d^2 hybridization are shown Figure 3.5.

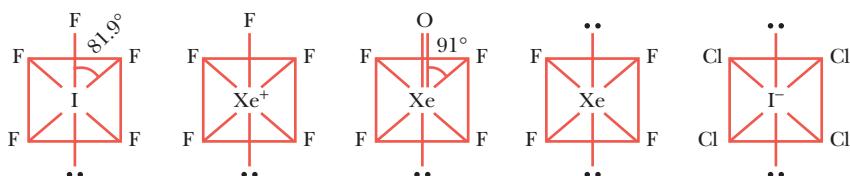


Figure 3.5 Geometry of some molecules with sp^3d^2 hybridization.

In case of IF_5 and $[XeF_5]^+$, distortion is observed in the shape because the lone pair-bond pair repulsion is greater than the bond pair-bond pair repulsion. But in case of $XeOF_4$, the lone pair-bond pair repulsion is almost equal to the double bond-single bond pair repulsion. Hence, the distortion is very less and the double bond repels slightly more here as compared to the lone pair, and the $O\bar{X}eF$ angle is 91° .

6. For sp^3d^2 hybridization

The steric number is 7.

The possible values of $Q + \frac{R}{2}$ are

- a. $7 + 0 \Rightarrow$ PBP geometry, e.g. IF_7^- ,
- b. $6 + 1 \Rightarrow$ This can have the following geometries

- (i) Distorted octahedral geometry, e.g. XeF_6^- , IF_6^- , etc., when the lone pair is present in stereochemically active s orbital.
- (ii) Perfect octahedral geometry, e.g. $[ICl_6]^-$, $[TeCl_6]^{2-}$, $[SbCl_6]^{3-}$, etc., where the lone pair is present in stereochemically inactive s orbital.

- c. $5 + 2 \Rightarrow$ Pentagonal planar geometry, e.g. $[XeF_5]^-$.

The structure of $[XeF_5]^-$ is shown in Figure 3.6. It appears contradictory that the two lone pairs are at the axial position in $[XeF_5]^-$, while in case of ClF_3 two lone pairs are at the equatorial position. It can be understood by an alternative statement of Bent's rule, i.e. "the orbital occupying more space around the central atom will have more s character". For TBP geometry, one axial orbital is having three neighbouring orbitals which are all at 90° , while one equatorial orbital is having four neighbouring orbitals, out of which two are at 90° and the other two are at 120° . Hence, the equatorial orbital occupies more space as compared to the axial orbital and will have more s character. It is also experimentally supported by the fact that the d_{p-Cl} (a) $>$ d_{p-Cl} (e) in PCl_5 and similar behaviour in many other compounds which are listed in Table 3.4.

Table 3.4 Axial and equatorial radii for compounds with sp^3d hybridization

Compound	r_e (pm)	r_a (pm)
PF_5	153.4	157.7
PCl_5	202	214
$SbCl_5$	231	243
SF_4	154	164
ClF_3	159.8	169.8
BrF_3	172.1	181.0

However, this generalization does not hold true when the atoms surrounding the central atom are different. For example, the bond lengths observed in PCl_3F_2 and PCl_2F_3 are as follows:

$$\begin{aligned} PCl_3F_2 : d_{p-F} (a) &= 159.6 \text{ pm}; d_{p-Cl} (e) = 200.5 \text{ pm} \\ PCl_2F_3 : d_{p-F} (a) &= 159.1 \text{ pm}; d_{p-F} (e) = 153.8 \text{ pm}; d_{p-Cl} (e) = 200.2 \text{ pm} \end{aligned}$$

It can be concluded that in such cases the orbital length (axial) is always greater than orbital length (equatorial) but not the bond length.

Similarly for PBP geometry, one axial orbital is having five neighbouring orbitals and all are at 90° , while one equatorial orbital is having four neighbouring orbitals, out of which two are at 90° and other two are at 72° . Hence the axial orbital occupies more space as compared to the equatorial orbital and the axial orbital has more s character. Thus the two lone pairs in PBP geometry occupy the axial position and this clearly explains the structure of $[XeF_5]^-$.

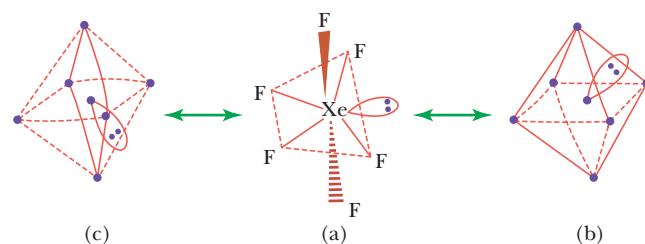


Figure 3.7 Possible structures for XeF_6 .

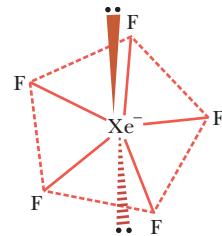


Figure 3.6 Pentagonal planar structure of $[XeF_5]^-$.

Again according to this theory, the position of the lone pair in XeF_6 molecule should be in axial position and the shape should be pentagonal pyramidal. But this is not observed and the actual shape of molecule is octahedral. This implies that the lone pair is placed at the equatorial position, and this explains the structure of XeF_6 shown in Figures 3.7 a, b and c.

According to Figure 3.7 μ_{expected} for XeF_6 is not equal to zero. But $\mu_{\text{real}}(\text{XeF}_6) \sim 0$. To explain the above facts, it is considered that the actual molecule is in dynamic equilibrium of all the three structures shown in Figure 3.7. Here it is considered that the lone pair is present in the stereochemically active *s* orbital and similar structure is observed in IF_6^- . But anions like $[\text{SbX}_6]^{3-}$, $[\text{TeX}_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $[\text{BrF}_6]^-$, $[\text{ICl}_6]^-$ have been assigned perfectly octahedral structure on the basis of X-ray crystallography and the lone pair is present in stereochemically inactive *s* orbital.

It is a common misconception that hybridization is the cause of a particular molecular shape. This is not so. The reason why any particular shape is adopted is its energy. It is also important to remember that the hybridized state is a theoretical step in going from an atom to a molecule, and the hybridized state never actually exists. It cannot be detected even spectroscopically, so the energy of hybrid orbitals cannot be measured and can only be estimated theoretically.

Effect of double bond

The effect of double bond is illustrated below for trigonal geometry (Figure 3.8a) and tetrahedral geometry (Figure 3.8b, c & d). Figure 3.8d shows that in SO_4^{2-} , all OSO bond angles are identical ($109^\circ 28'$) due to presence of resonating structures.

However, in case of H_2SO_4 , all OSO angles are not identical because resonating structures are not identical as in SO_4^{2-} , and their contribution is also not identical. This is shown in Figure 3.9.

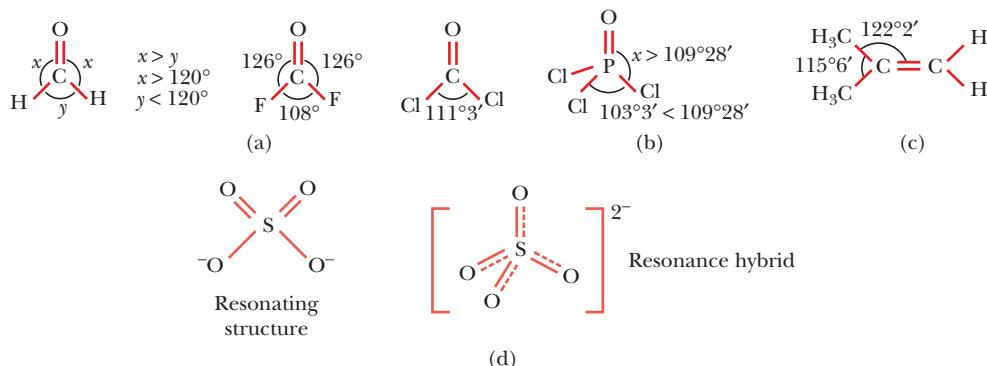


Figure 3.8 Bond angles in the presence of double bond: (a) trigonal geometry and (b) & (c) tetrahedral geometry.

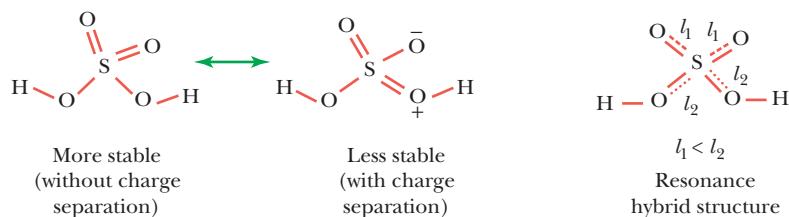


Figure 3.9 Non-identical resonating structures of H_2SO_4 .

The double bond – double bond repulsion is more as compared to double bond – single bond and single bond – single bond repulsion. Hence OSO angles are not identical, also there are two kinds of S–O bond lengths.

Note: Similar explanation is also applicable for HCO_2^- and HCO_2H , NO_3^- and HNO_3 , NO_2^- and HNO_2 , PO_4^{3-} and H_3PO_4 , etc.

Effect of electronegativity

The effect of electronegativity can be explained by considering the following cases.

1. When the central atom having lone pair is the same with different surrounding atoms.

NF_3 and NH_3 both have structures based on a tetrahedron with one corner occupied by a lone pair. The high electronegativity of F pulls the bonding electrons further away from N than in NH_3 . Thus repulsion between bond pairs is less in NF_3 than in NH_3 . Hence the lone pair in NF_3 causes a greater distortion from tetrahedral than NH_3 . The same effect is found in H_2O and F_2O .

NH_3 and NF_3	H_2O and F_2O
107° and 102°	104.5° and 103.1°

The following examples highlight the significance of ‘having lone pair’ on the central atom. In absence of lone pair, the effect of electronegativity is not observed.

CH_4 and CF_4	SiH_4 and SiF_4	BH_4^- and BF_4^-
$109^\circ 28'$ and $109^\circ 28'$	$109^\circ 28'$ and $109^\circ 28'$	$109^\circ 28'$ and $109^\circ 28'$

In the following case bond angles are distorted but, the decrease in bond angle is due to decrease in steric crowding.

PI_3	PBr_3	PCl_3	PF_3
102°	101°	100.3°	97.8°

Bent's rule is also consistent with Gillespie's VSEPR model, and may provide alternative rationalization for effect of electronegativity. So it is restated as: *‘more electronegative atom not only prefers to stay in the orbital having more p character but also can increase the p character in its attached orbital from the central atom depending on the circumstance’*. The rule can be applied to explain the effect of electronegativity on bond angle and bond length.

- a. Application on the bond angle: The different bond angles in CHF_3 and CH_2F_2 can be explained on the basis of (Figure 3.10a).

But it is not applicable for CHCl_3 and CH_2Cl_2 where the corresponding bond angles increase due to larger size of Cl atoms (Figure 3.10b).

- b. Application on bond length: With increase in p character in an orbital, bond length will increase while with increase in s character in an orbital, bond length will decrease. For example, $d_{\text{C}-\text{Cl}}$ in CH_3Cl (1.78\AA) $> d_{\text{C}-\text{Cl}}$ in CF_3Cl (1.75\AA).

Similarly,

$$\begin{aligned} d_{\text{N}-\text{N}} \text{ in } \text{N}_2\text{H}_4 &> d_{\text{N}-\text{N}} \text{ in } \text{N}_2\text{F}_4 \\ d_{\text{C}-\text{C}} \text{ in } \text{C}_2\text{H}_6 &> d_{\text{C}-\text{C}} \text{ in } \text{C}_2\text{F}_6 \\ d_{\text{O}-\text{O}} \text{ in } \text{O}_2\text{H}_2 &> d_{\text{O}-\text{O}} \text{ in } \text{O}_2\text{F}_2 \end{aligned}$$

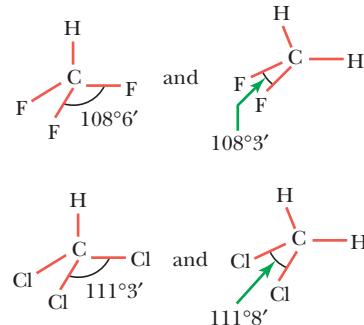


Figure 3.10: The increase in electronegativity of surrounding atoms affects the bond angle.

2. When the surrounding atom is the same with different central atom having lone pair.

NH_3	PH_3	AsH_3	SbH_3
107°	93.8°	91.8°	91.3°
H_2O	H_2S	H_2Se	H_2Te

104.5°	92°	91°	89.5°
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The effect of electronegativity as postulated in VSEPR theory explains the order of the angle for the above molecules but cannot rationalize very small angles ($\sim 90^\circ$) in PH_3 , AsH_3 ..., H_2S , H_2Se ... etc. with respect to NH_3 and H_2O respectively.

To explain this, Drago suggested an empirical rule which is compatible with the energetics of hybridization. It states that if the central atom is in the third row or below in the periodic table, the lone

pair will occupy a stereochemically inactive *s* orbital, and the bonding will be through *p* orbitals, and bond angles will be nearly 90° if the electronegativity of the surrounding atom is ≤ 2.5 .

The above rule is based upon the relation between hybridization and bond angle for two or more equivalent *s*-*p* hybrid orbitals, where the fraction of *s* character (*S*) or fraction of *p* character (*P*) is given by the relationship:

$$\cos \theta = \frac{S}{S-1} = \frac{P-1}{P} \quad (\text{for } 90^\circ < \theta < 180^\circ)$$

For example, for AsH_3 , $\overbrace{\text{HAsH}}$ angle is 91.8°, and from calculation it can be shown that each As–H bond consists of almost 97% *p* character and 3% *s* character. Hence, it can be concluded that there is no hybridization or the extent of hybridization is very less for PH_3 , AsH_3 , SbH_3 , H_2S , H_2Se and H_2Te molecules.

The cause for no hybridization in these molecules can be explained as follows. In case of P, the energy required for hybridization is about 600 kJ mol^{-1} which is not compensated by the energy released from the bond formation using hybrid orbitals. From the energy point of view alone, the most stable arrangement would be utilizing pure *p* orbitals in bonding with the lone pair ‘sinking’ into a pure *s* orbital.

Based upon the above discussion, we can explain the following facts.

- PH_3 has much lower solubility in water as compared to that of NH_3 .
- The formation of PH_4^+ is difficult as compared to that of NH_4^+ which is supported by the fact that



whereas,



The reason for the above observation is that the amount of $[\text{H}^+]$ is quantitatively less to protonate the lone pair that resides at almost pure *s* orbital in case of PH_3 . When $[\text{H}^+]$ increases in the presence of strong acids like HX ($\text{X} = \text{Cl}, \text{Br}$ and I), PH_4^+ is formed more readily.



- The complexing ability of NH_3 is much higher as compared to that of PH_3 .

These three observations can be explained on the basis that the lone pair donating ability for P in case of PH_3 is much less because the lone pair resides at almost pure *s* orbital. In case of NH_3 , the lone pair is present in one *sp*³ hybrid orbital and can be donated easily.

Back bonding

The phenomenon of back bonding involves transfer of lone pair from filled shell of an atom to the unfilled shell of the adjacent bonded atom.

It is a kind of coordinate π bonding which may be partial or full, depending on the relative donating and accepting ability of the donor and accepter atoms. In general, the donor atoms are the second period elements carrying lone pairs, such as F, O, N, C; sometimes Cl, Br, I, P, S can also act as donor atoms depending on circumstance.

1. Back bonding with F as donor atom

- Considering the electronegativity of the surrounding atoms, the expected bond angle order for PH_3 and PF_3 is $\text{PH}_3 > \text{PF}_3$. But in reality, it is $\text{PH}_3 < \text{PF}_3$. This is due to back bonding in PF_3 which is shown in Figure 3.11.

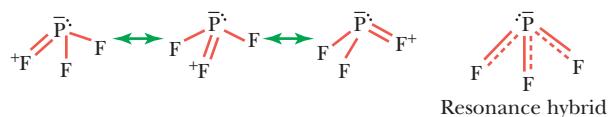


Figure 3.11 Back bonding in PF_3

Hence, due to back bonding the partial double bond character develops in a bond causing a decrease in the bond length; the bond angle may or may not increase, but it never decreases.

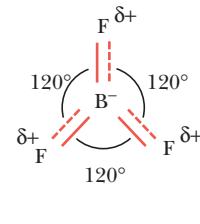
Hence, the following bond angles observed are well explained.

PH_3 and PF_3 AsH_3 and AsF_3

93.8° and 97.8° 91.8° and 96.2°

- b. In case of BF_3 , the extent of back bonding is more than that observed in PF_3 because of the $2p\pi - 2p\pi$ overlap in case of BF_3 , while that in P-F bond is $3d\pi - 2p\pi$. However, there is no change in the bond angle due to absence of the lone pair on the central atom.

Hence, it is also clear that $d_{\text{B-F}}$ in BF_3 is less than that in BF_4^- because back bonding is not possible in BF_4^- due to the non-availability of vacant orbital in B atom under sp^3 hybridization.



2. Back bonding with O as donor atom

- a. The expected bond angle order for H_2O , Cl_2O and F_2O is $\text{H}_2\text{O} > \text{Cl}_2\text{O} > \text{F}_2\text{O}$ based on the electronegativities of the surrounding atoms. But in reality, the order is Cl_2O (110°8') > H_2O (104°5') > F_2O (103°2'). This is also explained on the basis of back bonding in Cl_2O (Figure 3.12), which is not possible in H_2O and F_2O .

For the analogous compound SCl_2 , the bond angle is 102° since the lone pair of S or Cl atoms need not be delocalised due to the availability of vacant d orbitals of their own.

- b. The $d_{\text{B-O}}$ in $\text{B}(\text{OH})_3 < d_{\text{B-O}}$ in $[\text{B}(\text{OH})_4]^-$. This is because back bonding is possible in case of $\text{B}(\text{OH})_3$ from O atom to vacant p orbital of B atom, which is not available in case of $[\text{B}(\text{OH})_4]^-$ and hence no back bonding is possible.
- c. $(\text{CH}_3)_2\text{O}$ forms a complex with BF_3 easily, while $(\text{SiH}_3)_2\text{O}$ cannot do so because the availability of the lone pair on O atom decreases due to back bonding from O atom to vacant $3d$ orbital of Si atom. C atom has no such vacant orbital for back bonding.

In case of $(\text{CH}_3)_2\text{O}$, the positive deviation of the bond angle with respect to hybridization can be explained on the basis of steric crowding of two methyl groups. In case of $(\text{SiH}_3)_2\text{O}$, the huge bond angle increase is mainly due to back bonding and partly due to steric repulsion (Figure 3.13a).

If we consider the bond angles of Cl_2O and $(\text{SiH}_3)_2\text{O}$, in both the cases $3d\pi - 2p\pi$ type of back bonding takes place but the huge angle change in case of $(\text{SiH}_3)_2\text{O}$ is due to the much higher extent of back bonding as compared to Cl_2O . This is because of the presence of three lone pairs on each Cl atom which retard the flow of electrons from O atom. This phenomenon is not observed in case of $(\text{SiH}_3)_2\text{O}$ due to absence of lone pairs. (Figure 3.13b).

- d. The boroxine (B_3O_6) ring is planar due to back bonding and it is aromatic in nature (Figure 3.14). Here the back bond is considered as a full coordinate π bond in a particular resonating structure according to the bond order observed. Similarly $\text{B}_3\text{N}_3\text{H}_6$ is also planar and aromatic due to back bonding.
- e. In $\bar{\text{C}} \equiv \text{O}$ molecule also, the coordinate π bond may be considered as back bond from O atom to C atom. The structure before back bonding may be written as $:\text{C} = \ddot{\text{O}}:$ In this arrangement the lone pair from O atom is donated to the vacant orbital of electron deficient C atom.
- f. In $(\text{F}_3\text{C})_2\text{Al} - \text{O} - \text{Al}(\text{CF}_3)_2$, the AlOAl angle is almost 180° (i.e. 178°) so the $\text{Al}-\text{O}-\text{Al}$ skeleton is almost linear, and oxygen atom may be considered as sp hybridized (Figure 3.15).

Here the extent of back bonding is enhanced by the inductive effect of strongly electronegative CF_3 group which increases the electron deficiency of Al atom that is already electron deficient due to incomplete octet.

Another example of the compound where the O atom is sp hybridized is $\text{Ph}_3\text{Si}-\text{O}-\text{SiPh}_3$ in which the SiOSi angle is 180°.

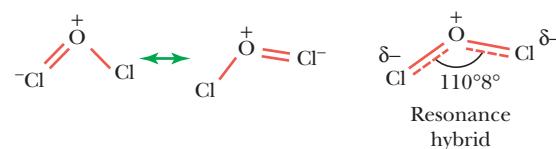


Figure 3.12 Back bonding in Cl_2O

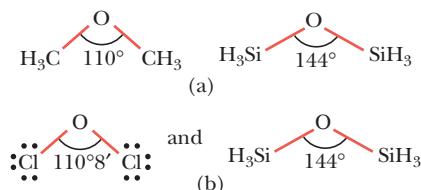


Figure 3.13 Bond angle deviation in (a) $(\text{CH}_3)_2\text{O}$ and $(\text{SiH}_3)_2\text{O}$. (b) Cl_2O and $(\text{SiH}_3)_2\text{O}$.

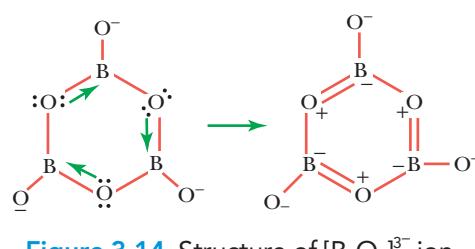


Figure 3.14 Structure of $[\text{B}_3\text{O}_6]^{3-}$ ion.

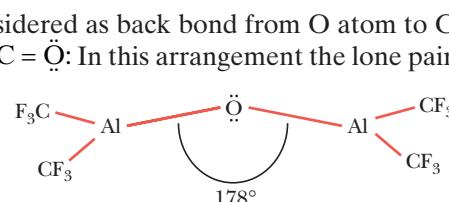
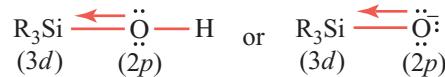


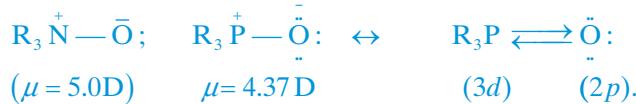
Figure 3.15 Structure of $(\text{F}_3\text{C})_2\text{Al} - \text{O} - \text{Al}(\text{CF}_3)_2$.

- g.** $\text{R}_3\text{Si}-\text{O}-\text{H}$ is more acidic than $\text{R}_3\text{C}-\text{O}-\text{H}$. This is also due to back bonding from O atom to Si atom which increases the polarity of O – H bond and stabilizes the conjugate base $\text{R}_3\text{Si}-\bar{\text{O}}$.



This also explains the bond angle order of $\widehat{\text{SiOH}} > \widehat{\text{COH}}$ in the above compounds.

- h.** R_3NO has a higher dipole moment as compared to R_3PO due to back bonding from O atom to P atom though the electronegativity difference between P and O is much larger as compared to that between N and O.



- i.** The $2p\pi-2p\pi$ back bonding in $\text{B}(\text{OH})_3$ or $\text{B}(\text{OMe})_3$ explains why the $\widehat{\text{BOH}}$ and $\widehat{\text{BOC}}$ angles are 112° and 113° respectively.

3. Back bonding with N as donor atom

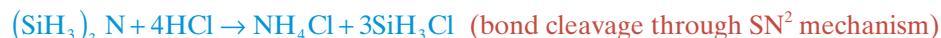
- a.** The bond angle order is $\text{NCl}_3(107^\circ 45') > \text{NH}_3(107^\circ) > \text{NF}_3(102^\circ)$.

This is due to very slight back bonding in NCl_3 from $2p$ orbital of N to $3d$ orbital of Cl the extent of which is very less because only one lone pair is distributed over three chlorine atoms.

- b.** $\text{B}_3\text{N}_3\text{H}_6$ is planar and aromatic due to back bonding from N to B atom in the form of $2p\pi-2p\pi$.

- c.** $(\text{CH}_3)_3\text{N}$ is pyramidal while $(\text{H}_3\text{Si})_3\text{N}$ is planar, and similarly $(\text{SiH}_3)_3\text{P}$ is pyramidal and $(\text{GeH}_3)_3\text{N}$ is planar. This can be explained on the basis of back bonding. In case of $(\text{CH}_3)_3\text{N}$, there is no back bonding, however $2p\pi-3d\pi$ and $2p\pi-4d\pi$ back bonding in $(\text{SiH}_3)_3\text{N}$ and $(\text{GeH}_3)_3\text{N}$ respectively makes them planar and N atom is forced to adopt sp^2 hybridization. In case of $\text{P}(\text{SiH}_3)_3$, the internuclear distance is large and P atom has its own vacant d orbital. Hence the tendency to donate lone pair is very less and it adopts pyramidal structure and P atom is sp^3 hybridized.

It is also observed that $(\text{CH}_3)_3\text{N}$ is more basic as compared to $(\text{SiH}_3)_3\text{N}$ due to the same reason and they behave differently towards HCl.



- d.** $\text{H}_3\text{C}-\text{NCS}$ is bent while SiH_3-NCS is linear.

In CH_3NCS there is no back bonding, while in SiH_3-NCS the extent of back bonding ($2p\pi-3d\pi$) is so large that $\text{Si}-\text{N}-\text{C}-\text{S}$ skeleton becomes linear.

Similarly, in analogous series, CH_3-NCO is bent and $\text{H}_3\text{Si}-\text{NCO}$ is linear but $\text{H}_3\text{Ge}-\text{NCO}$ is again bent. Here back bonding ($2p\pi-4d\pi$) is relatively ineffective as compared to ($2p\pi-3d\pi$) in $\text{H}_3\text{Si}-\text{NCO}$ and cannot stretch the angle up to 180° . Hence $\text{H}_3\text{Ge}-\text{NCO}$ is angular.

In contrast, it is notable that $(\text{SiH}_3)_3\text{N}$ and $(\text{GeH}_3)_3\text{N}$ are planar while $\text{H}_3\text{Si}-\text{NCO}$ is linear but GeH_3-NCO is bent. Back bonding occurs in both $(\text{GeH}_3)_3\text{N}$ and $\text{H}_3\text{Ge}-\text{NCO}$ and is $2p\pi-4d\pi$. The back bonding extent is enough to increase the bond angle from $109^\circ 28'$ to 120° in case of $(\text{GeH}_3)_3\text{N}$ but not enough to increase the bond angle from 120° to 180° in case of $\text{H}_3\text{Ge}-\text{NCO}$.

Note: It is interesting to note that $\widehat{\text{CNC}}$ angle in CH_3NCS is 142° while $\widehat{\text{HNN}}$ angle in HN_3 is 112° , though they have identical skeleton. This can be explained with the help of resonance hybrid structures shown in Figure 3.16.

The contribution of structure (III) is negligible because the π bonds between C and S, i.e., $2p\pi-3p\pi$ are ineffective and the resonance hybrid structure is contributed by structures (I) and (II). Hence the bond angle is in between 120° and 180° , i.e., 142° .

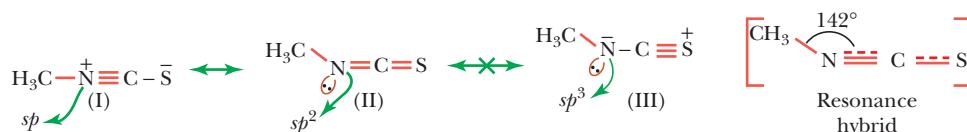


Figure 3.16 Resonating structures for CH_3NCS .

In case of HN_3 , the resonating structures are as shown in Figure 3.17.

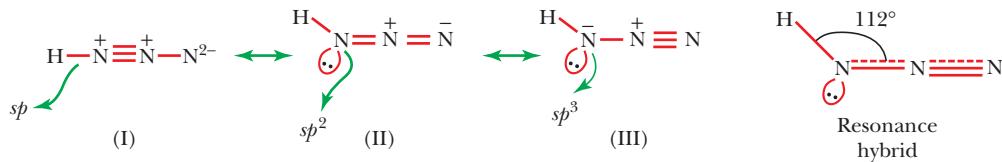


Figure 3.17 Resonating structures for HN_3 .

Here the contribution of structure (I) is very less. The hybrid structure is contributed largely by structures (II) and (III). Hence the bond angle is in between $109^{\circ}28'$ and 120° , i.e. 112° .

- e. The bond length order of the B–N bond in the following compounds is



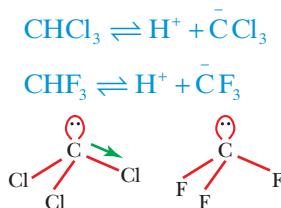
and the order of energy required for the rotation of the B–N bond is just reverse, i.e.



Here back bonding from N to B is most restricted in case of $\text{B}(\text{NR}_2)_3$ due to steric crowding and most relaxed in case of $\text{H}_2\text{B} - \text{NR}_2$. Hence, the above orders are well explained.

4. Back bonding with C as donor atom

- a. CHCl_3 is more acidic than CHF_3 which is explained as follows:



The lone pair on C atom gets delocalized through $2p\pi - 3d\pi$ bonding in Cl_3C^- , which is not possible in case of F_3C^- .

- b. $\text{R}_3\bar{\text{C}}$ is pyramidal while $(\text{CN})_3\bar{\text{C}}$ is planar due to the back bonding from the lone pair of C atom into the π^* orbital of the $\text{C} \equiv \text{N}$ group.

5. Back bonding with halogens (Cl, Br, I) as donor atom

- a. The Lewis acidity order of BX_3 molecules is explained in terms of back donation from X atom ($\text{X} = \text{F, Cl, Br, I}$) to B atom. The back donation ability order for halogens towards B atom is $\text{F} > \text{Cl} > \text{Br} > \text{I}$. This is because

(i) the size increases and mismatch of the overlapping orbital increases down the group, i.e. from F ($2p\pi - 2p\pi$) to I ($2p\pi - 5p\pi$).

(ii) F atom is a good donor due to its filled shell, while in general Cl, Br, I do not like to act as donor atoms; only act as donor atom when the adjacent atom is electrons deficient due to incomplete octet like B atom as shown in Figure 3.18.

Finally the Lewis acidity order is:



- b. The relative stability order for the diradicals is

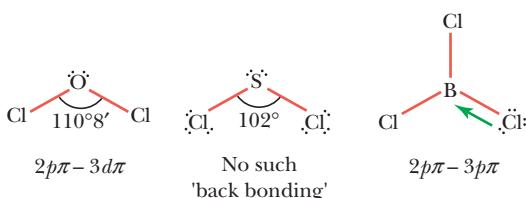


Figure 3.18 Effect of back bonding of halogen on Lewis acidity.

Here C atom is electron deficient due to incomplete octet and no back bonding is possible in $:\text{CH}_2$, while $2p\pi - 2p\pi$ and $2p\pi - 3p\pi$ kind of back donation takes place in $:\text{CF}_2$ and $:\text{CCl}_2$ respectively. Since the $2p\pi - 2p\pi$ back donation is most effective, $:\text{CF}_2$ is more stable as compared to $:\text{CCl}_2$ and $:\text{CH}_2$.

Note: An interesting phenomenon observed is that the direction of back bonding in $\bar{\text{C}}\text{Cl}_3$ and $:\text{CCl}_2$ is just reverse (Figure 3.19).

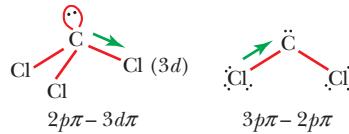


Figure 3.19 Back bonding in $\bar{\text{C}}\text{Cl}_3$ and $:\text{CCl}_2$

3.7 | THE EXTENT OF *d* ORBITAL PARTICIPATION IN MOLECULAR BONDING

The bonding in PCl_5 may be described using hybrids of the $3s$, $3p$ and $3d$ atomic orbitals for P – see below. However, there are doubts as to whether *d* orbitals can take part and this has led to the decline of valence bond theory.

Electronic structure of phosphorus atom – ground state	full inner shell	$3s$	$3p$	$3d$
Phosphorus atom – excited state				
Phosphorus having gained five electrons from chlorine atoms in PCl_5 molecule				

sp^3d hybridization, trigonal bipyramidal

However, *d* orbitals are in general too large and too high in energy to mix completely with *s* and *p* orbitals. The difference in size is illustrated by the mean values for the radial distance for different phosphorus orbitals: $3s = 0.47 \text{ \AA}$, $3p = 0.55 \text{ \AA}$ and $3d = 2.4 \text{ \AA}$. The energy of an orbital is proportional to its mean radial distance, and since the $3d$ orbital is much larger it is much higher in energy than the $3s$ and $3p$ orbitals. It would at first seem unlikely that hybridization involving *s*, *p* and *d* orbitals could possibly occur.

Several factors affect the size of orbitals. The most important is the charge on the atom. If the atom carries a formal positive charge then all the electrons will be pulled in towards the nucleus. The effect is greatest for the outer electrons. If the central P atom is bonded to a highly electronegative element such as F, O or Cl, then the electronegative element attracts more than its share of the bonding electrons and the F or Cl atom attains a $\delta-$ charge. This leaves a $\delta+$ charge on P, which makes the orbitals contract. Since the $3d$ orbital contracts in size very much more than the $3s$ and $3p$ orbitals, the energies of the $3s$, $3p$ and $3d$ orbitals may become close enough to allow hybridization to occur in PCl_5 . Hydrogen does not cause this large contraction, so PH_5 does not exist.

In a similar way the structure of SF_6 can be described by mixing the $3s$, three $3p$ and two $3d$ orbitals, that is sp^3d^2 hybridization.

Electronic structure of sulphur atom – ground state	full inner shell	$3s$	$3p$	$3d$
Electronic structure of sulphur atom – excited state				
Sulphur atom having gained six electrons from fluorine atoms in SF_6 molecule				

sp^3d^2 hybridization, octahedral structure

The presence of six highly electronegative F atoms causes a large contraction of the *d* orbitals, and lowers their energy, so mixing may be possible.

A second factor affecting the size of d orbitals is the number of d orbitals occupied by electrons. If only one $3d$ orbital is occupied on an S atom, the average radial distance is 2.46 \AA , but when two $3d$ orbitals are occupied the distance drops to 1.60 \AA . The effect of changing the charge can be seen in Table 3.5.

Table 3.5 Sizes of orbitals

$(sp^3 d^2$ configuration)	Mean radial distance (\AA)		
	$3s$	$3p$	$3d$
S atom (neutral, no charge)	0.88	0.94	1.60
S atom (charge +0.6)	0.87	0.93	1.40

A further small contraction of d orbitals may arise by coupling of the spins of electrons occupying different orbitals.

It seems probable that d orbitals do participate in bonding in cases where d orbital contraction occurs.

3.8 | TYPES OF COVALENT BONDS (SIGMA (σ) AND Pi (π) BONDS)

Covalent bonds are classified into two main types, i.e. σ bonds and π bonds.

- σ bond:** It is formed by head-on overlap of orbitals. In σ bond, the electron density is concentrated in between two atoms, and along the line joining the two atoms.

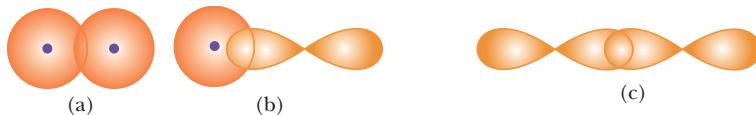


Figure 3.20 Different types of overlaps in σ bond: (a) $s - s$ overlap; (b) $s - p$ overlap; and (c) $p - p$ overlap

Different types of overlap for σ bonds:

- $s - s$ overlap, e.g. H_2 molecule (Figure 3.20a).
- $s - p$ overlap, e.g. HX molecule ($\text{X} = \text{F, Cl, Br, I}$) (Figure 3.20b).
- $p - p$ overlap, e.g. X_2 molecule ($\text{X} = \text{F, Cl, Br, I}$) (Figure 3.20c).

Keeping the internuclear distance same, the relative strength of bond resulting from three kinds of overlap is:

$$s - s < s - p < p - p$$

The order of bond strength can be explained on the basis of the fact that more the area of overlap, higher will be the strength. Since the p orbital has directional property, $p - p$ overlap provides more area for overlap for the same internuclear distance which is explained in Figure 3.21.

- π bond:** It is formed by sideways overlap of orbitals and it merely shortens the bond length.

Different types of overlap for π bonds (Figure 3.22):

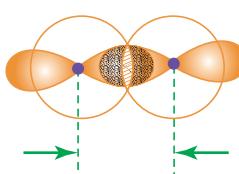


Figure 3.21 Area of overlap in $p - p$ overlap.

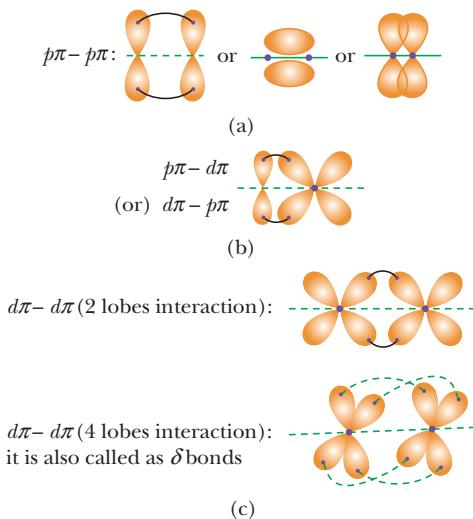


Figure 3.22 Different types of overlaps in π bond: (a) $p\pi-p\pi$ overlap; (b) $p\pi-d\pi$ or $d\pi-p\pi$ overlap; (c) $d\pi-d\pi$ overlap.

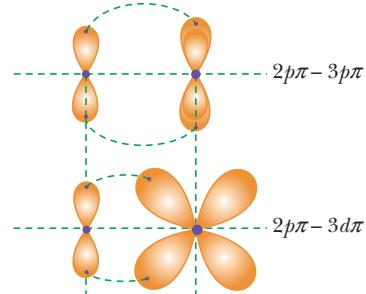


Figure 3.23 Nature of overlap between p and d orbitals in π bond formation.

The relative strength of the π bonds increases when the intermolecular distance decreases and the order is:



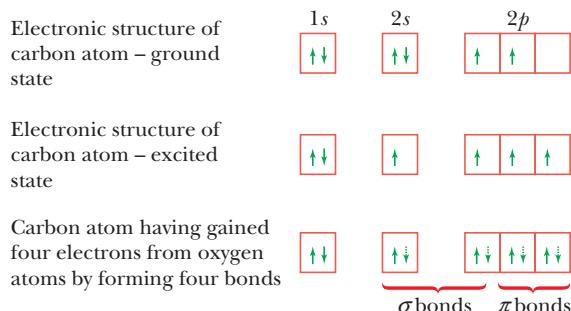
Due to the inclined nature of the d orbital, it is more close in case of $2p\pi - 3d\pi$ overlap and strength of bond is more as compared to $2p\pi - 3p\pi$ as shown in Figure 3.23.

The shape of the molecule is determined by the σ bonds (and lone pairs) but not by the π bonds.

Consider the structure of the carbon dioxide molecule. Since C has typically four valency and O has typically two valency, the bonding can be simply represented as



Triatomic molecules must be either linear or angular. In CO_2 , the C atom must be excited to provide four unpaired electrons to form the four bonds required.



There are two σ bonds and two π bonds in the molecule. π orbitals are ignored in determining the shape of the molecule. The remaining s and p orbitals are used to form the σ bonds. (These could be hybridized and the two sp orbitals will point in opposite directions. Alternatively, VSEPR theory suggests that these two orbitals will be oriented as far apart as possible). These two orbitals overlap with p orbitals from two O atoms, forming a linear molecule with a bond angle of 180° (Figure 3.24a). The $2p_y$ and $2p_z$ orbitals on C used for π bonding are at right angles to the bond, and overlap sideways

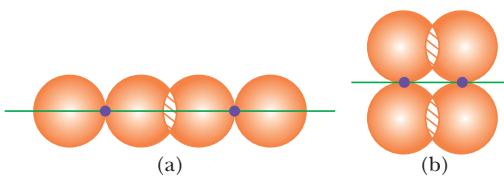


Figure 3.24 σ and π overlap: (a) σ overlap (lobes point along the nuclei); (b) π overlap (lobes are at right angles to the line joining the nuclei).

with p orbitals on the O atoms at either side (Figure 3.24b). This π overlap shortens the C—O distances, but does not affect the shape.

The sulphur dioxide molecule SO_2 may be considered in a similar way. S shows oxidation states of (+II), (+IV) and (+VI), whilst O has two valency. The structure may be represented as



Triatomic molecules are either linear or bent. The S atom must be excited to provide four unpaired electrons. The two electron pairs which form the π bonds do not affect the shape of the molecule. The remaining three orbitals point to the corners of a triangle, and result in a planar triangular structure for the molecule with two corners occupied by O atoms and one corner occupied by a lone pair. The SO_2 molecule is thus angular or V-shaped (Figure 3.25).

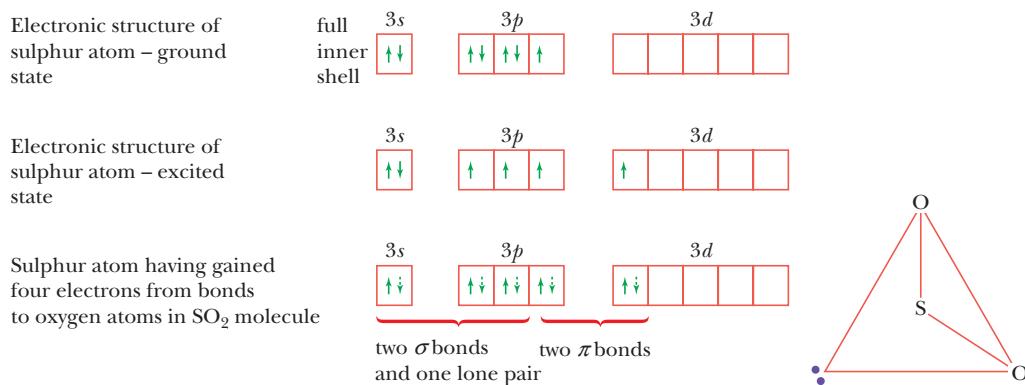
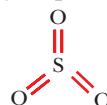


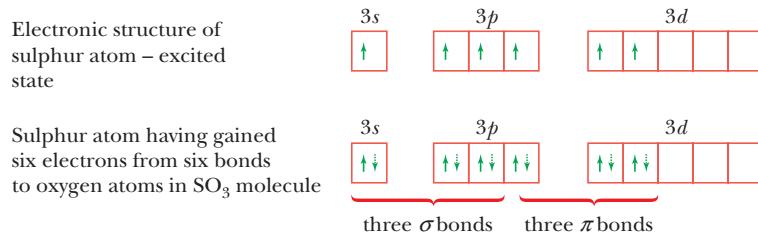
Figure 3.25 Sulphur dioxide molecule

The π bonds do not alter the shape, but merely shorten the bond lengths. The bond angle is reduced from the ideal value of 120° to $119^\circ 30'$ because of the repulsion by the lone pair of electrons. Problems arise when we examine exactly which AOs are involved in π overlap. If the σ bonding occurs in the xy plane, then π overlap can occur between the $3p_z$ orbital on S and the $2p_z$ orbital on one O atom to give one π bond. The second π bond involves a d orbital. Though the $3d_{z^2}$ orbital on S is in the correct orientation for π overlap with the $2p_z$ orbital on the other O atom, the symmetry of the $3d_{z^2}$ orbital is wrong (both lobes have a + sign); whilst for a p orbital one lobe is + and the other -. Thus, overlap of these orbitals does not result in bonding. The $3d_{xz}$ orbital on S is in the correct orientation, and has the correct symmetry to overlap with the $2p_z$ orbital on the second O atom, and could give the second π bond. It is surprising that π bonds involving p and d orbitals both have the same energy (and bond length). This calls into question whether it is correct to treat molecules with two π bonds as containing two discrete π bonds. A better approach is to treat the π bonds as being delocalized over several atoms. Examples of this treatment are given near the end of this chapter.

In the sulphur trioxide molecule SO_3 valency requirements suggest the structure



The central S atom must be excited to provide six unpaired electrons to form six bonds.



The three π bonds are ignored in determining the shape of the molecule. The three σ orbitals are directed towards the corners of an equilateral triangle, and the SO_3 molecule is a completely regular plane triangle (Figure 3.26). The π bonds shorten the bond lengths, but do not affect the shape. This approach explains the σ bonding and shape of the molecule, but the explanation of π bonding is unsatisfactory. It presumes that:

- One $3p$ and two $3d$ orbitals on S are in the correct orientation to overlap sideways with the $2p_y$ or $2p_z$ orbitals on three different O atoms.
- The π bonds formed are all of equal strength.

This calls into question the treatment of π bonds. In molecules with more than one π bond, or molecules where the π bond could equally well exist in more than one position, it is better to treat the π bonding as being delocalized over several atoms rather than localized between two atoms.

Bridge bonding

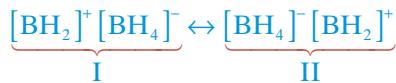
- Bridge bonding in BH_3 molecules:** It is observed that BH_3 molecules do not exist in monomeric form at ordinary conditions, and undergo dimerization readily as explained below (Figure 3.27).



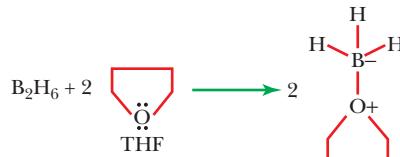
The driving force for this kind of dimerization is to achieve momentarily octet for B atoms in B_2H_6 . The B_2H_6 can be considered a hybrid structure of the following resonating structures (I) and (II), where the B atom in $[\text{BH}_4]^-$ unit has a complete octet, while the B atom in $[\text{BH}_2]^+$ has an incomplete octet.



Figure 3.27 Dimerization of BH_3 molecules.

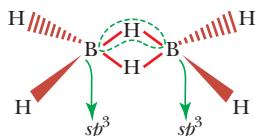


Hence the momentarily octet is achieved and B_2H_6 molecule is still electron deficient. This is further supported by the experimental fact that B_2H_6 readily reacts with tetrahydrofuran (THF) as shown below.



For the above reaction, the driving force is to complete the octet of B atom permanently.

- Hybridization of the B atoms in B_2H_6 : Observing the tetrahedral arrangement of four H atoms around the B atom, it is concluded that the hybridization of both B atoms is sp^3 and overall the molecule is non-planar.

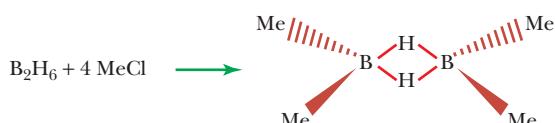


The electronic distribution of the bridge bond ($\text{B} - \text{H} - \text{B}$) has a banana-like appearance and is also called banana bond. This bridge bond is also called three centre–two electron (3c–2e) bond because only two electrons are responsible for attracting three positive centres or nucleus.

- Bond lengths and bond strength in B_2H_6 :

(i) $d_{\text{B}-\text{H}}$ (terminal bonds) $< d_{\text{B}-\text{H}}$ (bridge bonds)

- (ii) The energy required to replace H atoms from the bridged position is more than that needed for the terminal position. This is supported by the fact that on reaction with methyl chloride, terminal hydrogen atoms are replaced by methyl group in preference to bridged hydrogen atoms.



The reason for this could be to the fact that to break the bridge bond, the overlapping zone should be broken from both sides and the overall energy required is more as compared to do so for terminal bonds (Figure 3.28).

This kind of overlap is σ type and considered as $sp^3 - s - sp^3$ overlap.

- 2. Bridge bonding in BeH_2 and BeCl_2 :** The structures of BeH_2 , Be_2H_4 and $(\text{BeH}_2)_n$ can be explained in the light of bridge bonding as shown in Figure 3.29.

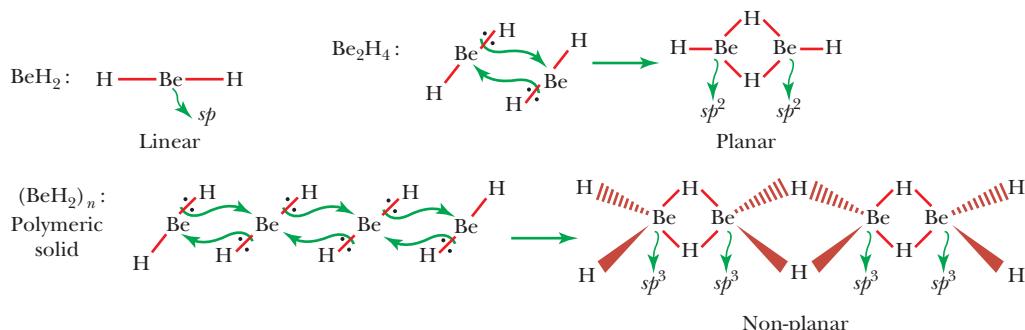


Figure 3.29 Bridge bonding in BeH_2 , Be_2H_4 and $(\text{BeH}_2)_n$.

BeCl_2 also undergoes dimerization and polymerization like BeH_2 , but the nature of bonding to fulfill the electron deficiency is different and is depicted in Figure 3.30. When a lone pair is present on the surrounding atom, the bond pair cannot be shared, which releases less energy compared to that when lone pair is shared.

The bridge bond in $\text{Be}-\text{Cl}-\text{Be}$ is called three centre–four electron (3c–4e) bond because total four electrons are involved in this bridge bond formation. But here also $d_{\text{Be}-\text{Cl}}$ (bridge bond) $> d_{\text{Be}-\text{Cl}}$ (terminal bond). The structure of $(\text{BeCl}_2)_n$ that exists as a polymeric solid is shown in Figure 3.31.

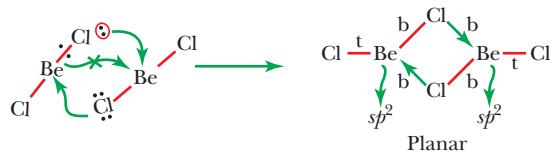


Figure 3.30 Bridge bonding in Be_2Cl_4 .

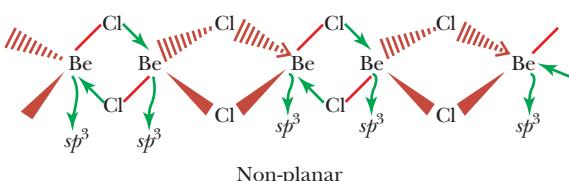


Figure 3.31 Polymeric structure of $(\text{BeCl}_2)_n$.

- 3. Bridge bonding in I_2Cl_6 :** Formation of I_2Cl_6 takes place by following reaction



In I_2Cl_6 both I atoms are sp^3d^2 hybridized and overall molecule is planar to minimize the repulsion between the lone pairs of I atoms (Figure 3.32).

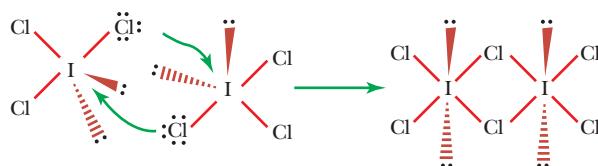


Figure 3.32 Structure of I_2Cl_6 .

The nature and planarity of bonds in some molecules that show bridge bonding is given in Table 3.6.

Table 3.6 Molecules which show bridge-bonding

Molecules	Nature of bonds (3c – 2e / 3c – 4e)	Planar (P) and Non-planar (NP)
Al ₂ Cl ₆	3c – 4e	NP
Al ₂ Br ₆	3c – 4e	NP
(AlH ₃) _n	3c – 2e	NP
Al ₂ I ₆	3c – 4e	NP
Al ₂ (CH ₃) ₆	3c – 2e	NP
I ₂ Cl ₆	3c – 4e	P

Note: The bridge bonding between two different atoms is also possible which is found in Al(BH₄)₃ and Be(BH₄)₂. (See Chapter 10, page 368 for further discussion.)

3.9 | MOLECULAR ORBITAL METHOD

In the valence bond (electron pair) theory, a molecule is considered to be made up of atoms. Electrons in atoms occupy atomic orbitals. These may or may not be hybridized. If they are hybridized, atomic orbitals *from the same atom* combine to produce hybrid orbitals which can overlap more effectively with orbitals from other atoms, thus producing stronger bonds. Thus the atomic orbitals (or the hybrid orbitals) are thought to remain even when the atom is chemically bonded in a molecule.

In the molecular orbital theory, the valency electrons are considered to be associated with all the nuclei in the molecule. Thus the atomic orbitals *from different atoms* must be combined to produce molecular orbitals.

Electrons may be considered either as particles or waves. An electron in an atom may therefore be described as occupying an atomic orbital, or by a wave function ψ , which is a solution to the Schrödinger wave equation. Electrons in a molecule are said to occupy molecular orbitals. The wave function describing a molecular orbital may be obtained by one of two procedures:

1. Linear combination of atomic orbitals (LCAO).
2. United atom method. (Beyond scope of discussion).

3.10 | LCAO METHOD

Consider two atoms A and B which have atomic orbitals described by the wave functions $\psi_{(A)}$ and $\psi_{(B)}$. If the electron clouds of these two atoms overlap when the atoms approach, then the wave function for the molecule (molecular orbital $\psi_{(AB)}$) can be obtained by a linear combination of the atomic orbitals $\psi_{(A)}$ and $\psi_{(B)}$:

$$\psi_{(AB)} = N(c_1\psi_{(A)} + c_2\psi_{(B)})$$

where N is a normalizing constant chosen to ensure that the probability of finding an electron in the whole of the space is unity, and c_1 and c_2 are constants chosen to give a minimum energy for $\psi_{(AB)}$. If atoms A and B are similar, then c_1 and c_2 will have similar values. If atoms A and B are the same, then c_1 and c_2 are equal.

The probability of finding an electron in a volume of space dv is $\psi^2 dv$, so the probability density for the combination of two atoms as above is related to the wave function squared:

$$\psi_{(AB)}^2 = (c_1^2\psi_{(A)}^2 + 2c_1c_2\psi_{(A)}\psi_{(B)} + c_2^2\psi_{(B)}^2)$$

If we examine the three terms on the right of the equation, the first term $c_1^2\psi_{(A)}^2$ is related to the probability of finding an electron on atom A if A is an isolated atom. The third term $c_2^2\psi_{(B)}^2$ is related to the probability

of finding an electron on atom B if B is an isolated atom. The middle term becomes increasingly important as the overlap between the two atomic orbitals increases, and this term is called the overlap integral. This term represents the main difference between the electron clouds in individual atoms and in the molecule. The larger this term the stronger the bond.

s-s combinations of orbitals

Suppose the atoms A and B are hydrogen atoms; then the wave functions $\psi_{(A)}$ and $\psi_{(B)}$ describe the 1s atomic orbitals on the two atoms. Two combinations of the wave functions $\psi_{(A)}$ and $\psi_{(B)}$ are possible:

1. Where the signs of the two wave functions are the same.
2. Where the signs of the two wave functions are different.

(If one of the wave functions $\psi_{(A)}$ is arbitrarily assigned a +ve sign, the other may be either +ve or -ve). Wave functions which have the same sign may be regarded as waves that are in phase, which when combined add up to give a larger resultant wave (Figure 3.33). Similarly wave functions of different signs correspond to waves that are completely out of phase and which cancel each other by destructive interference. (The signs + and - refer to signs of the wave functions, which determine their symmetry, and have nothing to do with electrical charges.) The two combinations are:

$$\Psi_{(g)} = N\{\psi_{(A)} + \psi_{(B)}\}$$

and

$$\Psi_{(u)} = N\{\psi_{(A)} + [-\psi_{(B)}]\} \equiv N\{\psi_{(A)} - \psi_{(B)}\}$$

The latter equation should be regarded as the summation of the wave functions and *not* as the mathematical difference between them.

When a pair of atomic orbitals $\psi_{(A)}$ and $\psi_{(B)}$ combine, they give rise to a pair of molecular orbitals $\Psi_{(g)}$ and $\Psi_{(u)}$. The number of molecular orbitals produced must always be equal to the number of atomic orbitals involved. The function $\Psi_{(g)}$ leads to increased electron density in between the nuclei, and is therefore a bonding molecular orbital. It is lower in energy than the original atomic orbitals. Conversely $\Psi_{(u)}$ results in two lobes of opposite sign cancelling and hence giving zero electron density in between the nuclei. This is an antibonding molecular orbital which is higher in energy (Figure 3.34).

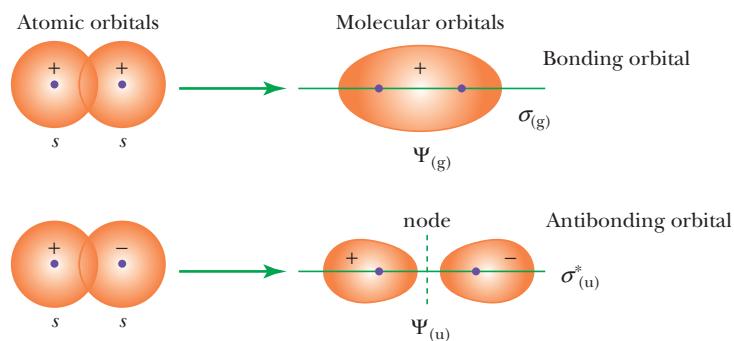


Figure 3.33 s-s combinations of atomic orbitals.

The molecular orbital wave functions are designated $\Psi_{(g)}$ and $\Psi_{(u)}$; g stands for *gerade* (even) and u for *ungerade* (odd), g and u refer to the symmetry of the orbital about its centre. If the sign of the wave function is unchanged when the orbital is reflected about its centre (i.e. x, y and z are replaced by -x, -y and -z) the orbital is *gerade*. An alternative method for determining the symmetry of the molecular orbital is to rotate the orbital about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remains the same, the orbital is *gerade*, and if the sign changes, the orbital is *ungerade*.

The energy of the bonding molecular orbital $\Psi_{(g)}$ passes through a minimum (Figure 3.34), and the distance between the atoms at this point corresponds to the internuclear distance between the atoms when they form a bond. Consider the energy levels of the two $1s$ atomic orbitals, and of the bonding $\Psi_{(g)}$ and antibonding $\Psi_{(u)}$ orbitals (Figure 3.35).

The energy of the bonding molecular orbital is lower than that of the atomic orbital by an amount Δ . This is known as the stabilization energy.

Similarly the energy of the antibonding molecular orbital is increased by Δ . Atomic orbitals may hold up to two electrons (provided that they have opposite spins) and the same applies to molecular orbitals. In the case of two hydrogen atoms combining, there are two electrons to be considered: one from the $1s$ orbital of atom A and one from the $1s$ orbital of atom B. When combined, these two electrons both occupy the bonding molecular orbital $\Psi_{(g)}$. This results in a saving of energy of 2Δ , which corresponds to the bond energy: It is only because the system is stabilized in this way that a bond is formed.

Consider the hypothetical case of two He atoms combining. The $1s$ orbitals on each He contain two electrons, making a total of four electrons to put into molecular orbitals. Two of the electrons occupy the bonding MO, and two occupy the antibonding MO. The stabilization energy 2Δ derived from filling the bonding MO is offset by the 2Δ destabilization energy from using the antibonding MO. Since overall there is no saving of energy, He_2 does not exist, and this situation corresponds to non-bonding.

Some further symbols are necessary to describe the way in which the atomic orbitals overlap. Overlap of the orbitals along the axis joining the nuclei produces σ molecular orbitals, whilst lateral overlap of atomic orbitals forms π molecular orbitals.

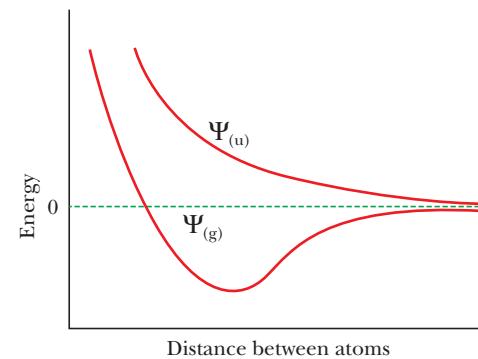


Figure 3.34 Energy of $\Psi_{(g)}$ and $\Psi_{(u)}$ molecular orbitals.

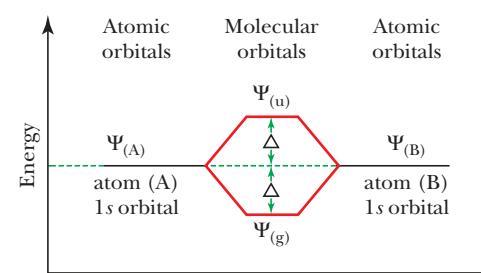


Figure 3.35 Energy levels of $s-s$ atomic and molecular orbitals.

s–p combinations of orbitals

An s orbital may combine with a p orbital provided that the lobes of the p orbital are pointing along the axis joining the nuclei. When the lobes which overlap have the same sign this results in a bonding MO with an increased electron density between the nuclei. When the overlapping lobes have opposite signs this gives an antibonding MO with a reduced electron density in between the nuclei (Figure 3.36).

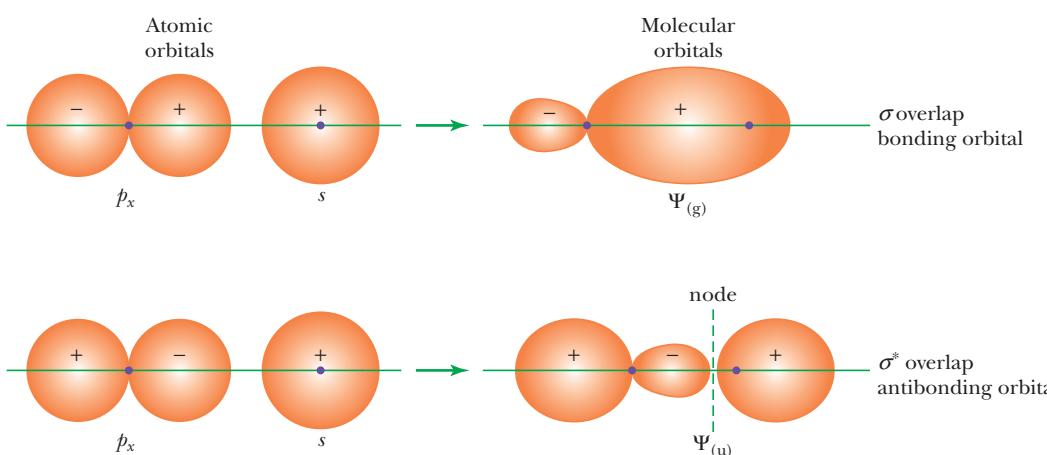


Figure 3.36 $s-p$ combination of atomic orbitals.

p–p combinations of orbitals

Consider first the combination of two p orbitals which both have lobes pointing along the axis joining the nuclei. Both a bonding MO and an antibonding MO are produced (Figure 3.37).

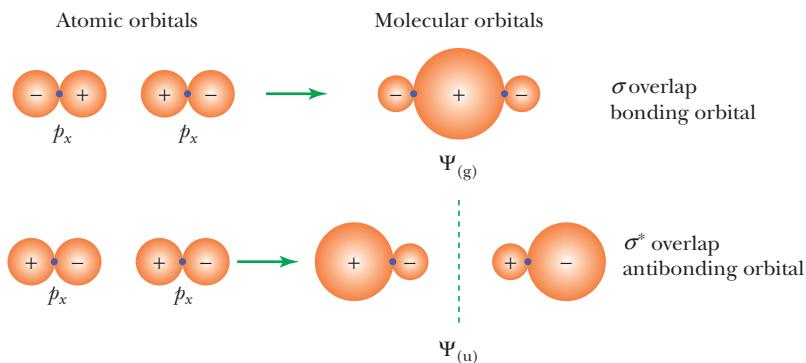


Figure 3.37 p – p combination of atomic orbitals.

Next consider the combination of two p orbitals which both have lobes perpendicular to the axis joining the nuclei. Lateral overlap of orbitals will occur, resulting in π bonding and π^* antibonding MOs being produced (Figure 3.38).

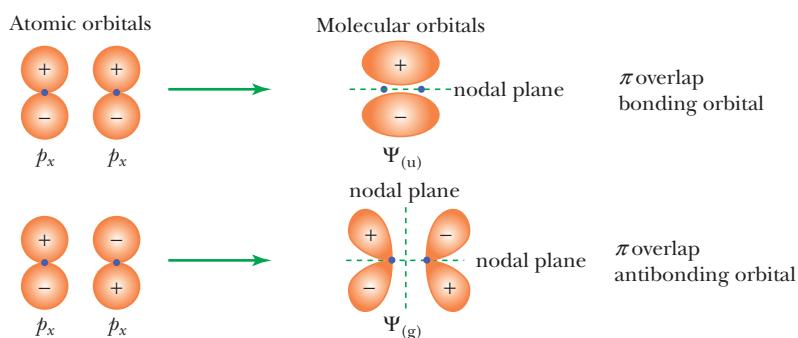


Figure 3.38 p – p combinations giving π bonding.

There are three points of differences between these molecular orbitals and the σ orbitals described previously:

1. For π overlap, the lobes of the atomic orbitals are perpendicular to the line joining the nuclei, whilst for σ overlap the lobes point along the line joining the two nuclei.
2. For π molecular orbitals, ψ is zero along the internuclear line and consequently the electron density ψ^2 is also zero. This is in contrast to σ orbitals.
3. The symmetry of π molecular orbitals is different from that shown by σ orbitals. If the bonding π MO is rotated about the internuclear line a change in the sign of the lobe occurs. The π bonding orbitals are therefore *ungerade*, whereas all σ bonding MOs are *gerade*. Conversely, the antibonding π MO is *gerade* whilst all σ antibonding MOs are *ungerade*.

π bonding is important in many organic compounds such as ethene (where there is one σ bond and one π bond between the two carbon atoms), ethyne (one σ and two π), and benzene, and also in a number of inorganic compounds such as CO_2 and CN^- .

Ethene contains a localized double bond, which involves only the two carbon atoms. Experimental measurements show that the two C atoms and the four H atoms are coplanar, and the bond angles are close to 120° . Each C atom uses its $2s$ and two $2p$ orbitals to form three sp^2 hybrid orbitals that form σ bonds to the other C atom and two H atoms. The remaining p orbital on each C atom is at right angles to the σ

bonds so far formed. In the valence bond theory these two p orbitals overlap sideways to give a π bond. This sideways overlap is not as great as the end to end overlap in σ bonds so a $\text{C} = \text{C}$, though stronger than a $\text{C} - \text{C}$ bond, is not twice as strong ($\text{C} - \text{C}$ in ethane 346 kJ mol^{-1} , $\text{C} = \text{C}$ in ethene 598 kJ mol^{-1}). The molecule can be twisted about the $\text{C} - \text{C}$ bond in ethane, but it cannot be twisted in ethene since this would reduce the amount of π overlap. In the molecular orbital theory the explanation of the π bonding is slightly different. The two p orbitals involved in π bonding combine to form two π molecular orbitals, one bonding and one antibonding. Since there are only two electrons involved, these occupy the π bonding MO since this has the lower energy. The molecular orbital explanation becomes more important in cases where there is non-localized π bonding, that is where π bonding covers several atoms as in benzene, NO_3^- and CO_3^{2-} .

In ethyne each C atom uses sp hybrid orbitals to form σ bonds to the other C atom and a H atom. These four atoms form a linear molecule. Each C atom has two p orbitals at right angles to one another, and these overlap sideways with the equivalent p orbitals on the other C atom, thus forming two π bonds. Thus a $\text{C} \equiv \text{C}$ triple bond is formed, which is stronger than a $\text{C} = \text{C}$ double bond ($\text{C} \equiv \text{C}$ in ethyne 813 kJ mol^{-1}).

The majority of strong π bonds occur between elements of the first short period in the periodic table, for example $\text{C} \equiv \text{C}$, $\text{C} \equiv \text{N}$, $\text{C} \equiv \text{O}$, $\text{C} = \text{C}$ and $\text{C} = \text{O}$. This is mainly because the atoms are smaller and hence the orbitals involved are reasonably compact, so it is possible to get substantial overlap of orbitals. There are a smaller number of cases where π bonding occurs between different types of orbitals, for example the $2p$ and $3d$ orbitals. Though these orbitals are much larger, the presence of nodes may concentrate electron density in certain parts of the orbitals.

p-d combinations of orbitals

A p orbital on one atom may overlap with a d orbital on another atom as shown, giving bonding and antibonding combinations. Since the orbitals do not point along the line joining the two nuclei, overlap must be of the π type (Figure 3.39). This type of bonding is responsible for the short bonds found in the oxides and oxoacids of phosphorus and sulphur. It also occurs in transition metal complexes such as the carbonyls and cyanides.

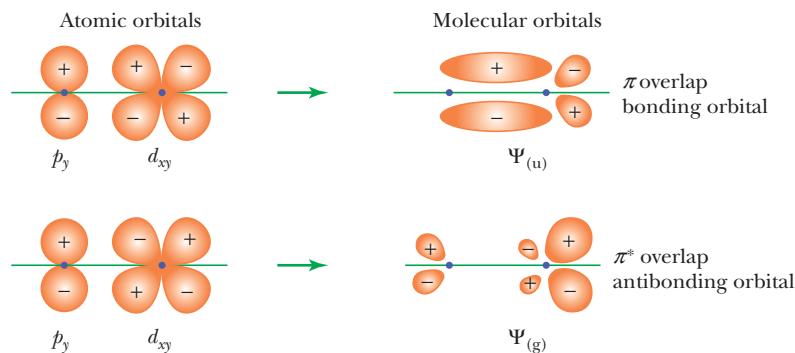


Figure 3.39 p - d combinations of atomic orbitals.

d-d combinations of orbitals

It is possible to combine two d atomic orbitals, producing bonding and antibonding MOs which are called δ and δ^* respectively. On rotating these orbitals about the internuclear axis, the sign of the lobes changes four times compared with two changes with π overlap and no change for σ overlap (Figure 3.40).

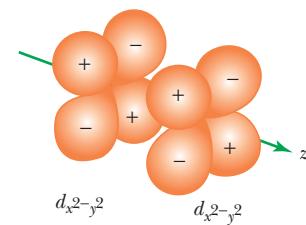


Figure 3.40 δ bonding by d orbitals (sideways overlap of two $d_{x^2-y^2}$ orbitals).

Non-bonding combinations of orbitals

All the cases of overlap of atomic orbitals considered so far have resulted in a bonding MO of lower energy, and an antibonding MO of higher energy. To obtain a bonding MO with a concentration of electron

density in between the nuclei, the signs (symmetry) of the lobes which overlap must be the same. Similarly for antibonding MOs the signs of the overlapping lobes must be different. In the combinations shown in Figure 3.41 any stabilization which occurs from overlapping + with + is destabilized by an equal amount of overlap of + with -. There is no overall change in energy, and this situation is termed non-bonding. It should be noted that in all of these non-bonding cases the symmetry of the two atomic orbitals is different, i.e. rotation about the axis changes the sign of one.

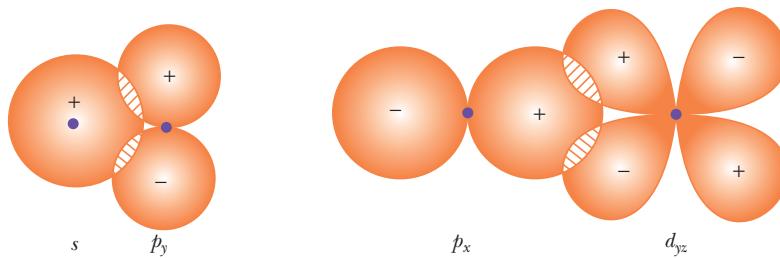


Figure 3.41 Some non-bonding combinations of atomic orbitals.

3.11 | RULES FOR LINEAR COMBINATION OF ATOMIC ORBITALS

In deciding which atomic orbitals may be combined to form molecular orbitals, three rules must be considered:

1. The atomic orbitals must be roughly of the same energy. This is important when considering overlap between two different types of atoms.
2. The orbitals must overlap one another as much as possible. This implies that the atoms must be close enough for effective overlap and that the radial distribution functions of the two atoms must be similar at this distance.
3. In order to produce bonding and antibonding MOs, either the symmetry of the two atomic orbitals must remain unchanged when rotated about the internuclear line, or both atomic orbitals must change symmetry in an identical manner.

In the same way that each atomic orbital has a particular energy, and may be defined by four quantum numbers, each molecular orbital has a definite energy, and is also defined by four quantum numbers.

1. The principal quantum number n has the same significance as in atomic orbitals.
2. The subsidiary quantum number l also has the same significance as in atomic orbitals.
3. The magnetic quantum number of atomic orbitals is replaced by a new quantum number λ . In a diatomic molecule, the line joining the nuclei is taken as a reference direction and λ represents the quantization of angular momentum in $h/2\pi$ units with respect to this axis. λ takes the same values as m takes for atoms, i.e.

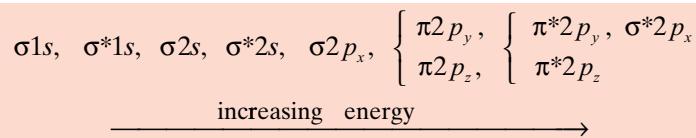
$$\lambda = -l, \dots, -3, -2, -1, 0, +1, +2, +3, \dots, +l$$

When $\lambda = 0$, the orbitals are symmetrical around the axis and are called σ orbitals. When $\lambda = \pm 1$ they are called π orbitals and when $\lambda = \pm 2$ they are called δ orbitals.

4. The spin quantum number is the same as for atomic orbitals and may have values of $\pm \frac{1}{2}$.

The Pauli exclusion principle states that *in a given atom no two electrons can have all four quantum numbers the same*. The Pauli principle also applies to molecular orbitals: *No two electrons in the same molecule can have all four quantum numbers the same*.

The order of energy of molecular orbitals has been determined mainly from spectroscopic data. In simple homonuclear diatomic molecules, the order is:



The molecular orbital diagram representing this order of energy levels is shown in Figure 3.42.

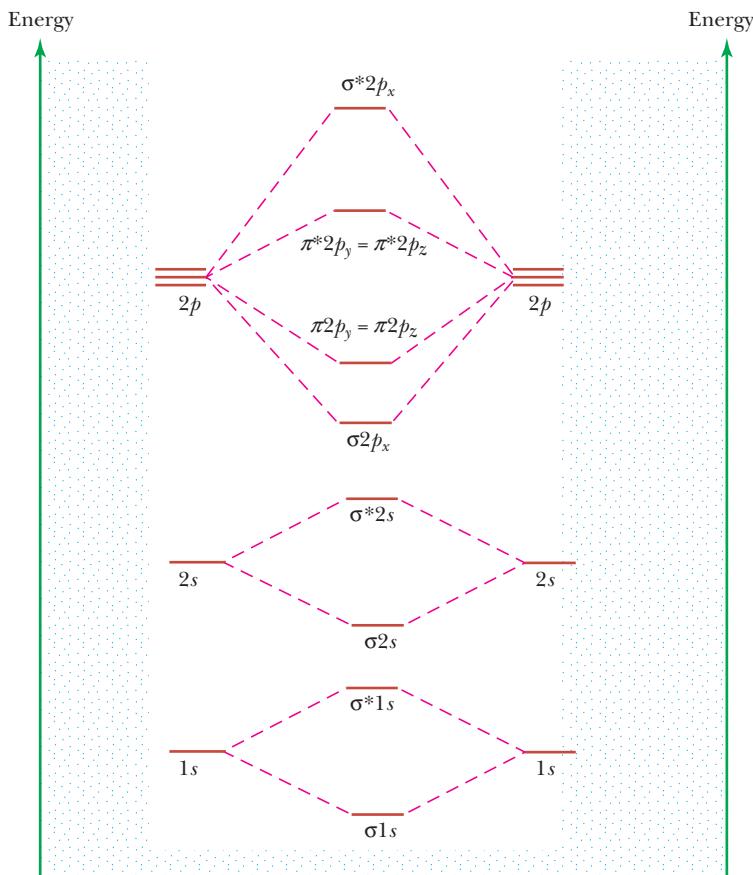
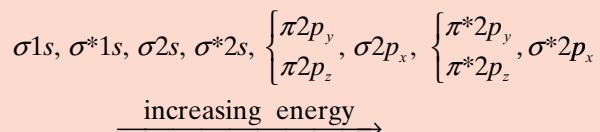


Figure 3.42 Electronic configuration, atomic orbital and molecular orbitals for simple homonuclear diatomic molecules.

Note that the $2p_y$ atomic orbital gives π bonding and π^* antibonding MOs and the $2p_z$ atomic orbital gives π bonding and π^* antibonding MOs. The bonding $\pi 2p_y$ and $\pi 2p_z$ MOs have exactly the same energy and are said to be double degenerate. In a similar way the antibonding $\pi^* 2p_y$ and $\pi^* 2p_z$ MOs have the same energy and are also doubly degenerate.

A similar arrangement of MOs exists from $\sigma 3s$ to $\sigma^* 3p_x$, but the energies are known with less certainty.

The energies of the $\sigma 2p$ and $\sigma 2p$ MOs are very close together. The order of MOs shown above is correct for oxygen and heavier elements, but for the lighter elements boron, carbon and nitrogen the $\pi 2p_y$ and $\pi 2p_z$ are probably lower than $\sigma 2p_x$. For these atoms the order is:



The molecular orbital diagram representing this order of energy levels is shown in Figure 3.43.

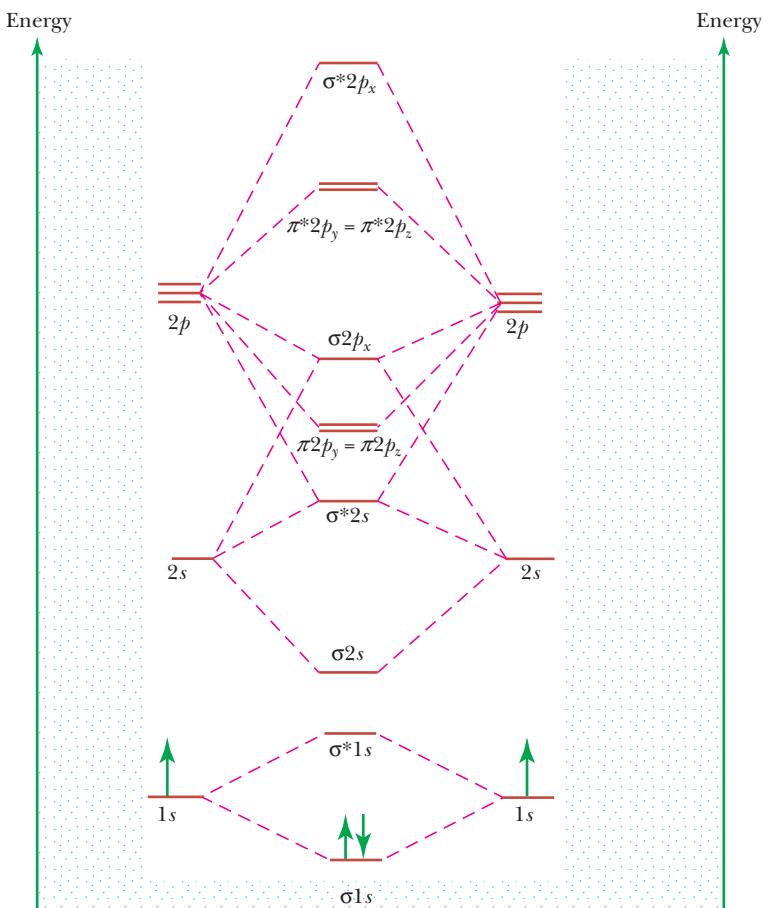


Figure 3.43 Electronic configuration, atomic and molecular orbitals for heavier homonuclear diatomic molecules.

This kind of energy reversal is due to mixing of 2s and 2p orbitals where the energy difference is very close, i.e. for B, C, N atoms. According to the symmetry interactions (non-crossing rule), the two orbitals of the same symmetry repel each other; and the lower energy orbital lowers down more while the higher energy orbital is energized more. Accordingly, σ_{2s} and σ_{2p_x} have same symmetry and similarly for σ_{2s}^* and $\sigma_{2p_x}^*$, the energy of σ_{2s} is lowered and that of the σ_{2p_x} becomes higher. Similarly the energy of σ_{2s}^* is lowered while that of $\sigma_{2p_x}^*$ becomes higher. Finally, the energy of the σ_{2p_x} becomes higher than $\pi 2p_y, \pi 2p_z$ which remain unchanged in the symmetry interaction. This kind of mixing of orbitals or symmetry interaction is not applicable for O₂ and F₂ molecule formation because of larger energy gap between 2s and 2p orbitals for these atoms.

Atoms	Li	Be	B	C	N	O	F	Ne
$\Delta E_{(2p-2s)}$	1.8	2.8	4.5	5.3	6.0	15.0	20.5	26.7
in (eV)								

3.12 | EXAMPLES OF MOLECULAR ORBITAL TREATMENT FOR HOMONUCLEAR DIATOMIC MOLECULES

In the build-up of atoms, electrons are fed into atomic orbitals. The *Aufbau* principle is used:

1. Orbitals of lowest energy are filled first.
2. Each orbital may hold up to two electrons, provided that they have opposite spins.

Hund's rule states that when several orbitals have the same energy (that is they are degenerate), electrons will be arranged so as to give the maximum number of unpaired spins.

In the molecular orbital method, we consider the whole molecule rather than the constituent atoms, and use molecular orbitals rather than atomic orbitals. In the build-up of the molecule, the total number of electrons from all the atoms in the molecule is fed into molecular orbitals. The *Aufbau* principle and Hund's rule are used as before.

For simplicity homonuclear diatomic molecules will be examined first. Homonuclear means that there is only one type of nucleus, that is one element present, and diatomic means that the molecule is composed of two atoms.

H_2^+ molecule ion

This may be considered as a combination of a H atom with a H^+ ion. This gives one electron in the molecular ion which occupies the lowest energy MO:



The electron occupies the $\sigma 1s$ bonding MO. The energy of this ion is thus lower than that of the constituent atom and ion, by an amount Δ , so there is some stabilization. This species exists but it is not common since H_2 is much more stable. However, H_2^+ can be detected spectroscopically when H_2 gas under reduced pressure is subjected to an electric discharge.

H_2 molecule

There is one electron from each atom, and hence there are two electrons in the molecule. These occupy the lowest energy MO:



This is shown in Figure 3.44. The bonding $\sigma 1s$ MO is full, so the stabilization energy is 2Δ . A σ bond is formed, and the H_2 molecule exists and is well known.

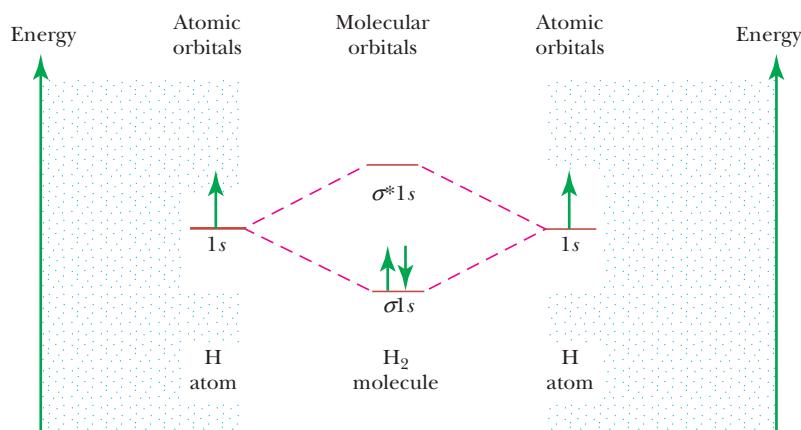


Figure 3.44 Electronic configuration, atomic and molecular orbitals for hydrogen.

He_2^+ molecule ion

This may be considered as a combination of a He atom and a He^+ ion. There are three electrons in the molecular ion, which are arranged in MOs:



The filled $\sigma 1s$ bonding MO gives 2Δ stabilization, whilst the half-filled $\sigma 1s^*$ gives Δ destabilization. Overall there is Δ stabilization. Thus the helium molecule ion can exist. It is not very stable, but it has been observed spectroscopically.

He₂ molecule

There are two electrons from each atom, and the four electrons are arranged in MOs:



The 2Δ stabilization energy from filling the $\sigma 2s$ MO is cancelled by the 2Δ destabilization energy from filling the $\sigma^* 1s$ MO. Thus a bond is not formed, and the molecule does not exist.

Li₂ molecule

Each Li atom has two electrons in its inner shell, and one in its outer shell, giving three electrons. Thus there is a total of six electrons in the molecule, and these are arranged in MOs:



The inner shell of filled $\sigma 1s$ and $\sigma^* 1s$ MOs do not contribute to the bonding in much the same way as in He₂. They are essentially the same as the atomic orbitals from which they were formed, and are sometimes written:



However, bonding occurs from the filling of the $\sigma 2s$ level, and Li₂ molecules do exist in the vapour state. However, in the solid it is energetically more favourable for lithium to form a metallic structure. Other Group 1 metals such as sodium behave in an analogous way:



Be₂ molecule

A beryllium atom has two electrons in the first shell plus two electrons in the second shell. Thus in the Be₂ molecule there are eight electrons. These are arranged in MOs:



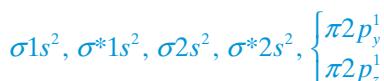
or



Ignoring the inner shell as before, it is apparent that the effects of the bonding $\sigma 2s$ and antibonding $\sigma^* 2s$ levels cancel, so there is no stabilization and the molecule would not be expected to exist.

B₂ molecule

Each boron atom has $2 + 3$ electrons. The B₂ molecule thus contains a total of ten electrons, which are arranged in MOs:



Note that B is a light atom and the order of energies of MOs is different from the 'usual' arrangement. Thus the $\pi 2p$ orbitals are lower in energy than the $\sigma 2p_x$. Since the $\pi 2p_y$ and $\pi 2p_z$ orbitals are degenerate (identical in energy), Hund's rule applies, and each is singly occupied. The inner shell does not participate in bonding. The effects of bonding and antibonding $\sigma 2s$ orbitals cancel but stabilization occurs from the filling of the $\pi 2p$ orbitals, and hence a bond is formed and B₂ exists.

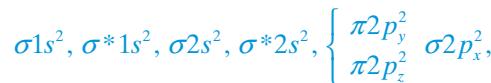
C₂ molecule

A carbon atom has $2 + 4$ electrons. A C₂ molecule would contain a total of 12 electrons, and these would be arranged in MOs:

The molecule should be stable, since the two $\pi 2p$ bonding orbitals provide 4Δ of stabilization energy, giving two bonds. In fact carbon exists as a macromolecule in graphite and diamond, since these are an even more stable arrangement (where each carbon forms four bonds): hence diamond and graphite are formed in preference to C₂.

N₂ molecule

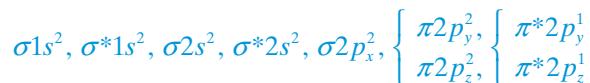
A nitrogen atom has $2 + 5 = 7$ electrons. Thus the N₂ molecule contains 14 electrons. These are arranged in MOs:



Assuming that the inner shell does not participate in bonding, and that the bonding and antibonding 2s levels cancel, one σ and two π bonding pairs remain, giving a total of three bonds. This is in agreement with the valence bond formulation as N \equiv N.

O₂ molecule

Each oxygen atom has $2 + 6 = 8$ electrons. Thus the O₂ molecule contains a total of 16 electrons. These are arranged in MOs:



The antibonding $\pi^* 2p_y$ and $\pi^* 2p_z$ orbitals are singly occupied in accordance with Hund's rule. Unpaired electrons give rise to paramagnetism. Since there are two unpaired electrons with parallel spins, this explains why dioxygen is paramagnetic. If this treatment is compared with the Lewis electron pair theory or the valence bond theory, these do not predict unpaired electrons or paramagnetism.



This was the first success of the molecular orbital theory in successfully predicting the paramagnetism of O₂, a fact not even thought of with a valence bond representation of O=O.

As in the previous examples, the inner shell does not participate in bonding and the bonding and antibonding 2s orbitals cancel each other. A σ bond results from the filling of $\sigma 2p_x^2$. Since $\pi^* 2p_y^1$ is half filled and therefore cancels half the effect of the completely filled $\pi 2p_y^2$ orbital, half of a π bond results. Similarly another half of a π bond arises from $\pi 2p_z^2$ and $\pi^* 2p_z^1$, giving a total of $1 + \frac{1}{2} + \frac{1}{2} = 2$ bonds. The bond order is thus two.

Instead of working out the bond order by cancelling the effects of filled bonding and antibonding MOs, the bond order may be calculated as half the difference between the number of bonding and antibonding electrons:

$$\text{Bond order} = \frac{\left(\begin{array}{c} \text{number of electrons} \\ \text{occupying bonding orbitals} \end{array} \right) - \left(\begin{array}{c} \text{number of electrons} \\ \text{in antibonding orbitals} \end{array} \right)}{2}$$

In the case of O₂ the bond order calculates as $(10 - 6)/2 = 2$, which corresponds to a double bond.

O₂⁻ ion

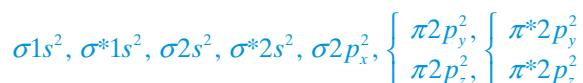
The compound potassium superoxide KO₂ contains the superoxide ion O₂⁻. The O₂⁻ ion has 17 electrons, and has one more electron than the O₂ molecule. This extra electron occupies either the $\pi^* 2p_y$ or $\pi^* 2p_z$ orbital. It does not matter which it occupies since they are the same energy.



The inner shell takes no part in bonding. The bonding and antibonding 2s orbitals completely cancel each other. The $\sigma 2p_x^2$ orbital bond is filled and forms a σ bond. The effects of the bonding $\pi 2p_y^2$ and antibonding $\pi 2p_y^2$ orbitals cancel, and the completely filled bonding $\pi 2p_z^2$ is half cancelled by half antibonding, thus giving half a π bond. The bond order is thus $1 + \frac{1}{2} = 1\frac{1}{2}$. This corresponds to a bond that is intermediate in length between a single and a double bond. Alternatively the bond order may be calculated as (bonding – antibonding)/2, that is $(10 - 7)/2 = 1\frac{1}{2}$.

F₂ molecule

Fluorine atoms have $2 + 7$ electrons, so an F₂ molecule contains 18 electrons. These are arranged:



The inner shell is non-bonding, and the filled bonding 2s, 2p_y and 2p_z are cancelled by the equivalent antibonding orbitals. This leaves a σ bond from the filled $\sigma 2p_x^2$ orbital, and thus a bond order of one. Alternatively the bond order may be calculated as (bonding – antibonding)/2, that is $(10 - 8)/2 = 1$.

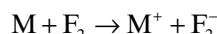
It should be noted that Cl₂ and Br₂ have structures analogous to F₂, except that additional inner shells of electrons are full.

The F–F bond is rather weak and this is attributed to the small size of fluorine and repulsion between lone pairs of electrons on adjacent atoms.



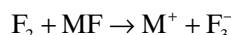
The formation of both F₂⁻ and F₃⁻ can be explained on the basis of MO theory. In case of F₂⁻, the extra electron enters into σ^*2p_x orbital while in case of F₃⁻ the donation from F⁻ is accepted in the σ^*2p_x orbital.

In an argon matrix at 15 K, F₂⁻ can be prepared according to the following reaction



where M = K, Rb, Cs

The F₃⁻ ion is prepared at 15 K on freezing argon gas which contains F₂ as well as gaseous MF (where M = Rb, Cs) in small amounts.



3.13 | EXAMPLES OF MOLECULAR ORBITAL TREATMENT FOR HETERONUCLEAR DIATOMIC MOLECULES

The same principles apply when combining atomic orbitals from two different atoms as applied when the atoms were identical, that is:

1. Only atomic orbitals of about the same energy can combine effectively.
2. They should have the maximum overlap.
3. They must have the same symmetry.

Since the two atoms are different, the energies of their atomic orbitals are slightly different. A diagram showing how they combine to form molecular orbitals after considering the symmetry interaction of 2s and 2p_x orbitals is given in Figure 3.45 (where the molecule is XY and Y is more electronegative than X).

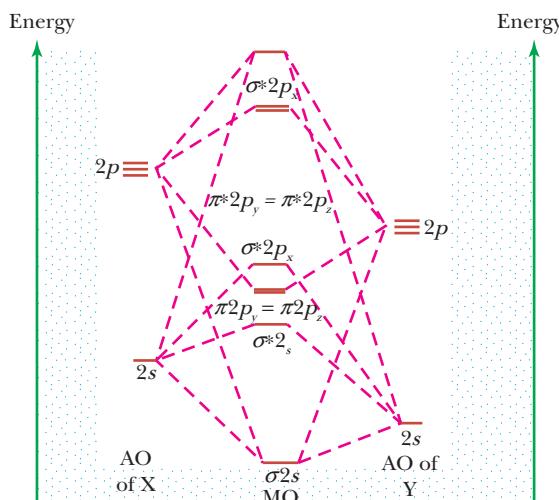


Figure 3.45 Electronic configuration, atomic and molecular orbitals for a heteronuclear molecule XY.

The problem is that in many cases the order of MO energy levels is not known with certainty. Thus we will consider first some examples where the two different atoms are close to each other in the periodic table, and consequently it is reasonable to assume that the order of energies for the MOs are the same as for homonuclear molecules.

NO molecule

There are total 15 electrons in the molecule and the order of energy levels of the various MOs is

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \left\{ \begin{array}{l} \pi 2p_y^2, \sigma 2p_x^2, \left\{ \begin{array}{l} \pi^* 2p_y^1 \\ \pi^* 2p_z^0 \end{array} \right. \end{array} \right.$$

An unpaired electron is present in the π^* orbital and is delocalized over the whole molecule, hence NO molecules is paramagnetic. Since the highest occupied molecular orbital (HOMO) is π^* and the energy of which is higher than the atomic orbitals of N atom and O atom, the ionization energy of NO is less than that of both N and O atoms.

Species	Ionization energy (in kJ mol^{-1})
N	1402
O	1314
NO	894

On ionization, the bond order 2.5 of NO is increased to 3.0 in NO^+ as a result of which bond length decreases from 113 pm in NO to 106 pm in NO^+ .

CO molecule

Some special features are introduced in the MO diagram of CO because the electronegativity difference between C and O atom is large. Since the $\Delta E_{(2p-2s)}$ for C atom (5.3 eV) is much less compared to $\Delta E_{(2p-2s)}$ for O atom (15.0 eV), the participation of $s - p$ hybrid orbitals are considered for the formation of MO diagram of CO, which is shown in Figure 3.46.

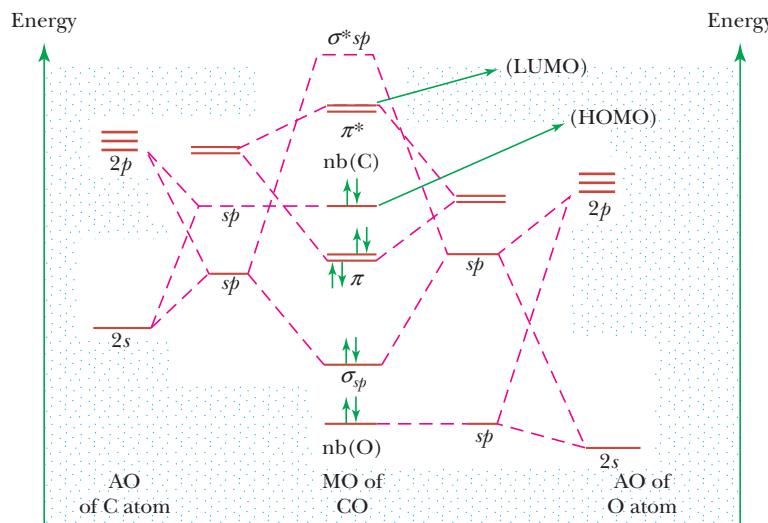


Figure 3.46 Electronic configuration, atomic orbital and molecular orbital for carbon monoxide.

In ionization of CO, i.e. $\text{CO} \rightarrow \text{CO}^+$, the removal of electron takes place from the non-bonding orbital of C atom (HOMO). Hence the interelectronic repulsion decreases and finally the bond length decreases from 112.8 pm to 111.5 pm.

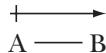
3.14 | DIPOLE MOMENT

Dipole moment of a bond A–B can be expressed as follows

$$\mu = q \times d \quad (3.1)$$

where μ = dipole moment of the bond A–B, q = charge accumulated on either A or B without sign, d = bond length of A–B bond.

It measures the polarity of the bond which is caused by the electronegativity difference between two atoms involved in that bond. It is a vector quantity because it has both direction as well as magnitude and the direction is shown by an arrow (\rightarrow) from low electronegative atom to high electronegative atom. For example, if B is more electronegative than A, then the direction is shown in A–B bond is as follows



Dipole moment is measured in *Debye* unit (symbol D) where $1 \text{ D} = 10^{-18} \text{ esu cm} = 3.33 \times 10^{-30} \text{ coulomb metre}$.

Bond moment: It is the dipole moment of a particular bond. The dipole moment of a molecule is determined by the bond moments of the bonds.

For diatomic heteroatomic molecules, the bond moment is equal to the dipole moment and for diatomic homoatomic molecule it is zero because there is no shifting of bond pair towards any atom. Hence q is zero in Eq. (3.1).

For polyatomic molecule (molecule having more than two atoms), the dipole moment is equal to the vector sum of all bond moments and lone pair moments.

Lone pair moment: The lone pair has no contribution to the dipole moment of the molecule, if the lone pair is present in the pure s or p orbital. This is because s orbital is spherically symmetrical and two lobes of a pure p orbital are projected equally in the opposite direction. However, when the lone pair is present in a hybrid orbital, the electronic density is not equal in two lobes of the hybrid orbital.



So, the direction of lone pair moment is from smaller lobe to larger lobe as shown above. Because of presence of lone pair in hybrid orbital it is also referred to as hybrid lone pair moment.

The value of lone pair moment depends upon the $\%s$ character of the hybrid orbital and as the $\%s$ character increases, the lone pair moment increases upto 50% and then falls down as it becomes more and more spherical. The lone pair moment order for different hybrid orbitals (consisting of s or p orbitals) is given as follows:

$$sp > sp^2 > sp^3$$

In general, the lone pair moments have larger magnitude compared to bond pair moment. For example, in case of the hybrid orbitals of carbon, it varies from 4.4 D (sp hybrid) to 3.7 D (sp^3 hybrid) while the largest value of some bond moments are

$$\begin{aligned} P \rightarrow B &: 4.4 \text{ D} \\ N \rightarrow O &: 4.28 \text{ D} \\ O \rightarrow B &: 3.6 \text{ D} \end{aligned}$$

Most of the other bond moments are less or much less than these values.

The contribution of lone pair moment to the dipole moment of the molecule can be understood with the help of the following examples.

1. The dipole moment of NH_3 is much higher compared to that of NF_3 though there is very small difference in $\Delta\chi$ (electronegativity difference) values of N–H bond ($\Delta\chi = 0.94$) and N–F bond ($\Delta\chi = 0.96$).

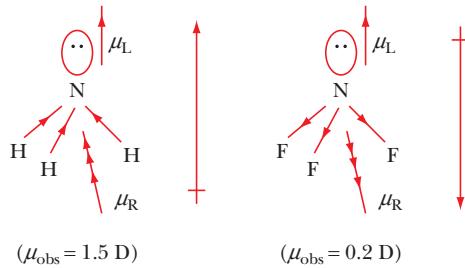


Figure 3.47 Dipole moment of NH_3 and NF_3 .

where μ_L = lone pair moment and μ_R = resultant vector of bond moments.

In case of NH_3 , $\mu_{\text{NH}_3} = (\mu_R + \mu_L)$ and it is much higher than $\mu_{\text{NF}_3} = (\mu_R - \mu_L)$. The overall direction of dipole moment in these molecules is shown in the Figure 3.47 and it can be predicted only when all individual data of lone pair moment and bond moment is available.

2. Similarly, in case of H_2O and F_2O , $\mu_{\text{F}_2\text{O}}$ is much less than $\mu_{\text{H}_2\text{O}}$ as shown in Figure 3.48.

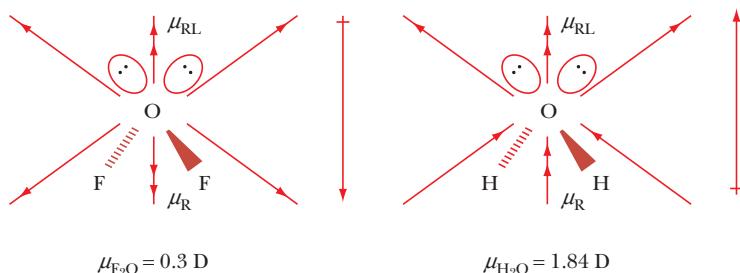


Figure 3.48 Dipole moment of F_2O and H_2O .

where μ_{RL} : Resultant vector of lone pair moment and

μ_R : Resultant vector of bond pair moment.

3. In case of *cis* and *trans* isomers of N_2F_2 , $\mu_{\text{N}_2\text{F}_2(\text{cis})}$ is also almost equal to zero like $\mu_{\text{N}_2\text{F}_2(\text{trans})}$ as shown in Figure 3.49.

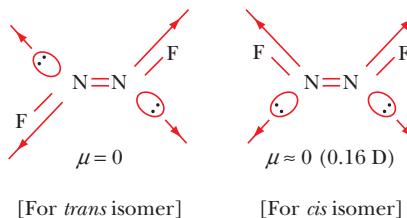


Figure 3.49 Dipole moment of N_2F_2 (*trans*) and N_2F_2 (*cis*).

4. For SO_2 molecule, the overall direction of dipole moment is upwards as shown in Figure 3.50.

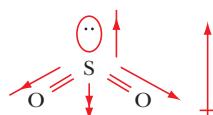


Figure 3.50 Dipole moment of SO_2 .

Applications of dipole moment

1. The percentage ionic character can be calculated in a bond (A–B) by the following equation

$$\begin{aligned}\% \text{ ionic character} &= \frac{\mu_{\text{obs.}}}{\mu_{\text{calc.}}} \times 100 \\ &= \frac{q_{\text{obs.}} \times d_{\text{A-B}}}{q_{\text{calc.}} \times d_{\text{A-B}}} \times 100 = \frac{q_{\text{obs.}}}{q_{\text{calc.}}} \times 100\end{aligned}$$

For example, we can calculate the % ionic character in Li–F from the following data:

$\mu_{\text{LiF}} = 6.32 \text{ D}$ and $d_{\text{LiF}} = 0.156 \text{ nm}$.

We have $\mu_{\text{obs.}}$ for LiF, and $\mu_{\text{calc.}}$ can be obtained as

$$\mu_{\text{calc.}} = (1.602 \times 10^{-19} \text{ C}) \times (0.156 \times 10^{-9} \text{ m}) = 2.496 \times 10^{-29} \text{ C m}$$

Hence, % ionic character is calculated as

$$\frac{\mu_{\text{obs.}}}{\mu_{\text{calc.}}} \times 100 = \frac{6.32 \times 3.33 \times 10^{-30} \text{ C m}}{2.496 \times 10^{-29} \text{ C m}} \times 100 = 84.32\%$$

Note: This result may be somewhat different than that obtained by using Haney–Smith equation. But the two approaches are completely different. Either neglect the difference or do not compare.

2. Prediction of the shape of the molecule can be done based on dipole moment measurements.

a. For AX_2 type of molecule

If $\mu = 0$; it must be linear. For example, BeCl_2 , XeF_2 , ICl_2^- , I_3^- , etc.

If $\mu \neq 0$; it must be angular. For example, H_2O , SCl_2 , SO_2 , etc.

b. For AX_3 type of molecule

If $\mu = 0$; it must be trigonal planar. For example, BH_3 , BF_3 , AlCl_3 , CH_3^+ etc.

If $\mu \neq 0$; it must be pyramidal or *T*-shaped. For example, NH_3 , CH_3^- are pyramidal and ClF_3 , XeF_3^+ are *T*-shaped.

c. For AX_4 type of molecule

If $\mu = 0$; it must be tetrahedral or square planar. For example, CH_4 , SiF_4 are tetrahedral and XeF_4 , ICl_4 are square planar.

If $\mu \neq 0$; it must be see-saw. For example, SF_4 .

d. For AX_5 type of molecule

If $\mu = 0$; it must be trigonal bipyramidal. For example, PF_5 , SbF_5 , etc. Only XeF_5^- has pentagonal planar structure.

If $\mu \neq 0$; it must be square pyramidal. For example, XeF_5^+ .

e. For AX_6 type of molecule

If $\mu = 0$; it must be regular octahedral. For example, SX_6 , TeCl_6 .

If $\mu \neq 0$; it must be distorted octahedral (known) or any other shape (but unknown). For example, XeH_6 .

f. For AX_7 type of molecule

If $\mu = 0$; it must be pentagonal bipyramidal. For example, IF_7 .

If $\mu \neq 0$; [Not known yet].

3. Prediction of *cis* – *trans* isomerism. For example, as shown for $\text{C}_2\text{H}_2\text{Cl}_2$ in Figure 3.51.

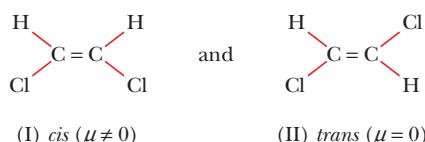


Figure 3.51 Dipole moment of $\text{C}_2\text{H}_2\text{Cl}_2$ (*cis*) and $\text{C}_2\text{H}_2\text{Cl}_2$ (*trans*).

But another structural isomer is possible from this formula which has non-zero dipole moment value as shown in Figure 3.52.

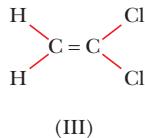


Figure 3.52 Dipole moment of $\text{C}_2\text{H}_2\text{Cl}_2$ (*cis*).

Hence, from non-zero value, it cannot be predicted if it is either *cis*-form (I) or (III).

4. Prediction of position of substituents in disubstituted benzene from their given relative dipole moment values. For example,

- a. if X is a halogen atom, then the dipole moment order is *ortho* > *meta* > *para*, for example as shown in Figure 3.53 for $\text{X} = -\text{Cl}$.

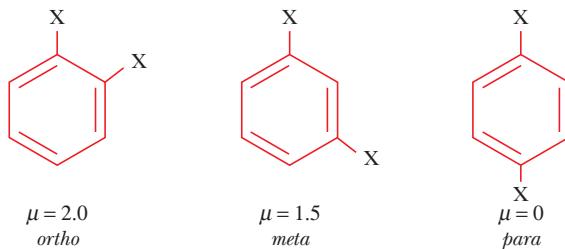


Figure 3.53 Dipole moment order of *ortho*, *meta* and *para* disubstituted benzene when both halogen atoms are same.

Note: If two halogen atoms are the same, then the above order is always obtained.

- b. For molecules like $\text{C}_6\text{H}_4\text{XY}$, where X is electron withdrawing in nature and Y is electron donating in nature, the order of dipole moment is observed as *ortho* < *meta* < *para* as shown in Figure 3.54.

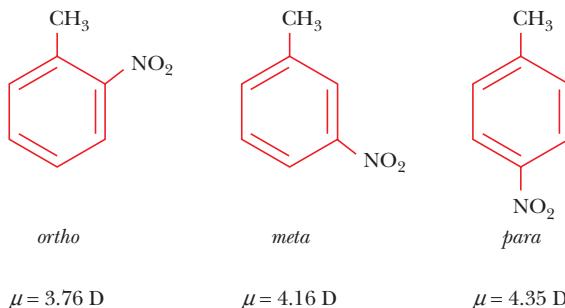


Figure 3.54 Dipole moment order of *ortho*, *meta* and *para* disubstituted benzene when both the atoms are different.

- c. Again consider molecules of the type $\text{C}_6\text{H}_4\text{XY}$ when $\text{X} \neq \text{Y}$ but X and Y are both electron withdrawing in nature, the dipole moment order is *ortho* > *meta* > *para*.

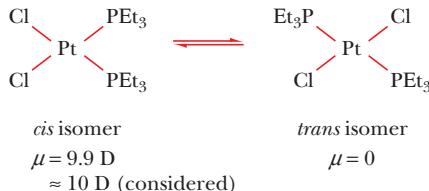
Some observed data is given for molecules of the type $\text{C}_6\text{H}_4\text{XY}$ in Table 3.7.

Table 3.7 Observed order of dipole moment of $\text{C}_6\text{H}_4\text{XY}$ type of molecule

	X	Y (Electron withdrawing type)	μ_{ortho}	μ_{meta}	μ_{para}
Electron donating type	CH ₃	Cl	1.35	<	1.78
	CH ₃	NO ₂	3.76	<	4.17
	NH ₂	NO ₂	3.64	<	4.85
Electron withdrawing type	Cl	NO ₂	4.6	>	3.69
	Cl	CN	4.75	>	3.4

5. Prediction of the isomeric equilibria and stability of different conformations.

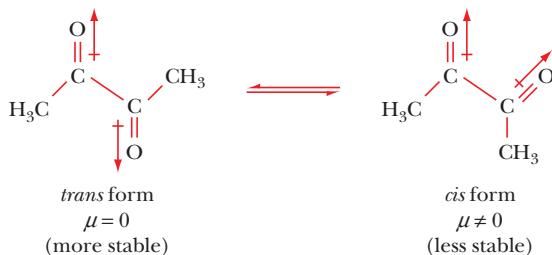
a. In several cases, *cis*- and *trans*-isomers and square planar and tetrahedral isomers are interconvertible into each other and they are in equilibrium under this circumstance. If these two isomers have distinctly different value of dipole moment, then by measuring the dipole moment, we can find out the percentage of each isomer and the position of the equilibria, that is, equilibrium constant can be measured. For example, consider the equilibrium between *cis*- and *trans*-isomers of the complex $\text{Pt}(\text{Et}_3\text{P})\text{Cl}_2$



The equilibrium is temperature dependent and if at a particular temperature the observed dipole moment is 4 D, then the percentage of *cis* isomer is 40 and that of *trans* isomer is 60 and

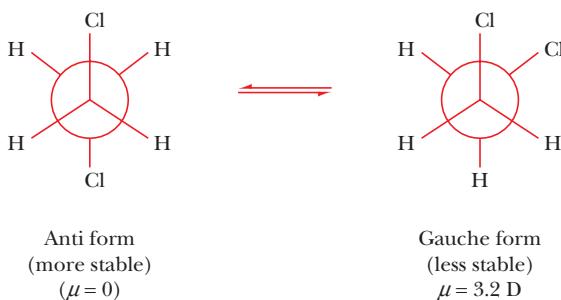
$$K_{\text{eq}} = \frac{60}{40} = 1.5$$

b. The stability of a particular conformation can be understood from dipolar repulsion. For example, consider two different forms of butane-2,3-dione.



The equilibrium is shifted towards more stable *trans*-form.

c. Consider two different forms of 1,2-dichloromethane and their relative dipole moments. The μ_{obs} in gaseous phase is 1.2 D which indicates the significant presence of Gauche form in gaseous phase.



Some special cases

1. The molecule HOOH is expected to have zero dipole moment value but it has the dipole moment value of 1.64 D. This is due to the presence of lone pair on O atom which is not involved in resonance with benzene ring.

2. Sometimes the value of dipole moment is lessened by the mesomeric effect and becomes reversed in direction also. For example,



Due to inductive effect, $\mu = 2.05$ D.

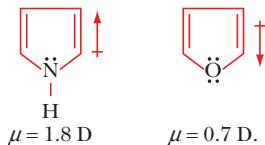
Due to mesomeric effect,



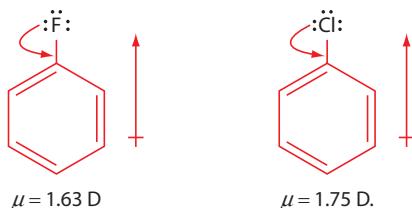
$\mu = 1.44$ D, where the inductive effect is opposed by $+R$ effect.

But in the case of $\text{H} - \text{C} \equiv \text{C} - \text{Cl}$, the direction of dipole moment just reversed because here $-I$ effect between sp hybridized C atom and Cl atom is very less hence net dipole moment is dominated by mesomeric effect.

- b. The direction of dipole moment in pyrrole and furan are just opposite as shown below and this is due to $-I$ effect of O atom which is more than that of N atom and mesomeric effect is almost same because both are $2p_{\pi} - 2p_{\pi}$ type.



- c. The dipole moment of $\text{Ph}-\text{F}$ is less than that of $\text{Ph}-\text{Cl}$ and it is due to more effective mesomeric effect in case of F ($2p_{\pi} - 2p_{\pi}$) as compared to that of Cl ($3p_{\pi} - 2p_{\pi}$).



3. The dipole moment of *p*-nitroaniline and *o*-nitroaniline are extra-ordinarily large compared to the expected value. This is because $+R$ effect of $-\text{NH}_2$ group and $-R$ effect of $-\text{NO}_2$ group are coupled together and the overall effect enhances dipole moment value.



4. CO molecule has very low dipole moment of 0.112 D due to the following reasons:

- a. In CO lone pair moments due to presence of two lone pairs can be considered as cancelled by each other as shown below.

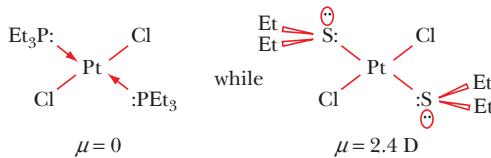


- b. In $:\text{CO}=\ddot{\text{O}}$; the bond moments are in the direction of CO .

- c. In $:\bar{\text{C}}=\ddot{\text{O}}^+$; the dative bond moment not only opposes the above bond moments but also reverses the direction from O to C atom.

Hence, the overall dipole moment is very less.

5. *trans* $(Et_3P)_2PtCl_2$ has zero dipole moment value while *trans* $(Et_2S)_2PtCl_2$ has significant value of dipole moment ($\mu = 2.4$ D).



The lone pairs on S atom (not used in coordinate bonding) are not oriented in a manner that their lone pair moments are cancelled by each other.

6. O_3 molecule is also polar due to its lone pair moments and resultant lone pair moment is not zero as shown in Figure 3.55.

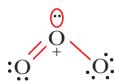


Figure 3.55 Dipole moment of ozone.

7. For halogenated derivatives, the observed dipole moment order is observed as follows
- $HF > HCl > HBr > HI$
 - $CH_3Cl > CH_3F > CH_3Br > CH_3I$
 - $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

3.15 | THE IONIC BOND

Ionic compounds include salts, oxides, hydroxides, sulphides, and the majority of inorganic compounds. Ionic solids are held together by the electrostatic attraction between the positive and negative ions. Plainly there will be repulsion if ions of the same charge are adjacent, and attraction will occur when positive ions are surrounded by negative ions, and vice versa. The attractive force will be a maximum when each ion is surrounded by the greatest possible number of oppositely charged ions. The number of ions surrounding any particular ion is called the coordination number. Positive and negative ions will both have the same coordination number when there are equal numbers of both types of ions, as in $NaCl$, but the coordination numbers for positive and negative ions are different when there are different numbers of the ions, as in $CaCl_2$.

Radius ratio rules

The structures of many ionic solids can be accounted for by considering the relative sizes of the positive and negative ions, and their relative numbers. Simple geometric calculations allow us to work out how many ions of a given size can be in contact with a smaller ion. Thus we can predict the coordination number from the relative sizes of the ions.

When the coordination number is three in an ionic compound AX , three X^- ions are in contact with one A^+ ion (Figure 3.56a). A limiting case arises (Figure 3.56b) when the X^- ions are also in contact

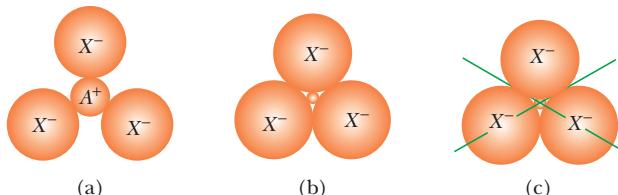


Figure 3.56 Sizes of ions for coordination number 3.

Table 3.8 Limiting radius ratios and structures

Limiting radius ratio r^+/r^-	Coordination number	Shape
<0.155	2	Linear
0.155 → 0.225	3	Planar triangle
0.225 → 0.414	4	Tetrahedral
0.414 → 0.732	4	Square planar
0.414 → 0.732	6	Octahedral
0.732 → 0.999	8	Body-centred cubic

with one another. By simple geometry this gives the ratio (radius A^+ /radius X^-) = 0.155. This is the lower limit for a coordination number of 3. If the radius ratio is less than 0.155 then the positive ion is not in contact with the negative ions, and it 'rattles' in the hole, and the structure is unstable (Figure 3.56c). If the radius ratio is greater than 0.155 then it is possible to fit three X^- ions round each A^+ ion. As the difference in the size of the two ions increases, the radius ratio also increases, and at some point (when the ratio exceeds 0.225), it becomes possible to fit four ions around one, and so on for six ions around one, and eight ions around one. Coordination numbers of 3, 4, 6 and 8 are common, and the appropriate limiting radius ratios can be worked out by simple geometry, and are shown in Table 3.8.

If the ionic radii are known, the radius ratio can be calculated and hence the coordination number and shape may be predicted. This simple concept predicts the correct structure in many cases.

Calculation of some limiting radius ratio values

- Coordination number 3 (planar triangle):** Figure 3.57a shows the smaller positive ion of radius r^+ in contact with three larger negative ions of radius r^- . Plainly $AB = BC = AC = 2r^-$, $BE = r^-$, $BD = r^+ + r^-$. Further, the angle $A-B-C$ is 60° , and the angle $D-B-E$ is 30° . By trigonometry

$$\begin{aligned}\cos 30^\circ &= \frac{BE}{BD} \\ BD &= \frac{BE}{\cos 30^\circ} \\ r^+ + r^- &= \frac{r^-}{\cos 30^\circ} = \frac{r^-}{0.866} = r^- \times 1.155 \\ r^+ &= (1.155r^-) - r^- = 0.155r^-\end{aligned}$$

Hence

$$\frac{r^+}{r^-} = 0.155$$

- Coordination number 4 (tetrahedral):** Figure 3.57b shows a tetrahedral arrangement inscribed in a cube. Part of this tetrahedral arrangement is drawn in Figure 3.57c. It can be seen that the angle ABC is the tetrahedral angle of $109^\circ 28'$ and hence the angle ABD is half of this, that is $54^\circ 44'$. In the triangle ABD

$$\sin ABD = 0.8164 = \frac{AD}{AB} = \frac{r^-}{r^+ + r^-}$$

Taking reciprocals

$$\frac{r^+ + r^-}{r^-} = \frac{1}{0.8164} + 1.225$$

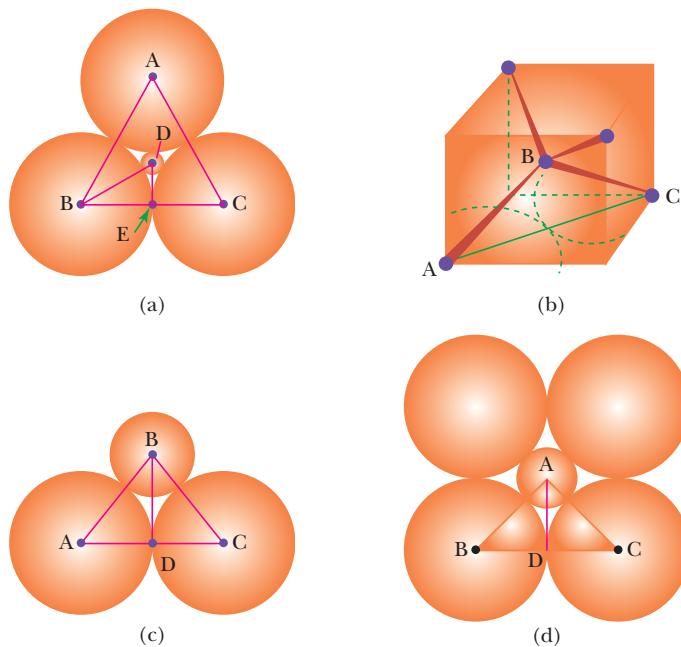


Figure 3.57 Limiting radius ratios for coordination numbers 3, 4 and 6. (a) Cross-section through a planar triangle site; (b) tetrahedron inscribed in a cube; (c) diagram for tetrahedral case; (d) cross-section through an octahedral site.

Rearranging

$$\frac{r^+}{r^-} + 1 = 1.225$$

Hence

$$\frac{r^+}{r^-} = 0.225$$

3. Coordination number 6 (octahedral): A cross-section through an octahedral site is shown in Figure 3.48d, and the smaller positive ion (of radius r^+) touches six larger negative ions (of radius r^-). (Note that only four negative ions are shown in this section, and one is above and another below the plane of the paper.) It is obvious that $AB = r^+ + r^-$ and $BD = r^-$. The angle ABC is 45° . In the triangle ABD

$$\cos ABD = 0.7071 = \frac{BD}{AB} = \frac{r^-}{r^+ + r^-}$$

Taking reciprocals

$$\frac{r^+ + r^-}{r^-} = \frac{1}{0.7071} = 1.414$$

Rearranging

$$\frac{r^+}{r^-} + 1 = 1.414$$

Hence

$$\frac{r^+}{r^-} = 0.414$$

3.16 | CLOSE PACKING

Many common crystal structures are related to, and may be described in terms of, hexagonal or cubic close-packed arrangements (Table 3.9). Because of their shape, spheres cannot fill space completely. In a close-packed arrangement of spheres, 74% of the space is filled. Thus 26% of the space is unoccupied, and may be regarded as holes in the crystal lattice. Two different types of hole occur. Some are bounded by four spheres and are called tetrahedral holes (marked T in Figure 3.58a), and others are bounded by six spheres and are called octahedral holes (marked O in Figure 3.58a). For every the close-packed arrangement there is one octahedral hole and two tetrahedral holes. The octahedral holes are larger than the tetrahedral holes (Figure 3.58 b, c).

Table 3.9 Some structures based on close packing

Formula		Type of cp	Tetrahedral	Octahedral	Coordination No. AX		
AX	NaCl	ccp	none	all	6	:	6
	NiAs	hcp	none	all	6	:	6
	ZnS (Zinc blende)	ccp	$\frac{1}{2}$	none	4	:	4
	ZnS (Wurtzite)	hcp	$\frac{1}{2}$	none	4	:	4
AX ₂	F ₂ Ca* (Fluorite)	ccp*	all	none	8	:	4
	CdI ₂	hcp	none	$\frac{1}{2}$	6	:	3
	CdCl ₂	ccp	none	$\frac{1}{2}$	6	:	3
	β -ZnCl ₂	hcp	$\frac{1}{4}$	none	4	:	2
MX ₄	SnI ₄	hcp	$\frac{1}{8}$	none	4	:	1
MX ₆	α -WCl ₆ and UCl ₆	ccp	none	$\frac{1}{6}$	6	:	1
M ₂ X ₃	α -Al ₂ O ₃ (Corundum)	hcp	none	$\frac{2}{3}$	6	:	4

* The metal ions adopt a face-centred cubic arrangement, which is exactly like cubic close packing except that the ions do not touch. (Note it is the M⁺ ions that are almost close packed, not the negative ions as with the other examples.)

An ionic structure is composed of oppositely charged ions. If the larger ions are close packed, then the smaller ions may occupy either the octahedral holes or the tetrahedral holes depending on their size. Normally the type of hole occupied can be determined from the radius ratio. An ion occupying a tetrahedral hole has a coordination number of 4, whilst one occupying an octahedral hole has a coordination number of 6. In some compounds the relative sizes of the ions are such that the smaller ions are too large to fit in the holes, and they force the larger ions out of contact with each other so that they are no longer close packed. Despite this, the relative positions of the ions remain unchanged, and it is convenient to retain the description in terms of close packing.

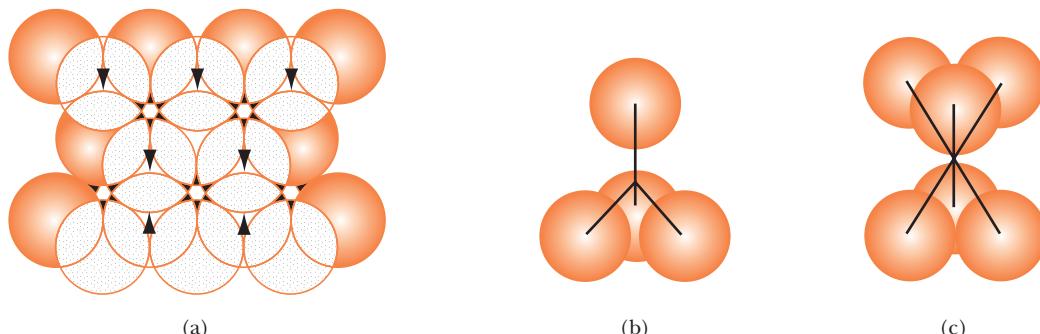


Figure 3.58 Tetrahedral and octahedral holes: (a) Tetrahedral and octahedral sites in a close-packed lattice; (b) tetrahedral site; and (c) octahedral

3.17 | IONIC COMPOUNDS OF THE TYPE AX (ZnS, NaCl, CsCl)

Three structural arrangements commonly found for ionic compounds of the type AX are the zinc sulphide, sodium chloride and caesium chloride structures.

Structures of zinc sulphide

In zinc sulphide, ZnS, the radius ratio of 0.40 suggests a tetrahedral arrangement. Each Zn^{2+} ion is tetrahedrally surrounded by four S^{2-} ions and each S^{2-} ion is tetrahedrally surrounded by four Zn^{2+} ions. The coordination number of both ions is 4, so this is called a 4:4 arrangement. Two different forms of zinc sulphide exist, zinc blende and wurtzite (Figure 3.59). Both are 4:4 structures.

These two structures may be considered as close-packed arrangements of S^{2-} ions. Zinc blende is related to a cubic close-packed structure whilst wurtzite is related to a hexagonal close-packed structure. In both structures the Zn^{2+} ions occupy tetrahedral holes in the lattice. Since there are twice as many tetrahedral holes as there are S^{2-} ions, it follows that to obtain a formula ZnS only half of the tetrahedral holes are occupied by Zn^{2+} ions (that is every alternate tetrahedral site is unoccupied).

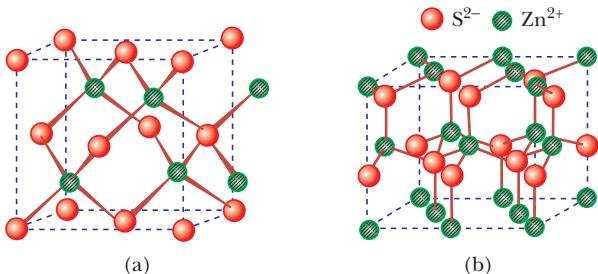


Figure 3.59 Structures of ZnS: (a) zinc blende and (b) wurtzite. (Reproduced with permission from Wells, A.F., *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, 1984.)

Sodium chloride structure

For sodium chloride, NaCl, the radius ratio is 0.52 and this suggests an octahedral arrangement. Each Na^+ ion is surrounded by six Cl^- ions at the corners of a regular octahedron and similarly each Cl^- ion is surrounded by six Na^+ ions (Figure 3.60). The coordination is thus 6:6. This structure may be regarded as a cubic close-packed array of Cl^- ions, with Na^+ ions occupying all the octahedral holes.

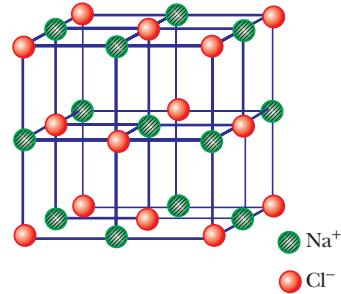


Figure 3.60 Rock salt (NaCl) structure. (Reproduced by permission of Wells, A.F., *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, 1984.)

Caesium chloride structure

In caesium chloride, CsCl, the radius ratio is 0.93. This indicates a body-centred cubic type of arrangement, where each Cs^+ ion is surrounded by eight Cl^- ions, and vice versa (Figure 3.61). The coordination is thus 8:8. Note that this structure is not close packed, and is not strictly body-centred cubic.

In a body-centred cubic arrangement, the atom at the centre of the cube is identical to those at the corners. This structure is found in metals, but in CsCl if the ions at the corners are Cl^- then there will be a Cs^+ ion at the body-centred position, so it is not strictly body-centred cubic. The caesium chloride structure should be described as a *body-centred cubic type of arrangement* and not *body-centred cubic*.

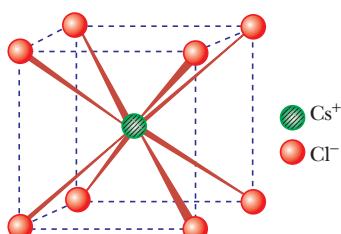


Figure 3.61 Caesium chloride (CsCl) structure. (Reproduced by permission of Wells, A.F., *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, 1984.)

3.18 | IONIC COMPOUNDS OF THE TYPE AX_2 (CaF_2 , TiO_2 , SiO_2)

The two most common structures are fluorite, CaF_2 (Figure 3.62), and rutile, TiO_2 (Figure 3.63), and many difluorides and dioxides have one of these structures. Another fairly common structure is one form of SiO_2 called β -cristobalite (Figure 3.64). These are true ionic structures. Layer structures are formed instead if the bonding becomes appreciably covalent.

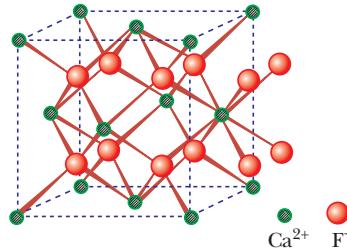


Figure 3.62 Fluorite (CaF_2) structure. (Reproduced by permission of Wells, A.F., *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, 1984.)

Calcium fluoride (fluorite) structure

In fluorite, each Ca^{2+} ion is surrounded by eight F^- ions, giving a body-centred cubic arrangement of F^- round Ca^{2+} . Since there are twice as many F^- ions as Ca^{2+} ions, the coordination number of both ions is different, and four Ca^{2+} ions are tetrahedrally arranged around each F^- ion. The coordination numbers are therefore 8 and 4, so this is called an 8:4 arrangement. The fluorite structure is found when the radius ratio is 0.73 or above.

An alternative description of the structure is that the Ca^{2+} ions form a face-centred cubic arrangement. The Ca^{2+} ions are too small to touch each other, so the structure is not close packed. However, the structure is related to a close-packed arrangement, since the Ca^{2+} occupy the same relative positions as for a cubic close-packed structure, and the F^- ions occupy all the tetrahedral holes.

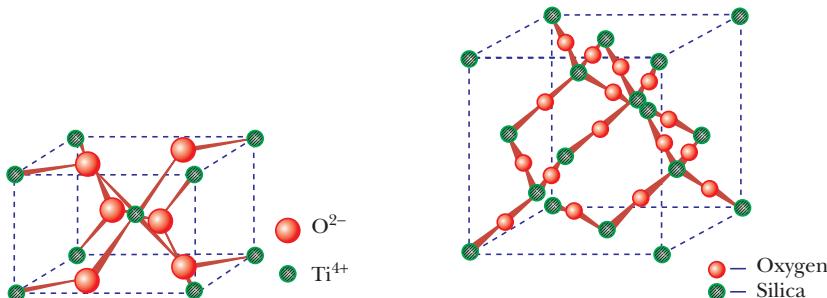


Figure 3.63 Rutile (TiO_2) structure.

Figure 3.64 β -cristobalite structure.

Rutile structure

TiO_2 exists in three forms called anatase, brookite and rutile. The rutile structure is found in many crystals where the radius ratio is between 0.41 and 0.73. This suggests a coordination number of 6 for one ion, and from the formula it follows that the coordination number of the other ion must be 3. This is a 6:3 structure. Each Ti^{4+} is octahedrally surrounded by six O^{2-} ions and each O^{2-} ion has three Ti^{4+} ions round it in a plane triangular arrangement (Figure 3.63).

The rutile structure is not close packed. The unit cell, i.e. the repeating unit of this structure, is not a cube, since one of the axes is 30% shorter than the other two. It is convenient to describe it as a considerably distorted cube (though the distortion is rather large). The structure may then be described as a considerably distorted body-centred cubic lattice of Ti^{4+} ions. Each Ti^{4+} ion is surrounded octahedrally by six O^{2-} ions, and the O^{2-} are in positions of threefold coordination, that is each O^{2-} is surrounded by three Ti^{4+} ions at the corners of an equilateral triangle. Three-coordination is not common in solids. There are no examples of three-coordination in compounds of the type AX , but there is another example in the compounds of

type AX_2 , that is CdI_2 , though in this case the shape is not an equilateral triangle. The structure of $CaCl_2$ is also a 6:3 structure, and is similar to CdI_2 . These are described later (Section 3.19).

There are only a few cases where the radius ratio is below 0.41. Examples include silica SiO_2 and beryllium fluoride BeF_2 . These have coordination numbers of 4 and 2, but radius ratio predictions are uncertain since they are appreciably covalent.

β -cristobalite (silica) structure

Silica SiO_2 exists in six different crystalline forms as quartz, cristobalite and tridymite, each with an α and β form, β -cristobalite is related to zinc blende, with two interpenetrating close-packed lattices, one lattice arising from Si occupying the S^{2-} positions, and the other lattice from Si occupying the Zn^{2+} positions (i.e. the tetrahedral holes in the first lattice). The oxygen atoms lie midway between the Si atoms, but are shifted slightly off the line joining the Si atoms, so the bond angle $Si-O-Si$ is not 180° . The radius ratio predicts a coordination number of 4, and this is a 4:2 structure.

3.19 | LAYER STRUCTURES (CdI_2 , $CdCl_2$, $[NiAs]$)

Cadmium iodide structure

Many AX_2 compounds are not sufficiently ionic to form the perfectly regular ionic structures described. Many chlorides, bromides, iodides and sulphides crystallize into structures which are very different from those described. Cadmium fluoride CdF_2 forms an ionic lattice with the CaF_2 structure, but in marked contrast cadmium iodide CdI_2 is much less ionic, and does not form the fluorite structure. The radius ratio for CdI_2 is 0.45, and this indicates a coordination number of 6 for cadmium. The structure is made up of electrically neutral layers of Cd^{2+} ions with layers of I^- ions on either side – rather like a sandwich where a layer of Cd^{2+} corresponds to the meat in the middle, and layers of I^- correspond to the bread on either side. This is called a layer structure, and it is not a completely regular ionic structure. With a sandwich, bread is separated from bread by the meat, but in a pile of sandwiches, bread from one sandwich touches bread from the next sandwich. Similarly, in CdI_2 , two sheets of I^- ions are separated by Cd^{2+} within a ‘sandwich’, but between one ‘sandwich’ and the next, two I^- layers are in contact. Whilst there is strong electrostatic bonding between Cd^{2+} and I^- layers, there are only weak van der Waals forces holding the adjacent layers of I^- together. The packing of layers in the crystal structure is not completely regular, and the solid is flaky, and it cleaves into two parallel sheets quite easily. This structure is adopted by many transition metal diiodides (Ti , V , Mn , Fe , Co , Zn , Cd) and by some main group diiodides and dibromides (Mg , Ca , Ge and Pb). Many hydroxides have similar layer structures $Mg(OH)_2$, $Ca(OH)_2$, $Fe(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, and $Cd(OH)_2$.

In cadmium iodide, the third layer of I^- ions is directly above the first layer, so the repeating pattern is ABABAB... The I^- ions may be regarded as an approximately hexagonal close-packed arrangement. The Cd^{2+} ions occupy half of the octahedral sites. Rather than half filling the octahedral sites in a regular way throughout the whole structure, all of the octahedral sites are filled between two I^- layers, and none of the octahedral sites is filled between the next two layers of I^- ions. All of the octahedral holes are filled between the next two layers of I^- ions, none between the next pair, and so on (Figure 3.65).

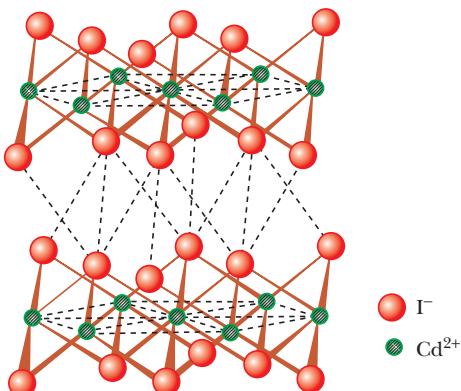


Figure 3.65 Part of two layers of cadmium iodide (CdI_2) structure.

Cadmium chloride structure

Cadmium chloride forms a closely related layer structure, but in this the chloride ions occur approximately in a cubic close-packed arrangement (ABCABC...).

Layer structures are intermediate in type between the extreme cases of:

1. A totally ionic crystal with a regular arrangement of ions and strong electrostatic forces in all directions.
2. A crystal in which small discrete molecules are held together by weak residual forces such as van der Waals forces and hydrogen bonds.

Nickel arsenide structure

The structure of nickel arsenide NiAs is related to the structure of CdI₂. In NiAs (Figure 3.66), the arsenic atoms form a hexagonal close-packed type of lattice with nickel atoms occupying all of the octahedral sites between all of the layers of arsenic atoms. (In CdI₂ all of the octahedral sites between half of the layers are filled, whilst with NiAs all of the octahedral sites between all of the layers are filled.)

In the nickel arsenide structure each atom has six nearest neighbours of the other type of atom. Each arsenic atom is surrounded by six nickel atoms at the corners of a trigonal prism. Each nickel atom is surrounded octahedrally by six arsenic atoms, but with two more nickel atoms sufficiently close to be bonded to the original nickel atom. This structure is adopted by many transition elements combined with one of the heavier elements from the *p*-block (Sn, As, Sb, Bi, S, Se, Te) in various alloys. These are better regarded as intermetallic phases rather than true compounds. They are opaque, have metallic lustre, and sometimes have a variable composition.

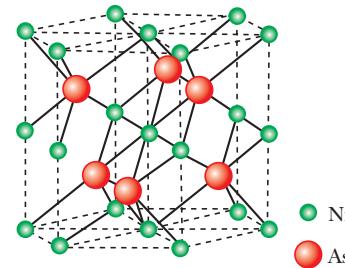


Figure 3.66 Nickel arsenide structure.

3.20 | LATTICE ENERGY

The lattice energy (*U*) of a crystal is the energy evolved when one gram molecule of the crystal is formed from gaseous ions:



Lattice energies cannot be measured directly, but experimental values are obtained from thermodynamic data using the Born–Haber cycle.

Theoretical values for lattice energy may be calculated. The ions are treated as point charges, and the electrostatic (coulombic) energy *E* between two ions of opposite charge is calculated:

$$E = -\frac{z^+ z^- e^2}{r}$$

where *z*⁺ and *z*⁻ are the charges on the positive and negative ions, *e* is the charge on an electron, *r* is the inter-ionic distance

For more than two ions, the electrostatic energy depends on the number of ions, and also on *A* their arrangement in space. For one mole, the attractive energy is:

$$E = -\frac{N_o A z^+ z^- e^2}{r}$$

where *N*_o is the Avogadro constant – the number of molecules in a mole – which has the value 6.023×10^{23} mol⁻¹. *A* is the Madelung constant, which depends on the geometry of the crystal.

Values for the Madelung constant have been calculated for all common crystal structures, by summing the contributions of all the ions in the crystal lattice. Some values are given in Table 3.10.

The equation for the attractive forces between the ions gives a negative value for energy, that is energy is given out when a crystal is formed. The inter-ionic distance r occurs in the denominator of the equation. Thus the smaller the value of r , the greater the amount of energy evolved when the crystal lattice is formed, and hence the more stable the crystal will be. Mathematically, the equation suggests that an infinite amount of energy should be evolved if the distance r is zero. Plainly this is not so. When the inter-ionic distance becomes small enough for the ions to touch, they begin to repel each other. This repulsion originates from the mutual repulsion of the electron clouds on the two atoms or ions. The repulsive forces increase rapidly as r decreases. The repulsive force is given by B/r^n , where B is a constant that depends on the structure, and n is a constant called the Born exponent. For one gram molecule the total repulsive force is $(N_0 B)/r^n$. The Born exponent may be determined from compressibility measurements. Often chemists use a value of 9, but it is better to use values for the particular ions in the crystal as given in Table 3.11.

The total energy holding the crystal together is U the lattice energy. This is the sum of the attractive and the repulsive forces.

Table 3.10 Madelung constants

Type of structure	A
Zinc blende ZnS	1.63806
Wurtzite ZnS	1.64132
Sodium chloride NaCl	1.74756
Caesium chloride CsCl	1.76267
Rutile TiO ₂	2.408
Fluorite CaF ₂	2.51939
Corundum Al ₂ O ₃	4.17186

Table 3.11 Average values for the Born exponent

Electronic structure of ion	<i>n</i>	Examples
He	5	Li^+ , Be^{2+}
Ne	7	Na^+ , Mg^{2+} , O^{2-} , F^-
Ar	9	K^+ , Ca^{2+} , S^{2-} , Cl^- , Cu^+
Kr	10	Rb^+ , Br^- , Ag^+
Xe	12	Cs^+ , I^- , Au^+

Average values are used, e.g. in LiCl, $\text{Li}^+ = 5$, $\text{Cl}^- = 9$, hence for LiCl, $n = (5 + 9)/2 = 7$

$$U = -\frac{N_o A z^+ z^- e^2}{r} + \frac{N_o B}{r^n} \quad (3.2)$$

attractive	repulsive
force	force

(A is the Madelung constant and B is a repulsion coefficient, which is a constant which is approximately proportional to the number of nearest neighbours.)

The equilibrium distance between ions is determined by the balance between the attractive and repulsion terms. At equilibrium, $dU/dr = 0$ and the equilibrium distance $r = r_0$.

$$\frac{dU}{dr} = \frac{N_o A z^+ z^- e^2}{r^2} - \frac{n N_o B}{r^{n+1}} = 0 \quad (3.3)$$

Rearranging this gives an equation for the repulsion coefficient B :

$$B = \frac{Az^+ z^- e^2 r_{\text{o}}^{n-1}}{n} \quad (3.4)$$

Substituting equation (3.4) into (3.2)

$$U = -\frac{N_o A z^+ z^- e^2}{r_o} \left(1 - \frac{1}{n}\right)$$

This equation is called the *Born–Landé equation*. It allows the lattice energy to be calculated from a knowledge of the geometry of the crystal, and hence the Madelung constant, the charges z^+ and z^- , and the inter-ionic distance. When using SI units, the equation takes the form:

$$U = -\frac{N_o A z^+ z^- e^2}{4\pi\epsilon_o r_o} \left(1 - \frac{1}{n}\right) \quad (3.5)$$

where ϵ_o is the permittivity of free space $= 8.854 \times 10^{-12} \text{ F m}^{-1}$

This equation gives a calculated value of $U = -778 \text{ kJ mol}^{-1}$ for the lattice energy for sodium chloride, which is close to the experimental value of -775 kJ mol^{-1} at 25°C (obtained using the Born–Haber cycle). The experimental and theoretical values for the alkali metal halides and the oxides and halides of the alkaline earths (excluding Be), all agree within 3%.

Other expressions, for example the Born–Mayer and Kapustinskii equations, are similar, but calculate the repulsive contribution in a slightly different way. Agreement is even better if allowances are made for van der Waals forces and zero point energy.

Several important points arise from the Born–Landé equation:

1. The lattice becomes stronger (i.e. the lattice energy U becomes more negative), as r the inter-ionic distance decreases. U is proportional to $1/r$.

	r (Å)	U (kJ mol $^{-1}$)
LiF	2.01	-1004
CsI	3.95	-527

2. The lattice energy depends on the product of the ionic charges, and U is proportional to $(z^+ \cdot z^-)$.

	r (Å)	$(z^+ \cdot z^-)$	U (kJ mol $^{-1}$)
LiF	2.01	1	-1004
MgO	2.10	4	-3933

3. The close agreement between the experimental lattice energies and those calculated by the Born–Landé equation for the alkali metal halides does not of itself prove that the equation itself, or the assumptions on which it is based, are correct. The equation is remarkably self-compensating, and tends to hide errors. There are two opposing factors in the equation. Increasing the inter-ionic distance r reduces the lattice energy. It is almost impossible to change r without changing the structure, and therefore changing the Madelung constant A . Increasing A increases the lattice energy: hence the effects of changing r and A may largely cancel each other.

This may be illustrated by choosing a constant value for n in the Born–Landé equation. Then changes in inter-ionic distance can be calculated for either changes in the coordination number, or in crystal structure. Taking a constant value of $n = 9$, we may compare the inter-ionic distances with those for six-coordination:

Coordination number	12	8	6	4
Ratio of inter-ionic distance	1.091	1.037	1.000	0.951

For a change of coordination number from 6 (NaCl structure) to 8 (CsCl structure) the inter-ionic distance increases by 3.7%, and the Madelung constants (NaCl $A = 1.74756$, and CsCl $A = 1.76267$) change by only 0.9%. Thus a change in coordination number from 6 to 8 would result in a reduction in

lattice energy, and in theory the NaCl structure should always be more stable than the CsCl structure. In a similar way reducing the coordination number from 6 to 4 decreases r by 4.9%. The decrease in A is 6.1% or 6.3% (depending on whether a zinc blende or wurtzite structure is formed), but in either case it more than compensates for the change in r , and in theory coordination number 6 is more stable than 4.

This suggests that neither four-nor eight-coordinate structures should exist, since the six-coordinate NaCl structure is more stable. Since ZnS is known (coordination number 4), and CsCl, CsBr and CsI have a coordination number of 8, this suggestion is plainly incorrect. We must therefore look for a mistake in the theoretical assumptions made. First the value of n was assumed to be 9, when it may vary from 5 to 12. Second, the calculation of electrostatic attraction assumes that the ions are point charges. Third, the assumption is made that there is no reduction in charge because of the interaction (i.e. the bonds are 100% ionic).

4. Crystals with a high lattice energy usually melt at high temperatures, and are very hard. Hardness is measured on Mohs' scale. (See Appendix K.) High lattice energy is favoured by a small inter-ionic distance, and a high charge on the ions (Table 3.12).

It has been seen that a number of salts which might be expected from radius ratio considerations to have a CsCl structure in fact adopt a NaCl structure. The Madelung constant for CsCl is larger than for NaCl, and would give an increased lattice energy. However, the inter-ionic distance r will be larger in a CsCl type of structure than in a NaCl type of structure, and this would decrease the lattice energy. These two factors work in opposite directions and partly cancel each other. This makes the lattice energy more favourable for a NaCl type of lattice in some cases where a CsCl structure is geometrically possible. Consider a case such as RbBr, where the radius ratio is close to borderline between six-coordination (NaCl structure) and eight-coordination (CsCl structure). If the CsCl structure is adopted, the Madelung constant is larger than for NaCl, and *this increases the lattice energy by 0.86 %*.

Table 3.12 Inter-ionic distances and ionic charges related to m.p. and hardness

	$r(\text{\AA})$	$(z^+ \cdot z^-)$	m.p. (°C)	Hardness (Mohs' scale)
NaF	2.310	1	990	3.2
BeO	1.65	4	2530	9.0
MgO	2.106	4	2800	6.5
CaO	2.405	4	2580	4.5
SrO	2.580	4	2430	3.5
BaO	2.762	4	1923	3.3
TiC	2.159	16	3140	8–9

At the same time the inter-ionic distance in a CsCl structure increases by 3%, and *this decreases the lattice energy by 3%*. Clearly the NaCl structure is preferred.

3.21 | STOICHIOMETRIC DEFECTS

The essential feature of crystalline solids is that the constituent molecules, atoms or ions are arranged in a completely regular three-dimensional pattern. Models built to show the detailed structure of crystalline materials are usually grossly misleading, for they imply a perfect static pattern. Since the atoms or ions have a considerable degree of thermal vibration, the crystalline state is far from static, and the pattern is seldom perfect. Many of the most useful properties of solids are related to the thermal vibrations of atoms, the presence of impurities and the existence of defects.

Stoichiometric compounds are those where the numbers of the different types of atoms or ions present are exactly in the ratios indicated by their chemical formulae. They obey the law of constant composition that '*the same chemical compound always contains the same elements in the same composition by weight*'. At one time these were called Daltonide compounds, in contrast to Berthollide or nonstoichiometric compounds where the chemical composition of a compound was variable, not constant.

Two types of defects may be observed in stoichiometric compounds, called Schottky and Frenkel defects respectively. At absolute zero, crystals tend to have a perfectly ordered arrangement. As the temperature increases, the amount of thermal vibration of ions in their lattice sites increases, and if the vibration of a particular ion becomes large enough, it may jump out of its lattice site. This constitutes a point defect. The higher the temperature, the greater the chance that lattice sites may be unoccupied. Since the number of defects depends on the temperature, they are sometimes called thermodynamic defects.

Schottky defects

A Schottky defect consists of a pair of 'holes' in the crystal lattice. One positive ion and one negative ion are absent (see Figure 3.67). This sort of defect occurs mainly in highly ionic compounds where the positive and negative ions are of a similar size, and hence the coordination number is high (usually 8 or 6), for example NaCl, CsCl, KCl and KBr.

The number of Schottky defects formed per cm^3 (n_s) is given by

$$n_s = N \exp\left(-\frac{W_s}{2kT}\right)$$

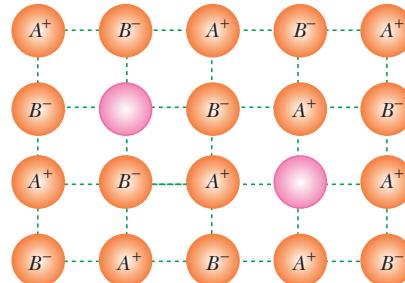


Figure 3.67 Schottky defect.

where N is the number of sites per cm^3 that could be left vacant, W_s is the work necessary to form a Schottky defect, k is the gas constant and T the absolute temperature.

Frenkel defects

A Frenkel defect consists of a vacant lattice site (a 'hole'), and the ion which ideally should have occupied the site now occupies an interstitial position (see Figure 3.68).

Metal ions are generally smaller than the anions. Thus it is easier to squeeze A^+ into alternative interstitial positions, and consequently it is more common to find the positive ions occupying interstitial positions. This type of defect is favoured by a large difference in size between the positive and negative ions, and consequently the coordination number is usually low (4 or 6). Since small positive ions are highly polarizing and large negative ions are readily polarized, these compounds have some covalent character. This distortion of ions, and the proximity of like charges, leads to a high dielectric constant. Examples of this type of defect are ZnS, AgCl, AgBr and AgI.

The number of Frenkel defects formed per cm^3 (n_f) is given by

$$n_f = \sqrt{NN'} \exp\left(-\frac{W_f}{2kT}\right)$$

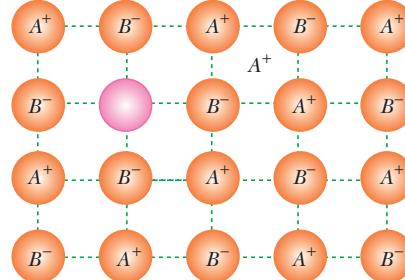


Figure 3.68 Frenkel defect.

where N is the number of sites per cm^3 that could be left vacant, N' is the number of alternative interstitial positions per cm^3 , W_f is the work necessary to form a Frenkel defect, k is the gas constant and T the absolute temperature.

The energy needed to form either a Schottky defect or a Frenkel defect depends on the work needed to form the defect, and on the temperature. In a given compound one type generally predominates.

In NaCl, the energy to form a Schottky defect is about 200 kJ mol^{-1} compared with a lattice energy of approximately 750 kJ mol^{-1} . It is therefore much easier to form a defect than to break the lattice. The number of defects formed is relatively small, and at room temperature NaCl has only one defect in 10^{15} lattice sites, this value rising to one in 10^6 sites at 500°C and one in 10^4 sites at 800°C .

A consequence of these defects is that a crystalline solid that has defects may conduct electricity to a small extent. Electrical conductivity in a chemically pure, stoichiometric semiconductor is called '*intrinsic semiconductor*'. In the above cases, intrinsic semiconductor occurs by an ionic mechanism. If an ion moves from its lattice site to occupy a 'hole', it creates a new 'hole'. If the process is repeated many times, a 'hole'

may migrate across a crystal, which is equivalent to moving a charge in the opposite direction. (This type of semiconduction is responsible for the unwanted background noise produced by transistors.)

Crystals with Frenkel defects have only one type of hole, but crystals containing Schottky defects have holes from both positive and negative ions, and conduction may arise by using either one type of hole or both types. Migration of the smaller ion (usually the positive ion) into the appropriate holes is favoured at low temperatures, since moving a small ion requires less energy. However, migration of both types of ions in opposite directions (using both types of holes) occurs at high temperatures. For example, at temperatures below 500 °C the alkali halides conduct by migration of the cations, but at higher temperatures both anions and cations migrate. Further, the amount of anionic conduction increases with temperature, as shown in Table 3.13.

Table 3.13 Percentage of conduction by cations and anions

Temp. (°C)	NaF		NaCl		NaBr	
	cation %	anion %	cation %	anion %	cation %	anion %
400	100	0	100	0	98	2
500	100	0	98	2	94	6
600	92	8	91	9	89	11

The density of a defect lattice should be different from that of a perfect lattice. The presence of 'holes' should lower the density, but if there are too many 'holes' there may be a partial collapse or distortion of the lattice – in which case the change in density is unpredictable. The presence of ions in interstitial positions may distort (expand) the lattice and increase the unit cell dimensions.

3.22 | NONSTOICHIOMETRIC DEFECTS

Nonstoichiometric or Berthollide compounds exist over a range of chemical composition. The ratio of the number of atoms of one kind to the number of atoms of the other kind does not correspond exactly to the ideal whole number ratio implied by the formula. Such compounds do not obey the law of constant composition. There are many examples of these compounds, particularly in the oxides and sulphides of the transition elements. Thus in FeO, FeS or CuS the ratio of Fe : O, Fe : S or Cu : S differs from that indicated by the ideal chemical formula. If the ratio of atoms is not exactly 1 : 1 in the above cases, there must be either an excess of metal ions, or a deficiency of metal ions (e.g. $\text{Fe}_{0.84}\text{O}$ – $\text{Fe}_{0.94}\text{O}$, $\text{Fe}_{0.9}\text{S}$). Electrical neutrality is maintained either by having extra electrons in the structure, or changing the charge on some of the metal ions. This makes the structure irregular in some way, i.e. it contains defects, which are in addition to the normal thermodynamic defects already discussed.

Metal excess

This may occur in two different ways.

F-centres

A negative ion may be absent from its lattice site, leaving a 'hole' which is occupied by an electron, thereby maintaining the electrical balance (see Figure 3.69). This is rather similar to a Schottky defect in that there are 'holes' and not interstitial ions, but only one 'hole' is formed rather than a pair. This type of defect is formed by crystals which would be expected to form Schottky defects. When compounds such as NaCl, KCl, LiH or δTiO are heated with excess of their constituent metal vapours, or treated with high energy radiation, they become deficient in the negative ions, and their formulae may be represented by $\text{AX}_{1-\delta}$, where δ is a small fraction. The nonstoichiometric form of NaCl is yellow, and the nonstoichiometric form of KCl is blue – lilac in colour. Note the similarity with the flame colorations for Na and K.

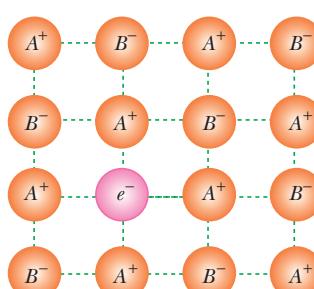


Figure 3.69 Metal excess defect because of absent anion.

The crystal lattice has vacant anion sites, which are occupied by electrons. Anion sites occupied by electrons in this way are called *F*-centres. (*F* is an abbreviation for *Farbe*, the German word for colour.) These *F*-centres are associated with the colour of the compound and the more *F*-centres present, the greater the intensity of the coloration. Solids containing *F*-centres are paramagnetic, because the electrons occupying the vacant sites are unpaired. When materials with *F*-centres are irradiated with light they become photoconductors. When electrons in the *F*-centres absorb sufficient light (or heat) energy, the electron is promoted into a conduction band, rather similar to the conduction bands present in metals. Since conduction is by electrons it is *n-type semiconduction*.

Interstitial ions and electrons

Metal excess defects also occur when an extra positive ion occupies an interstitial position in the lattice, and electrical neutrality is maintained by the inclusion of an interstitial electron (see Figure 3.70). Their composition may be represented by the general formula $A_{1+\delta}X$.

This type of defect is rather like a Frenkel defect in that ions occupy interstitial positions, but there are no 'holes', and there are also interstitial electrons. This kind of metal excess defect is much more common than the first, and is formed in crystals which would be expected to form Frenkel defects (i.e. the ions are appreciably different in size, have a low coordination number, and have some covalent character). Examples include ZnO , CdO , Fe_2O_3 and Cr_2O_3 .

If this type of defect oxide is heated in dioxygen, then cooled to room temperature, its conductivity decreases. This is because the dioxygen oxidizes some of the interstitial ions, and these subsequently remove interstitial electrons, which reduces the conductivity.

Crystals with either type of metal excess defect contain free electrons, and if these migrate they conduct an electric current. Since there are only a small number of defects, there are only a few free electrons that can conduct electricity. Thus the amount of current carried is very small compared with that in metals, fused salts or salts in aqueous solutions, and these defect materials are called *semiconductors*. Since the mechanism is normal electron conduction, these are called *n-type semiconductors*. These free electrons may be excited to higher energy levels giving absorption spectra, and in consequence their compounds are often coloured, e.g. nonstoichiometric $NaCl$ is yellow, nonstoichiometric KCl is lilac, and ZnO is white when cold but yellow when hot.

Metal deficiency

Metal-deficient compounds may be represented by the general formula $A_{1-\delta}X$. In principle metal deficiency can occur in two ways. Both require variable valency of the metal, and might therefore be expected with the transition metals.

Positive ions absent

If a positive ion is absent from its lattice site, the charges can be balanced by an adjacent metal ion having an extra positive charge (see Figure 3.71). Examples of this are FeO , NiO , δ - TiO , FeS and CuI . (If an Fe^{2+} is missing from its lattice site in FeO , then there must be two Fe^{3+} ions somewhere in the lattice to balance the electrical charges. Similarly if a Ni^{2+} is missing from its lattice site in NiO , there must be two Ni^{3+} present in the lattice.)

Crystals with metal deficiency defects are semiconductors. Suppose the lattice contains A^+ and A^{2+} metal ions. If an electron 'hops' from an A^+ ion to the positive centre (an A^{2+} ion), the original A^+ becomes a new positive centre. There has been an apparent

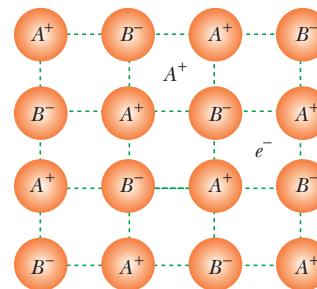


Figure 3.70 Metal excess defects caused by interstitial cations.

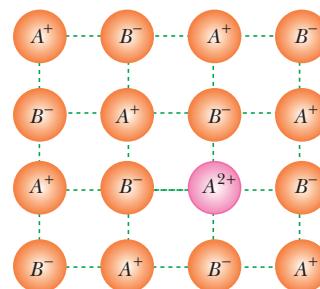


Figure 3.71 Metal deficiency caused by missing positive ion.

movement of A^{2+} . With a series of similar 'hops', an electron may be transferred in one direction across the structure, and at the same time the positive hole migrates in the opposite direction across the structure. This is called positive hole, or *p-type semiconductor*.

If a defect oxide of this type is heated in dioxygen, its room temperature conductivity increases, because the dioxygen oxidizes some of the metal ions, and this increases the number of positive centres.

Extra interstitial negative ions

In principle it might be possible to have an extra negative ion in an interstitial position and to balance the charges by means of an extra charge on an adjacent metal ion (see Figure 3.72). However, since negative ions are usually large, it would be difficult to fit them into interstitial positions. No examples of crystals containing such negative interstitial ions are known at present.

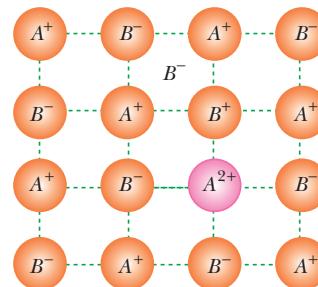


Figure 3.72 Metal deficiency caused by interstitial negative ions.

3.23 | BORN-HABER CYCLE

This cycle devised by Born and Haber in 1919 relates the lattice energy of a crystal to other thermochemical data. The energy terms involved in building a crystal lattice such as sodium chloride may be taken in steps. The elements in their standard state are first converted to gaseous atoms, and then to ions, and finally packed into the crystal lattice.

The enthalpies of sublimation and dissociation and the ionization energy are positive since energy is supplied to the system. The electron affinity and lattice energy are negative since energy is evolved in these processes.

According to Hess's law, the overall energy change in a process depends only on the energy of the initial and final states and not on the route taken. As can be seen from Figure 3.73 the enthalpy of formation of ΔH_f is the algebraic sum of the terms going round the cycle (paying heed to the exothermic or endothermic nature of each step).

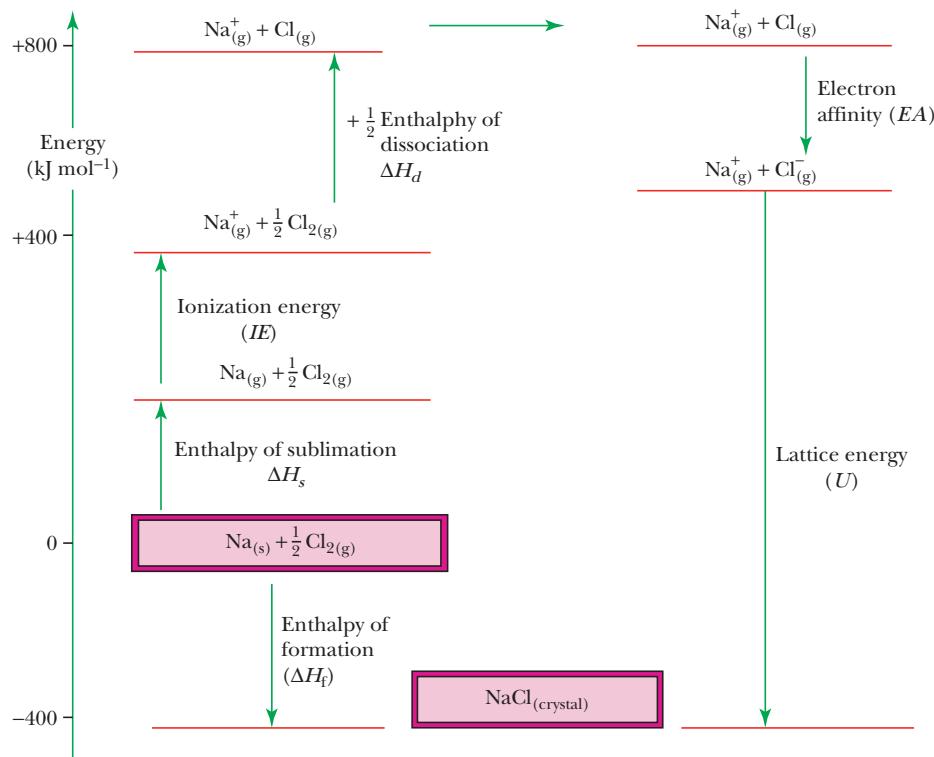


Figure 3.73 Born-Haber cycle for the formation of NaCl.

$$\Delta H_f = \Delta H_s + IE + \frac{1}{2} \Delta H_d + EA + U$$

All the terms except the lattice energy and electron affinity can be measured. Originally the cycle was used to calculate electron affinities. By using known crystal structures, it was possible to calculate the lattice energy, and hence values were obtained for the electron affinity.

$$\Delta H_f = + \Delta H_s + IE + \frac{1}{2} \Delta H_d + EA + U$$

For NaCl

$$381.2 = +108.4 + 495.4 + 120.9 + EA - 757.3$$

hence

$$EA = -348.6 \text{ kJ mol}^{-1}$$

Now that some electron affinity values are known, the cycle is used to calculate the lattice energy for unknown crystal structures.

It is useful to know the lattice energy, as a guide to the solubility of the crystal. When a solid dissolves, the crystal lattice must be broken up (which requires that energy is put in). The ions so formed are solvated (with the evolution of energy). When the lattice energy is high a large amount of energy is required to break the lattice. It is unlikely that the enthalpy of solvation will be big enough (and evolve sufficient energy to offset this), so the substance will probably be insoluble.

The 'noble behaviour' of many transition metals, that is their resistance to chemical attack, is related to a similar series of energy changes. Noble character is favoured by a high heat of sublimation, high ionization energy and low enthalpy of solvation of the ions.

Lattice energies may also provide some information about the ionic/covalent nature of the bonding. If the lattice energy is calculated theoretically assuming ionic bonding then the value can be compared with the experimental value for the lattice energy obtained from the experimentally measured quantities in the Born–Haber cycle. Close agreement indicates that the assumption that bonding is ionic is in fact true, whilst poor agreement may indicate that the bonding is not ionic. A number of lattice energies are compared in Table 3.14. The agreement is good for all the compounds listed except for CdI₂, confirming that these are ionic. The large discrepancy for CdI₂ indicates that the structure is not ionic, and in fact it forms a layer structure which is appreciably covalent.

Table 3.14 Comparison of theoretical and experimental lattice energies

	Theoretical lattice energy (kJ mol ⁻¹)	Born–Haber lattice energy (kJ mol ⁻¹)	% difference
LiCl	-825	-817	0.8
NaCl	-764	-764	0.0
KCl	-686	-679	1.0
KI	-617	-606	1.8
CaF ₂	-2584	-2611	1.0
CdI ₂	-1966	-2410	22.6

3.24 | POLARIZING POWER AND POLARIZABILITY – FAJANS' RULES

Consider making a bond theoretically by bringing two ions A⁺ and B⁻ together to their equilibrium distance. Will the bond remain ionic, or will it become covalent? Ionic and covalent bonding are two extreme types of bonding, and almost always the bonds formed are intermediate in type, and this is explained in terms of polarizing (that is deforming) the shape of the ions.

The type of bond between A⁺ and B⁻ depends on the effect one ion has on the other. The positive ion attracts the electrons on the negative ion and at the same time it repels the nucleus, thus distorting or polarizing the negative ion. The negative ion will also polarize the positive ion, but since anions are usually large, and cations small, the effect of a large ion on a small one will be much less pronounced. If the degree of polarization is quite small, then the bond remains largely ionic. If the degree of polarization is large,

electrons are drawn from the negative ion towards the positive ion, resulting in a high concentration of electrons between the two nuclei, and a large degree of covalent character results.

The extent to which ion distortion occurs depends on the power of an ion to distort the other ion (that is on its polarizing power) and also on how susceptible the ion is to distortion (that is on its polarizability). Generally the polarizing power increases as ions become smaller and more highly charged. The polarizability of a negative ion is greater than that of a positive ion since the electrons are less firmly bound because of the differences in effective nuclear charge. Large negative ions are more polarizable than small ones.

Fajans put forward four rules which summarize the factors favouring polarization and hence covalency.

1. A small positive ion favours covalency.

In small ions the positive charge is concentrated over a small area. This makes the ion highly polarizing, and very good at distorting the negative ion.

2. A large negative ion favours covalency.

Large ions are highly polarizable, that is easily distorted by the positive ion, because the outermost electrons are shielded from the charge on the nucleus by filled shells of electrons.

3. Large charges on either ion, or on both ions, favour covalency.

This is because a high charge increases the amount of polarization.

4. Polarization, and hence covalency, is favoured if the positive ion does not have a noble gas configuration.

Examples of ions which do not have a noble gas configuration include a few main group elements such as Ti^+ , Pb^{2+} and Bi^{3+} , many transition metal ions such as Ti^{3+} , V^{3+} , Cr^{2+} , Mn^{2+} and Cu^+ , and some lanthanide metal ions such as Ce^{3+} and Eu^{2+} . A noble gas configuration is the most effective at shielding the nuclear charge, so ions without the noble gas configuration will have high charges at their surfaces, and thus be highly polarizing.

Exceptions of 'smaller size cation causes higher polarization' are as follows.

Metal ion	Ionic radius
Zn^{2+}	0.6 Å
Cd^{2+}	0.78 Å
Hg^{2+}	0.96 Å

The radius increases down the group and it is expected that the polarizing power should also decrease. But it actually increases, and this is because $Z_{\text{effective}}$ increases down the group as much as the number of low shielding electron increases. The above observation is supported by the fact that the covalent character order is



and the dissociation observed is



Similarly the colour for the sulphides of these metals is also intensified.



Properties of ionic compounds affected by polarization

Higher polarization brings the following changes in the properties of ionic compounds:

1. Covalent character increases.
2. Lattice energy decreases.

3. Melting point decreases.
4. Hardness decreases.
5. Solubility in polar solvent decreases while that in relatively non-polar solvent increases.
6. Electrical conductivity decreases.
7. Intensity of colour increases.
8. Acidic character of oxide increases.

3.25 | MELTING POINT OF IONIC COMPOUNDS

Melting point of ionic compounds depends upon the lattice energy as well as polarization. But we can have the theoretical prediction of melting point orders only when polarization is in one extreme situation, i.e. either polarization is negligible or polarization is dominating.

1. **When the polarization is negligible:** Oxide or fluoride ions are very difficult to polarize due to their small size and high electronegativity and only a few cations like Li^+ , Be^{2+} , Al^{3+} , etc. can polarize them to some extent. Under this circumstance, the melting point order of the compounds is decided by the lattice energy.

Lattice energy can be defined by

$$\text{Lattice energy} = \int_{\infty}^r \frac{k \cdot q_1 q_2}{r^2} = -\frac{k \cdot q_1 q_2}{r}$$

when two opposite charges q_1 and q_2 are brought to the internuclear distance of r from infinity and k is the proportionality constant. Here, $q_1 = z^+ e$ and $q_2 = z^- e$ and z^+ and z^- are the charges in positive and negative ions and e is the charge on an electron.

Hence

$$\text{Lattice energy} \propto q_1 q_2$$

and

$$\text{Lattice energy} \propto \frac{1}{r}$$

The variations in the lattice energy with change in the charge and distance factor, in different situations, are discussed as follows:

- a. When the internuclear distance factor is kept same and the charge factor ($q_1 q_2$) is varied. For example,

Compounds	NaF	MgO	ScN	TiC
$q_1 q_2$	1	4	9	16

Hence,

Lattice energy order: $\text{NaF} < \text{MgO} < \text{ScN} < \text{TiC}$

Melting point order: $\text{NaF} < \text{MgO} < \text{ScN} < \text{TiC}$

Hardness order: $\text{NaF} < \text{MgO} < \text{ScN} < \text{TiC}$

- b. When charge factor ($q_1 q_2$) is fixed and the internuclear distance factor is varied, then with the increase in the value of r , the lattice energy and melting point decreases. For example,

- (i) For the series BeO , MgO , CaO , SrO and BaO

Melting point order: $\text{MgO} > \text{CaO} > \text{BeO} > \text{SrO} > \text{BaO}$

Lattice energy order: $\text{BeO} > \text{MgO} > \text{CaO} > \text{SrO} > \text{BaO}$

- (ii) For the series $\text{BeF}_2, \text{MgF}_2, \text{CaF}_2, \text{SrF}_2, \text{BaF}_2$
 Melting point order: $\text{CaF}_2 > \text{MgF}_2 > \text{SrF}_2 > \text{BaF}_2 > \text{BeF}_2$
 Lattice energy order: $\text{BeF}_2 > \text{MgF}_2 > \text{CaF}_2 > \text{SrF}_2 > \text{BaF}_2$

It is apparent that

$$\text{Melting point} \propto \frac{1}{P} \text{ and lattice energy} \propto \frac{1}{P}$$

where P stands for polarization. With the increase in polarization, the melting point and lattice energy order both are affected, but their variation may not be identical and hence there is no changes in the lattice energy order. Again, Be^{2+} causes polarization to some extent for both F^- and O^{2-} and hence BeO and BeF_2 are not in their expected position of melting point order. Mg^{2+} also shows little polarization towards F^- ion and exchanges its position with CaF_2 in their melting point order.

Note: Even though it appears odd that the extent of polarization by the same cation in case of F^- is less compared to O^{2-} ion, but the effect of polarization on melting point is more in case of fluoride in comparison to oxide. This is due to just double value of $q_1 q_2$ for oxide (4) as compared to that of fluoride (2). Hence the polarization order or covalent character order is $\text{MO} > \text{MF}_2$ but m.p. order is also $\text{MO} > \text{MF}_2$. For example,

Compound	m.p. ($^{\circ}\text{C}$)
BeO	2530
BeF_2	800
MgO	2850
MgF_2	1261
CaO	2580
CaF_2	1403

- c. For alkali metal halides, where the extent of polarization is less due to lower charge on cation, i.e. M^+ compared to M^{2+} in the cases discussed above.

Lattice energy order: $\text{LiX} > \text{NaX} > \text{KX} > \text{RbX} > \text{CsX}$ (where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)

But the melting point order is: $\text{NaX} > \text{KX} > \text{RbX} > \text{CsX} > \text{LiX}$ (where $\text{X} = \text{Cl}, \text{Br}$)

and $\text{KI} > \text{NaI} > \text{RbI} > \text{CsI} > \text{LiI}$

$\text{NaF} > \text{KF} > \text{LiF} > \text{RbF} > \text{CsF}$

Compounds LiX are not in their original position due to polarization in LiX and in case of iodide, Na^+ also causes polarization to some extent and the effect of this is observed in the melting point order.

- d. When $(q_1 q_2)$ factor increases as well as distance factor r decreases, then both lattice energy and melting point increase. For example,

Compounds:	NaF	MgF_2	AlF_3
$ q_1 q_2 $	1	2	3
r order:	$\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$		

Hence

Lattice energy order: $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$

Melting point order: $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$
 $995^{\circ}\text{C} 1261^{\circ}\text{C} 1291^{\circ}\text{C}$

Polarization order is also same like $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$

- 2. When the polarization is dominating factor:** When P increases and melting point decreases. Again polarization will vary with the following factors.

- a. When the charge on the cation increases and the radius decreases.

Covalent character order: $\text{NaX} < \text{MgX}_2 < \text{AlX}_3$

Melting point order: $\text{NaX} > \text{MgX}_2 > \text{AlX}_3$

where $\text{X} = \text{Cl}, \text{Br}, \text{I}$

- b.** When the charge on the cation remains the same but the size of the cation increases, the polarization decreases and melting point increases. For example,

- (i) For the series $\text{BeX}_2, \text{MgX}_2, \text{CaX}_2, \text{SrX}_2, \text{BaX}_2$

Covalent character order: $\text{BeX}_2 > \text{MgX}_2 > \text{CaX}_2 > \text{SrX}_2 > \text{BaX}_2$

Melting point order: $\text{BeX}_2 < \text{MgX}_2 < \text{CaX}_2 < \text{SrX}_2 < \text{BaX}_2$

- (ii) For the series $\text{LiX}, \text{NaX}, \text{KX}, \text{RbX}, \text{CsX}$

Covalent character order: $\text{LiX} > \text{NaX} > \text{KX} > \text{RbX} > \text{CsX}$

where $\text{X} = \text{Cl}, \text{Br}, \text{I}$

But the melting point order is not decided accordingly, since the extent of polarization is low enough due to lower charges of cation.

- c.** When the size of the anion increases, polarization increases and melting point decreases. For example,

- (i) For the series where M^+ is Li^+ to Cs^+ .

Covalent character order: $\text{MF} < \text{MCl} < \text{MBr} < \text{MI}$

Melting point order: $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$

- (ii) For the series where M^{2+} is Be^{2+} to Ba^{2+} .

Covalent character order: $\text{MF}_2 < \text{MCl}_2 < \text{MBr}_2 < \text{MI}_2$

Melting point order: $\text{MF}_2 > \text{MCl}_2 > \text{MBr}_2 > \text{MI}_2$

- (iii) For the series AlX_3 , where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$

Covalent character order: $\text{AlF}_3 < \text{AlCl}_3 < \text{AlBr}_3 < \text{AlI}_3$

Melting point order: $\text{AlF}_3 > \text{AlCl}_3 > \text{AlI}_3 > \text{AlBr}_3$

Here another parameter works to decide the melting point order, i.e. for the covalently bonded molecule, higher the molecule weight, higher will be the melting point. Hence the expected order is



and the overall order is as above.

3.26 | SOLUBILITY OF IONIC COMPOUNDS

The solubility of ionic compounds depends upon several parameters like lattice energy, hydration energy, polarization, packing pattern, entropy, etc. But no equation is available which can correlate all these parameters with solubility. Hence we have to study the solubility in situation where only one of the parameters is dominating.

1. When polarization is the dominating factor

- a. In polar solvent: higher polarization will cause less solubility. For example,

- (i) $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$

- (ii) $\text{PbF}_2 > \text{PbCl}_2 > \text{PbBr}_2 > \text{PbI}_2$

- (iii) $\text{HgF}_2 > \text{HgCl}_2 > \text{HgBr}_2 > \text{HgI}_2$

- b. In relatively non-polar solvents, e.g. acetone, the solubility order is



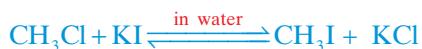
Since the covalent character order is



more the covalent character, higher will be the solubility in relatively non-polar solvent.

more the covalent character, higher will be the solubility in relatively non-polar solvent.

This information helps us choose the correct solvent for a reaction. For example, in Finkelstein reaction,

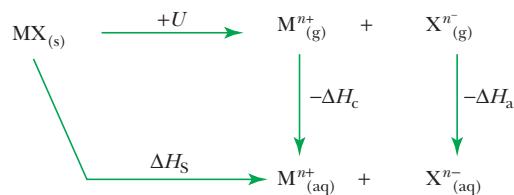


and in acetone



In water the reaction is reversible and the yield of CH_3I is not good. However, in acetone the percentage yield is very good in acetone because KCl is insoluble in acetone and makes the reaction unidirectional.

- 2. When the lattice energy and hydration energy are the dominating factors:** The mechanism for dissolution process of an ionic compound is shown below.



According to Hess's law,

$$\Delta H_s = U + \Delta H_h$$

and

$$\Delta G_s = \Delta H_s - T\Delta S_s$$

where, ΔH_s : Heat of dissolution

U : Lattice energy of MX

ΔH_h : Total hydration energy of cation and anion

ΔG_s : Gibb's free energy change for dissolution of MX

ΔS_s : Total entropy change for dissolution of MX .

T : Temperature in Kelvin

If the above thermodynamical and thermochemical data is known, we can predict if the compound is soluble or not.

- If ΔH_s is negative, then ΔG_s must be negative and the compound is soluble, because for all dissolution processes, ΔS_s is always positive (since the ions are free to move in a solution whereas they are rigidly held in a solid).
- If ΔH_s is positive, two cases are possible:

(i) If $|\Delta H_s| > |T\Delta S_s|$, then ΔG is positive and the compound is insoluble at the temperature T . For example, PbCl_2 and $\text{CH}_3\text{CO}_2\text{Ag}$ are sparingly soluble in cold water while completely soluble in hot water because with the increase in temperature, the situation reverses and $|\Delta H_s| < |T\Delta S_s|$ and ΔG_s becomes negative.

(ii) If $|\Delta H_s| < |T\Delta S_s|$, then ΔG_s is negative and the compound is soluble and this solubility is governed by huge the entropy change only. For example, solubility of NaNO_3 and KNO_3 , etc.

Prediction of solubility order in ionic compounds

We know that hydration energy

$$\Delta H_h \propto \frac{1}{r_{\text{ion}}}$$

$$\Delta H_c = \frac{k_1}{r_c} \quad \text{and} \quad \Delta H_a = \frac{k_2}{r_a} \quad (\text{where } \Delta H_h = \Delta H_c + \Delta H_a)$$

Also, lattice energy

$$U \propto \frac{1}{r_c + r_a}$$

$$U = \frac{k_3}{r_c + r_a}$$

or

where r_c and r_a are the radii of cation and anion respectively. Therefore

$$\begin{aligned} \Delta H_s &= \Delta H_h + U \\ &= \Delta H_c + \Delta H_a + U \end{aligned}$$

$$\Delta H_s = \frac{k_1}{r_c} + \frac{k_2}{r_a} + \frac{k_3}{r_c + r_a} \quad (3.6)$$

Let us consider two cases described as follows

1. If $r_c \ll r_a$, then $r_c + r_a \approx r_a$, and equation 3.6 reduces to

$$\Delta H_s = \frac{k_1}{r_c} + \frac{k_2}{r_a} + \frac{k_3}{r_a} \quad (3.7)$$

For the compounds having the same anion $(k_2/r_a) + (k_3/r_a)$ remains constant, therefore

$$\Delta H_s \propto \frac{1}{r_c}$$

Thus with increase in radius of the cation down the group, ΔH_s becomes less and less negative and so does ΔG_s . Hence the solubility decreases down the group. For example,

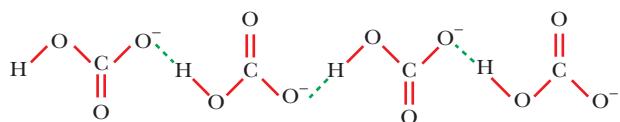
- a.** $\text{LiClO}_4 > \text{NaClO}_4 > \text{KClO}_4 > \text{RbClO}_4 > \text{CsClO}_4$
- b.** $\text{LiNO}_3 > \text{NaNO}_3 > \text{KNO}_3 > \text{RbNO}_3 > \text{CsNO}_3$
- c.** $\text{NaI} > \text{LiI} > \text{KI} > \text{RbI} > \text{CsI}$
- Lithium iodide is the alkali metal halide which has maximum polarization, and this high polarization causes lower solubility in polar solvent. Hence it is not at the expected position in the order.
- d.** $\text{LiBr} > \text{NaBr} > \text{KBr} > \text{RbBr} > \text{CsBr}$
- e.** $\text{CaCrO}_4 > \text{SrCrO}_4 > \text{BaCrO}_4$
- f.** $\text{Be}(\text{NO}_3)_2 > \text{Mg}(\text{NO}_3)_2 > \text{Ca}(\text{NO}_3)_2 > \text{Sr}(\text{NO}_3)_2 > \text{Ba}(\text{NO}_3)_2$
- g.** $\text{BeCO}_3 > \text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$
- h.** $\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$
- i.** $\text{CaSO}_3 > \text{SrSO}_3 > \text{BaSO}_3$
- j.** $\text{CaS}_2\text{O}_3 > \text{SrS}_2\text{O}_3 > \text{BaS}_2\text{O}_3$
- k.** $\text{BeX}_2 > \text{MgX}_2 > \text{CaX}_2 > \text{SrX}_2 > \text{BaX}_2$ (where $\text{X} = \text{Cl, Br, I}$)

Exceptions where $r_c \ll r_a$ but solubility increases down the group, are given as follows:

- a.** $\text{CaC}_2\text{O}_4 < \text{SrC}_2\text{O}_4 < \text{BaC}_2\text{O}_4 < \text{BeC}_2\text{O}_4$
 BeC_2O_4 is the exception of this trend.
- b.** $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$
- c.** $\text{NaHCO}_3 < \text{KHCO}_3 < \text{RbHCO}_3 < \text{CsHCO}_3$

LiHCO_3 is absent in the trend because it does not exist in the solid form.

In case of NaHCO_3 it is observed that HCO_3^- ions are attracted to each other by very strong hydrogen bonds which are formed by ion-dipole interaction.



The voids generated by the HCO_3^- ions in the lattice are best fitted with Na^+ ion. As the size of cation increases down the group, HCO_3^- ions become far apart from each other to accommodate the cation, and the hydrogen bonds become weaker. Hence the energy required to break the crystal becomes less and less, and the solubility increases down the group.

2. When $r_c \approx r_a$, then the lattice energy parameter is the deciding factor for solubility order. For the compounds having same $(q_1 q_2)$ factor, as the inter-ionic distance ($r_c + r_a$) increases, the lattice energy decreases and solubility increases down the group. This can be explained as follows.

$$\Delta H_s = \frac{k_1}{r_c} + \frac{k_2}{r_a} + \frac{k_3}{r_c + r_a}$$

$$\Delta H_s = \frac{k_1}{r_c} + \frac{k_2}{r_a} + \frac{k_3}{2r_c}$$

(as $r_c \approx r_a$)

For the compounds having the same anion like LiF to CsF , the k_2/r_a term is constant. It is observed that the variation of lattice energy term $k_3/2r_c$ is more prominent as compared to the hydration energy term k_1/r_c for the variation of r_c from Li^+ to Cs^+ . Hence the solubility increases down the group. For example,

- a. $\text{LiF} < \text{NaF} < \text{KF} < \text{RbF} < \text{CsF}$
- b. $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$
- c. $\text{Be}(\text{OH})_2 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$
- d. $\text{MgF}_2 < \text{CaF}_2 < \text{SrF}_2 < \text{BaF}_2 < \text{BeF}_2$.

BeF_2 is the exception to the trend

The solubility of alkali metals halides at a glance:

$\text{LiF} < \text{NaF} < \text{KF} < \text{RbF} < \text{CsF}$

* $\text{LiCl} > \text{NaCl} > \text{KCl} < \text{RbCl} < \text{CsCl}$

$\text{LiBr} > \text{NaBr} > \text{KBr} > \text{RbBr} > \text{CsBr}$

$\text{NaI} > \text{LiI} > \text{KI} > \text{RbI} > \text{CsI}$

(*Based on experimental data: $\text{LiCl} > \text{CsCl} > \text{RbCl} > \text{NaCl} > \text{KCl}$)

3.27 | ELECTRICAL CONDUCTIVITY AND COLOUR

As the polarization increases, the electrical conductivity decreases because ionization tendency decreases due to increase in the covalent character. For example,

- 1. $\text{LiCl} > \text{BeCl}_2$
- 2. $\text{NaCl} > \text{MgCl}_2$

The intensity of colour in ionic compounds increases with the increase in polarization. For example,

Colourless compounds:	AgCl, PbCl ₂ , HgCl ₂ , SnCl ₄
Coloured compounds:	Agl, Pbl ₂ , Hgl ₂ , Snl ₄ Yellow Yellow Scarlet red Orange red

Some important points related to the colour of halides are listed as follows:

1. It is not mandatory that all iodides will be coloured, e.g. NaI, KI, CuI are colourless.
2. For a particular metal ion, if the iodide is colourless, other halides must be colourless.
3. For a particular metal ion, if the bromide is colourless, then its iodide may be coloured but fluoride and chloride must be colourless.

3.28 | ACIDIC NATURE OF OXIDES

It is observed that as the polarization increases, the acidic nature of oxides increases. For example,

1. Li₂O < BeO < B₂O₃ < CO₂ < N₂O₅
2. Na₂O < MgO < Al₂O₃ < SiO₂ < P₂O₅ < SO₃ < Cl₂O₇
3. CO < CO₂
4. SO₂ < SO₃
5. N₂O < NO < N₂O₃ < NO₂ < N₂O₅

One empirical rule that can be used to predict the nature of oxides, states that if

1. $\sqrt{\phi_{M^{n+}}}$ > 3.2: then the oxide is acidic.
2. $\sqrt{\phi_{M^{n+}}}$ is between 2.2 and 3.2 : then the oxide is amphoteric.
3. $\sqrt{\phi_{M^{n+}}}$ < 2.2 : then the oxide is basic.

where ϕ is called the ionic potential which is defined as

$$\phi = \frac{\text{charge}}{\text{radius (in } \text{\AA})}$$

For example,

1. In BeO: for Be²⁺, $\phi = \frac{2.0}{0.31} = 6.45$ and $\sqrt{\phi_{M^{n+}}} = 2.54$

Hence BeO is amphoteric.

2. In Al₂O₃: for Al³⁺, $\phi = \frac{3.0}{0.5} = 6.0$ and $\sqrt{\phi_{M^{n+}}} = 2.45$

Hence Al₂O₃ is amphoteric.

3. In MgO: for Mg²⁺, $\phi = \frac{2.0}{0.72} = 2.77$ and $\sqrt{\phi_{M^{n+}}} = 1.66$

Hence MgO is basic.

4. In N₂O₅: for N⁵⁺, $\phi = \frac{5.0}{0.044} = 113.6$ and $\sqrt{\phi_{M^{n+}}} = 10.66$

Hence N₂O₅ is acidic.

Note: (i) If the oxide of any element is acidic/amphoteric/basic in nature, then the respective hydroxide also (if exists) must be acidic/amphoteric/basic in nature.

(ii) Amphoteric oxide include ZnO, Al₂O₃, PbO, PbO₂, SnO, SnO₂, Sb₂O₃, BeO, Cr₂O₃, MnO₂ and V₂O₅.

3.29 | THERMAL STABILITY OF IONIC COMPOUNDS

Ionic compounds are categorized into two based on their thermal stability.

- For binary compounds having smallest stoichiometric ratio, the thermal stability order is decided by the inter-ionic distance. Larger the inter-ionic distance, lower will be the lattice energy and lower the lattice energy, lower will be the thermal stability. For example,
 - $\text{Li}_3\text{N} > \text{Na}_3\text{N} > \text{K}_3\text{N}$
 - $\text{Li}_2\text{O} > \text{Na}_2\text{O} > \text{K}_2\text{O} > \text{Rb}_2\text{O} > \text{Cs}_2\text{O}$
 - $\text{LiX} > \text{NaX} > \text{KX} > \text{RbX} > \text{CsX}$
(where $\text{X} = \text{F, Cl, Br, I}$)
 - $\text{BeX}_2 > \text{MgX}_2 > \text{CaX}_2 > \text{SrX}_2 > \text{BaX}_2$
(where $\text{X} = \text{F, Cl, Br, I}$)
 - $\text{Be}_3\text{N}_2 > \text{Mg}_3\text{N}_2 > \text{Ca}_3\text{N}_2 > \text{Sr}_3\text{N}_2 > \text{Ba}_3\text{N}_2$
 - $\text{BeO} > \text{MgO} > \text{CaO} > \text{SrO} > \text{BaO}$
- For the ionic compounds having multiatomic anion, the efficient packing of the larger size cation and the larger size anion leads to the formation of thermally more stable compounds. Thus the thermal stability increases down the group for the compounds having the same anion. For example,
 - $\text{LiClO}_3 < \text{NaClO}_3 < \text{KClO}_3 < \text{RbClO}_3 < \text{CsClO}_3$
 - $\text{LiNO}_3 < \text{NaNO}_3 < \text{KNO}_3 < \text{RbNO}_3 < \text{CsNO}_3$
 - $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$
 - $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$
 - $\text{Be}(\text{NO}_3)_2 < \text{Mg}(\text{NO}_3)_2 < \text{Ca}(\text{NO}_3)_2 < \text{Sr}(\text{NO}_3)_2 < \text{Ba}(\text{NO}_3)_2$
 - $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3$
 - $\text{Be}(\text{OH})_2 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$
 - $\text{BeC}_2\text{O}_4 < \text{MgC}_2\text{O}_4 < \text{CaC}_2\text{O}_4 < \text{SrC}_2\text{O}_4 < \text{BaC}_2\text{O}_4$
 - $\text{BeSO}_4 < \text{MgSO}_4 < \text{CaSO}_4 < \text{SrSO}_4 < \text{BaSO}_4$.
 - Super oxides, peroxides, and ozonides of alkali metals and alkaline earth metals also have the same order of thermal stability, i.e. it increases down the group.

3.30 | WEAK FORCES

Attractive intermolecular forces

In the kinetic theory of gases, it is assumed that there are no forces of attraction between gas molecules. However, the fact that gases like O_2 , H_2 etc. can be liquefied, implies that the molecules are aggregated together and are obviously held together by some forces of attraction. This kind of existence of intermolecular forces is also proved by other facts like non-ideal behaviour of real gases and Joule–Thomson effect, etc.

There are three types of intermolecular attractive forces, which are described as follows and the sum of these three forces is called as van der Waals forces of attraction.

- Dipole–dipole interaction (or Keesom forces):** These forces arises due to dipolar nature of a molecule. The opposite ends of two molecules are attracted electrostatically in two ways, head–tail arrangement (Figure 3.74a) and anti-parallel arrangement (Figure 3.74b).

For fatty molecules, the head–tail arrangement is more stable. In other molecules, anti-parallel arrangement is more stable. Both the arrangements will have the same energy when the longer axis is 1.12 times as

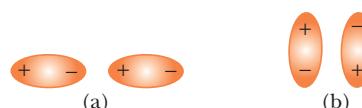


Figure 3.74 (a): Head-Tail arrangement

(b) Anti parallel arrangement.

long as the shorter axis. Both the arrangements may exist together only when the molecule is having higher attractive forces than the thermal energy, and it is true for both solids and liquids. With increase in temperature, these orientations become more random. The hydrogen bonding is a special case of this type of interaction due to its high energy release.

- 2. Dipole-induced dipole interaction (or Debye forces):** When the dipolar end of a polar molecule is introduced in the environment of a non-polar molecule, it can induce a dipole moment in the adjacent non-polar molecule (Figure 3.75). Then this induced dipole can interact electrostatically with the polarizing dipole.



Figure 3.75 Induced dipole.

This kind of interaction explains the solubility of noble gases in water, and formation of noble gas hydrates like $\text{Ar}\cdot 6\text{H}_2\text{O}$, $\text{Kr}\cdot 6\text{H}_2\text{O}$, and $\text{Xe}\cdot 6\text{H}_2\text{O}$. The solubility order for noble gases in water is: $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$. This is due to the increased polarizability of the larger inert gas molecules. Similarly, other derivatives of inert gases, $\text{Kr}(\text{phenol})_2$, $\text{Xe}(\text{phenol})_2$, and $\text{Rn}(\text{phenol})_2$ result from this kind of interaction.

Note: He and Ne do not form clathrate compounds due to their small size.

- 3. Instantaneous dipole-induced dipole interaction (London forces):** Molecules or atoms which have no permanent dipole are also attracted to each other and this is evident from the formation of liquid X_2 (where $\text{X} = \text{H, F, O, N, Cl, etc.}$) and liquid He. In such a molecule, at any point of time an instantaneous dipole is developed which induces dipole in the other nearby non-polar molecule, thereby producing dipole-induced dipole interactions. These interactions are known as London forces. London forces can be used to explain the formation of the following:

- a. Formation of liquid H_2 : The electronic distribution in H_2 molecules can be represented as shown in Figure 3.76.

On the time average these molecules are non-polar but at a particular moment, the molecule may become polar and the actual molecules may be a combination of all the three structure shown in Figure 3.76.

The development of induced dipole and its interaction in H_2 molecule is shown in Figure 3.77.

- b. Formation of liquid He: It is observed that two electrons in $1s$ orbital of He are not diametrically opposite always. Hence an instantaneous dipole is developed that induces dipole in adjacent atoms (Figure 3.78).

London forces work in polar and non-polar molecules and are dependent on the following factors and increases rapidly with increase in:

- (i) Number of polarizable electrons.
- (ii) Molecular weight.
- (iii) Molecular volume and surface area available for interaction.

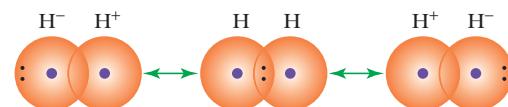


Figure 3.76 Electronic distribution in H_2 molecule.

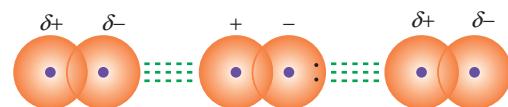


Figure 3.77 Instantaneous dipole-induced dipole interaction in H_2 molecule.

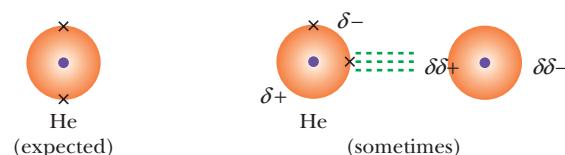
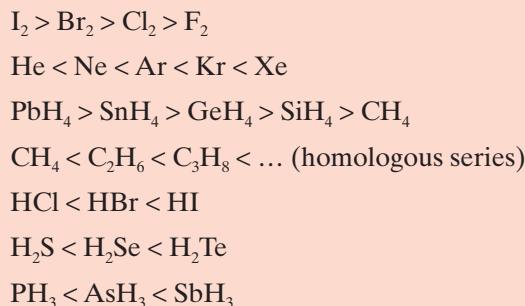


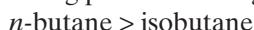
Figure 3.78 Instantaneous dipole-induced dipole interaction in He molecule.

Based on these, the effects of London forces on melting and boiling points of compounds are described as follows:

- a. Within the same group:



- b. When molecular weight is the same, molecular surface area is the responsible factor. For example, in isomeric alkanes as branching increases the surface area available for interaction decreases, resulting in the following melting/boiling point order in general:



n -pentane > iso-pentane > neo-pentane (for boiling point)
 But the melting point order is neo-pentane > iso-pentane > n -pentane.

- c. When the number of electrons is the same but molecular weight varies, boiling/melting point increases with increase in molecular weight. For example,



Boiling point: 20 K 23 K 25 K

- d. When polarizability of the attached groups is dominating over molecular weight, boiling point increases with increase in polarizability. For example, since methyl group is more polarizable than F atom, the boiling point order is



- e. The boiling point of H_2 (20 K) is more as compared to that of He (4.2 K). The extent of induction is more prominent in case of H_2 (which is caused by full positive or negative charge) as compared to that in He (which is caused by partial positive or negative charge).
 f. The molecular weight of fluorocarbons are significantly higher than those of corresponding hydrocarbons, yet their melting points and boiling points are less, particularly for higher members. The boiling points of some fluorocarbons and corresponding hydrocarbons are given in Table 3.15.

Table 3.15 Boiling points (°C) of C_nH_{2n+2} and C_nF_{2n+2}

n	1	2	3	5	6	8	10
C_nH_{2n+2}	-161	-88	-44	36	68	125	285
C_nF_{2n+2}	-128	-78	-38	22	51	104	240

Since fluorine is more electronegative as compared to carbon, a negative charge cloud density is developed at the periphery of the molecule which repels other molecules. This kind of repulsive force reduces the attraction among the molecules and is responsible for the observed order of boiling points.

- g. The boiling point order for $SiCl_4$ and CCl_4 is $CCl_4 > SiCl_4$ though the molecular weight of $SiCl_4$ is more than that of CCl_4 . The reason is the same as discussed above for hydrocarbons and fluorocarbons. The partial negative cloud density in case of $SiCl_4$ is more as compared to that in CCl_4 because the ΔEN ($Cl - Si$) = $3.16 - 1.8 = 1.36$ while ΔEN ($Cl - C$) = $3.16 - 2.5 = 0.66$. The increase in ΔEN value is sufficient to overcome the percentage increase in molecular weight which is only 10–11%.

Note: The van der Waals forces denoted by $E_{\text{attractive}}$ and the net $E_{\text{attractive}} = E_K + E_D + E_L$

where E_K : Keesom forces

E_D : Debye forces

E_L : London forces

Repulsive intermolecular forces

When the molecules come closer, the van der Waals forces increase gradually, but beyond a particular distance the electron–electron and nucleus–nucleus repulsions also increase, and finally the attractive and repulsive forces remain in equilibrium. The above repulsive energy is expressed by

$$E_{\text{repulsive}} = \frac{B}{r^n}$$

where B is a constant, n is of large value and depends upon the electronic configuration.

Lennard–Jones potential

The net interaction energy (also called as Lennard–Jones potential) is expressed by E_T .

$$\begin{aligned} E_T &= E_{\text{attractive}} + E_{\text{repulsive}} \\ &= \frac{A}{r^6} + \frac{B}{r^n} \end{aligned}$$

The plot of E_T with r is shown in Figure 3.79.

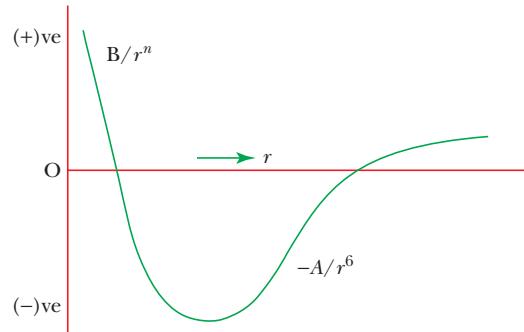


Figure 3.79 Plot of Lennard–Jones potential with internuclear distance.

3.31 | INTERACTIONS BETWEEN IONS AND COVALENT MOLECULES

- 1. Ion–dipole interactions:** These interactions explain the solubilities of ionic compounds in polar solvents. When an ionic compound is dissolved in polar solvents, the positive end of the polar solvent gets oriented towards anion, while the negative end of the polar solvent gets oriented towards cation, as shown in Figure 3.80.
- 2. Ion–induced dipole interaction:** The electrical field of an ion can polarize a non-polar molecule to induce a new dipole in the molecule. The electrostatic interaction between this ion and the induced dipole is called ion–induced dipole interaction (Figure 3.81). The formation of polyhalide ions like X_3^- ($X = F, Cl, Br, I$) and the solubility of ionic compounds in non-polar solvent can be explained on the basis of this interaction.

The stability order of X_3^- is $F_3^- < Cl_3^- < Br_3^- < I_3^-$. Among halides, I^- is the largest ion and has the largest polarizability. Hence the donating ability is maximum and produces the most stable species.

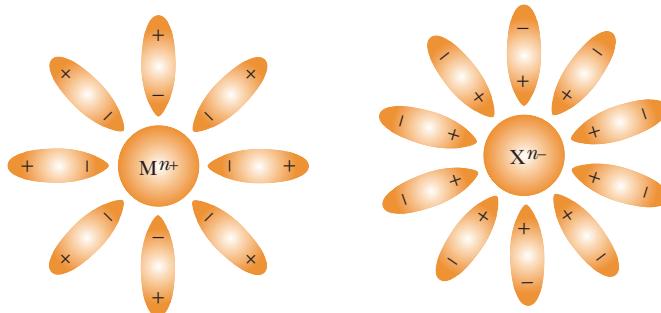


Figure 3.80 Ion–dipole interactions between ionic compounds and polar solvents.

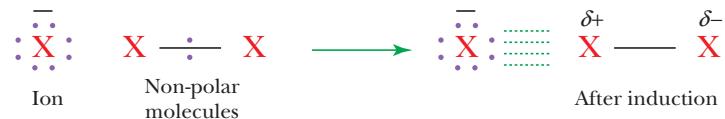


Figure 3.81 Ion–induced dipole interactions between ionic compounds and polar or non-polar molecules.

All the above interactions depend on the internuclear distance, and decrease with increase in this distance. Their energy–distance relation is given in Table 3.16.

Table 3.16 Energy–distance function for different ion-covalent interactions

Type of interaction	Energy–distance function
Ionic bond	$1/r$
Ion–dipole	$1/r^2$
Dipole–dipole	$1/r^3$
Ion–induced dipole	$1/r^4$
Dipole–induced dipole	$1/r^6$
London forces	$1/r^6$

3.32 | THE METALLIC BOND

All metals have characteristic physical properties:

1. They are exceptionally good conductors of electricity and heat.
2. They have a characteristic metallic lustre – they are bright, shiny and highly reflective.
3. They are malleable and ductile.
4. Their crystal structures are almost always cubic close-packed, hexagonal close-packed, or body-centred cubic.
5. They form alloys readily.

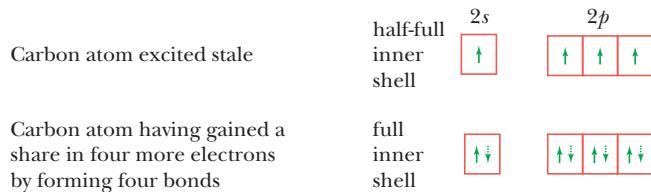
Conductivity

All metals are exceptionally good conductors of heat and electricity. Electrical conduction arises by the movement of electrons. This is in contrast to the movement of ions which is responsible for conduction in aqueous solution or fused melts of ionic compounds like sodium chloride, where sodium ions migrate to the cathode, and chloride ions migrate to the anode. In the solid state, ionic compounds may conduct to a very small extent (semiconduction) if defects are present in the crystal. There is an enormous difference in the conductivity between metals and any other type of solid (Table 3.17).

Most of the elements to the left of carbon in the periodic table are metals. A carbon atom has four outer electrons. If these are all used to form four bonds, the outer shell is complete and there are no electrons free to conduct electricity.

Table 3.17 Electrical conductivity of various solids

Substance	Type of bonding	Conductivity (ohm cm ⁻¹)
Silver	Metallic	$6.3 \cdot 10^5$
Copper	Metallic	$6.0 \cdot 10^5$
Sodium	Metallic	$2.4 \cdot 10^5$
Zinc	Metallic	$1.7 \cdot 10^5$
Sodium chloride	Ionic	10^{-7}
Diamond	Covalent giant molecule	10^{-14}
Quartz	Covalent giant molecule	10^{-14}



Elements to the left of carbon have fewer electrons, and so they must have vacant orbitals. Both the number of electrons present in the outer shell, and the presence of vacant orbitals in the valence shell, are important features in explaining the conductivity and bonding of metals.

The conductivity of metals decreases with increasing temperature. Metals show some degree of paramagnetism, which indicates that they possess unpaired electrons.

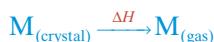
Lustre

Smooth surfaces of metals typically have a lustrous shiny appearance. All metals except copper and gold are silvery in colour. (Note that when finely divided most metals appear dull grey or black.) The shininess is rather special, and is observed at all viewing angles, in contrast to the shininess of a few non-metallic elements such as sulphur and iodine which appear shiny when viewed at low angles. Metals are used as mirrors because they reflect light at all angles. This is because of the 'free' electrons in the metal, which absorb energy from light and re-emit it when the electron drops back from its excited state to its original energy level. Since light of all wavelengths (colours) is absorbed, and is immediately re-emitted, practically all the light is reflected back – hence the lustre. The reddish and golden colours of copper and gold occur because they absorb some colours more readily than others.

Many metals emit electrons when exposed to light – the photoelectric effect. Some emit electrons when irradiated with short-wave radiation, and others emit electrons on heating (thermionic emission).

Malleability and cohesive force

The mechanical properties of metals are that they are typically malleable and ductile. This shows that there is not much resistance to deformation of the structure, but that a large cohesive force holds the structure together.



The cohesive force may be measured as the heat of atomization. Some numerical values of ΔH° , the heats of atomization at 25 °C, are given in Table 3.17. The heats of atomization (cohesive energy) decrease on descending a group in the periodic table Li–Na–K–Rb–Cs, showing that they are inversely proportional to the internuclear distance.

The cohesion energy increases across the periodic table from Group 1 to Group 2 to Group 13. This suggests that the strength of metallic bonding is related to the number of valency electrons. The cohesive energy increases at first on crossing the transition series Sc–Ti–V as the number of unpaired *d* electrons increases. Continuing across the transition series the number of electrons per atom involved in metallic bonding eventually falls, as the *d* electrons become paired, reaching a minimum at Zn.

The melting points and to an even greater extent the boiling points of the metals follow the trends in the cohesive energies. The cohesive energies vary over an appreciable range, and they approach the magnitude of the lattice energy which holds ionic crystals together. The cohesive energies are much larger than the weak van der Waals forces which hold discrete covalent molecules together in the solid state.

There are two rules about the cohesive energy and structure of metals (or alloys), and these are examined as follows:

Rule 1. The bonding energy of a metal depends on the average number of unpaired electrons available for bonding on each atom.

*Rule 2. The crystal structure adopted depends on the number of *s* and *p* orbitals on each atom that are involved with bonding.*

Consider the first rule – Group 1 metals have the outer electronic configuration ns^1 , and so have one electron for bonding. In the ground state (lowest energy), Group 2 elements have the electronic configuration ns^2 , but if the atom is excited, an outer electron is promoted, giving the configuration ns^1, np^1 , with two unpaired electrons, which can form two bonds. Similarly Group 13 elements in the ground state have the configuration ns^2, np^1 , but when excited to ns^1, np^2 , they can use three electrons for metallic bonding.

Table 3.18 Enthalpies of atomization ΔH° (kJ mol⁻¹) (Measured at 25 °C except for Hg)

Metal	ΔH°	Melting point (°C)	Boiling point (°C)
Li	162	181	1331
Na	108	98	890
K	90	64	766
Rb	82	39	701
Cs	78	29	685
Be	324	1277	2477
Mg	146	650	1120
Ca	178	838	1492
Sr	163	768	1370
Ba	178	714	1638
B	565	2030	3927
Al	326	660	2447
Ga	272	30	2237
Sc	376	1539	2480
Ti	469	1668	3280
V	562	1900	3380
Cr	397	1875	2642
Mn	285	1245	2041
Fe	415	1537	2887
Co	428	1495	2887
Ni	430	1453	2837
Cu	339	1083	2582
Zn	130	420	908

Enthalpies of atomization from Brewer, L., *Science*, 1968, **161**, 115, with some additions.

The second rule attempts to relate the number of *s* and *p* electrons available for bonding to the crystal structure adopted (Table 3.19). Apart from Group 1 metals, the atoms need to be excited, and the structures adopted are shown in Table 3.20.

Group 1 elements have a body-centred cubic structure, and follow the rule. In Group 2, only Be and Mg have a hexagonal close-packed structure and strictly follow the rule. In Group 13, Al has a cubic close-packed structure as expected. However, not all the predictions are correct. There is no obvious reason why Ca and Sr form cubic close-packed structures. However, the high temperature forms of Ca and Sr, and the room temperature form of Ba, form body-centred cubic structures (like Group 1), instead of the expected hexagonal close-packed structure. The explanation is probably that the paired *s* electron is excited to a *d* level instead of a *p* level, and hence there is only one *s* or *p* electron per atom participating in metallic bonding. This also explains why the first half of the transition metals also form

Table 3.19 Prediction of metal structures from the number of *s* and *p* electrons involved in metallic bonding

Number of <i>s</i> and <i>p</i> electrons per atom involved in bonding	Structure
Less than 1.5	Body-centred cubic
1.7–2.1	Hexagonal close-packed
2.5–3.2	Cubic close-packed
Approaching 4	Diamond structure – not metallic

Table 3.20 Type of structure adopted by metals in the periodic table (The room temperature structure is shown at the bottom. Other structures which occur at higher temperatures are listed above this in order of temperature stability)

Li	Be													B	C	N	
bcc	hcp																
Na	Mg													Al	Si	P	S
bcc	hcp													ccp	d		
K	Ca	Sc	Ti	V	Cr	Mn bcc ccp β	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se		
bcc	hcp	bcc		bcc	bcc	X	bcc	hcp	ccp	ccp	hcp	•	d	a			
bcc	ccp	hcp	hcp	bcc	bcc	X	bcc	hcp	ccp	ccp	hcp	•	d	a			
Rb	Sr bcc hcp	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te		
bcc	ccp	hcp	hcp	bcc	bcc	hcp	hcp	ccp	ccp	ccp	hcp	ccp*	d	α			
Cs	Ba	La bcc ccp	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl bcc	Pb	Bi	Po		
bcc	bcc	hcp	hcp	bcc	bcc	hcp	hcp	hcp	ccp	ccp	hcp	hep	ccp	a			

bcc = body-centred cubic

d = diamond structure

ccp = cubic close-packed

a = rhombohedral – puckered sheets

ccp* = distorted cubic close-packed

X = other structure

hcp = hexagonal close-packed

• = special case (see individual group)

body-centred cubic structures. In the second half of the transition series, the extra electrons may be put in the *p* level, to avoid pairing *d* electrons, and so allow the maximum participation of *d* orbitals in metallic bonding. This increases the number of *s* and *p* electrons involved in metallic bonding, and for example in Cu, Ag and Au the excited electronic state involved in bonding is probably d^8, s^1, p^2 , giving a cubic close-packed structure and five bonds per atom (two *d*, one *s* and two *p* electrons). At Zn the *d* orbitals are full, and the excited state used for bonding is $3d^{10}, 4s^1, 4p^1$, giving two bonds per atom and a body-centred cubic structure. The enthalpies of atomization are in general agreement with these ideas on bonding.

Crystal structures of metals

Metallic elements usually have a close-packed structure with a coordination number of 12. There are two types of close packing depending on the arrangement of adjacent layers in the structure: cubic close packing ABCABC and hexagonal close packing ABAB. However, some metals have a body-centred cubic type of structure (which fills the space slightly less efficiently) where there are eight nearest neighbours, with another

six next-nearest neighbours about 15% further away. If this small difference in distance between nearest and next-nearest neighbours is disregarded, the coordination number for a body-centred cubic structure may be regarded loosely as 14. The mechanical properties of malleability and ductility depend on the ease with which adjacent planes of atoms can glide over each other, to give an equivalent arrangement of spheres. These properties are also affected by physical imperfections such as grain boundaries and dislocations, by point defects in the crystal lattice and by the presence of traces of impurity in the lattice. The possibility of planes gliding is greatest in cubic close-packed structures, which are highly symmetrical and have possible slip planes of close-packed layers in four directions (along the body diagonals), compared with only one direction in the hexagonal close-packed structure. This explains why cubic close-packed structures are generally softer and more easily deformed than hexagonal or body-centred cubic structures. Impurities may cause dislocations in the normal metal lattice, and the localized bonding increases the hardness. Some soft metals like Cu become work hardened – it is harder to bend the metal a second time. This is because dislocations are caused by the first bending, and these disrupt the slip planes. Other metals such as Sb and Bi are brittle. This is because they have directional bonds, which pucker layers, preventing one layer from slipping over another.

The type of packing varies with the position of the element in the periodic table (Table 3.20), which is related to the number of *s* and *p* electrons on each atom that can take part in metallic bonding. This has been described earlier.

Metallic elements commonly react with other metallic elements, often over a wide range of composition, forming a variety of alloys which look like metals, and have the properties of metals.

Bond lengths

If the valence electrons in a metal are spread over a large number of bonds, each bond should be weaker and hence longer. The alkali metals exist as diatomic molecules in the vapour state, and the interatomic distances in the metal crystal are longer than in the diatomic molecule (Table 3.21).

Table 3.21 Interatomic distances in M_2 molecules and metal crystals

	Distance in metal (Å)	Distance in M_2 molecule (Å)
Li	3.04	2.67
Na	3.72	3.08
K	4.62	3.92
Rb	4.86	4.22
Cs	5.24	4.50

Though the bonds in the metal are longer and weaker, there are many more of them than in the M_2 molecule, so the total bonding energy is greater in the metal crystal. This can be seen by comparing the enthalpy of sublimation of the metal crystal with the enthalpy of dissociation of the M_2 molecules (Table 3.22).

Table 3.22 Comparison of enthalpies of sublimation and dissociation

	Enthalpy of sublimation of metal (kJ mol^{-1})	$\frac{1}{2}$ enthalpy of dissociation of M_2 molecule (kJ mol^{-1})
Li	161	54
Na	108	38
K	90	26
Rb	82	24
Cs	78	21

3.33 | THEORIES OF BONDING IN METALS

The bonding and structures adopted by metals and alloys are less fully understood than those with ionic and covalent compounds. Any successful theory of metallic bonding must explain both the bonding between a large number of identical atoms in a pure metal, and the bonding between widely different metal atoms in alloys. The theory cannot involve directional bonds, since most metallic properties remain even when the metal is in the liquid state (for example mercury), or when dissolved in a suitable solvent (for example solutions of sodium in liquid ammonia). Further, the theory should explain the great mobility of electrons.

Free electron theory

As early as 1900, Drude regarded a metal as a lattice with electrons moving through it in much the same way as molecules of a gas are free to move. The idea was refined by Lorentz in 1923, who suggested that metals comprised a lattice of rigid spheres (positive ions), embedded in a gas of free valency electrons which could move in the interstices. This model explains the free movement of electrons, and cohesion results from electrostatic attraction between the positive ions and the electron cloud. Whilst it does explain in a rough qualitative way why an increased number of valency electrons results in an increased cohesive energy, quantitative calculations are much less successful than similar calculations for the lattice energies of ionic compounds.

Valence bond theory

Consider a simple metal such as lithium, which has a body-centred cubic structure, with eight nearest neighbours and six next-nearest neighbours at a slightly greater distance. A lithium atom has one electron in its outer shell, which may be shared with one of its neighbours, forming a normal two-electron bond. The atom could equally well be bonded to any of its other eight neighbours, so many different arrangements are possible, and Figures 3.69a and b are two examples.

A lithium atom may form two bonds if it ionizes, and it can then form many structures similar to those in Figures 3.69c and d. Pauling suggested that the true structure is a mixture of all the many possible bonding forms. The more possible structures there are, the lower the energy. This means that the cohesive force which holds the structure together is large, and in metallic lithium the cohesive energy is three times greater than in a Li_2 molecule. The cohesive energy increases from Group 1 to 2 to 13, and this is explained by the atoms being able to form an increased number of bonds, and give an even larger number of possible structures. The presence of ions could explain the electrical conduction, but the theory does not explain the conduction of heat in solids, or the uster, or the retention of metallic properties in the liquid state or in solution.

Molecular orbital or band theory

The electronic structure of a lithium atom is as shown in Figure 3.82.

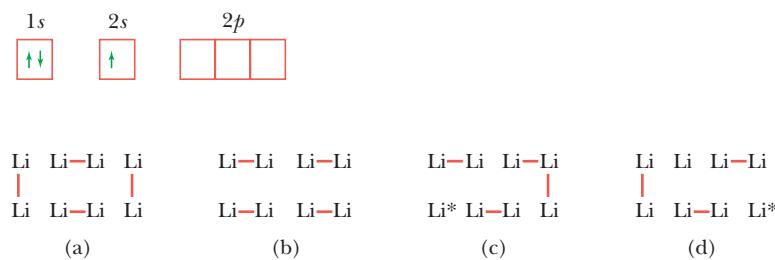


Figure 3.82 Representations of some bonding possibilities in lithium.

The Li_2 molecule exists in the vapour state, and bonding occurs using the 2s atomic orbital. There are three empty 2p orbitals in the valence shell, and the presence of empty AOs is a prerequisite for metallic properties. (Carbon in its excited state, nitrogen, oxygen, fluorine, and neon all lack empty AOs in the valence shell and are all non-metals.)

The valence shell has more AOs than electrons, so even if the electrons are all used to form normal two-electron bonds, the atom cannot attain a noble gas structure. Compounds of this type are termed 'electron deficient'.

Empty AOs may be utilized to form additional bonds in two different ways:

1. Empty AOs may accept lone pairs of electrons from other atoms or ligands, forming coordinate bonds.
2. Cluster compounds may be formed, where each atom shares its few electrons with several of its neighbours, and obtains a share in their electrons. Clustering occurs in the boron hydrides and carboranes, and is a major feature of metals.

The molecular orbital description of an Li_2 molecule has been discussed earlier in Section 3.12, in the examples of MO treatment. There are six electrons arranged in molecular orbitals:



Bonding occurs because the $\sigma 2s$ bonding MO is full and the corresponding antibonding orbital is empty. Ignoring any inner electrons, the 2s AOs on each of the two Li atoms combine to give two MOs – one bonding and one antibonding. The valency electrons occupy the bonding MO (Figure 3.83a).

Suppose three Li atoms joined to form Li_3 . Three 2s AOs would combine to form three MOs – one bonding, one non-bonding and one antibonding. The energy of the non-bonding MO is between that for the bonding and antibonding orbitals. The three valency electrons from the three atoms would occupy the bonding MO (two electrons) and the non-bonding MO (one electron) (Figure 3.83b).

In Li_4 , the four AOs would form four MOs – two bonding, and two antibonding. The presence of two non-bonding MOs between the bonding and antibonding orbitals reduces the energy gap between the orbitals. The four valency electrons would occupy the two lowest energy MOs, which are both bonding orbitals, as shown in Figure 3.83c.

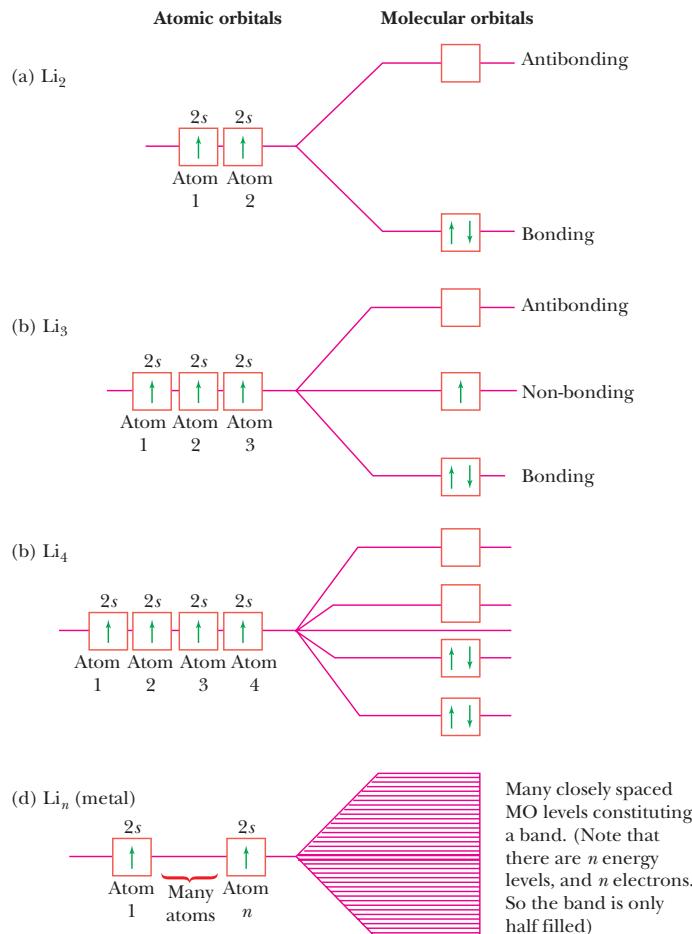


Figure 3.83 Development of molecular orbitals into bands in metals.

As the number of electrons in the cluster increases, the spacing between the energy levels of the various orbitals decreases further, and when there are a large number of atoms, the energy levels of the orbitals are so close together that they almost form a continuum (Figure 3.83d).

The number of MOs must by definition be equal to the number of constituent AOs. Since there is only one valence electron per atom in lithium, and a MO can hold two electrons, it follows that only half the MOs in the $2s$ valence band are filled –i.e. the bonding MOs. It requires only a minute amount of energy to perturb an electron to an unoccupied MO.

The MOs extend in three dimensions over all the atoms in the crystal, so electrons have a high degree of mobility. The mobile electrons account for the high thermal and electrical conduction of metals.

If one end of a piece of metal is heated, electrons at that end gain energy and move to an unoccupied MO where they can travel rapidly to any other part of the metal, which in turn becomes hot. In an analogous manner, electrical conduction takes place through a minor perturbation in energy promoting an electron to an unfilled level, where it can move readily. In the absence of an electric field, equal numbers of electrons will move in all directions. If a positive electrode is placed at one end, and a negative electrode at the other, then electrons will move towards the anode much more readily than in the opposite direction; hence an electric current flows.

Conduction occurs because the MOs extend over the whole crystal, and because there is effectively no energy gap between the filled and unfilled MOs. The absence of an energy gap in lithium is because only half the MOs in the valence band are filled with electrons (Figure 3.84a).

In beryllium there are two valence electrons, so the valence electrons would just fill the $2s$ valence band of MOs. In an isolated beryllium atom, the $2s$ and $2p$ atomic orbitals differ in energy by 160 kJ mol^{-1} . In much the same way as the $2s$ AOs form a band of MOs, the $2p$ AOs form a $2p$ band of MOs. The upper part of the $2s$ band overlaps with the lower part of the $2p$ band (Figure 3.84b). Because of this overlap of the bands some of the $2p$ band is occupied and some of the $2s$ band is empty. It is both possible and easy to perturb electrons to an unoccupied level in the conduction band, where they can move throughout the crystal. Beryllium therefore behaves as a metal. It is only because the bands overlap that there is no energy gap, so perturbation from the filled valence band to the empty conduction band can occur.

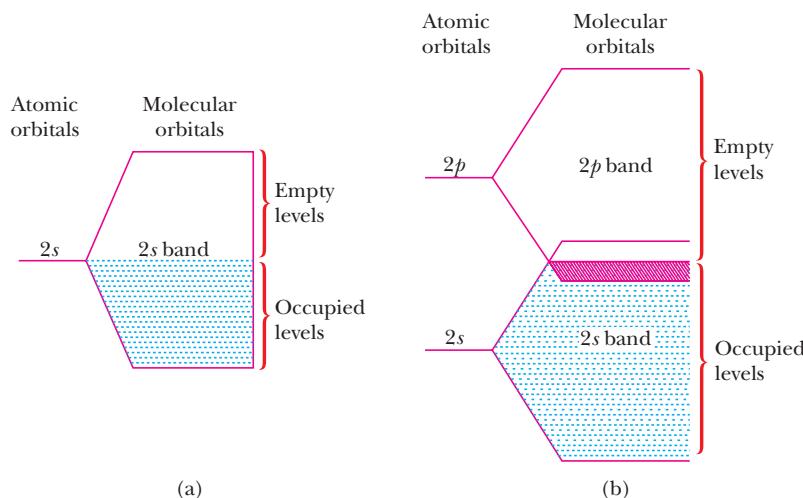


Figure 3.84 Two methods by which conduction can occur: (a) metallic molecular orbitals for lithium showing half-filled band; (b) metallic molecular orbitals for beryllium showing overlapping bands.

3.34 | CONDUCTORS, INSULATORS AND SEMICONDUCTORS

In electrical conductors (metals), either the valence band is only partly full, or the valence and conduction bands overlap. There is therefore no significant gap between filled and unfilled MOs, and perturbation can occur readily.

In insulators (non-metals), the valence band is full, so perturbation within the band is impossible, and there is an appreciable difference in energy (called the band gap) between the valence band and the next empty band. Electrons cannot therefore be promoted to an empty level where they could move freely.

Intrinsic semiconductors are basically insulators, where the energy gap between adjacent bands is sufficiently small for thermal energy to be able to promote a small number of electrons from the full valence band to the empty conduction band. Both the promoted electron in the conduction band and the unpaired electron left in the valence band can conduct electricity. The conductivity of semiconductors increases with temperature, because the number of electrons promoted to the conduction band increases as the temperature increases. Both *n*-type and *p*-type semiconductors are produced by doping an insulator with a suitable impurity. The band from the impurity lies in between the valence and conduction bands in the insulator, and acts as a bridge, so that electrons may be excited from the insulator bands to the impurity bands, or vice versa (Figure 3.85).

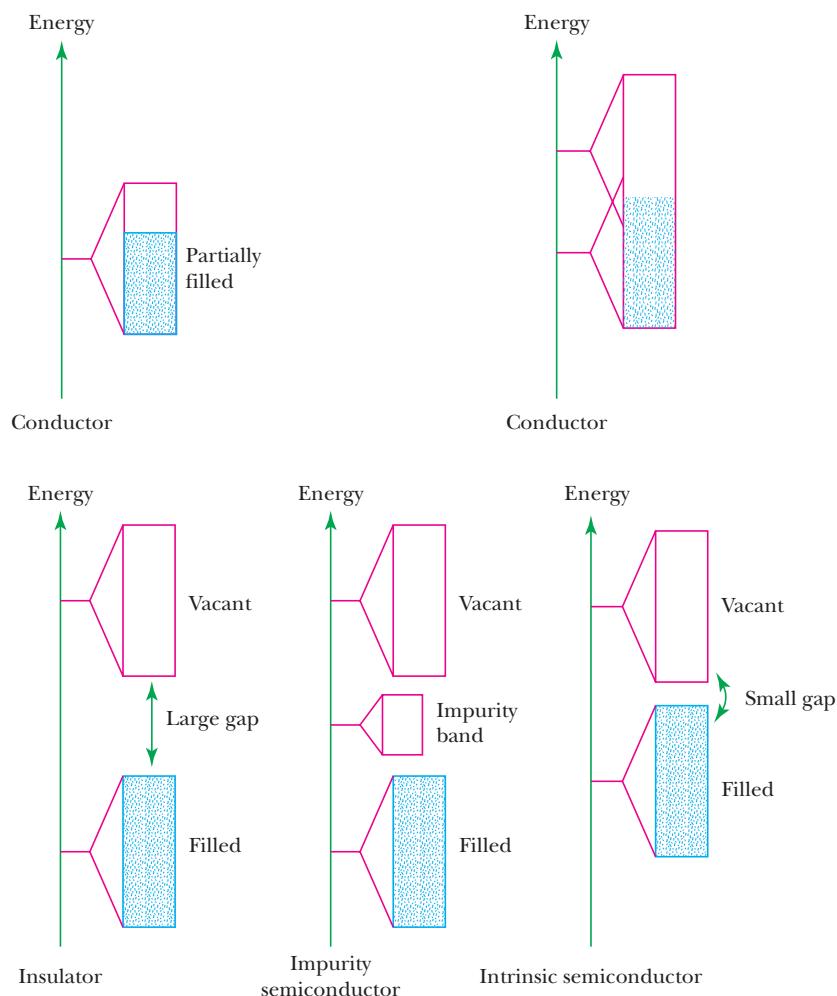
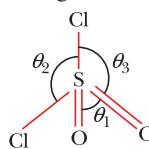
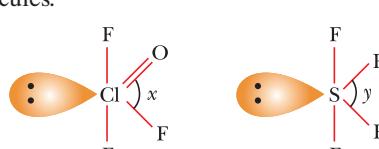


Figure 3.85 Conductors, insulators, impurity and intrinsic semiconductors.

SINGLE CORRECT CHOICE TYPE QUESTIONS

- If all bond angles in AX_3 molecule are the same, then which of the following conclusions is correct about AX_3 ?
 - AX_3 must be polar.
 - AX_3 must be planar.
 - AX_3 must have at least 5 valence electrons.
 - X must connect from central atom with either single bond or double bond.
- Which of the following statements is correct for BrF ?
 - Total number of lone pairs present in 15.
 - Total number of maximum number of atoms in one plane = 5.
 - Molecule is polar.
 - Bromine has its maximum covalency in this molecule.

3. What is the shape of the cationic part of solid Cl_2O_6 ?
- Distorted octahedral
 - Square pyramidal
 - Square planar
 - None of these
4. Which of the following orders of boiling point is incorrect?
- $\text{CH}_4 < \text{CF}_4$
 - $\text{BF}_3 < \text{BMe}_3$
 - $\text{I}_2 < \text{Br}_2 < \text{Cl}_2 < \text{F}_2$
 - $\text{Br}_2 < \text{I} - \text{Cl}$
5. The $\widehat{\text{CNC}}$ bond angle in CH_3NCS is:
- $< 109^\circ 28'$
 - $< 120^\circ$
 - $> 120^\circ$
 - 112°
6. Which of the following orders is incorrect? ($\text{X} = \text{F}/\text{Cl}$)
- $\text{CH}_2\text{F}_2 < \text{CHF}_3 < (\text{FCF})$
 - $\text{CH}_2\text{F}_2 < \text{CH}_2\text{Cl}_2 (\widehat{\text{XCX}})$
 - $\text{CHF}_3 < \text{CHCl}_3 (\widehat{\text{XCX}})$
 - $\text{CF}_4 < \text{CCl}_4 (\widehat{\text{XCX}})$
7. Which of the following statements is correct?
- $\text{C}-\text{F}$ bond length: $\text{CH}_3\text{F} < \text{CHF}_3$
 - $\text{O}-\text{F}$ bond length: $\text{O}_2\text{F}_2 < \text{OF}_2$
 - $(\widehat{\text{XCX}})$ bond angle: $\text{OCF}_2 < \text{OCCl}_2$
 - $(\widehat{\text{CICCI}})$ bond angle in $\text{OCCl}_2 > \widehat{\text{HCH}}$ bond angle in $\text{O} = \text{CH}_2$
8. Which of the following statements is/are correct for $\text{H}_2\text{C} = \text{SF}_4$?
- Double bond lies in equatorial position.
 - It is a non-planar and polar molecule.
 - Maximum number of atoms in a plane is 6.
- I, II
 - II, III
 - I, III
 - I, II, III
9. Which of the following molecules is polar as well as non-planar?
- $\text{P}(\text{CH}_3)_3 (\text{CF}_3)_2$
 - POF_3
 - OF_2
 - SO_2
10. Consider the following statements:
- In OSF_4 , $\text{F}_{\text{eq}} - \hat{\text{S}} - \text{F}_{\text{eq}} > \text{F}_{\text{eq}} - \hat{\text{S}} = \text{O}$
 - The bond angle of PF_3 is greater than PH_3 but the bond angle of NF_3 is lesser than NH_3 .
 - The % s-character in the orbital containing lone pair of H_2O molecule is 30%.
- $[(\widehat{\text{HOH}}) = 104^\circ 5 \text{ and } \cos(104.5) = -0.25]$
- Which of the following statements is/are correct?
- I, II
 - II, III
 - I, III
 - I, II, III
11. Choose the correct order of boiling point.
- $\text{H}_2 < \text{He}$
 - $\text{B}(\text{OH})_3 < \text{B}(\text{OMe})_3$
 - $\text{NF}_3 < \text{NMe}_3$
 - $\text{CCl}_4 < \text{SiCl}_4$
12. Which of the following interactions is responsible for the formation of clathrate compounds?
- Instantaneous dipole-induced dipole interaction
 - Ion-dipole interaction
 - Dipole-dipole interaction
 - Dipole-induced dipole interaction
13. Which of the following orders is correct?
- $\text{CH}_3\text{F} > \text{CH}_3\text{Cl}$ (dipole moment)
 - $\text{HF} > \text{H}_2\text{O}$ (extent of hydrogen bonding)
 - $\text{C}_5\text{H}_{12} > \text{C}_5\text{F}_{12}$ (boiling point)
 - $\text{KCl} > \text{NaCl}$ (solubility in water)
14. Which of the following statements is correct for
- 
- It contains $p_{\pi} - p_{\pi}$ and $p_{\pi} - d_{\pi}$
 - It has regular tetrahedral geometry.
 - $\theta_1 > \theta_3$
 - Plane which contains maximum number of atom is 4.
15. In which of the following processes electron is not added to molecular orbital having *gerade* symmetry?
- $\text{O}_2^+ \rightarrow \text{O}_2^-$
 - $\text{N}_2^+ \rightarrow \text{N}_2^-$
 - $\text{B}_2 \rightarrow \text{B}_2^-$
 - $\text{C}_2 \rightarrow \text{N}_2^{2-}$
16. If Hund's rule and *sp* intermixing is/are not considered, then which of the following characteristics is changed in C_2 ?
- Number of electrons in *gerade* molecular orbital
 - Bond order
 - Magnetic behaviour
 - Magnetic moment
17. A silicate mineral has chemical formula $\text{Ca}_2\text{Mg}_x\text{Si}_8\text{O}_{22}(\text{OH})_2$ and is known as tremolite. Predict the value of x .
- 3
 - 4
 - 2
 - 5
18. In which of the following N–N bond length is the shortest?
- N_2O
 - N_3^-
 - N_2O_4
 - N_2O_3 (unsymmetrical)
19. Select the correct order of H–M–H bond angle.
- $\text{PH}_3 > \text{PH}_4^+$
 - $\text{P}_2\text{H}_4 > \text{PH}_4^+$
 - $\text{PH}_3 > \text{NH}_4^+$
 - $\text{PH}_4^+ > \text{NH}_3$
20. Compare bond angle x and y in the following molecules.
- 

- (A) $x > y$ (B) $y > x$
 (C) $x = y$ (D) None of these
- 21.** Choose the correct statement from the following options.
 (A) All d_{C-O} in H_2CO_3 are identical.
 (B) All d_{Sb-Cl} in $SbCl_5$ are identical.
 (C) \widehat{HCH} (in H_2CO) $<$ \widehat{FCF} (in F_2CO)
 (D) All above statements are incorrect
- 22.** The maximum % of *s*-character in N–H bond is observed in
 (A) NH_3 (B) NH_4^+
 (C) N_2H_4 (D) N_2H_2
- 23.** Consider the following statements and select the correct set of codes using **T**(True) and **F**(False) in the given sequence.
 (I) $PI_5(s)$ does not exist due to steric crowding.
 (II) All possible angle in BF_2Cl are 120° .
 (III) In $N(SiH_3)_3$, lone pair of N is present in sp^3 hybrid orbital.
 (IV) *d* orbital used in hybridization of P in $PBr_5(s)$ is d_{z^2}
 (A) T F T T (B) F T T T
 (C) F F F F (D) T F T F
- 24.** Choose the incorrect statement from the following.
 (A) Bond angles are not affected in BF_3 due to back bonding.
 (B) Bond angles are affected in PF_3 due to back bonding.
 (C) Bond angles are not affected in $B(OMe)_3$ due to back bonding.
 (D) None of these.
- 25.** There is no hybridization of the central atom in AsH_3 because
 (A) it is a third period element.
 (B) the energy gap between $3s$ and $3p$ orbital is large enough.
 (C) the energy gap between $3s$ and $3p$ orbital is sufficiently less.
 (D) the energy gap between $4s$ and $4p$ orbital is large enough.
- 26.** In which of the following cases, the strength of back bonding is the maximum?
 (A) PF_3 (B) BF_3
 (C) $(H_3Si)_3N$ (D) $(SiH_3)_2O$
- 27.** If the % *s*-character in one $Sb-H$ bond in SbH_3 is 1.0%. What is the % *p*-character in the orbital occupied by its lone pair?
 (A) 99.0 (B) 97
 (C) 90 (D) None of these
- 28.** In which of the following all the given characteristics are present?
 (I) Vacant orbitals involved in hybridization.
 (II) Octet of underlined atom is complete.
 (III) Geometry at underlined atom is tetrahedral.
 (A) \underline{B}_2H_6 (B) \underline{Si}_2H_6
 (C) \underline{Al}_2Cl_6 (D) \underline{I}_2Cl_6
- 29.** Which of the following molecules is non-planar?
 (A) $\dot{C}FH_2$ (B) $\dot{C}F_2H$
 (C) ClO_3 (D) All of these
- 30.** Which of the following is correct with regard to bonding of $Al_2(CH_3)_6$?
 (A) 2 ($2c - 2e$) bond and 2 ($3c - 2e$) bond.
 (B) 4 ($2c - 2e$) bond and 2 ($3c - 4e$) bond.
 (C) All central atoms are having complete octet.
 (D) Molecule is non-planar.
- 31.** Which of the following orders of bond angle is correct?
 (A) $B(OH)_3 < B(OMe)_3$
 (B) \widehat{OBX} , where X = H, Me
 (C) $BF_3 < BCl_3$ (\widehat{XBX})
 (D) $SiCl_4 < CCl_4$
 (E) \widehat{ClACl} , where A = Si, C
- 32.** Which of the following chemical species is linear, planar as well as polar?
 (A) HCN (B) XeF_2
 (C) I_3^- (D) XeF_4
- 33.** Match the overlapping of orbitals with the type of bond formed. (Consider *x*-axis as internuclear axis.)
- | Column-I | Column-II |
|-----------------------|-----------------------|
| (P) $2s + 2p_x$ | (1) π bond |
| (Q) $2p_y + 2p_y$ | (2) σ bond |
| (R) $d_{xy} + p_z$ | (3) δ bond |
| (S) $d_{yz} + d_{yz}$ | (4) no bond formation |
- Code:**
- | P | Q | R | S |
|-------|---|---|---|
| (A) 1 | 2 | 3 | 4 |
| (B) 2 | 1 | 4 | 3 |
| (C) 3 | 1 | 2 | 4 |
| (D) 4 | 3 | 2 | 1 |
- 34.** Which of the following statements is correct?
 (A) Noble gases are insoluble in water.
 (B) The solubility of noble gases in water is fairly high due to London dispersion force.
 (C) The solubility of noble gases increases with the decrease in size of the noble gas atom.
 (D) The solubility of noble gases in water is fairly high due to dipole–induced dipole interaction.
- 35.** Choose the correct order for the energy barrier to rotation around the B–N bond.
 (A) $H_2B - NR_2 < BH(NR_2)_2 < B(NR_2)_3$
 (B) $B(NR_2)_3 < BH(NR_2)_2 < BH_2 - NR_2$
 (C) $BH(NR_2)_2 > B(NR_2)_3 > BH_2NR_2$
 (D) $BH_2NR_2 > B(NR_2)_3 > BH(NR_2)_2$
- Note:** R = CH_3 in all the above cases.

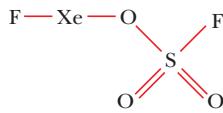
- 36.** Calculate the percentage of p character in the orbital occupied by the lone pair of electrons in water molecule. [Given HOH is 104.5° and $\cos(104.5^\circ) = -0.25$]
 (A) 80% (B) 20% (C) 70% (D) 75%
- 37.** Give the correct order of initials **True (T)** or **False (F)** for the following statements.
 (I) sp^3 hybrid orbitals are at 90° to one another.
 (II) Adjacent sp^3d^2 hybrid orbitals are at 90° to one another.
 (III) sp^2 hybrid orbitals are at 120° to one another.
 (IV) Bond order of N – O bond in NO_3^- is $1\frac{1}{3}$.
 (A) TFTF (B) TTFF (C) FTTT (D) FTFT
- 38.** Which among the following species is not perfectly planar?
 (A) $\dot{\text{C}}\text{H}_3$ (B) $\dot{\text{C}}\text{HF}_2$ (C) $:\text{CF}_2$ (D) $\dot{\text{N}}\text{O}_2$
- 39.** Which of the following molecules has the maximum number of A–X bonds of identical length, where 'A' is the central atom and 'X' is the surrounding atom?
 (A) SF_6 (B) IF_7
 (C) PF_5 (D) ClO_4^- .
- 40.** Which of the following sequences shows the correct bond angle order for isoelectronic species O_3 , NO_2^- and NOF ?
 (A) $\text{NO}_2^- > \text{NOF} > \text{O}_3$ (B) $\text{O}_3 > \text{NO}_2^- > \text{NOF}$
 (C) $\text{O}_3 < \text{NO}_2^- < \text{NOF}$ (D) Cannot be predicted
- 41.** The shape of $[\text{ClF}_4^-]$ and $[\text{ClF}_2^-]$ ions is respectively
 (A) See-saw and linear.
 (B) See-saw and bent.
 (C) Tetrahedral and linear.
 (D) Square planar and linear.
- 42.** Which of the following d orbitals is not involved in d^3 hybridization?
 (A) $d_{x^2-y^2}$ (B) d_{xy} (C) d_{yz} (D) d_{zx}
- 43.** Which among the following statements is incorrect?
 (A) Half-filled configuration is less stable as compared to fully filled configuration.
 (B) SbF_5 is a hypervalent species.
 (C) SbF_5 can act as a Lewis acid.
 (D) All are incorrect.
- 44.** Which of the following orders is correct with respect to the given property?
 (A) $\text{SiF}_4 > \text{SiCl}_4$: B.P. order.
 (B) $\text{MgCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$; p_{CO_2} order when kept at fixed temperature in a closed container.
 (C) $\text{XeF}_2 > \text{XeF}_4$: Dipole moment order.
 (D) $\text{XeF}_2 > \text{XeF}_4$: Fluoride-accepting tendency order.
- 45.** Which of the following statements is correct for $\text{F}_3\text{C}-\text{CF}_2-\text{CF}_3$?
 (A) All C–F bond lengths are identical.
 (B) Two C–F bonds attached to middle carbon atom are longer as compared to the other C–F bond at the terminal carbon.
 (C) Two C–F bonds attached to the middle carbon atom are shorter as compared to the other C–F bond at the terminal carbon.
 (D) None of these.
- 46.** Which of the following statements is not correct regarding NO_2 molecule?
 (A) Paramagnetic behaviour decreases when it undergoes in dimerization.
 (B) It is coloured in its dimeric form.
 (C) The colour is due to the presence of unpaired electron.
 (D) The free electron is present in one of the sp^2 hybrid orbital.
- 47.** $\text{PCl}_{x}\text{F}_{5-x}$ molecule will be polar and non-polar for what values of x respectively?
 Polar Non-polar Polar Non-polar
 (A) 2, 3, 5 and 0, 4, 1 (B) 0, 2, 5 and 3, 1, 4
 (C) 4, 3, 0 and 2, 0, 4 (D) 2, 1, 4 and 3, 0, 5
- 48.** Which of the following molecules/species has the minimum number of lone pairs?
 (A) ICl_3 (B) BF_4^- (C) SnCl_2 (D) XeF_4
- 49.** Find the pair of species having the same shape but different hybridization of the central atom.
 (A) SO_3 , CO_3^{2-} (B) NO_2^- , ClO_2^-
 (C) BeCl_2 , HCN (D) XeF_2 , SnCl_2
- 50.** Which of the following statements is incorrect regarding Cl_2O molecule?
 (A) The molecule is planar.
 (B) The shape of the molecule is bent.
 (C) The hybridization of the central atom is sp^3 .
 (D) The molecule is non-planar.
- 51.** The hybridization of all carbon atoms in benzene is
 (A) sp^2 (B) sp^3
 (C) sp^2 and sp^3 (D) sp^2 and sp
- 52.** The ratio of σ bond and π bond in naphthalene is _____.
 (A) 11 : 5 (B) 2 : 1 (C) 19 : 5 (D) 10 : 4
- 53.** The strongest π bond is present in which of the following species?
 (A) $\text{HC} \equiv \text{CH}$ (B) $\text{H}-\text{C} \equiv \text{P}$
 (C) SO_4^{2-} (D) $\text{H}_2\text{C}=\text{CH}_2$
- 54.** Which of the following pairs is iso-structural?
 (A) BO_3^{3-} and SO_3^{2-} (B) NO_2^+ and CO_2
 (C) HNC and SnCl_2 (D) SnCl_3^- and SO_3
- 55.** The d_{z^2} orbital is involved in which of the following hybridizations?
 (A) sp^3d (square pyramidal) (B) sp^3
 (C) sp^3d^2 (D) None of these

56. Which of the following species has incomplete octet?
 (A) SiF_4 (B) N^{3-} (C) PBr_3 (D) B^{3-}
57. Which of the following statements is correct for the two molecules, C_6H_6 and $\text{B}_3\text{N}_3\text{H}_6$?
 (A) C–H bond length is identical with N–H and B–H bond lengths.
 (B) The nature of double bond is perfectly identical in both.
 (C) Both the molecules are planar.
 (D) C_6H_6 is non-polar while $\text{B}_3\text{N}_3\text{H}_6$ is polar.
58. Which of the following species has the same number of X – O – X linkages, where X = S or P?
 (I) $\text{S}_4\text{O}_6^{2-}$ (II) S_3O_9 (III) $\text{S}_2\text{O}_5^{3-}$ (IV) $\text{P}_3\text{O}_9^{3-}$
 (A) II & IV (B) II & III (C) I & III (D) I & IV
59. In which of the following processes, the value of magnetic moment does not change?
 (A) $\text{N}_2 \rightarrow \text{N}_2^-$ (B) $\text{N}_2 \rightarrow \text{N}_2^+$
 (C) $\text{O}_2 \rightarrow \text{O}_2^+$ (D) $\text{O}_2^+ \rightarrow \text{O}_2^-$
60. Which of the following statements is not correct?
 (A) $(s + p_y)$ produces sp hybrid orbitals which are lying in the yz plane.
 (B) $(s + p_y)$ produces sp hybrid orbitals which are lying in the xz plane.
 (C) $(s + p_x + p_z)$ produces sp^2 hybrid orbitals which are lying in the xz plane.
 (D) $(s + p_y)$ produces sp hybrid orbitals which are lying along the y axis.
61. Which is the correct order of the bond angle?
 (A) $\text{NH}_3 < \text{NF}_3$ (B) $\text{H}_2\text{O} > \text{Cl}_2\text{O}$
 (C) $\text{PH}_3 < \text{SbH}_3$ (D) $\text{H}_2\text{Te} < \text{H}_2\text{S}$
62. The electronic configurations of three elements are as follows:
 L: $1s^2 2s^2 2p^6 3s^1$, M: $1s^2 2s^2 2p^4$, N: $1s^2 2s^2 2p^6 3s^2 3p^1$
 Choose the correct formula of the ionic compounds formed by the above given elements where the cations are written first as usual.
 (A) N_3M_2 , LM (B) ML_2 , M_3N_2
 (C) LN, M_2L (D) N_2M_3 , L_2M

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. Which of the following options is/are correct regarding the XeO_3F_2 and XeOF_4 molecules?
 (A) Bond length $d_{\text{Xe}-\text{O}(\text{XeO}_3\text{F}_2)} < d_{\text{Xe}-\text{O}(\text{XeOF}_4)}$
 (B) Bond length $d_{\text{Xe}-\text{F}(\text{XeO}_3\text{F}_2)} < d_{\text{Xe}-\text{F}(\text{XeOF}_4)}$
 (C) Shapes are trigonal bipyramidal and square pyramidal, respectively.
 (D) The nature of π -bond is of $5d_{\pi} - 2p_{\pi}$ type.
2. Choose the incorrect statement(s) from the following.
 (A) HOMO for N_2 molecule is π_b MO.
 (B) LUMO for N_2^- ion is π^* MO.
 (C) HOMO for CO molecule is NBMO from C-atom.
 (D) Among halogens, pale yellow colour of F_2 only is not due to HOMO – LUMO transition.
3. Which of the following statements is/are correct?
 (A) On increasing s -character hybrid orbital's energy decreases.
 (B) Bond angle is generally unaffected due to the presence of lone pair.
 (C) On increasing s -character hybrid orbital's length decreases.
 (D) Valence shell electron pairs play important role to decide the shape of a molecule.
4. The correct order for Lewis basic strength is/are
 (A) $\overline{\text{C}}\text{Cl}_3 < \overline{\text{C}}\text{F}_3$
 (B) $(\text{CH}_3)_2\text{O} < \text{O}(\text{SiH}_3)_2$
 (C) $(\text{CH}_3)_3\text{N} > \text{N}(\text{SiH}_3)_3$
 (D) $\text{NH}_3 > \text{PH}_3$
5. Which of the following molecules/ions does not exist?
 (A) KHF_2 (B) OF_4^-
 (C) BeF_5^{3-} (D) SH_4^-
6. In which of the following reactions, the magnitude of change in bond angle with respect to underlined atom is $\geq 20^\circ$?
 (A) $\underline{\text{Be}}\text{F}_2 + 2\text{F}^- \rightarrow \text{Be}\underline{\text{F}}_4^{2-}$
 (B) $\underline{\text{B}}\text{F}_3 + \text{F}^- \rightarrow \text{BF}_4^-$
 (C) $\underline{\text{N}}\text{H}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$
 (D) $\underline{\text{C}}_2\text{H}_2 + 2\text{H}_2 \rightarrow \text{C}_2\text{H}_6$
7. Which of the following is correct order for indicated bond length?
 (A) $d_{\text{N}-\text{N}}$ in $\text{N}_2\text{H}_2 > d_{\text{N}-\text{N}}$ in N_2F_4
 (B) $d_{\text{N}-\text{N}}$ in $\text{NH}_2 - \text{NH}_2 > d_{\text{N}-\text{N}}$ in $\overset{+}{\text{NH}_3} - \overset{+}{\text{NH}_3}$
 (C) $d_{\text{Si}-\text{Cl}}$ in $\text{SiClF}_3 > d_{\text{Si}-\text{Cl}}$ in SiClH_3
 (D) $d_{\text{C}-\text{C}}$ in $\text{C}_2\text{H}_6 > d_{\text{C}-\text{C}}$ in C_2F_6
8. Which of the following statements is/are not correct?
 (A) The bond angle $\widehat{\text{SiOSi}}$ in $(\text{SiH}_3)_2\text{O}$ is larger than that of C–O–C in $(\text{CH}_3)_2\text{O}$.
 (B) BF_3 has more Lewis acidic nature than BI_3 .
 (C) $p\pi-d\pi$ bond electrons get delocalized between B and N atoms in $\text{B}_3\text{N}_3\text{H}_6$.
 (D) CH_3NCS is linear, while SiH_3NCS is bent structure.
9. Which of the following pairs of molecules is/are not isostructural?
 (A) NMe_3 and $\text{N}(\text{SiMe}_3)_3$
 (B) XeOF_4 and SOF_4
 (C) CF_3 and PF_3
 (D) SiO_2 and CO_2

10. Which of the following statements is/are correct for XeFOSO_2F ?



- (A) The number of sp^3 hybridized central atom is 3.
 (B) The number of identical S–O bond is 2.
 (C) Maximum number of atoms that may lie in one plane is 5.
 (D) All atoms are lying in the same plane.

11. Select the correct statement(s) about the following chemical species:



- (A) Magnetic moment of NO is greater than that of O_2 .
 (B) The bond length of O_2^+ is shorter than that of O_2 due to removal of electron from π^* .
 (C) The ionization energy of N_2 is greater than that of N.
 (D) H_2^+ is more stable than H_2^- although both have the same bond order.

12. Which of the following orders is/are incorrect, against the indicated properties?

- (A) $\text{AgF} > \text{AgCl} > \text{AgI}$: Covalent character
 (B) $\text{NaHCO}_3 > \text{KHCO}_3 < \text{RbHCO}_3$: Solubility in water
 (C) $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$: Melting point
 (D) $\text{MgC}_2\text{O}_4 > \text{CaC}_2\text{O}_4 > \text{BaC}_2\text{O}_4$: Solubility in water

13. Select the correct statement(s) among the following.

- (A) When lone pair of surrounding atom is involved in back bonding, the bond angle does not change anywhere.
 (B) When lone pair of central atom is involved in back bonding, the bond angle does not change.
 (C) In $\text{B}_3\text{N}_3\text{H}_6$, all B – N bond lengths are equal and these are shorter than the single B – N covalent bonds due to delocalization of π electrons.
 (D) BF_3 , BCl_3 are gaseous, BBr_3 is liquid and BI_3 is solid because when size increases, instantaneous dipole-induced dipole interaction increases.

14. Which of the following molecule have $3c - 2e$ bond?

- (A) Al_2Cl_6 (B) $\text{Al}_2(\text{CH}_3)_6$
 (C) $[\text{Be}(\text{OMe})_2]_n$ (D) $[\text{Be}(\text{CH}_3)_2]_n$

15. Types of bonds in B_2H_6 :

- (A) B – B ($2c - 2e$) (B) B B B ($3c - 2e$)
 (C) B – H ($2c - 2e$) (D) B H B ($3c - 2e$)

16. $\text{Be}(\text{OH})_2$ forms bridge bonding structure in their polymeric form of the compounds as given below.

(I) $[\text{Be}_3(\text{OH})_8]^{2-}$ (II) $[\text{Be}_4(\text{OH})_{10}]^{2-}$

Which types of bonds are present in the above compounds?

- (A) $2c - 2e$ bond (B) $3c - 2e$ bond
 (C) $3c - 4e$ bond (D) All of these

17. If polarizing power is in the order of $\text{M}_a^+ > \text{M}_b^+ > \text{M}_c^+$ and polarizability is in the order of $\text{X}^- > \text{Y}^- > \text{Z}^-$, then select which of the following compounds have more covalent character as compared to M_b^+Y^- ?

- (A) M_a^+Y^- (B) M_b^+X^-
 (C) M_c^+Y^- (D) M_b^+Z^-

18. Which of the following compounds are thermally more stable than compound CaO_2 ?

- (A) BeO_2 (B) BaO_2
 (C) SrO_2 (D) MgO_2

19. IE_1 , IE_2 and IE_3 of an atom X are 170 kcal/mole, 340 kcal/mole and 1280 kcal/mole, respectively. If this atom X forms compounds with O, Cl and N, then which of following compounds has the least chance to exist?

- (A) X_2O_3 (B) XCl
 (C) XCl_2 (D) X_3N_2

20. In which of following processes, do(es) the value of magnetic moment change?

- (A) $\text{CO} \rightarrow \text{CO}^+$ (B) $\text{N}_2^- \rightarrow \text{N}_2^+$
 (C) $\text{Zn} \rightarrow \text{Zn}^{2+}$ (D) $\text{O}_2 \rightarrow \text{O}_2^-$

21. Choose the correct statement(s) among the following for HPO_3^{2-} ions.

- (A) All three $\widehat{\text{HPO}}$ angles are identical due to resonance.
 (B) All bond lengths are identical due to resonance.
 (C) The bond order of all P – O bond is 1.33.
 (D) None of these.

22. London force works in

- (A) gaseous state. (B) solid state.
 (C) liquid state. (D) none of these.

23. Which of the following d orbitals may participate in sp^3d hybridization?

- (A) d_{z^2} (B) d_{xy} (C) d_{yz} (D) $d_{x^2-y^2}$

24. Which of the following options represent incorrect hybridization of its central atom for the respective species?

- (A) $\text{SeCl}_4 : sp^3d$ (B) $\text{BrF}_4^- : sp^3d^2$
 (C) $\text{SiF}_2\text{Cl}_2 : sp^3d$ (D) $\text{XeO}_6^{4-} : sp^3d^3$

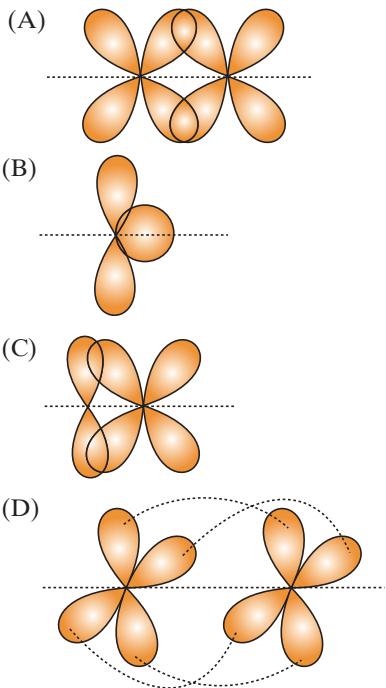
25. Which of the following compounds have the same shape?

- (A) SF_4 (B) XeF_4
 (C) $[\text{AsF}_4]^-$ (D) $[\text{SnCl}_3]^-$

26. Which of the following Lewis acid – base interactions are associated with the further involvement of d -orbitals?

- (A) $\text{SbF}_5 + \text{HF} \rightarrow \text{H}^+ [\text{SbF}_6]^-$
 (B) $\text{NH}_3 + \text{BF}_3 \rightarrow \text{H}_3^+ \text{N}^- \text{BF}_3^-$
 (C) $\text{AlCl}_3 + \text{Cl}^- \rightarrow [\text{AlCl}_4]^-$
 (D) $\text{SF}_4 + \text{F}^- \rightarrow [\text{SF}_5]^-$

27. Which of the following diagrams indicate the formation of π bonds?



28. Which of the following can be calculated from the Born–Haber cycle of formation of Al_2O_3 ?
- (A) Lattice energy of Al_2O_3 .
 (B) Electron affinity of O atom.
 (C) Hydration energy of Al^{3+} .
 (D) Ionization energy of Al.

29. Which of the following set of molecules have the same shape but different hybridization?
- (A) H_2O , SnCl_2 (B) XeO_3 , BrF_3
 (C) XeO_4 , SF_4 (D) BeCl_2 , I_3^-
30. Which of the following types of bonds are present in NaNO_3 ?
- (A) Ionic bond (B) Covalently bonded σ bond
 (C) π bond (D) Coordinate bond

31. Which of the following compounds are planar as well as non-polar?
- (A) XeF_4 (B) XeF_2
 (C) XeF_5^- (D) XeF_5^+

32. Choose the correct statement.
- (A) d_{yz} orbital lies in the xz plane.
 (B) p_z orbital lies along the x axis.
 (C) Lobes of $d_{x^2-y^2}$ orbital are at 90° with the z axis.
 (D) Lobes of d_{xy} orbital are at 90° with the z axis.

33. From octahedral electron geometry of the central atom, which of the following shapes of the molecule/species may be possible.

- (A) Square pyramidal (B) Linear
 (C) Square planar (D) Bent

34. Which of the following species has the maximum number of lone pairs on the central atom?

- (A) BrF_4^- (B) SO_4^{2-}
 (C) CO_3^{2-} (D) XeF_3^+

35. Which of following energy terms are associated with the Born–Haber cycle of dissolution of BaCl_2 in water?

- (A) Hydration energy of Ba^{2+} .
 (B) Lattice energy of BaCl_2 .
 (C) Sublimation energy of Ba.
 (D) Electron affinity of Cl^- .

36. The formal charges on different atoms in the Lewis structure of N_3^- are:

- (A) $-1, +1, -1$ (B) $-1, +1, 0$
 (C) $-2, +1, 0$ (D) $0, +1, -2$

37. Choose the correct angle order.

- (A) $\widehat{\text{H}}\text{P}\text{H}$ in PH_4^- $<$ $\widehat{\text{H}}\text{C}\text{H}$ in CH_4 .
 (B) $\widehat{\text{H}}\text{N}\text{H}$ in NH_3 $<$ $\widehat{\text{H}}\text{P}\text{H}$ in PH_3
 (C) $\widehat{\text{H}}\text{N}\text{H}$ in NH_3 $<$ $\widehat{\text{H}}\text{P}\text{H}$ in PH_4^+
 (D) $\widehat{\text{O}}\text{S}\text{O}$ in SO_3^{2-} $<$ $\widehat{\text{O}}\text{N}\text{O}$ in NO_3^-

38. Select the correct statement(s) about O_3 molecule.

- (A) Correct structure of ozone is $\text{O}=\text{O}=\text{O}$.
 (B) Molecule is planar and polar.
 (C) It is diamagnetic.
 (D) It has bent structure.

39. Choose the correct statements from the following.

- (A) The ratios of σ bond to π bond in SO_3 and SO_2 are identical.
 (B) The hybridization of S in SO_3 and SO_2 is identical.
 (C) The S atom in SO_3 is more electronegative as compared to that in SO_2 .
 (D) SO_3 is planar while SO_2 is non-planar.

40. Which of the following species are isoelectronic and also have the same number of atoms?

- (A) SF_4 (B) $[\text{BeF}_4]^{2-}$ (C) BF_4^- (D) NF_4^+

41. Consider the following four monoatomic ions M^+ , N^+ , X^- and Y^- .

If lattice energy order is $\text{MX} > \text{NX}$ and hydration energy order is $\text{NY} > \text{NX}$, which of the following must be true?

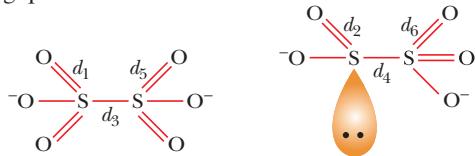
- (A) Covalent character order is $\text{MX} > \text{MY}$.
 (B) Thermal stability order is $\text{MY} > \text{NY}$.
 (C) Hydration energy order is $\text{MX} > \text{NX}$.
 (D) Hydration energy order is $\text{MX} < \text{NX}$.

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1–2

According to Bent's rule, more electronegative atom prefers to stay in that hybrid orbital which has less *s*-character and lone pair prefers to stay in that hybrid orbital which has more *s*-character.

Consider the molecules given below and answer the following questions.



- Which of the following bond length order is correct?
 (A) $d_1 < d_3$ (B) $d_1 = d_3$
 (C) $d_5 > d_1$ (D) Both (A) and (B)
- Out of d_1, d_2, d_3, d_4, d_5 and d_6 which bond length is the maximum?
 (A) d_3 (B) d_4
 (C) d_1 (D) d_5

Passage 2: For Questions 3–4

Molecular orbital theory is based on linear combination of atomic orbitals (LCAO). According to LCAO when respective atomic orbitals of the atoms interact, they undergo constructive and destructive interference giving rise to two types of molecular orbitals, that is, bonding and antibonding molecular orbitals.

- If z is the molecular axis then which of the following overlapping results in non-bonding molecular orbital?
 (A) $(d_{x^2-y^2} + d_{x^2-y^2})$ (B) $(d_{xy} + d_{xy})$
 (C) $(d_{yz} + p_y)$ (D) $(d_{xz} + p_z)$
- Calculate the bond order and magnetic nature of the Fe_2^{2+} , if *sp* intermixing is not considered and Hund's rule is also violated.
 (A) 1, diamagnetic
 (B) 1, paramagnetic
 (C) 2, paramagnetic
 (D) 2, diamagnetic

Passage 3: For Questions 5–6

Consider two homodiatomic molecules C_2 [carbon] and X_2 which have following properties:

- Both have the same bond order.
- X_2 has more number of antibonding electrons than C_2 molecule.

Then answer the following questions.
 $(\text{X}_2$ has total number of electron $< 20)$.

- In X_2 molecule, total number of antibonding electrons is

- (A) 4 (B) 6
 (C) 5 (D) 2

- Select the incorrect statement.
 (A) Total number of electrons in X_2 is 16.
 (B) X_2 has two π -bonds.
 (C) X_2 has one σ and one π -bond.
 (D) Total number of bonding electrons in X_2 is 10.

Passage 4: For Questions 7–8

As implied by the mechanism of hydrolysis, diborane and many other light boron hybrids act as Lewis acids and they are cleaved by reaction with Lewis bases.

Two different cleavage patterns have been observed, namely, symmetric cleavage and unsymmetric cleavage. In symmetric cleavage, B_2H_6 is broken symmetrically into two BH_3 fragments with NMe_3 . While hydrolysis with NH_3 , MeNH_2 , MeNH results in unsymmetrical cleavage, which is a cleavage leading to an ionic product.

- Which of the following statements is incorrect regarding the reaction of B_2H_6 with NH_3 ?
 (A) B_2H_6 with NH_3 gives ionic product $[\text{BH}_2(\text{NH}_3)_2]^+[\text{BH}_4]^-$.
 (B) The hybridization state of boron atom is unchanged from reactant to ionic products.
 (C) B_2H_6 is non-planar and each boron atom is in sp^3 hybridized state.
 (D) None of the above statements are incorrect.
- $\text{B}_2\text{H}_6 + 2\text{NH}_3 \rightarrow \text{X}[\text{Ionic product}] \xrightarrow[140^\circ\text{C}]{\Delta} \text{Y}$
 Here Y is inorganic benzene.
 Which of the following statements is incorrect about Y molecule?
 (A) Y is a planar molecule.
 (B) Y is aromatic and sp^3 hybridization of each B and N-atom.
 (C) Y is a non-polar molecule.
 (D) Back bonding takes place from N-atom to B-atom in Y .

Passage 5: For Questions 9–10

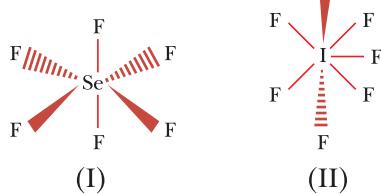
Silicon forms a very large number of compounds containing SiO_4^{4-} anion as the basic unit. The structure of this basic unit is a tetrahedron in which oxygen atoms are arranged in a tetrahedral around the silicon atom.

- Which of the following types of silicate represents the mineral $\text{Mg}_3(\text{OH})_2[\text{Si}_4\text{O}_{10}]$?
 (A) Linear silicate
 (B) Cyclic silicate
 (C) 3-D-Silicate
 (D) Sheet silicate

10. The total number of oxygen atoms shared per unit of SiO_4^{4-} in beryl $[\text{Be}_2\text{Al}_2\text{Si}_6\text{O}_{18}]$ is
 (A) 4 (B) 3
 (C) 2 (D) 1

Passage 6: For Questions 11–12

In the following structures of two compounds

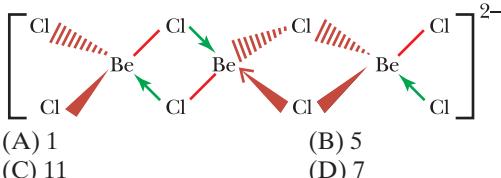


11. Find the ratio of 90° angles in (I) and (II).
 (A) 6 : 5 (B) 5 : 2
 (C) 8 : 10 (D) 4 : 5
12. Choose the correct statement from the following options.
 (A) The number of identical bonds in (I) is equal to that in (II).
 (B) The number of identical bonds in (I) is equal to that in $\text{S}_2\text{O}_7^{2-}$.
 (C) All bond lengths in (II) are identical.
 (D) Smallest bond angle value is available in (I) among these two structures.

Passage 7: For Questions 13–14

There are some cases in which the number of available valence electrons is not sufficient to displace normal electron pair bond (i.e., 2 centre – 2 electron, $2c - 2e$) among all the constituent atoms.

13. Find the maximum number of atom(s) that is/are present in one plane in the given complex.



14. Select the correct order of bond angle in B_2H_6 . (Here H_t and H_b are terminal and bonding hydrogens, respectively.)

- (A) $\widehat{\text{H}_t - \text{B} - \text{H}_t} > \widehat{\text{H}_b - \text{B} - \text{H}_b}$
 (B) $\widehat{\text{H}_t - \text{B} - \text{H}_t} < \widehat{\text{H}_b - \text{B} - \text{H}_b}$
 (C) $\widehat{\text{H}_t - \text{B} - \text{H}_t} = \widehat{\text{H}_b - \text{B} - \text{H}_b}$
 (D) None of these

Passage 8: For Questions 15–17

The binary boron-hydrogen compounds are called boranes. Experimental and theoretical studies of the

boranes have had a fundamental impact on all of chemistry, organic as well as inorganic.

There are two series of boranes.

- (1) B_nH_{n+4} (called nidoboranes)
 (2) B_nH_{n+6} (called Arachno-boranes)

15. Select correct statements about B_2H_6 (diborane).

- (I) It is isoelectronic with ethane.
 (II) It is isostructural with ethane.
 (III) Hybridization of each boron is sp^3 .
 (IV) All B-H bonds are identical.
 (V) It is a nidoborane.
 (A) I, II, III (B) II, III, V
 (C) II, IV, V (D) I, III, V

16. Find the maximum number of atoms present in one plane which is perpendicular to that plane which contains all $2c - 2e$ bonds of B_2H_6 .

- (A) Two (B) Four
 (C) Six (D) Eight

17. In which of the following compounds at least one valence shell orbital of underlined atom remains unhybridized?

- (A) $\underline{\text{B}}_2\text{H}_6$ (B) $\underline{\text{B}}\text{H}_4^-$
 (C) $\underline{\text{B}}\text{Cl}_3$ (D) None of these

Passage 9: For Questions 18–19

Different kind of molecules are available in chemistry, like molecules having single central atom, molecules having more than one central atom, molecules having odd number of electrons and even if some molecules do not exist with theoretical support.

18. The reason for non-existence of which molecule is not the same with the molecules in other options?

- (A) XeH_6 (B) HFO_4
 (C) SH_6 (D) IH_7

19. Which of the following statements is incorrect?

- (A) The free electron of ClO_3 molecule is not present in the d -orbital of Cl atom.
 (B) The hybridization of central atom of ClCO_2 is sp^2 .
 (C) The $d_{\text{C-H}}$ in CH_3 is smaller than $d_{\text{C-F}}$ in CF_3 .
 (D) The hybridization of N-atom(s) in NO_2 and its dimer is different.

Passage 10: For Questions 20–22

Molecular orbital theory is completely based upon the wave mechanical approach. The MO diagram gives the energy comparison between different orbitals.

20. Choose the correct ionization energy order from the following options.

- (A) $\text{F}_2 > \text{F}$ (B) $\text{B} > \text{B}_2$
 (C) $\text{N}_2 < \text{N}$ (D) $\text{B}_2 > \text{B}$

21. Which of the following orbital is having maximum number of nodal planes?

- (A) σ_{p-p}^* (B) π_{d-d} (2 lobes interaction)
 (C) π_{p-p}^* (D) π_{d-p}

Passage 11: For Questions 23–24

According to Molecular orbital theory, electrons in a molecule are present in molecular orbitals. Molecular orbital is defined as the region or space around two or more nuclei where electron finding probability is the maximum.

Passage 12: For Questions 25–26

Dipole moment gives an idea of the polar character of a covalent molecule. It is a vector quantity as it has a direction as well as magnitude. A molecule with $\mu = 0$ is non-polar and with $\mu \neq 0$ is polar.

- 25.** If the dipole moment of NF_3 is 0.80×10^{-30} Cm, then the dipole moment of NH_3 is
 (A) 0.80×10^{-30} Cm (B) 1.2×10^{-31} Cm
 (C) 4.90×10^{-30} Cm (D) 0.7×10^{-30} Cm

26. Which of the following dipole moment order is correct?
 (A) $\text{XeF}_2 < \text{XeF}_4$ (B) $\text{SiH}_4 < \text{CF}_4$
 (C) $\text{H}_2\text{O} < \text{OF}_2$ (D) $\text{PCl}_5 < \text{PCl}_3$

Passage 13: For Questions 27–29

The hybrid orbital is obtained by mixing of atomic orbitals of comparable energy.

- (C) length of the orbital increases.
(D) thinness of the orbital increases.

29. For which of the following sets of geometry, both axial and equatorial positions are present?

(A) Octahedral and trigonal bipyramidal.
(B) Tetrahedral and octahedral.
(C) Trigonal bipyramidal and pentagonal bipyramidal.
(D) Tetrahedral and pentagonal bipyramidal.

Passage 14: For Questions 30–32

Bent's rule explains the relative position of atoms and lone pairs in trigonal bipyramidal and pentagonal bipyramidal geometries mainly. However, the bond lengths and bond angles are also well explained in several places.

Passage 15: For Questions 33–36

IF_7 is a molecule in which I atom is in the maximum oxidation state, and the hybridization for I atom is sp^3d^3 .

33. The number of $\widehat{\text{FIF}}$ adjacent angles in IF_7 molecule is
(A) 10 (B) 15
(C) 20 (D) 14

34. The number of $\widehat{\text{FIF}}$ angles less than 90° and equal to 90° are respectively
(A) 5 and 5 (B) 10 and 5
(C) 5 and 10 (D) 10 and 15

35. The number of I – F bonds having the longest and shortest lengths are respectively
(A) 5 and 2 (B) 2 and 5
(C) 5 and 5 (D) 2 and 2

36. The number of planes of symmetry in IF_7 is
(A) 5 (B) 7 (C) 4 (D) 6

Passage 16: For Questions 37–39

One more electron or atom can change the system a lot in several aspects.

37. Choose the correct bond angle order:

- (A) $\overset{+}{\text{CH}_3} > \overset{-}{\text{CH}_3} > \overset{\cdot}{\text{CH}_3}$ (B) $\overset{+}{\text{CH}_3} = \overset{\cdot}{\text{CH}_3} > \overset{-}{\text{CH}_3}$
 (C) $\overset{\cdot}{\text{CH}_3} > \overset{+}{\text{CH}_3} > \overset{-}{\text{CH}_3}$ (D) $\overset{+}{\text{CH}_3} > \overset{-}{\text{CH}_3} = \overset{\cdot}{\text{CH}_3}$

38. Choose the correct bond angle order.

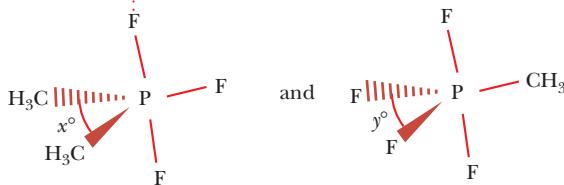
- (A) $\text{CH}_4 > \overset{-}{\text{CH}_3} > \overset{+}{\text{CH}_3}$ (B) $\overset{-}{\text{CH}_3} > \text{CH}_4 > \overset{+}{\text{CH}_3}$
 (C) $\overset{+}{\text{CH}_3} > \text{CH}_4 > \overset{-}{\text{CH}_3}$ (D) $\text{CH}_4 > \overset{-}{\text{CH}_3} > \overset{+}{\text{CH}_3}$

39. Choose the correct order for C – H bond length.

- (A) $\text{CH}_3^- > \text{CH}_4 > \text{CH}_3^+$
 (B) $\text{CH}_4 = \overset{-}{\text{CH}_3} > \text{CH}_3^+$
 (C) $\text{CH}_4 = \overset{+}{\text{CH}_3} = \overset{\cdot}{\text{CH}_3}$
 (D) $\overset{\cdot}{\text{CH}_3} > \text{CH}_4 > \overset{-}{\text{CH}_3}$

Passage 17: For Questions 40–42

The structures of $\text{P}(\text{CH}_3)_2\text{F}_3$ and $\text{P}(\text{CH}_3)\text{F}_4$ are shown below:



40. Which of the following are correct values for x and y in the above figure?

- (A) $x > 120^\circ, y > 120^\circ$ (B) $x > 120^\circ, y < 120^\circ$
 (C) $x = y = 120^\circ$ (D) $x < 120^\circ, y < 120^\circ$

41. Which of the following statements is true regarding the above two structures?

- (A) $d_{\text{P-C}} > d_{\text{P-F}}$ (axial) in both.
 (B) $d_{\text{P-C}} > d_{\text{P-F}}$ (equatorial) in both.
 (C) $d_{\text{P-F}}$ (axial) $> d_{\text{P-F}}$ (equatorial) in both.
 (D) All are correct.

42. For molecules $\text{P}(\text{CH}_3)_n\text{F}_{5-n}$, when the value of n increases from 1 to 4, which of the following statements is incorrect regarding the change observed?

- (A) $d_{\text{P-C}}$ (equatorial) increases.
 (B) $d_{\text{P-F}}$ (axial) increases.
 (C) $d_{\text{P-F}}$ (axial) decreases.
 (D) $d_{\text{P-F}}$ (axial) $> d_{\text{P-F}}$ (equatorial) wherever it is applicable.

Passage 18: For Questions 43–44

London force depends upon molecular weight, the number of polarizable electrons and molecular size.

43. Which type of interaction is involved in the solubility of noble gas in water?

- (A) Instantaneous dipole-induced dipole interaction.
 (B) Dipole-dipole interaction.
 (C) Dipole-induced dipole interaction.
 (D) Ion-dipole interaction.

44. Choose the correct order for boiling point.

- (A) $\text{GeH}_4 > \text{SiH}_4 < \text{CH}_4$ (B) $\text{Xe} > \text{Ne} > \text{He}$
 (C) $\text{He} > \text{H}_2$ (D) $\text{CH}_4 > \text{CD}_4$

Passage 19: For Questions 45–47

'No ionic compound is 100% ionic as well as no covalent compound is 100% covalent.'

45. Correct solubility order is

- (A) $\text{CaCrO}_4 > \text{BaCrO}_4$ (B) $\text{BeCO}_3 < \text{BaCO}_3$
 (C) $\text{LiNO}_3 < \text{CsNO}_3$ (D) $\text{NaClO}_4 < \text{KClO}_4$

46. Choose the incorrect order of the given properties.

- (A) $\text{BeCl}_2 < \text{LiCl}$: Electrical conductivity
 (B) $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$: Covalent character order
 (C) $\text{BeSO}_4 < \text{MgSO}_4 < \text{CaSO}_4$: Thermal stability order
 (D) $\text{HgCl}_2 < \text{HgBr}_2 < \text{HgI}_2$: Solubility order in water

47. Which of the following options give incorrect melting point order?

- (A) $\text{H}_2 < \text{T}_2$ (B) $\text{He} > \text{T}_2$ (C) $\text{D}_2 > \text{He}$ (D) $\text{T}_2 > \text{D}_2$

Passage 20: for Questions 48–50

Valence shell electron repulsion theory (VSEPR) can be used to predict the approximate shape of a molecule. Electrons in bonds and in lone pairs can be thought of as "charge cloud" that repel one another and stay as far apart possible, thus causing molecules to assume specific shapes.

The repulsive interactions of electron pairs decrease in the order:

Lone pair-lone pair $>$ Lone pair-bond pair $>$ Bond pair-bond pair.

These repulsions result in deviations from idealized shapes and alteration in bond angles in molecules.

48. Molecular shape of XeF_3^+ , SF_3^+ and CF_3^+ are

- (A) the same with 2, 1 and 0 lone pairs of electrons, respectively.
 (B) different with 2, 1 and 0 lone pairs of electrons, respectively.
 (C) different with 0, 1 and 2 lone pairs of electrons, respectively.
 (D) the same with 2, 0 and 1 lone pairs of electrons, respectively.

49. Which of the following statements is correct with respect to bond angle?

- (A) The F-S-F angle in SF_2 is more than 109.5° .
 (B) The H-N-N angle in N_2H_2 is approximately 180° .
 (C) The F-Kr-F angle in KrF_4 is 90° .
 (D) The Cl-N-O angle in NOCl is more than 120° .

50. Which of the following statements is incorrect?
- In ClF_3 , the axial Cl–F bond length is larger than equatorial Cl–F bond length.
 - In SF_4 , F–S–F equatorial bond angle is not 120° and 104° due to lone pair–bond pair repulsions.
 - In ICl_4^- , bond angles is 90° .
 - In OBr_2 , the bond angle is less than OCl_2 .

Passage 21: For Questions 51–53

HCN and HNC molecules are formed by the same atoms.

51. Which of the following properties are identical for HCN and HNC molecules?
- The number of σ bonds.
 - The number of π bonds.
 - The number of lone pairs.
 - All of these.
52. The correct set of formal charges for HNC is
- 0, 0, 0
 - 0, -1, +1
 - 0, +1, -1
 - +1, 0, -1
53. Which of the following statements is incorrect regarding the HCN and HNC molecules?
- The hybridization of the central atom is same for both.
 - They produce different ions in solution.
 - They produce the same ions in solution.
 - They produce the same number of ions in solution.

Passage *22: For Questions 54–56

The Lewis structure drawing is the first step to draw the structure of a compound. This method has a lot of limitations which are overcome by the theory of hybridization to explain many properties of molecules/ species.

54. Which of the following species have a π bond as well as coordinate σ bond in their Lewis structure?
- SiF_4
 - CO_2
 - SO_3
 - NO_3^-
55. What are the different kinds of bonds and interactions present within $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?
- σ bond
 - π bond
 - Coordinate bond
 - Electrostatic forces of attraction
 - Hydrogen bond (dipole – dipole)
 - Hydrogen bond (ion – dipole)
- I, II, III only
 - II, III, and IV only
 - II, VI, and VI only
 - All six kinds of forces of attraction are present.
56. Which of the following statements is/are incorrect regarding the real structure and Lewis structure of phosphate ion?
- The number of σ bonds is same in both the structures.
 - The number of lone pairs is same in both the structures.
 - The number of π bonds is same in both the structures.
 - The shape remains unchanged in both the structures.

*One or more than one correct answers.

ASSERTION–REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
- If Statement I is true but Statement II is false.
- If Statement I is false but Statement II is true.

1. **Statement I:** The shape of the molecule depends upon hybridization of the central atom.

Statement II: Hybridization can explain the shape of the molecule.

2. **Statement I:** sp^3d^2 hybrid orbitals are at 90° to one another.

Statement II: There are twelve 90° angles in regular octahedral geometry.

3. **Statement I:** Hydrocarbons with cumulated double bonds are non-polar irrespective of the number of double bonds present in them.

Statement II: The resultant bond vectors of two C–H bonds at two ends are lying in the same line with opposite direction.

4. **Statement I:** The $d_{\text{O}-\text{O}}$ in O_2F_2 is almost same with that in O_2 molecule.

Statement II: O_2F_2 exists in the form of $[\text{O}=\overset{+}{\text{O}}-\text{F}]^{\text{F}}^-$ also.

5. **Statement I:** XeH_4 does not exist but XeF_4 exists.

Statement II: F is more electronegative than H and causes lesser extent of d orbital contraction as compared to that by H atom.

6. **Statement I:** The removal of an electron takes place from π_{bonding} orbital when N_2 converts to N_2^+ .

Statement II: The bond order decreases by 0.5 when N_2 converts to N_2^+ .

7. **Statement I:** $(\text{AlCl}_3)_2$ is not electron deficient but $[\text{Al}(\text{CH}_3)_3]_2$ is electron deficient.

Statement II: $(\text{AlCl}_3)_2$ possesses $3c - 4e$ bond while $[\text{Al}(\text{CH}_3)_3]_2$ possesses $3c - 2e$ bond.

- 8. Statement I:** Allene molecule is non-polar.
Statement II: Allene molecule is non-planar.
- 9. Statement I:** On addition of two electrons to NO_2^+ , the N–O bond length increases by ~ 9 pm while on adding only one electron to NO^+ , the N–O bond length increases by ~ 9 pm.
Statement II: In both the above processes, the bond order of N–O bond is decreased by 0.5.
- 10. Statement I:** When BF_3 and BCl_3 are mixed together, it produces BF_2Cl and BFCl_2 through halogen exchange.
Statement II: Figure below is the intermediate for the above process.
-
- 11. Statement I:** The delocalization energy for $\text{B}_3\text{N}_3\text{H}_6$ is less as compared to C_6H_6 .
Statement II: $\text{B}_3\text{N}_3\text{H}_6$ is polar while C_6H_6 is non-polar.
- 12. Statement I:** $[\text{AlBr}_4]^-$ exists while the existence of $[\text{BBr}_4]^-$ is questionable.
Statement II: Al is larger in size as compared to B atom.
- 13. Statement I:** SiH_4 is highly reactive towards water while CH_4 is non-reactive.
Statement II: Polarity of Si – H bond is just reverse of that of C – H bond.
- 14. Statement I:** HgF_2 is colourless while HgI_2 is coloured.
Statement II: I[–] is more polarizable than F[–].
- 15. Statement I:** S_2F_2 has the structure $\text{S}=\text{S}^{\text{F}}_{\text{F}}$, but S_2Cl_2 has no such analogous structure.
Statement II: F being more electronegative than Cl causes better *d* orbital contraction as compared to Cl.

- 16. Statement I:** In TlI_3 , the oxidation state of Tl is +1.
Statement II: TlI_3 is isomorphous with NH_4I_3 and CsI_3 .
- 17. Statement I:** The $d_{\text{C}-\text{O}}$ in $\text{CH}_3\text{CO}_2\text{H}$ are different while that in $\text{CH}_3\text{CO}_2\text{Na}$ are identical.
Statement II: Resonance takes place in $\text{CH}_3\text{CO}_2\text{Na}$ but does not take place in $\text{CH}_3\text{CO}_2\text{H}$.
- 18. Statement I:** The direction of back bonding in $\bar{\text{CCl}}_3$ and $:\text{CCl}_2$ is the same.
Statement II: In $\bar{\text{CCl}}_3$, $2p\pi-3d\pi$ bonding and in $:\text{CCl}_2$, $2p\pi-3p\pi$ bonding takes place.
- 19. Statement I:** $d_{\text{p}-\text{F}}$ is greater than $d_{\text{p}-\text{Cl}}$ in PF_2Cl_3 .
Statement II: The axial orbital has no *s* character while equatorial orbital has 33.33% *s* character in trigonal bipyramidal geometry.
- 20. Statement I:** Be_2Cl_4 molecule has an incomplete octet.
Statement II: In Be_2Cl_4 each Be atom is *sp*² hybridized.
- 21. Statement I:** The nodal planes of π bonds of 1,3 – butadiene lie in the same plane.
Statement II: π bonds are also lying in the same plane in 1,3 – butadiene.
- 22. Statement I:** $d_{\text{Mn}-\text{O}}$ in MnO_4^- is less than that in MnO_4^{2-} .
Statement II: The higher oxidation state of an element causes higher extent of *d* orbital contraction and forms more effective π bond with O atoms.
- 23. Statement I:** Mercurous ion is always diamagnetic.
Statement II: The 79th electron of each Hg atom gets paired up to form a bond between two Hg atoms.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

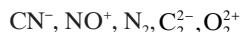
- Find the number of compounds of Xe which is/are associated with 180° bond angles.
 XeF_2 , ICl_2 , I_3^- , XeF_4 , XeO_6^{4-} , XeO_4 , XeCl_4 , TeCl_4
- Find the total number of *d*-orbitals used for bonding in XeO_2F_2 .
- Among the following, find the number of processes in which ion-dipole interaction is not observed.
I[–] in I_2 , KCl in water, CO_2 in water, Xe in ice CHCl_3 in water.
- Find the total number specie(s) among the following, containing 3c–2e bond.
 Be_2H_4 , $(\text{BeH}_2)_n$, Be_2Cl_4 , $\text{Al}_2(\text{CH}_3)_6$, Al_2Cl_6 , I_2Cl_6 , B_2H_6 , $\text{B}_2\text{H}_2(\text{CH}_3)_4$

- Find the total number of chemical species in which mentioned bond length decreases due to back bonding.

BF_3	(B–F)	$\text{B}(\text{OMe})_3$	(B–O)
PF_3	(P–F)	H_3SiNCO	(N–Si),
$\text{B}_3\text{N}_3\text{H}_6$	(B–N)	NO_2^-	(N–O)
O_3	(O–O)		

- Find the total number of compounds whose bond order is unaffected whether the *s*-*p* mixing is considered or not.
 B_2 , C_2 , N_2 , O_2
- Calculate the value of *n* in
 $\text{Zn}_n\text{Ca}_2(\text{Si}_3\text{O}_{10})\cdot 2\text{H}_2\text{O}$.
- Find the maximum number of hydrogen atoms that may lie in one plane in $\text{BH}_2(\text{CH}_3)_4$ molecules.

9. Find the number of chemical species which are iso-electronic and have the same bond order as of CO.



10. Find the number of chemical species which are planar and d_{xy} orbital of central atom participates in the hybridization.



11. Find the total number of compound(s), which is/are repelled by magnetic field.



12. In the compound $\text{PCl}_k \text{F}_{5-k}$, possible values of k are 0 to 5. Then sum of all possible value of k for the compounds having zero dipole moment is _____.

13. Find the number of 90° angles in XeF_5^- molecules.

14. The sum of oxidation states of N atom in the following compounds of nitrogen is _____.



15. The maximum number of atoms lying in the same plane in B_2H_6 is _____.

16. In a molecule of CH_3Cl , the number of planes consisting of maximum number of atoms where at least two atoms are same is _____.

17. The number of planes of symmetry in TeCl_6 is _____.

18. The number of planes which divide TeCl_6 molecule into two equal halves is _____.

19. The number of planes of symmetry in SbF_5 is _____.

20. The number of planes of symmetry in SiH_4 is _____.

21. The maximum number of atoms lying in the same plane in $[\text{AlCl}_4^-]$ and the number of such planes are respectively _____ and _____.

22. In Me_4C molecule, the maximum number of atoms that may lie in the same plane and the number of such planes are respectively _____ and _____.

23. The maximum number of atoms that may lie in the same plane of eclipsed form of C_2H_6 and the number of such planes are respectively _____ and _____.

24. The maximum number of atoms that may lie in the same plane in $\text{P}(\text{CH}_3)_3 (\text{CF}_3)_2$ is _____ and the number of such planes is _____.

25. The maximum number of equal angles in CH_2F_2 is _____.

26. The number of lone pairs in BF_4^- is _____.

27. The maximum number of atoms that may lie in the same plane in $(\text{CH}_3)_2\text{C}=\text{SF}_2(\text{CH}_3)_2$ is _____.

28. The maximum number of atoms that may lie in the same plane in $\text{N}(\text{SiH}_3)_3$ and the number of atoms are out of that plane are respectively _____ and _____.

29. The number of nodal planes when two d_{xy} orbitals from two atoms produce antibonding δ bonds is _____.

30. The maximum number of atoms that may lie in the same plane of staggered form of C_2H_6 and the number of such planes are respectively _____ and _____.

31. The sum of the number of d -orbitals whose lobes are available along the axis and are involved in the hybridization of central atoms of XeF_5^- and XeF_5^+ is _____.

32. The number of triatomic molecules, which are non-planar is _____.



33. The sum of oxidation states of all P atoms in the following compound of phosphorus is _____.



MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the molecules with the type of overlap in their bridge bonds.

Column I	Column II
(A) Be_2H_4	(P) $sp^3 - s - sp^3$
(B) B_2H_6	(Q) $sp^2 - s - sp^2$
(C) $\text{Al}_2(\text{CH}_3)_6$	(R) $sp^2 - sp^3 - sp^2$
(D) $\text{Be}_2(\text{CH}_3)_4$	(S) $sp^3 - sp^3 - sp^3$

2. Match the molecules with their properties.

Column I	Column II
(A) N_2H_2 (<i>trans</i>)	(P) It has only two lone pairs.
(B) N_2H_4 (<i>gauche</i>)	(Q) It shows geometrical isomerism.
(C) N_2O_4	(R) It has shortest N–N distance.
(D) N_2H_5^+	(S) It is non-planar.
	(T) It has zero value of dipole moment.

3. Match the compounds with their properties.

Column I	Column II
(A) XeO_3	(P) Pyramidal geometry.
(B) XeO_2F_4	(Q) Non-planar molecule.
(C) XeO_2F_2	(R) One lone pair is present on Xe.
	(S) d_{z^2} orbital is involved in hybridization of central atom.

4. Match the compounds with their properties.

Column I	Column II
(A) BH_3	(P) All atoms are central atom.
(B) SiF_4	(Q) It has no lone pair.
(C) $\text{B}_3\text{N}_3\text{H}_6$	(R) It has only σ -bond.
(D) SiC	(S) It is non-planar.

5. Match the compounds with their Lewis structures.

Column I	Column II
(A) SO_3^{2-}	(P) The central atom does not have lone pair.
(B) HNC	(Q) All atoms of the species have lone pair(s).
(C) SiF_4	(R) It has co-ordinate bond.
(D) NO_3^-	(S) It has σ - bond and π - bond as well as coordinate bond.
	(T) Species having only σ bond.

6. Match the type of hybridization with the orbital involved.

Column I	Column II
(A) sp^3d (TBP)	(P) p_z
(B) sp^2 (orbitals lying in xz plane)	(Q) p_x
(C) sp^3d^2	(R) $d_{x^2-y^2}$
	(S) d_{z^2}

7. Match the molecules/species with their properties.

Column I	Column II
(A) AlBr_3	(P) It has zero dipole moment.
(B) ClF_3	(Q) It is planar.
(C) ICl_4^-	(R) The central atom of the molecule is sp^3d hybridized.
(D) PCl_2F_3	(S) It is non-planar.
	(T) Maximum four atoms are lying in the same plane.

8. Match the molecules/species with their properties.

Column I	Column II
(A) IF_7	(P) The axial bond length is larger than the equatorial bond length.
(B) $[\text{SiF}_6]^{2-}$	(Q) The axial bond length is shorter than the equatorial bond length.
(C) BrF_3	(R) $d_{x^2-y^2}$ orbitals are involved in bonding.
(D) $[\text{PI}_4]^+$	(S) All possible bond angles are not identical.
	(T) All possible bond angles are identical.

9. Match the molecules/species with their properties.

Column I	Column II
(A) BrF_5	(P) It has atleast one angle less than 90° .
(B) ICl_3	(Q) The central atom is sp^3d hybridized.
(C) H_3O^+	(R) It is non-planar.
	(S) The central atom is having only one lone pair.

10. Match the molecules with their properties.

Column I	Column II
(A) O_3	(P) π bond is present in the molecule.
(B) XeF_2	(Q) σ bonds are only present.
(C) BeH_2	(R) It is hyperoctet.
(D) CO	(S) It is hypovalent.
	(T) It is linear.

11. Match the molecules/species with correct statement related to their property.

Column I	Column II
(A) $[\text{BH}_4]^-$	(P) All atoms are p -block elements.
(B) $[\text{BeF}_4]^{2-}$	(Q) The central atom is a s -block element.
(C) SiC	(R) The central atom(s) is(are) sp^3 hybridized.
(D) $[\text{BF}_4]^-$	(S) All atoms are s -block elements.
	(T) The central atom is p -block element but the surrounding atoms are s -block elements.

ANSWERS

Single Correct Choice Type Questions

- | | | | | | |
|--------|---------|---------|---------|---------|---------|
| 1. (D) | 6. (D) | 11. (C) | 16. (A) | 21. (D) | 26. (B) |
| 2. (C) | 7. (C) | 12. (D) | 17. (D) | 22. (D) | 27. (D) |
| 3. (D) | 8. (D) | 13. (C) | 18. (A) | 23. (C) | 28. (C) |
| 4. (C) | 9. (B) | 14. (C) | 19. (D) | 24. (C) | 29. (D) |
| 5. (C) | 10. (B) | 15. (C) | 20. (A) | 25. (D) | 30. (D) |

- | | | | | | |
|----------------|----------------|----------------|----------------|----------------|----------------|
| 31. (A) | 37. (C) | 43. (D) | 49. (B) | 55. (C) | 61. (D) |
| 32. (A) | 38. (B) | 44. (B) | 50. (D) | 56. (D) | 62. (D) |
| 33. (B) | 39. (A) | 45. (B) | 51. (A) | 57. (C) | |
| 34. (D) | 40. (B) | 46. (B) | 52. (C) | 58. (A) | |
| 35. (B) | 41. (D) | 47. (D) | 53. (A) | 59. (D) | |
| 36. (C) | 42. (A) | 48. (C) | 54. (B) | 60. (B) | |

Multiple Correct Choice Type Questions

- | | | | | | |
|-------------------------|--------------------------|---------------------|--------------------------|-------------------------------|--------------------------|
| 1. (A), (C), (D) | 8. (B), (C), (D) | 15. (C), (D) | 22. (A), (B), (C) | 29. (A), (D) | 35. (A), (B) |
| 2. (A), (D) | 9. (A), (B), (D) | 16. (A), (C) | 23. (A), (D) | 30. (A), (B), (C), (D) | 36. (A), (C), (D) |
| 3. (A), (C), (D) | 10. (B), (C) | 17. (A), (B) | 24. (C), (D) | 31. (A), (B), (C) | 37. (A), (C), (D) |
| 4. (A), (C), (D) | 11. (B), (C), (D) | 18. (B), (C) | 25. (A), (C) | 32. (C), (D) | 38. (B), (C), (D) |
| 5. (B), (C), (D) | 12. (A), (D) | 19. (A), (B) | 26. (A), (D) | 33. (A), (C) | 39. (A), (B), (C) |
| 6. (A), (D) | 13. (C), (D) | 20. (A), (D) | 27. (A), (C), (D) | 34. (A), (D) | 40. (B), (C), (D) |
| 7. (A), (B), (D) | 14. (B), (D) | 21. (A), (C) | 28. (A), (B), (D) | 41. (A), (B), (C) | |

Comprehension Type Questions

- | | | | | | |
|----------------|----------------|----------------|----------------|----------------|--------------------------|
| 1. (D) | 11. (A) | 21. (C) | 31. (A) | 41. (D) | 51. (D) |
| 2. (B) | 12. (B) | 22. (A) | 32. (C) | 42. (C) | 52. (C) |
| 3. (D) | 13. (D) | 23. (D) | 33. (B) | 43. (C) | 53. (B) |
| 4. (D) | 14. (A) | 24. (A) | 34. (C) | 44. (B) | 54. (B), (C), (D) |
| 5. (B) | 15. (D) | 25. (C) | 35. (A) | 45. (A) | 55. (D) |
| 6. (B) | 16. (B) | 26. (D) | 36. (D) | 46. (D) | 56. (B), (C), (D) |
| 7. (D) | 17. (C) | 27. (B) | 37. (B) | 47. (B) | |
| 8. (B) | 18. (B) | 28. (B) | 38. (C) | 48. (B) | |
| 9. (D) | 19. (D) | 29. (C) | 39. (A) | 49. (C) | |
| 10. (C) | 20. (D) | 30. (B) | 40. (B) | 50. (D) | |

Assertion–Reasoning Type Questions

- | | | | | | |
|---------------|---------------|----------------|----------------|----------------|----------------|
| 1. (D) | 5. (C) | 9. (A) | 13. (A) | 17. (C) | 21. (C) |
| 2. (D) | 6. (D) | 10. (A) | 14. (A) | 18. (D) | 22. (A) |
| 3. (A) | 7. (A) | 11. (C) | 15. (A) | 19. (D) | 23. (A) |
| 4. (A) | 8. (B) | 12. (A) | 16. (B) | 20. (B) | |

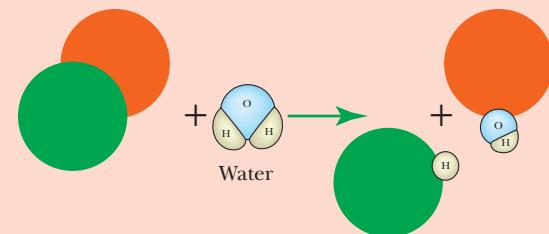
Integer Answer Type Questions

- | | | | | | |
|-------------|--------------|---------------|------------------|-----------------|---------------|
| 1. 4 | 7. 2 | 13. 0 | 19. 4 | 25. 4 | 31. 4 |
| 2. 3 | 8. 4 | 14. 9 | 20. 6 | 26. 12 | 32. 0 |
| 3. 4 | 9. 5 | 15. 6 | 21. 3, 10 | 27. 8 | 33. 16 |
| 4. 5 | 10. 1 | 16. 7 | 22. 6, 12 | 28. 7, 6 | |
| 5. 5 | 11. 4 | 17. 9 | 23. 4, 6 | 29. 3 | |
| 6. 4 | 12. 8 | 18. 13 | 24. 7, 4 | 30. 4, 6 | |

Matrix-Match Type Questions

- | | | | |
|--|---|---|--|
| 1. (A) \rightarrow (Q)
(B) \rightarrow (P)
(C) \rightarrow (S)
(D) \rightarrow (R) | 4. (A) \rightarrow (Q), (R)
(B) \rightarrow (R), (S)
(C) \rightarrow (Q)
(D) \rightarrow (P), (Q), (R), (S) | 7. (A) \rightarrow (P), (Q), (T)
(B) \rightarrow (Q), (R), (T)
(C) \rightarrow (P), (Q)
(D) \rightarrow (R), (S), (T) | 10. (A) \rightarrow (P)
(B) \rightarrow (Q), (R), (T)
(C) \rightarrow (Q), (S), (T)
(D) \rightarrow (P), (T) |
| 2. (A) \rightarrow (P), (Q), (R), (T)
(B) \rightarrow (P), (S)
(C) \rightarrow (T)
(D) \rightarrow (S) | 5. (A) \rightarrow (Q), (R), (T)
(B) \rightarrow (P), (R), (S)
(C) \rightarrow (P), (T)
(D) \rightarrow (P), (R), (S) | 8. (A) \rightarrow (Q), (R), (S)
(B) \rightarrow (R), (S)
(C) \rightarrow (P), (S)
(D) \rightarrow (T) | 11. (A) \rightarrow (R), (T)
(B) \rightarrow (Q), (R)
(C) \rightarrow (P), (R)
(D) \rightarrow (P), (R) |
| 3. (A) \rightarrow (P), (Q), (R)
(B) \rightarrow (Q), (S)
(C) \rightarrow (Q), (R), (S) | 6. (A) \rightarrow (P), (Q), (S)
(B) \rightarrow (P), (Q)
(C) \rightarrow (P), (Q), (R), (S) | 9. (A) \rightarrow (P), (R), (S)
(B) \rightarrow (P), (Q)
(C) \rightarrow (R), (S) | |

Hydrolysis



Schematic representation of hydrolysis.

4.1 | INTRODUCTION

When a substance undergoes nucleophilic substitution reaction and the nucleophile is the solvent itself, then the reaction is known as solvolysis. In solvolysis reaction, if the solvent used is water then the reaction is called as hydrolysis.

Hydrolysis can occur through several mechanisms. Some of these mechanisms are

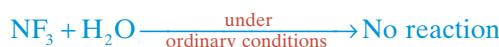
1. Unimolecular nucleophilic substitution (SN^1)
2. Bimolecular nucleophilic substitution (SN^2)
3. Addition–elimination mechanism
4. Addition mechanism
5. Redox reaction
6. Push–pull mechanism

These mechanisms are discussed in the following sections.

4.2 | HYDROLYSIS THROUGH SN^1 MECHANISM

This mechanism is explained by the following examples.

1. **Hydrolysis of NF_3 :** When hydrolysis of NF_3 is carried out at ordinary conditions, no reaction is observed by SN^2 mechanism.



This is because the nucleophile H_2O cannot attack either at N atom or at F atom due to non-availability of energetically low-lying vacant orbitals.

Contents

- 4.1 Introduction
- 4.2 Hydrolysis Through SN^1 Mechanism
- 4.3 Hydrolysis Through SN^2 Mechanism
- 4.4 Hydrolysis Through Addition–Elimination Mechanism
- 4.5 Hydrolysis Through Addition Mechanism
- 4.6 Hydrolysis Through Redox Reaction
- 4.7 Hydrolysis Through Push–Pull Mechanism
- 4.8 Hydrolysis Through Mixed Mechanism

However, NF_3 undergoes hydrolysis under drastic conditions to give N_2O_3 and HF through SN^1 mechanism as shown in Figure 4.1 which is finally decomposed into NO_2 and NO .

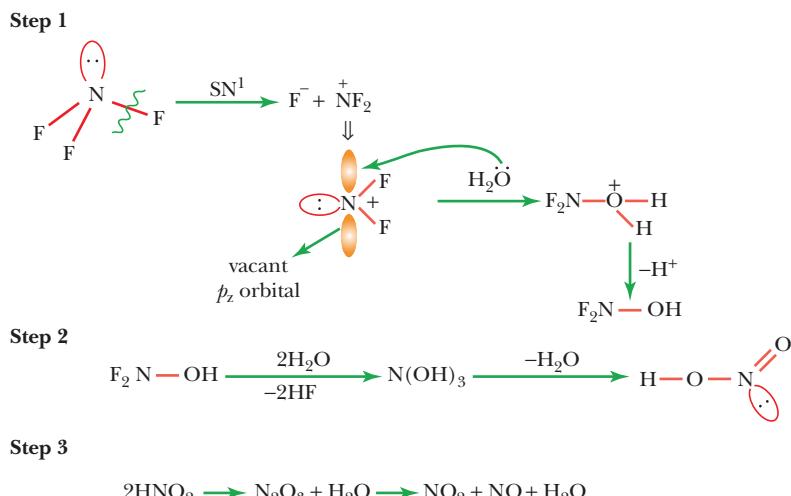
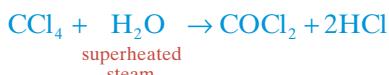


Figure 4.1 Hydrolysis of NF_3 by SN^1 mechanism.

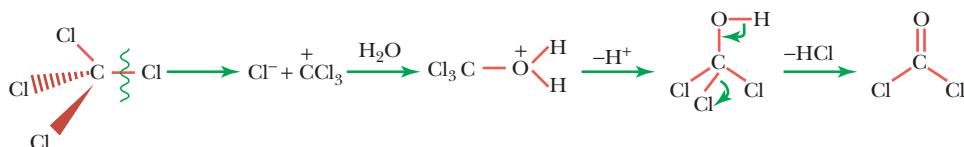
2. Hydrolysis of CCl_4 : CCl_4 is inert towards hydrolysis under ordinary conditions through SN^2 mechanism due to the following reasons:

- The non-availability of vacant low-lying d orbitals.
- Steric crowding due to presence of four Cl atoms around C atom which do not allow water molecule to approach antibonding orbitals of $\text{C}-\text{Cl}$ bonds.
- The nucleophile also cannot attack the vacant $3d$ orbital of Cl atom because of polarity of the bond. The negative charge (δ^-) developed on Cl atoms repels the incoming nucleophile.

However, CCl_4 undergoes partial hydrolysis under drastic conditions, using superheated steam, through SN^1 mechanism.



Out of the four leaving groups (Cl), only two groups leave while two are left on the parent molecule. Hence the reaction is referred to as partial hydrolysis.



4.3 | HYDROLYSIS THROUGH SN^2 MECHANISM

This mechanism is explained by the following examples.

- Hydrolysis of SiCl_4 :** In contrast to CCl_4 being inert to hydrolysis, SiCl_4 undergoes hydrolysis readily by SN^2 mechanism. In case of SiCl_4 , Si atom has a vacant d orbital to accommodate the incoming nucleophile, giving rise to a transition state with sp^3d hybridization and trigonal bipyramidal geometry. The mechanism is shown in Figure 4.2.

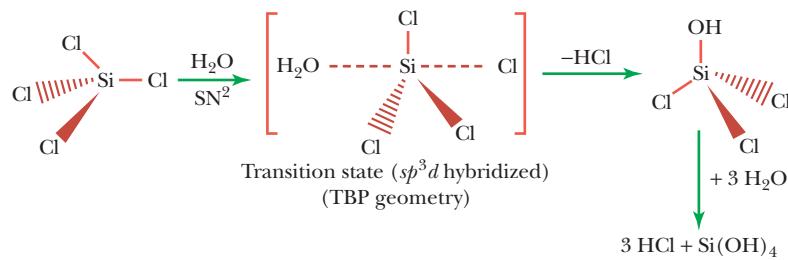


Figure 4.2 Hydrolysis of $SiCl_4$ by SN^2 mechanism.

Some important observations related to hydrolysis of $SiCl_4$ by SN^2 mechanism are listed below:

- When $R_1R_2R_3SiCl$ undergoes hydrolysis, it is associated with an inversion of configuration.
- If we compare the rate of hydrolysis for SiX_4 (where $X = F, Cl, Br, I$), it is in the same order as that of their Lewis acid strength order, i.e.



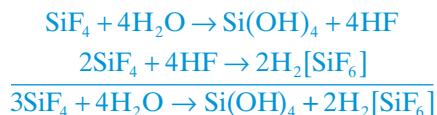
This is because the effect of π back bonding is less dominant over the negative inductive effect.

- For $SnCl_4$ and $SnCl_2$, the hydrolysis rate is $SnCl_4 > SnCl_2$ due to higher charges on the former. While for $SnCl_4$ and $SnMe_4$, the hydrolysis rate is $SnCl_4 > SnMe_4$ because the positive inductive effect of the methyl group reduces the Lewis acidity of Sn^{4+} ion, which leads to reduction in the rate of nucleophilic attack.

2. Hydrolysis of SiF_4 and BF_3 :

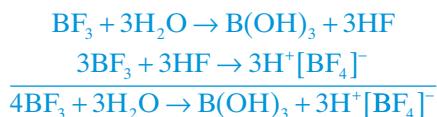
Both these molecules show partial hydrolysis.

For SiF_4 :

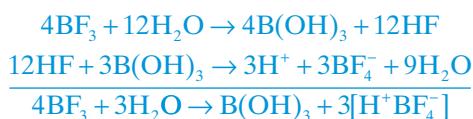


The complexation reaction is so fast that unless all HF molecules are consumed by SiF_4 , the H_2O molecule cannot attack the next molecule of SiF_4 . Out of three moles of SiF_4 , only one mole of SiF_4 gives the hydrolyzed product, hence it is called partial hydrolysis.

Similarly for BF_3 :



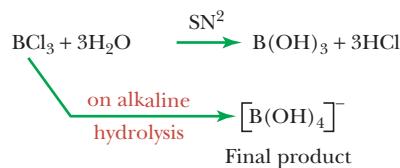
Alternatively,



Again out of four moles of BF_3 , only one mole of BF_3 gives the hydrolysed product. Hence it is called partial hydrolysis.

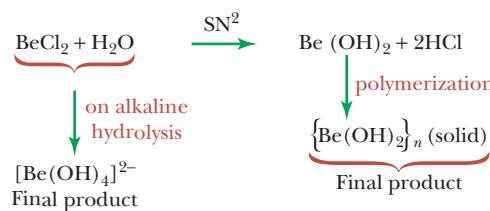
3. Hydrolysis of BCl_3 and BeCl_2 : Both these molecules undergo complete hydrolysis.

For BCl_3 :



The rate of hydrolysis for BX_3 ($\text{X} = \text{F, Cl, Br, I}$) is $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$.

Similarly, for BeCl_2 :



4. Hydrolysis of NCl_3 , PCl_3 , AsCl_3 , SbCl_3 and BiCl_3 : The hydrolysis of these compounds is discussed as follows:

a. NCl_3 produces NH_3 and HOCl on hydrolysis as shown in Figure 4.3.

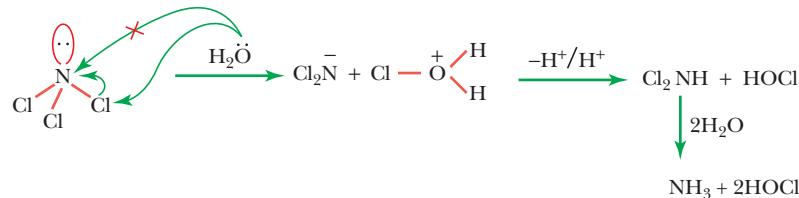


Figure 4.3 Hydrolysis of NCl_3 by S_{N}^2 mechanism.

Here the nucleophilic attack on N atom cannot take place due to the non-availability of vacant orbital. The attack on Cl atom is favoured because the N–Cl bond is almost non-polar, and the attack takes place through electromeric effect.

b. PCl_3 produces H_3PO_3 and HCl as shown in Figure 4.4.

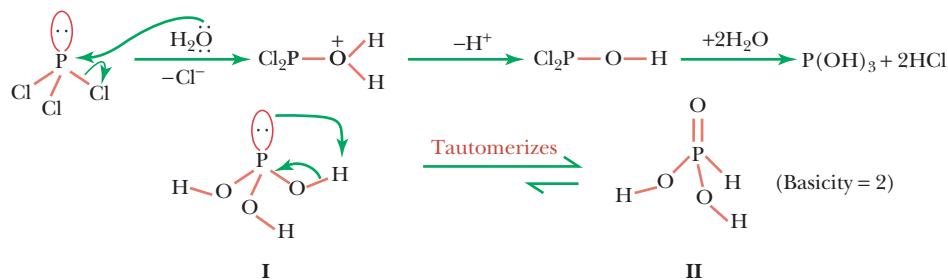


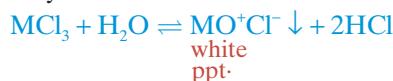
Figure 4.4 Hydrolysis of PCl_3 by $\text{S}^{\text{N}}2$ mechanism.

The driving force for the tautomerization reaction is the larger bond energy of II as compared to that of I.

- c. AsCl_3 produces H_3AsO_3 and HCl by the mechanism depicted in Figure 4.5.

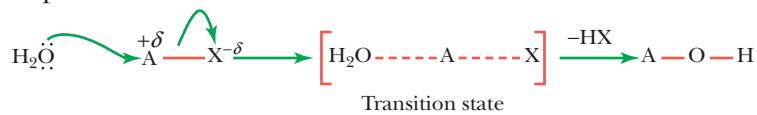
Here tautomerization does not take place because the $(4d\pi - 2p\pi)$ bond in $\text{As}=\text{O}$ is not so effective as compared to $(3d\pi - 2p\pi)$ bond in $\text{P}=\text{O}$ of H_3PO_3 .

- d. SbCl_3 and BiCl_3 on hydrolysis produce HCl and MO^+Cl^- type of product, whereas the expected product according to the S^2 mechanism is $\text{M}(\text{OH})_3 + \text{HCl}$. This is because of the fact that as we move down the group, the electropositive character increases and hence the tendency to form ionic compound increases. Hence $[\text{MO}^+\text{Cl}^-]$ formed truly consists of $[\text{M}^{3+}\text{O}^{2-}]^+\text{Cl}^-$ and finally

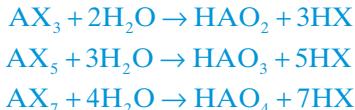


where $\text{M} = \text{Sb, Bi}$.

- 5. Hydrolysis of interhalogen compounds:** Interhalogens have the general formula AX_n where n is always odd, i.e. 1, 3, 5, and 7; and X is more electronegative halogen atom. As a result A acquires $\delta(+)$ charge and accepts nucleophilic attack on it.



Similarly,



These are the products generally formed and sometimes other side products are also formed, but they are specific to the case.

4.4 | HYDROLYSIS THROUGH ADDITION-ELIMINATION MECHANISM

This mechanism is explained by the following examples.

- 1. Hydrolysis of SO_2Cl_2 :** In the mechanism depicted in Figure 4.6, Step I involves only the addition of the nucleophile because π bond is more flexible as compared to the σ bond. In Step II, the leaving group (Cl^-) is eliminated and then in Step III, deprotonation occurs. Thus, the process is called addition-elimination mechanism.

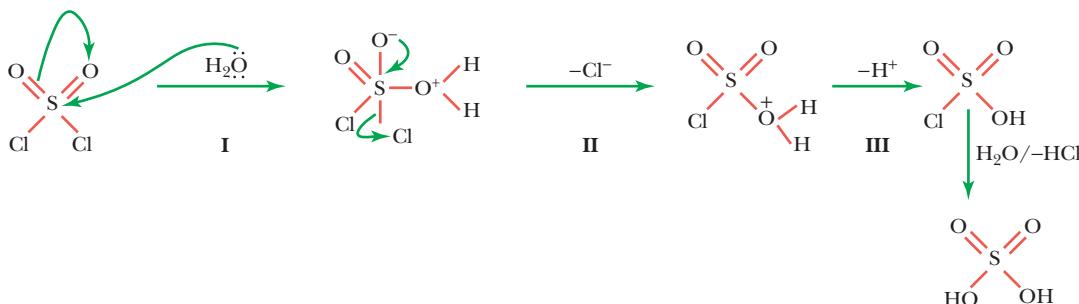


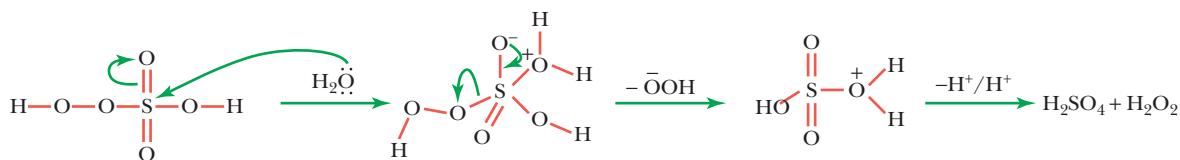
Figure 4.6 Hydrolysis of SO_2Cl_2 through addition-elimination mechanism.

Similarly for SOCl_2 and POCl_3



2. Hydrolysis of Caro's acid and Marshall's acid:

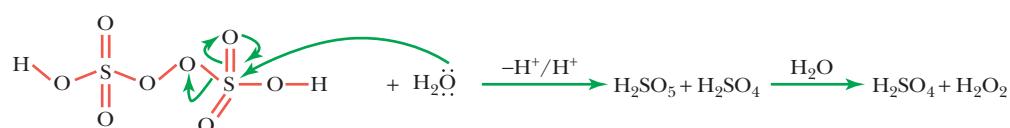
The addition-elimination mechanism for Caro's acid is depicted below.



Hence,



Similarly for Marshall's acid



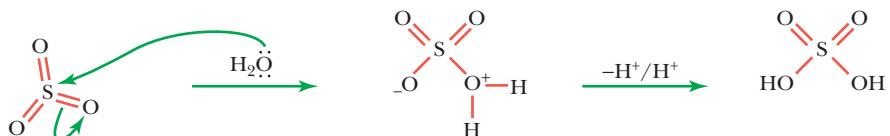
Hence,



3. Hydrolysis of N₂O₃ and N₂O₅: These compounds on hydrolysis produce HNO₂ and HNO₃, respectively.

4.5 | HYDROLYSIS THROUGH ADDITION MECHANISM

This mechanism can be explained using hydrolysis of SO₃ as an example.



In the hydrolysis of SO₃, only the nucleophile, i.e. water, is added to the molecule without any elimination of the leaving group. Hence the process is called as addition mechanism.

Similarly for SO₂ and CO₂



4.6 | HYDROLYSIS THROUGH REDOX REACTION

This mechanism can be explained using hydrolysis of XeF₂ and XeF₄ as examples.



However, XeF₆ undergoes hydrolysis through SN² mechanism, not by redox mechanism



4.7 | HYDROLYSIS THROUGH PUSH–PULL MECHANISM

This mechanism is explained by the following examples.

- 1. Hydrolysis of SiH_4 :** Silanes are hydrolyzed readily in the presence of traces of alkali. The mechanism of the reaction is depicted in Figure 4.7.

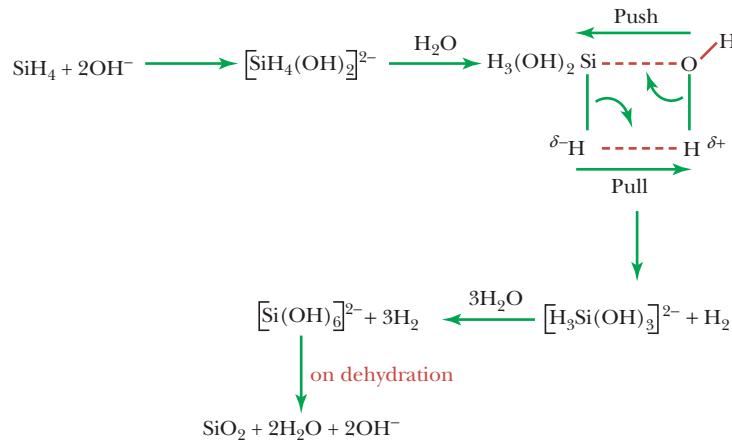
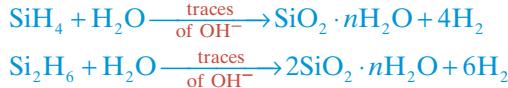


Figure 4.7 Hydrolysis of SiH_4 through push-pull mechanism.

Hence,



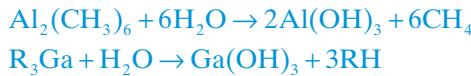
However, CH_4 does not undergo hydrolysis.



The reason behind this is the difference in polarities of $\text{C}-\text{H}$ and $\text{Si}-\text{H}$ bonds. (Electronegativities of C, Si, H are 2.5, 1.8, and 2.1 respectively). Hence C atom of CH_4 cannot be attacked by a nucleophile. Apart from this, Si also has a vacant $3d$ orbital to accommodate the incoming nucleophile.

Similarly GeH_4 and SnH_4 are inert towards hydrolysis due to insufficient bond polarity of $\text{M}-\text{H}$ bond as the electronegativities of Ge and Sn are closer to that of hydrogen

- 2. Hydrolysis of $\text{Al}_2(\text{CH}_3)_6$ and R_3Ga :**



where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$, etc.

- 3. Hydrolysis of carbides, nitrides and phosphides:** Some examples are



4.8 | HYDROLYSIS THROUGH MIXED MECHANISM

Some compounds undergo hydrolysis by more than one mechanisms or mixed mechanism. The following are some examples of hydrolysis through mixed mechanism.

1. **Hydrolysis of PCl_5 :** This hydrolysis proceeds through SN^2 mechanism followed by addition–elimination mechanism as shown in Figure 4.8.

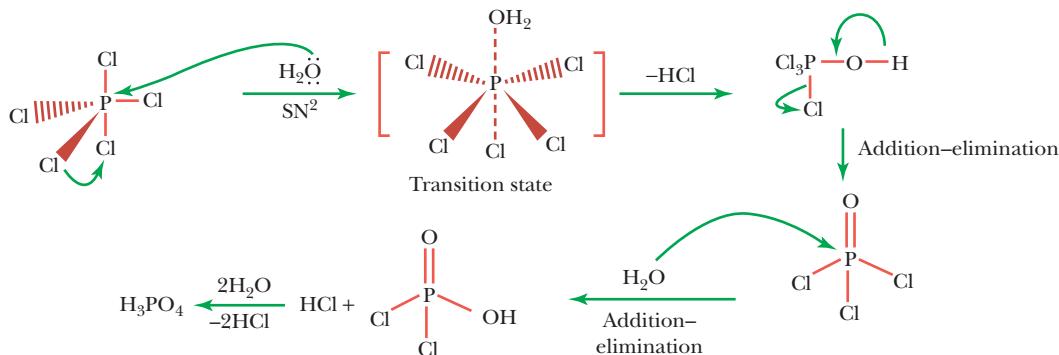


Figure 4.8 Hydrolysis of PCl_5 through SN^2 and addition–elimination mechanism.

2. **Hydrolysis of SF_4 versus SF_6 :** SF_4 undergoes hydrolysis very easily to produce H_2SO_3 and HF through SN^2 mechanism as shown in Figure 4.9.

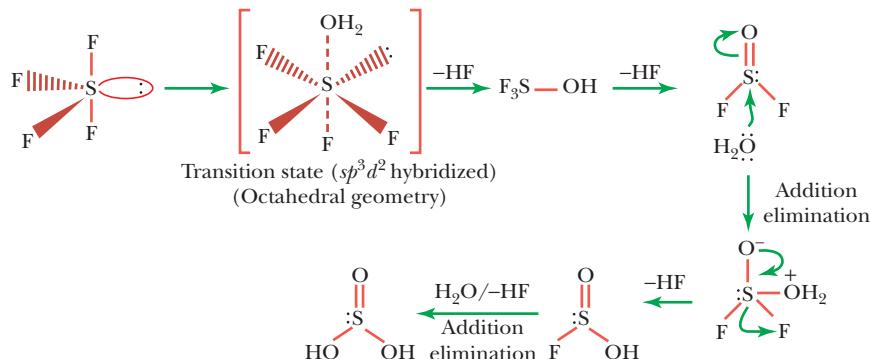
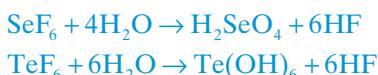


Figure 4.9 Hydrolysis of SF_4 by SN^2 mechanism followed by addition elimination mechanism.

Unlike SF_4 , SF_6 is inert towards hydrolysis even though it has vacant d orbitals available with the central atom S. This is due to steric crowding around sulphur atom; and this reason is supported by the fact that the order for rate of hydrolysis of SF_6 , SeF_6 and TeF_6 is $\text{SF}_6 < \text{SeF}_6 < \text{TeF}_6$. As the size of the central atom increases, this steric crowding decreases; and the surface of the central atom becomes more exposed for the nucleophilic attack.

Though SeF_6 is inert like SF_6 , it undergoes hydrolysis to a very little extent, on the other hand TeF_6 hydrolyzes readily and completely.



Here also, the nature of products formed is different due to steric crowding. The expected product from SeF_6 hydrolysis is $\text{Se}(\text{OH})_6$ but to avoid steric crowding it condenses into H_2SeO_4 .

- 3. Hydrolysis of P_4O_{10} :** This hydrolysis also proceeds through addition and addition–elimination mechanism as shown in Figure 4.10.

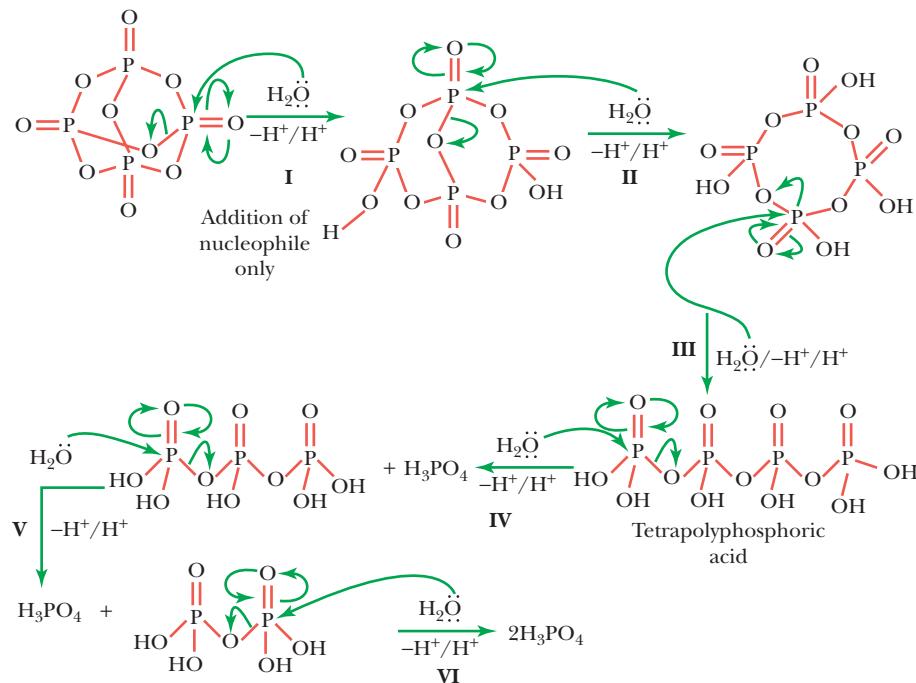
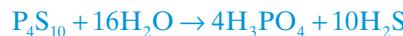


Figure 4.10 Hydrolysis of P_4O_{10} through addition and addition–elimination mechanism.

In the first three steps (I, II and III) of hydrolysis of P_4O_{10} , there is no elimination. Hence these three steps follow addition mechanism for the nucleophile. However, in the last three steps (IV, V and VI) one PO_4^- unit is left which acts as the leaving group. So the overall mechanism is addition and addition–elimination.

Similarly for P_4S_{10} ,



- 4. Hydrolysis of P_4 :** Disproportionation of P_4 in alkaline medium can be easily explained through addition and addition–elimination mechanisms as shown in Figure 4.11.

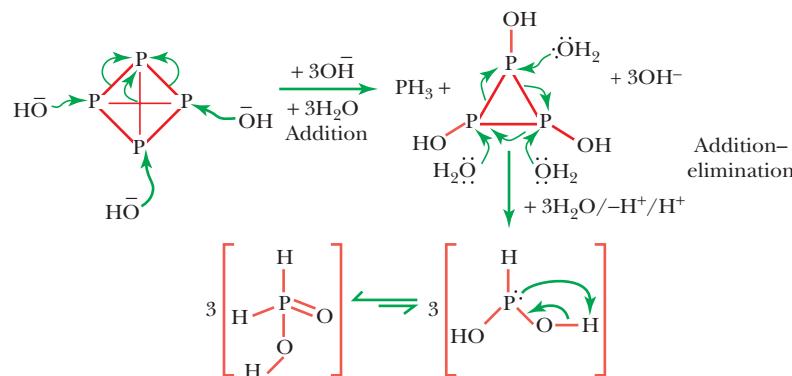


Figure 4.11 Hydrolysis of P_4 through addition and addition–elimination mechanism.

SINGLE CORRECT CHOICE TYPE QUESTIONS

- Which of the following orders is incorrect for the rate of hydrolysis?
 (A) $\text{SnCl}_2 > \text{SnCl}_4$
 (B) $\text{SnCl}_4 > \text{SnMe}_4$
 (C) $\text{AlCl}_3 < \text{CCl}_4$
 (D) $\text{BF}_3 < \text{BCl}_3$
- Which of the following statements is incorrect?
 (A) Disproportionation reaction takes place for the hydrolysis of XeF_4 .
 (B) In the hydrolysis of PCl_3 , tautomers of P(OH)_3 are formed as final product.
 (C) In the hydrolysis of NCl_3 , HOCl is not formed.
 (D) CH_4 is inert towards the hydrolysis at normal conditions.
- Which of the following reaction is correct?
 (A) $\text{PCl}_3 + 4\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 5\text{HCl} + \frac{1}{2}\text{O}_2$
 (B) $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$
 (C) $2\text{BCl}_3 + 6\text{HOH}$ (excess) $\rightarrow \text{B}_2\text{H}_6 + 6\text{HOCl}$
 (D) $\text{B}_2\text{H}_6 + 2\text{N}(\text{CH}_3)_3 \rightarrow [\text{BH}_2\text{N}(\text{CH}_3)_3]_2^+ [\text{BH}_4]^-$
- In which of the following all the chlorine atoms are substituted, as given, on hydrolysis?

$$\text{MCl}_n + n\text{H}_2\text{O} \xrightarrow[\text{temperature}]{\text{room}} \text{M(OH)}_n + n\text{HCl}$$
 (A) NCl_3
 (B) BCl_3
 (C) CCl_4
 (D) None of these
- Which of the following statements is correct?
 (A) On hydrolysis of SeF_6 and TeF_6 four water molecules are consumed.
 (B) On hydrolysis of PCl_3 the product obtained has basicity 3.
 (C) On hydrolysis of SF_4 , hybridization of S in transition state is sp^3d .
 (D) All molecules of BF_3 are not hydrolyzed in water.
- Which of the following compounds produce acid having basicity of two on hydrolysis?
 (A) NCl_3
 (B) $\text{Al}_2(\text{CH}_3)_6$
 (C) SO_2Cl_2
 (D) Mg_3N_2
- In which of the following reactions oxidation number of underlined atom will be +6 in atleast one of the products?
 (A) $\underline{\text{SO}}_2\text{F}_2 \xrightarrow{\text{Hydrolysis}}$
 (B) $\underline{\text{Xe}}\text{F}_4 \xrightarrow{\text{Hydrolysis}}$
 (C) $\underline{\text{Xe}}\text{F}_6 \xrightarrow{\text{Hydrolysis}}$
 (D) All of the these
- Select the incorrect trend for extent of hydrolysis.
 (A) $\text{SF}_4 > \text{SF}_6$
 (B) $\text{NCl}_3 > \text{NF}_3$
- Which of the following chain controlling unit for silicone is
 (A) R_3SiCl
 (B) R_2SiCl_2
 (C) RSiCl_3
 (D) SiCl_4
- The products of hydrolysis of Br-Cl are
 (A) $\text{HBr} + \text{HCl} + \frac{1}{2}\text{O}_2$
 (B) $\text{HOBr} + \text{HCl}$
 (C) $\text{HOCl} + \text{HBr}$
 (D) $\text{HOBr} + \text{HOCl}$
- The hydrolysis of Na_2SO_3 makes the solution
 (A) alkaline.
 (B) acidic.
 (C) neutral.
 (D) None of these.
- Which of the following compounds produces only basic product(s) on hydrolysis?
 (A) Mg_3N_2
 (B) NCl_3
 (C) BBr_3
 (D) LiH
- When CH_3Cl undergoes alkaline hydrolysis to produce CH_3OH , the state of hybridization of C atom in the transition state is
 (A) sp
 (B) sp^3d
 (C) sp^3
 (D) sp^2
- When SiCl_4 undergoes hydrolysis to produce $\text{Si}(\text{OH})_4$, the state of hybridization of Si atom in the transition state is
 (A) sp
 (B) sp^3d
 (C) sp^3
 (D) sp^2
- The basicity of the acid produced from the central atom in the hydrolysis of AsCl_3 is
 (A) 1
 (B) 2
 (C) 3
 (D) 4
- Which of the following statements is incorrect?
 (A) PCl_5 produces POCl_3 as intermediate product on hydrolysis.
 (B) BCl_3 produces $\text{B}(\text{OH})_3$ on alkaline hydrolysis.
 (C) SiH_4 gives rise to H_2 gas on hydrolysis.
 (D) N_2O_5 produces two molecules of HNO_3 on hydrolysis.

17. Which of the following statements is correct?

(A) BiCl_3 produces $\text{Bi}(\text{OH})_3$ (white ppt.) on hydrolysis.

(B) d orbital participates in the alkaline hydrolysis of CH_3Cl .

(C) d orbital participates in the hydrolysis of SF_6 .

(D) d orbital participates in the hydrolysis of PCl_5 .

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1 to 3

Silicones are the organo-silicon polymers. Compounds like R_2SiCl_2 on hydrolysis produce silicone like $-O-Si(R_2)-O-Si(R_2)-O-Si(R_2)-$. It may be of chain or cyclic type.

1. The water repelling characteristic of silicones is due to
(A) the presence of alkyl group pointed towards surface.
(B) strong Si—O—Si bonds.

- (C) low surface area.
(D) high van der Waals forces.

2. Hardness of silicone polymer can be controlled by using
(A) R_2SiCl_2
(B) $RSiCl_3$
(C) R_3SiCl
(D) $AlCl_3$

3. Which is not the use of silicones?
(A) As lubricant in gear box.

- (B) In masonry works in buildings.
 (C) Cosmetics and nail polish manufacture.
 (D) As electrical insulator.

Passage 2: For Questions 4 to 6

Hydrolysis of different polyphosphoric acids occurs through addition-elimination mechanism.

4. The product(s) of hydrolysis of hypophosphoric acid is (are)
 (A) H_3PO_4 only.
 (B) H_3PO_3 and H_3PO_4 .
 (C) H_3PO_3 only.
 (D) $\text{H}_3\text{PO}_4 + \text{H}_2$.
5. The product(s) of hydrolysis of pyrophosphoric acid is (are)
 (A) H_3PO_4 only.
 (B) H_3PO_3 and H_3PO_4 .
 (C) H_3PO_3 only.
 (D) $\text{H}_3\text{PO}_4 + \text{H}_2$.
6. The product(s) of hydrolysis of isohypophosphoric acid is (are)
 (A) H_3PO_4 only.
 (B) H_3PO_3 and H_3PO_4 .
 (C) H_3PO_3 only.
 (D) $\text{H}_3\text{PO}_4 + \text{H}_2$.

Passage 3: For Questions 7 to 9

Hydrolysis is a reaction in which the substance undergoes nucleophilic substitution with the solvent water. If the solvents are NH_3 and ROH , then the corresponding terms are known as ammonolysis and alcoholysis respectively.

7. Ammonolysis of SiCl_4 followed by heating produces
 (A) $\text{Si}(\text{NH}_2)_4$
 (B) Si_3N_4
 (C) $\text{Si}(\text{OH})_4$
 (D) SiO_2
8. Alcoholysis of $\text{Al}(\text{CH}_3)_3$ by CH_3OH gives rise to
 (A) AlH_3
 (B) $\text{Al}(\text{OH})_3$
 (C) $\text{Al}(\text{OCH}_3)_3 + \text{CH}_4$
 (D) Al_2O_3
9. Which of the following compounds shows least tendency towards hydrolysis?
 (A) BF_3
 (B) BCl_3
 (C) BBr_3
 (D) BI_3

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

Passage 4: For Questions 10 to 12

Latest definition says that the reaction of any substance with water is called as hydrolysis and it may happen by different mechanism.

10. Which of the following statements shows similarities between the hydrolysis of NCl_3 and PCl_3 ?
 (A) In both cases the nucleophilic attack takes place at the central atom.
 (B) In both cases, products are acidic in nature.
 (C) In both cases, one of the product is HCl .
 (D) None of these.
11. Which of the following compounds involves SN^1 mechanism for its hydrolysis (if any)?
 (A) AsCl_3
 (B) NF_3
 (C) SiCl_4
 (D) BCl_3
12. The product of hydrolysis of CCl_4 from its central atom under drastic conditions is
 (A) HCl
 (B) $\text{CO}(\text{OH})_2$
 (C) $\text{C}(\text{OH})_4$
 (D) COCl_2

Passage 5: For Questions 13 to 15

Hydrolysis of different compounds may take place by different kinds of mechanisms.

13. In which of the following molecules, the nucleophilic attack by the H_2O molecule does not take place at the Br atom?
 (A) BrF_3
 (B) $\text{Br}-\text{F}$
 (C) $\text{I}-\text{Br}$
 (D) None of these
14. Which of the following molecules involve(s) redox reaction in their hydrolysis reaction?
 (A) XeF_4
 (B) XeF_2
 (C) POCl_3
 (D) Both (A) and (B)
15. Which of the following statements is correct?
 (A) In the hydrolysis of NCl_3 , the nucleophilic attack takes place at N atom.
 (B) In the hydrolysis of Marshall's acid ($\text{H}_2\text{S}_2\text{O}_8$), the Caro's acid (H_2SO_5) is formed as intermediate.
 (C) $\text{F}-\text{Cl} + \text{H}_2\text{O} \rightarrow \text{H}-\text{O}-\text{H} + \text{HCl}$
 (D) All of the above statements are correct.

ASSERTION-REASONING TYPE QUESTIONS

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.

- (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
 (C) If Statement I is true but Statement II is false.
 (D) If Statement I is false but Statement II is true.

- 1. Statement I:** Mg_2C_3 and Al_4C_3 both produce the same gaseous products on their hydrolysis.

Statement II: The nature of hydrocarbon produced from a particular carbide depends upon the anionic part present in it.

- 2. Statement I:** Hydrolysis of $\text{Al}_2(\text{CH}_3)_6$ is highly spontaneous.

Statement II: $\text{Al}_2(\text{CH}_3)_6$ gives $\text{Al}(\text{OH})_3$ (white ppt.) and CH_4 (gaseous product) on hydrolysis.

- 3. Statement I:** SiH_4 is prone towards hydrolysis while SnH_4 is inert.

Statement II: Sn–H bond has insufficient polarity compared to Si–H bond.

- 4. Statement I:** TeF_6 produces H_2TeO_4 as hydrolyzed product.

Statement II: $\text{Te}(\text{OH})_6$ exists and there is no steric crowding to accommodate six OH^- groups around it.

- 5. Statement I:** P_4S_{10} produces H_3PO_4 and H_2S , not H_2SO_4 and PH_3 , on hydrolysis.

Statement II: S atom being more electronegative, the nucleophilic attack takes place on P atom and protonation takes place on S atom.

- 6. Statement I:** Silicones are resistant towards hydrolysis.

Statement II: +I effect of CH_3 groups reduces the $\delta(+)$ character of Si atoms.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

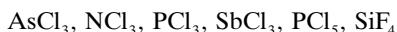
- 1.** Find the total number of molecules which give hydro acid as one of the products when they undergo complete hydrolysis.



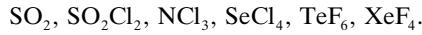
- 2.** Find the number of molecules which produce Na_2SO_4 on hydrolysis followed by the treatment of resulting solution with excess NaOH .



- 3.** The number of compounds among the following, forming oxyacids from the central atom on hydrolysis is _____.



- 4.** The number of compounds among the following that do not produce only acidic product(s) on their hydrolysis is _____.



- 5.** When SF_4 is hydrolysed, the change in oxidation state of S atom during the process is _____.

- 6.** Among the following orders, the number of incorrect orders with respect to rate of hydrolysis is _____.

- (i) $\text{SnCl}_2 > \text{SnCl}_4$
- (ii) $\text{BBr}_3 > \text{BI}_3$
- (iii) $\text{SeF}_6 > \text{TeF}_6$
- (iv) $\text{SiCl}_4 < \text{SiBr}_4$
- (v) $\text{SiH}_4 > \text{GeH}_4$
- (vi) $\text{SF}_6 < \text{SeF}_6$

- 7.** When SnCl_4 is converted into $[\text{SnCl}_6]^{2-}$ by the nucleophilic addition of Cl^- , the coordination number is increased by _____.

- 8.** The number of HCl molecules formed from the hydrolysis of one molecule of NCl_3 is _____.

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as **(A)**, **(B)**, **(C)** and **(D)**, while those in Column II are labelled as **(P)**, **(Q)**, **(R)**, **(S)** and **(T)**. Any given statement in Column I can have correct matching with *one or more* statements in Column II.

- 1.** Match the compounds with their properties.

Column I	Column II
(A) BeCl_2	(P) d orbital participation does not take place during hydrolysis.
(B) BF_3	(Q) $p\pi-p\pi$ back bonding is present in the molecule.
(C) SiF_4	(R) Partial hydrolysis takes place due to complex formation.
(S)	(T) $(3c - 4e)$ bond is present in the hydrolyzed product.

- (A) BeCl_2 (P) d orbital participation does not take place during hydrolysis.

- (B) BF_3 (Q) $p\pi-p\pi$ back bonding is present in the molecule.

- (C) SiF_4 (R) Partial hydrolysis takes place due to complex formation.

- (S) (T) $(3c - 4e)$ bond is present in the hydrolyzed product.

2. Match the compounds with the mechanism involved in their hydrolysis.

Column I	Column II
(A) PCl_5	(P) Addition mechanism only.
(B) SiCl_4	(Q) SN^2 mechanism only.
(C) SO_3	(R) Addition–elimination mechanism only.
(D) CrO_2Cl_2	(S) SN^2 and addition–elimination mechanism.

3. Match the compounds with the correct statement regarding their hydrolysis reactions.

Column I	Column II
(A) PCl_3	(P) At least one of the hydrolysis products undergoes tautomerism.
(B) SO_2Cl_2	(Q) Produces acid(s) having basicity of two on hydrolysis.
(C) NCl_3	(R) Follows purely SN^1 mechanism for hydrolysis.
(D) H_2SO_5	(S) The nucleophilic attack takes place on the surrounding atoms during hydrolysis.
	(T) The nucleophilic attack takes place at the central atom on hydrolysis.

ANSWERS

Single Correct Choice Type Questions

- | | | | | | |
|--------|--------|--------|---------|---------|---------|
| 1. (C) | 4. (B) | 7. (D) | 10. (B) | 13. (D) | 16. (B) |
| 2. (C) | 5. (D) | 8. (C) | 11. (A) | 14. (B) | 17. (D) |
| 3. (B) | 6. (C) | 9. (A) | 12. (A) | 15. (C) | |

Multiple Correct Choice Type Questions

- | | | |
|------------------|------------------|------------------|
| 1. (B), (C), (D) | 3. (B), (C), (D) | 5. (A), (C) |
| 2. (C), (D) | 4. (A), (C) | 6. (A), (C), (D) |

Comprehension Type Questions

- | | | | | |
|--------|--------|--------|---------|---------|
| 1. (A) | 4. (B) | 7. (B) | 10. (D) | 13. (C) |
| 2. (B) | 5. (A) | 8. (C) | 11. (B) | 14. (D) |
| 3. (C) | 6. (B) | 9. (A) | 12. (D) | 15. (B) |

Assertion–Reasoning Type Questions

- | | | |
|--------|--------|--------|
| 1. (D) | 3. (A) | 5. (A) |
| 2. (B) | 4. (D) | 6. (A) |

Integer Answer Type Questions

- | | | | |
|------|------|------|------|
| 1. 4 | 3. 4 | 5. 0 | 7. 2 |
| 2. 3 | 4. 2 | 6. 4 | 8. 0 |

Matrix–Match Type Questions

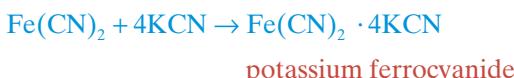
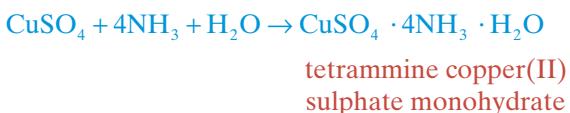
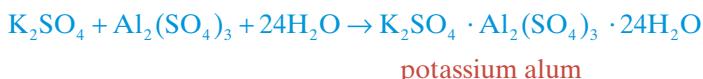
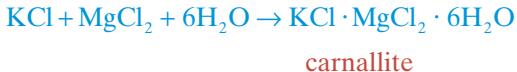
- | | | |
|--|---|---|
| 1. (A) \rightarrow (P), (Q), (S)
(B) \rightarrow (P), (Q), (R)
(C) \rightarrow (R) | 2. (A) \rightarrow (S)
(B) \rightarrow (Q)
(C) \rightarrow (P)
(D) \rightarrow (R) | 3. (A) \rightarrow (P), (Q), (T)
(B) \rightarrow (Q), (T)
(C) \rightarrow (S)
(D) \rightarrow (Q), (T) |
|--|---|---|

5

Coordination Compounds

5.1 | DOUBLE SALTS AND COORDINATION COMPOUNDS

Addition compounds are formed when stoichiometric amounts of two or more stable compounds join together. For example:

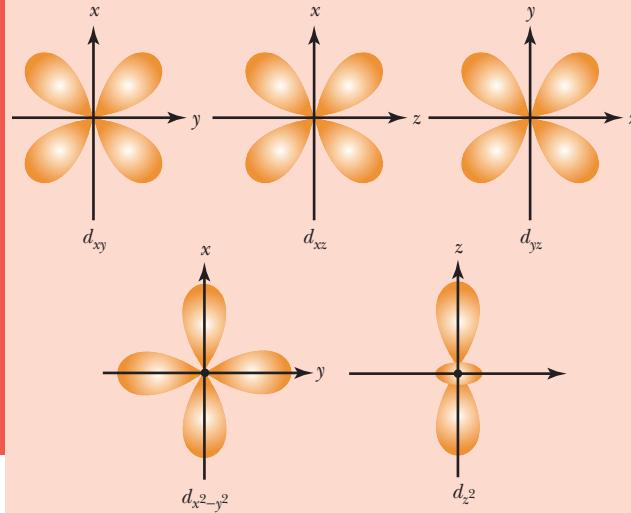


Addition compounds are of two types:

1. Those which lose their identity in solution (double salts)
2. Those which retain their identity in solution (complexes)

When crystals of carnallite are dissolved in water, the solution shows the properties of K^+ , Mg^{2+} and Cl^- ions. In a similar way, a solution of potassium alum shows the properties of K^+ , Al^{3+} and SO_4^{2-} ions. These are both examples of double salts which exist only in the crystalline state.

When the other two examples of coordination compounds dissolve they do not form simple ions – Cu^{2+} , or Fe^{2+} and CN^- – but instead their complex ions remain intact. Thus the cuproammonium ion $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ and the

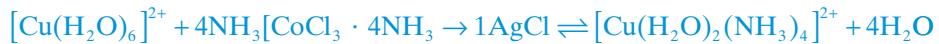


Shapes of *d* orbitals.

Contents

- 5.1 Double Salts and Coordination Compounds
- 5.2 Werner's Work
- 5.3 More Recent Methods of Studying Complexes
- 5.4 Classification of Ligands
- 5.5 Effective Atomic Numbers
- 5.6 Shapes of *d* Orbitals
- 5.7 Bonding in Transition Metal Complexes
- 5.8 Valence Bond Theory
- 5.9 Crystal Field Theory
- 5.10 Effects of Crystal Field Splitting
- 5.11 Tetragonal Distortion of Octahedral Complexes (Jahn-Teller Distortion)
- 5.12 Square Planar Arrangements
- 5.13 Tetrahedral Complexes
- 5.14 Magnetism
- 5.15 Extension of the Crystal Field Theory to Allow for Some Covalency
- 5.16 Nomenclature of Coordination Compounds
- 5.17 Isomerism

ferrocyanide ion $[\text{Fe}(\text{CN})_6]^{4-}$ exist as distinct entities both in the solid and in solution. Complex ions are shown by the use of square brackets. Compounds containing these ions are called coordination compounds. *The chemistry of metal ions in solution is essentially the chemistry of their complexes. Transition metal ions, in particular, form many stable complexes.* In solution 'free' metal ions are coordinated either to water or to other ligands. Thus Cu^{2+} exists as the pale blue complex ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution (and also in hydrated crystalline salts). If aqueous ammonia is added to this solution, the familiar deep blue cuproammonium ion is formed:



Note that this reaction is a substitution reaction, and the NH_3 replaces water in the complex ion.

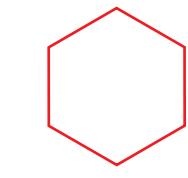
5.2 | WERNER'S WORK

Werner's coordination theory in 1893 was the first attempt to explain the bonding in coordination complexes. It must be remembered that this imaginative theory was put forward before the electron had been discovered by J.J. Thompson in 1896, and before the electronic theory of valency. This theory and his painstaking work over the next 20 years won Alfred Werner the Nobel Prize for Chemistry in 1913.

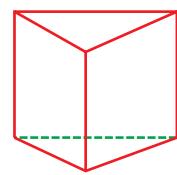
Complexes must have been a complete mystery without any knowledge of bonding or structure. For example, why does a stable salt like CoCl_3 react with a varying number of stable molecules of a compound such as NH_3 to give several new compounds: $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$? What are their structures? At that time X-ray diffraction, which is the most powerful method of determining the structures of crystals, had yet to be discovered. Werner did not have at his disposal any of the modern instrumental techniques, and all his studies were made using simple reaction chemistry. *Werner was able to explain the nature of bonding in complexes, and he concluded that in complexes the metal shows two different sorts of valency:*

- 1. Primary valencies:** These give rise to first order compounds (e.g. CoCl_3 from cobalt and chlorine) and correspond to the valency (now known as oxidation state) of the central atom. These are non-directional. In modern terms, the number of primary valencies corresponds to the number of charges on the central metal atom. The complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ actually exists as $[\text{Co}(\text{NH}_3)_6]^{3+}$ and 3Cl^- . Thus the primary valency is three. Similarly, in case of $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$, the primary valency is also three.
- 2. Secondary valencies:** These give rise to the higher order compounds (e.g. $\text{CoCl}_3 \cdot n\text{NH}_3$ from CoCl_3 and NH_3). These are directional. In modern terms the number of secondary valencies equals the number of ligand atoms coordinated to the metal. This is now called the coordination number. Ligands are commonly negative ions such as Cl^- , or neutral molecules such as NH_3 . Less commonly, ligands may be positive ions such as NO_3^+ . Each metal has a characteristic number of secondary valencies. Thus in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ the three Cl^- are held by primary valencies. The six NH_3 groups are held by secondary valencies.

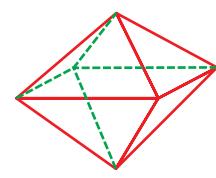
Werner also attempted to find the shapes of the complexes. The possible arrangements of six groups round one atom are a planar hexagon, a trigonal prism, and an octahedron (Figure 5.1). Werner then compared the number of isomeric forms he had obtained with the theoretical number for each of the possible shapes (Table 5.1).



Planar hexagon



Trigonal prism



Octahedron

Figure 5.1 Possible geometric shapes for six-coordination.

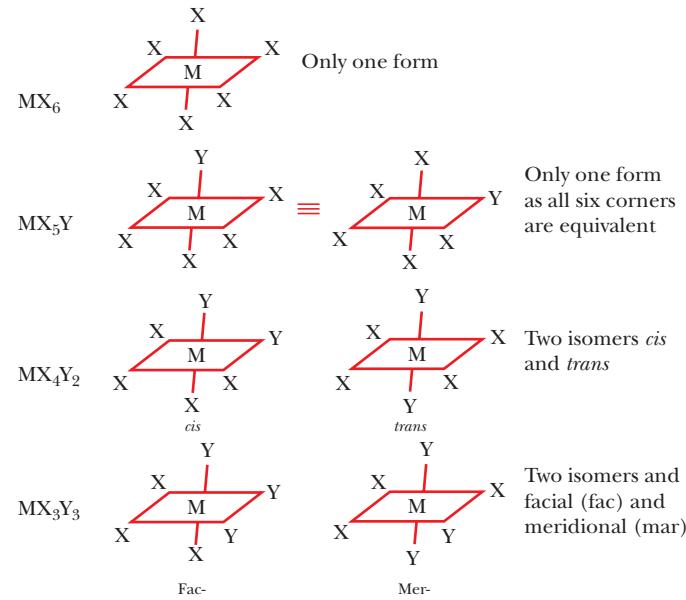
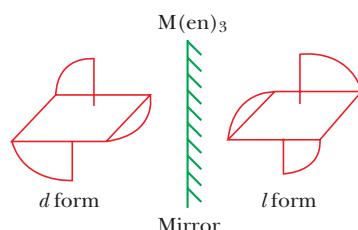
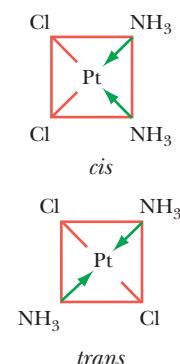
Table 5.1 Number of isomers predicted and actually found

Complex	Observed	Predicted		
		Octahedral	Planar hexagon	Trigonal prism
$[\text{MX}_6]$	1	1	1	1
$[\text{MX}_5\text{Y}]$	1	1	1	1
$[\text{MX}_4\text{Y}_2]$	2	2	3	3
$[\text{MX}_3\text{Y}_3]$	2	2	3	3

These results strongly suggested that these complexes have an octahedral shape. This proof was not absolute proof, as it was just possible that the correct experimental conditions had not been found for preparing all the isomers. More recently the X-ray structures have been determined, and these establish that the shape is octahedral (Figure 5.2).

More recently, with a bidentate ligand such as ethylenediamine (1,2-diaminoethane), two optically active isomers of octahedral complexes have been found (Figure 5.3).

In a similar way, Werner studied a range of complexes which included $[\text{Pt}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pd}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]$. The coordination number is 4, and the shape could be either tetrahedral or square planar. Werner was able to prepare two different isomers for these complexes. A tetrahedral complex can only exist in one form, but a square planar complex can exist in two isomeric forms. This proved these complexes are square planar rather than tetrahedral (Figure 5.4).

**Figure 5.2** Isomers in octahedral complexes.**Figure 5.3** Optical isomerism in octahedral complexes.**Figure 5.4** Isomerism in square planar complexes.

5.3 | MORE RECENT METHODS OF STUDYING COMPLEXES

The electrical conductivity of a solution of an ionic material depends on:

1. The concentration of solute.
2. The number of charges on the species which are formed on dissolution.

Molar conductivities relate to a 1 M solution and thus the concentration factor is removed. The total number of charges on the species formed when the complex dissolves can be deduced by comparison of its molar

conductivity with that of known simple ionic materials (Table 5.2). These conductivities suggest the same structures for the cobalt/ammonia/chlorine complexes mentioned earlier, as do the results from Werner's AgCl experiments, shown in Table 5.3.

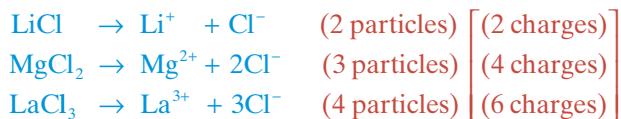
Table 5.2 Conductivities of salts and complexes (molar conductivities measured at 0.001 M concentration)

$\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$		
$\text{LiCl} \rightarrow \text{Li}^+ + \text{Cl}^-$	(total of 2 charges)	112.0
$\text{CaCl}_2 \rightarrow \text{Ca}^{2+} + 2\text{Cl}^-$	(total of 4 charges)	260.8
$\text{CoCl}_3 \cdot 5\text{NH}_3$		261.3
$\text{CoBr}_3 \cdot 5\text{NH}_3$		257.6
$\text{LaCl}_3 \rightarrow \text{La}^{3+} + 3\text{Cl}^-$	(total of 6 charges)	393.5
$\text{CoCl}_3 \cdot 6\text{NH}_3$		431.6
$\text{CoBr}_3 \cdot 6\text{NH}_3$		426.9

Table 5.3 Number of charges related to modern and Werner structures

Charges	Primary valency	Ionizable chlorines	Secondary valency
$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$	6	3	$6\text{NH}_3 = 6$
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} 2\text{Cl}^-$	4	3	$5\text{NH}_3 + 1\text{Cl}^- = 6$
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \text{Cl}^-$	2	3	$4\text{NH}_3 + 2\text{Cl}^- = 6$

The freezing point of a liquid is lowered when a chemical substance is dissolved in it. Cryoscopic measurements involve measuring how much the freezing point is lowered. The depression of freezing point obtained depends on the number of particles present. Cryoscopic measurements can be used to find if a molecule dissociates, and how many ions are formed. If a molecule dissociates into two ions it will give twice the expected depression for a single particle. If three ions are formed this will give three times the expected depression. Thus:



The number of particles formed from a complex molecule determines the size of the depression of freezing point. Note that the number of particles formed may be different from the total number of charges which can be obtained from conductivity measurements. These two types of information can be used together to establish the structure (Table 5.4).

Table 5.4 Establishing the structure of complexes

Formula	Cryoscopic measurement	Molar conductivity	Structure
$\text{CoCl}_3 \cdot 6\text{NH}_3$	4 particles	6 charges	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$
$\text{CoCl}_3 \cdot 5\text{NH}_3$	3 particles	4 charges	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} 2\text{Cl}^-$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	2 particles	2 charges	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \text{Cl}^-$
$\text{CoCl}_3 \cdot 3\text{NH}_3$	1 particle	0 charge	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
$\text{Co}(\text{NO}_2)_3 \cdot \text{KNO}_2 \cdot 2\text{NH}_3$	2 particles	2 charges	$\text{K}^+ [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$
$\text{Co}(\text{NO}_2)_3 \cdot 2\text{KNO}_2 \cdot \text{NH}_3$	3 particles	4 charges	$2\text{K}^+ [\text{Co}(\text{NH}_3)(\text{NO}_2)_5]^{2-}$
$\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$	4 particles	6 charges	$3\text{K}^+ [\text{Co}(\text{NO}_2)_6]^{3-}$

The magnetic moment can be measured and this provides information about the number of unpaired electron spins present in a complex. From this it is possible to decide how the electrons are arranged and which orbitals are occupied. Sometimes the structure of the complex can be deduced from this. For example, the compound $\text{Ni}^{\text{II}}(\text{NH}_3)_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ might contain four ammonia molecules coordinated to Ni in a square planar $[\text{Ni}(\text{NH}_3)_4]^{2+}$ ion and two molecules of water of crystallization and have no unpaired electrons. Alternatively the water might be coordinated to the metal, giving an octahedral $[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ complex with two unpaired electrons. Both these complex ions exist and their structures can be deduced from magnetic measurements.

Dipole moments may also yield structural information but only for non-ionic complexes. For example, the complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is square planar, and can exist as *cis* or *trans* forms. The dipole moments from the various metal-ligand bonds cancel out in the *trans* configuration. However, a finite dipole moment is given by the *cis* arrangement (Figure 5.4).

Electronic spectra (UV and visible) also provide valuable information on the energy of the orbitals, and on the shape of the complex. By this means it is possible to distinguish between tetrahedral and octahedral complexes, and whether the shape is distorted or regular.

The most powerful method, however, is the X-ray determination of the crystal structure. This provides details of the exact shape and the bond lengths and angles of the atoms in the structure.

5.4 | CLASSIFICATION OF LIGANDS

There are several ways to classify ligands and these are discussed as follows:

1. Based upon charges

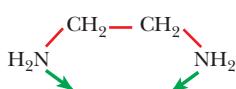
- a. Neutral ligands: H_2O , NO , CO , C_6H_6 , etc.
- b. Positive ligands: NO^+ and NH_2^+ – NH_3^+
- c. Negative ligands: Cl^- , NO_2^- , CN^- , OH^-

2. Based upon denticity of the ligand

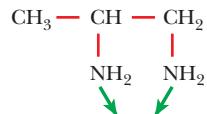
The number of donations accepted by a central atom from a particular ligand is known as the denticity of the ligand. Ligands may be classified as follows based on their denticity:

- a. **Monodentate:** Only one donation is accepted from the ligand. For example, H_2O , NO , CO , NH_3 , CO_3^{2-} , Cl^- , etc.
- b. **Bidentate:** Two donations are accepted from the ligand. For example,

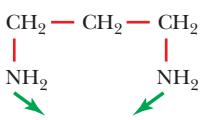
(i) en: ethylenediamine



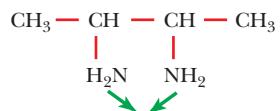
(ii) pn: propylenediamine



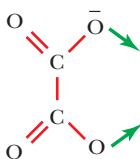
(iii) tn: trimethylenediamine



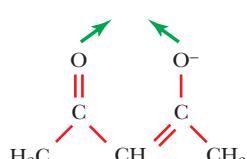
(iv) bn: butylenediamine

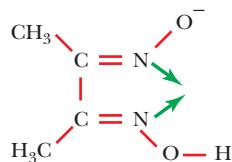
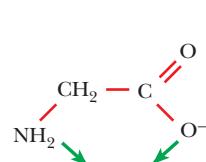
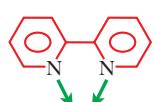
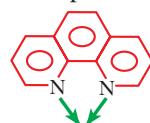
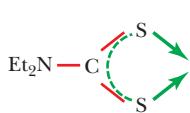


(v) ox²⁻: oxalate

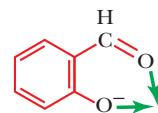


(vi) acac⁻: acetylacetone

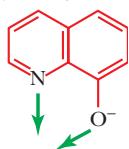
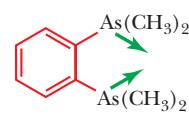


(vii) dmg^- : dimethylglyoximate(viii) gly^- : glycinate(ix) dipy : dipyridyl(x) o-phen : *ortho*- phenanthroline(xi) $\text{N, N}'$ - Diethylthiocarbamate ion

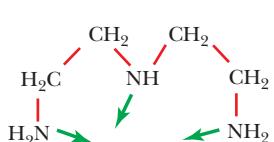
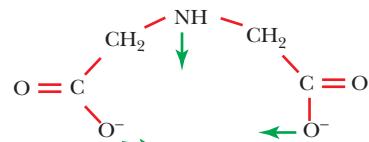
(xii) Salicylaldehyde anion



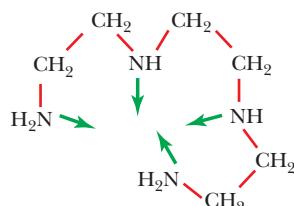
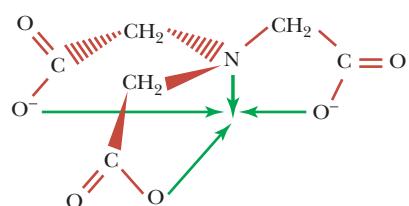
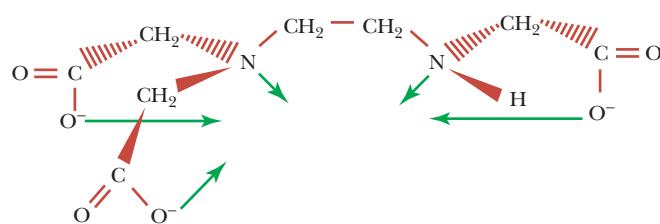
(xiii) 8-Hydroxyquinolinol ion (oxine)

(xiv) $\text{o-Phenylenebisdimethylarsine}$ (diarsine)**c. Tridentate:** Three donations are accepted from the ligand. For example,

(i) dien: diethylenetriamine

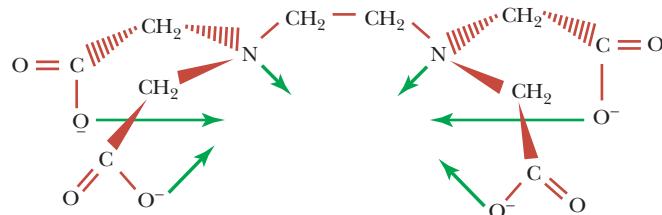
(ii) idma^{2-} : iminodiacetate**d. Tetridentate:** Four donations are accepted from the ligand. For example,

(i) trien: triethylenetetraamine

(ii) NTA^{3-} : nitrilotriacetate**e. Pentadentate:** Five donations are accepted from the ligand. For example, EDTA^{3-} : ethylenediamine triacetate

f. Hexadentate: Six donations are accepted from the ligand. For example,

EDTA⁴⁻: ethylenediamine tetracetate

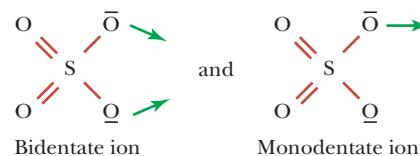


Note:

1. Flexidentate: A ligand which shows variable denticity is called a flexidentate ligand.

For example,

(i)



(ii) $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Br}$

and $[\text{Co}(\text{NH}_2)_5\text{CO}_2]\text{Br}$

374 31

(iii) NO_3^- , CH_3COO^- , $\text{S}_2\text{O}_3^{2-}$

may also act as flexidentate ligand

2. Chelating: A ligand that can form a ring structure with the central atom is called a chelating ligand.

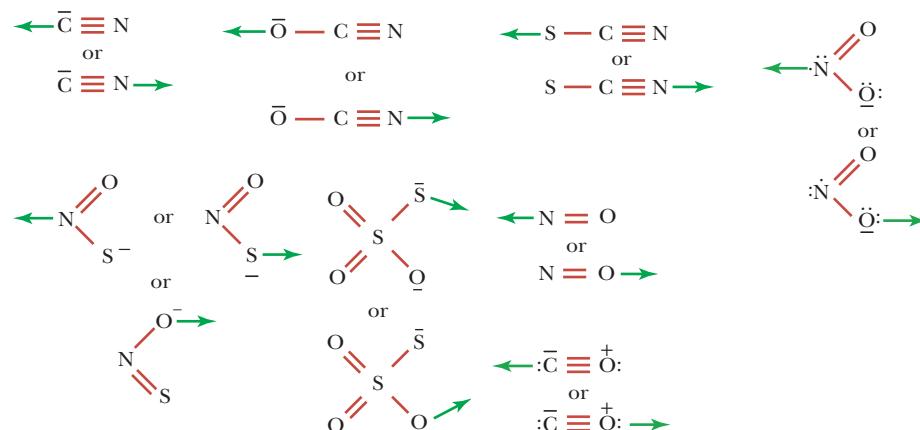
All polydentate ligands are the example of chelating ligands.

Chelated complexes are more stable than similar complexes with monodentate ligands as dissociation of the complex involves breaking two bonds rather than one.

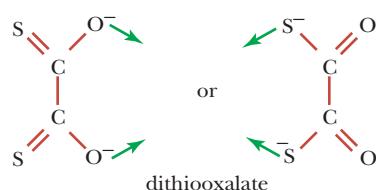
However, it must be noted that NH_2NH_2 and $\text{N}(\text{CH}_2 - \text{CH}_2)_3\text{N}$ cannot act as chelating ligands due to the formation of three membered ring and locked structure, respectively.

3. Ambidentate ligand: A ligand that may have more than one kind of donor sites but at a time only one kind of donor site is utilized for donation is called as ambidentate ligand. Ambidentate ligand may be of two types.

a. Monodentate and ambidentate:



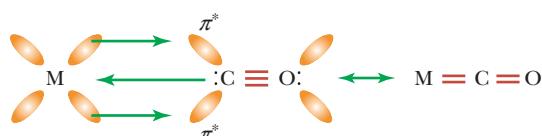
b. Bidentate and ambidentate:



3. Based upon bonding interaction between the ligand and the central atom

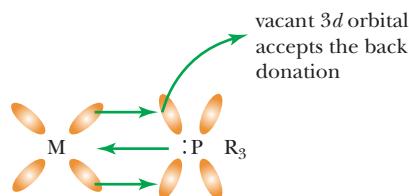
- a. **Classical or simple donor ligand:** These ligands only donate the lone pair of electrons to the central atom. For example, O^{2-} , OH^- , F^- , NH_2^- , NH_3^- , N^{3-} , etc.
- b. **Non-classical or π -acid or π -acceptor ligand:** These ligands not only donate the lone pair of electrons to the central atom but also accept the electron cloud from the central atom in their low-lying vacant orbitals. This kind of back donation is known as 'synergic effect' or 'synergic bonding'. For example, CO , CN^- , NO^+ , PF_3^+ , PR_3 ($R = H, Et, Ph...$), C_2H_4 , C_2H_2 , CO_2 , etc.

(i) In case of CO , the back donation to the π^* orbital of central atom may be depicted as:

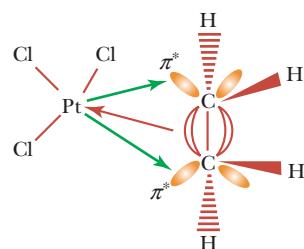


By valence bond or molecular orbital theory, it is well understood that the bond order of $C - O$ bond decreases but the $C - O$ bond length must increase due to synergic effect. Similarly, as CN^- and NO^+ are isoelectronic with CO , so back donation takes place in these species also in the π^* orbitals and the same conclusion can be drawn for the bond order and bond lengths.

(ii) In case of PR_3 , the back donation may be depicted as:



(iii) In case of C_2H_4 , the back donation may be depicted using the example of Zeise's salt.



Here the back donation is accepted in the π^* orbital of $C - C$ bond. Hence, the bond order of $C - C$ bond decreases and the bond length increases as compared to free C_2H_4 molecule. Due to backbonding, C_2H_4 molecule loses its planarity. Similarly, C_2H_2 molecule loses its linearity not the planarity.

5.5 | EFFECTIVE ATOMIC NUMBER (EAN)

Physically EAN signifies the number of electrons available around a central atom within a complex, including the electrons accepted from ligands. It is mathematically defined as follows:

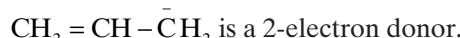
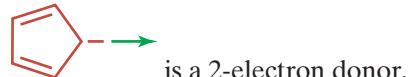
EAN of a central atom in a complex = Atomic number of the central atom (Z)

– (oxidation number of the central atom with sign)

+ (number of electrons collected from the ligands).

The following points need to be noted with regard to EAN.

1. All donations contribute two electrons, while NO is considered as a 3-electron donor.
2. For π -donors, the number of π -electrons involved in donation from a particular ligand are to be considered. For example,



3. For the compounds having δ bond, for example, $\text{Mn}_2(\text{Co})_{10}$, the EAN of each Mn atom is calculated as:

$$\text{EAN of Mn} = \frac{1}{2}[2 \times 25 - 0 + 10 \times 2 + 2^*] = 36$$

*These two electrons are considered for δ -bond.

The EAN of some metal atoms in different complexes are given in Table 5.5.

Table 5.5 Effective atomic numbers of some metals in complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN
Cr	24	$[\text{Cr}(\text{CO})_6]$	0	12	36
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12	36
Fe	26	$[\text{Fe}(\text{CO})_5]$	0	10	36
Co	27	$[\text{Co}(\text{NH}_3)_6]^{3+}$	3	12	36
Ni	28	$[\text{Ni}(\text{CO})_4]$	0	8	36
Cu	29	$[\text{Cu}(\text{CN})_4]^{3-}$	1	8	36
Pd	46	$[\text{Pd}(\text{NH}_3)_6]^{4+}$	4	12	54
Pt	78	$[\text{PtCl}_6]^{2-}$	4	12	86
Fe	26	$[\text{Fe}(\text{CN})_6]^{3-}$	3	12	35
Ni	28	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2	12	38
Pd	46	$[\text{PdCl}_4]^{2-}$	2	8	52
Pt	78	$[\text{Pt}(\text{NH}_3)_4]^{2+}$	2	8	84
Ti	22	$[\text{Ti}(\sigma-\text{C}_5\text{H}_5)_2(\pi-\text{C}_5\text{H}_5)_2]^0$	4	16	34
Fe	26	$[\text{Fe}(\pi-\text{C}_5\text{H}_5)_2]^0$	2	12	36
Fe	26	$[\text{Fe}(\text{CO})_2(\text{NO})_2]^0$	0	10	36
Co	27	$[\text{Co}(\text{CO})_4]^-$	-1	8	36
V	23	$[\text{V}(\text{CO})_6]^-$	-1	12	36

Sidgwick EAN rule

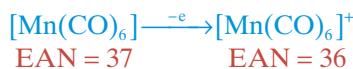
In 1927, Sidgwick suggested that electron pairs from ligands were added to the central metal atom until the central atom was surrounded by the same number of electrons as the next noble gas. The stability of the resulting state can be explained on the basis of the molecular orbital theory. However, this rule fails in many cases and works best for metals in low oxidation state.

Metal carbonyls exhibit a strong tendency to achieve Sidgwick EAN values and as a result of this:

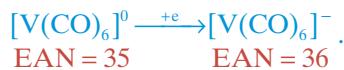
1. The number of CO molecule attached in mononuclear carbonyls can be predicted. For example, in



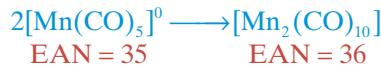
2. $[\text{Mn}(\text{CO})_6]^0$ can act as a reducing agent. The complex loses an electron to attain the noble gas configuration and hence obey Sidgwick EAN rule.



3. $[\text{V}(\text{CO})_6]^0$ can act as oxidizing agent. The complex gains an electron to attain the noble gas configuration and hence obey Sidgwick EAN rule.



4. $[\text{Mn}(\text{CO})_5]^0$ undergoes dimerization to attain the noble gas configuration and hence obey Sidgwick EAN rule.



5.6 | SHAPES OF d ORBITALS

Since d orbitals are often used in coordination complexes it is important to study their shapes and distribution in space. The five d orbitals are not identical and the orbitals may be divided into two sets. The three t_{2g} orbitals have identical shape and point between the axes, x , y and z . The two e_g orbitals have different shapes and point along the axes (Figure 5.5). Alternative names for t_{2g} and e_g are $d\epsilon$ and $d\gamma$ respectively.

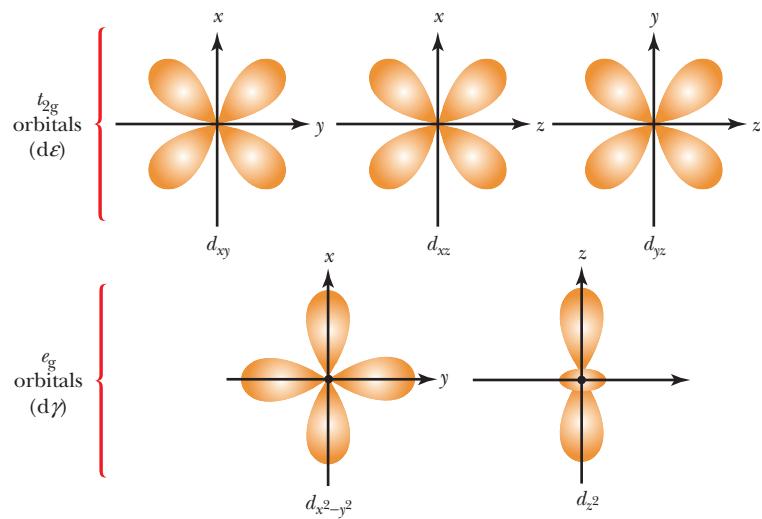


Figure 5.5 Shapes of d orbitals.

5.7 | BONDING IN TRANSITION METAL COMPLEXES

There are three theories of metal to ligand bonding in complexes, all dating back to the 1930s.

Valence bond theory

This theory was developed by Pauling. Coordination compounds contain complex ions, in which ligands form coordinate bonds to the metal. Thus the ligand must have a lone pair of electrons, and the metal must have an empty orbital of suitable energy available for bonding. The theory considers which atomic orbitals on the metal are used for bonding. From this the shape and stability of the complex are predicted. The theory has two main limitations. Most transition metal complexes are coloured, but the theory provides no explanation for their electronic spectra. Further, the theory does not explain why the magnetic properties vary with temperature. For these reasons it has largely been superseded by the crystal field theory. However, it is of interest for study as it shows the continuity of the development of modern ideas from Werner's theory.

Crystal field theory

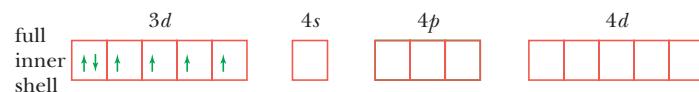
This theory was proposed by Bethe and van Vleck. The attraction between the central metal and ligands in the complex is considered to be purely electrostatic. Thus bonding in the complex may be ion–ion attraction (between positive and negative ions such as Co^{3+} and Cl^-). Alternatively, ion–dipole attractions may give rise to bonding (if the ligand is a neutral molecule such as NH_3 or CO). NH_3 has a dipole moment with a $\delta-$ charge on N and $\delta+$ charges on H. Thus in $[\text{Co}(\text{NH}_3)_6]^{3+}$ the $\delta-$ charge on the N atom of each NH_3 points towards the Co^{3+} . This theory is simple. It has been remarkably successful in explaining the electronic spectra and magnetism of transition metal complexes, particularly when allowance is made for the possibility of some covalent interaction between the orbitals on the metal and ligand. When some allowance is made for covalency, the theory is often renamed as the ligand field theory. Three types of interaction are possible: σ overlap of orbitals, π overlap of orbitals, or $d\pi-p\pi$ bonding (back bonding) due to π overlap of full d orbitals on the metal with empty p orbitals on the ligands.

Molecular orbital theory

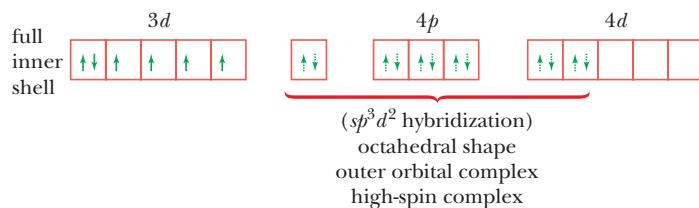
Both covalent and ionic contributions are fully allowed for in this theory. Though this theory is probably the most important approach to chemical bonding, it has not displaced the other theories. This is because the quantitative calculations involved are difficult and lengthy, involving the use of extensive computer time. Much of the qualitative description can be obtained by other approaches using symmetry and group theory.

5.8 | VALENCE BOND THEORY

The formation of a complex may be considered as a series of hypothetical steps. First the appropriate metal ion is taken, e.g. Co^{3+} . A Co atom has the outer electronic structure $3d^74s^2$. Thus a Co^{3+} ion will have the structure $3d^6$, and the electrons will be arranged:



If this ion forms a complex with six ligands, then six empty atomic orbitals are required on the metal ion to receive the coordinated lone pairs of electrons. The orbitals used are the $4s$, three $4p$ and two $4d$. These are hybridized to give a set of six equivalent sp^3d^2 hybrid orbitals. A ligand orbital containing a lone pair of electrons forms a coordinate bond by overlapping with an empty hybrid orbital on the metal ion. In this way a σ bond is formed with each ligand. The d orbitals used are the $4d_{x^2-y^2}$ and $4d_{z^2}$. In the diagrams below, electron pairs from the ligands are shown as $\uparrow\downarrow$.

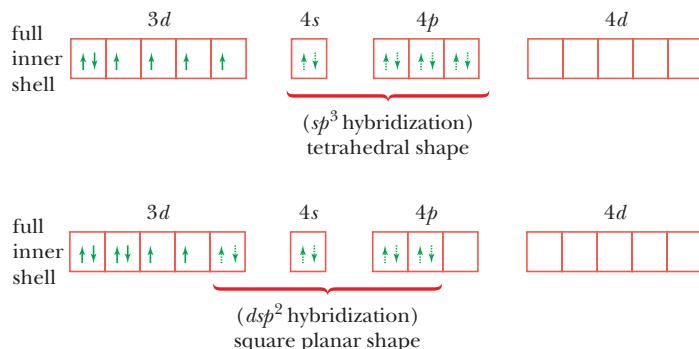


Since the outer 4d orbitals are used for bonding this is called an *outer orbital complex*. The energy of these orbitals is quite high, so that the complex will be reactive or labile. The magnetic moment depends on the number of unpaired electrons. The 3d level contains the maximum number of unpaired electrons for a d^6 arrangement, so this is sometimes called a *high-spin* or a *spin-free complex*. An alternative octahedral arrangement is possible when the electrons on the metal ion are rearranged as shown below. As before, lone pairs from the ligands are shown as $\uparrow\downarrow$.



Since low energy inner *d* orbitals are used this is called an *inner orbital complex*. Such complexes are more stable than the outer orbital complexes. The unpaired electrons in the metal ion have been forced to pair up, and so this is now a low-spin complex. In this particular case all the electrons are paired, so the complex will be diamagnetic.

The metal ion could also form four-coordinate complexes, and two different arrangements are possible. *It must be remembered that hybrid orbitals do not actually exist.* Hybridization is a mathematical manipulation of the wave equations for the atomic orbitals involved.



The theory does not explain the colour and spectra of complexes. The theory shows the number of unpaired electrons and from this the magnetic moment can be calculated. However, it does not explain why the magnetic moment varies with temperature.

5.9 | CRYSTAL FIELD THEORY

The crystal field theory is now much more widely accepted than the valence bond theory. It assumes that the attraction between the central metal and the ligands in a complex is purely electrostatic. The transition metal which forms the central atom in the complex is regarded as a positive ion of charge equal to the oxidation state. This is surrounded by negative ligands or neutral molecules which have a lone pair of electrons. If the ligand is a neutral molecule such as NH_3 , the negative end of the dipole in the molecule is directed towards the metal ion. The electrons on the central metal are under repulsive forces from those

on the ligands. Thus the electrons occupy the d orbitals furthest away from the direction of approach of ligands. In the crystal field theory the following assumptions are made.

1. Ligands are treated as point charges.
2. There is no interaction between metal orbitals and ligand orbitals.
3. The d orbitals on the metal all have the same energy (that is degenerate) in the free atom. However, when a complex is formed the ligands destroy the degeneracy of these orbitals, i.e. the orbitals now have different energies. In an isolated gaseous metal ion, the five d orbitals do all have the same energy, and are termed degenerate. If a spherically symmetrical field of negative charges surrounds the metal ion, the d orbitals remain degenerate. However, the energy of the orbitals is raised because of repulsion between the field and the electrons on the metal. In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both of these cases the field produced by the ligands is not spherically symmetrical. Thus the d orbitals are not all affected equally by the ligand field.

Octahedral complexes

In an octahedral complex, the metal is at the centre of the octahedron, and the ligands are at the six corners. The directions x , y and z point to three adjacent corners of the octahedron as shown in Figure 5.6.

The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x , y and z . The lobes of the t_{2g} orbitals (d_{xy} , d_{xz} and d_{yz}) point in between the axes. It follows that the approach of six ligands along the x , y , z , $-x$, $-y$ and $-z$ directions will increase the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals (which point along the axes) much more than it increases the energy of the d_{xy} , d_{xz} and d_{yz} orbitals (which point between the axes). Thus under the influence of an octahedral ligand field the d orbitals split into two groups of different energies (Figure 5.7).

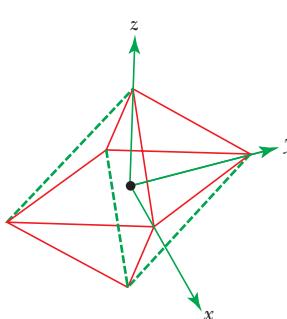


Figure 5.6 The directions in an octahedral complex.

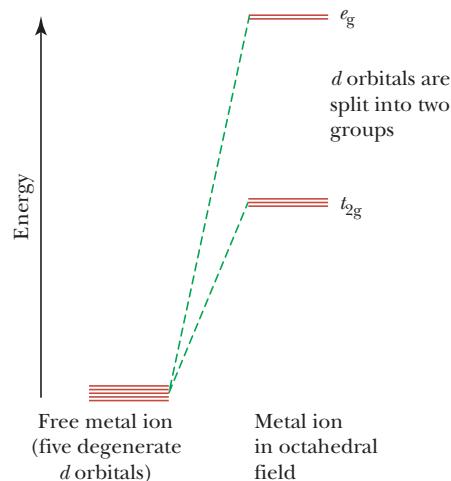


Figure 5.7 Crystal field splitting of energy levels in an octahedral field.

Rather than referring to the energy level of an isolated metal atom, the weighted mean of these two sets of perturbed orbitals is taken as the zero: this is sometimes called the Bari centre. The difference in energy between the two d levels is given either of the symbols Δ_o or $10 Dq$. It follows that the e_g orbitals are $+0.6\Delta_o$ above the average level, and the t_{2g} orbitals are $-0.4\Delta_o$ below the average (Figure 5.8).

The size of the energy gap Δ_o between the t_{2g} and e_g levels can be measured easily by recording the UV-visible spectrum of the complex. Consider a complex like $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. The Ti^{3+} ion has one d electron.

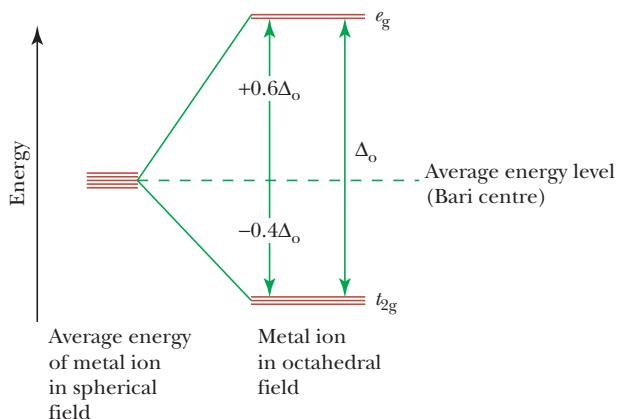


Figure 5.8 Diagram of the energy levels of d orbitals in an octahedral field.

In the complex this will occupy the orbital with the lowest energy, that is one of the t_{2g} orbitals (Figure 5.9a). The complex absorbs light of the correct wavelength (energy) to promote the electron from the t_{2g} level to the e_g level (Figure 5.9b).

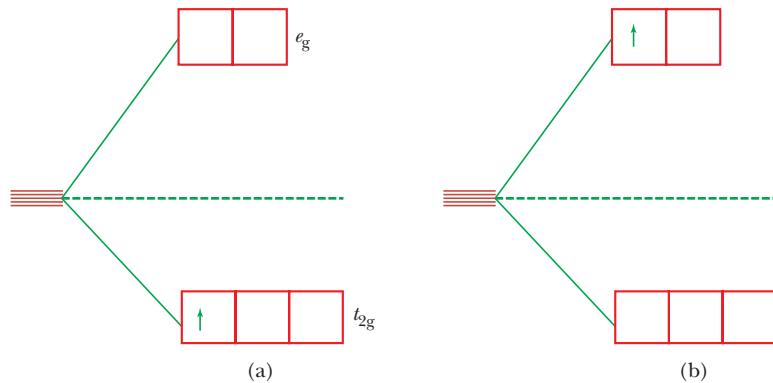


Figure 5.9 d^1 configuration: (a) ground state, (b) excited state.

The electronic spectrum for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is given in Figure 5.10. The steep part of the curve from $27\ 000$ to $30\ 000\text{ cm}^{-1}$ (in the UV region) is due to charge transfer. The $d-d$ transition is the single broad peak with a maximum at $20\ 300\text{ cm}^{-1}$. Since $1\text{ kJ mol}^{-1} = 83.7\text{ cm}^{-1}$, the value of Δ_o for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is $20\ 300/83.7 = 243\text{ kJ mol}^{-1}$. This is much the same as the energy of many normal single bonds (see Appendix F).

The above method is the most convenient way of measuring Δ_o values. However, Δ_o values can also be obtained from values of observed lattice energies and those calculated using the Born–Landé equation (see Chapter 3).

Solutions containing the hydrated Ti^{3+} ion are reddish violet coloured. This is because yellow and green light are absorbed to excite the electron. Thus the transmitted light is the complementary colour red–violet (Table 5.6).

Because of the crystal field splitting of d orbitals, the single d electron in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ occupies an energy level $2/5\Delta_o$ below the average energy of the d orbitals. As a result the complex is more stable. The crystal field stabilization energy (CFSE) is in this case $2/5 \times 243 = 97\text{ kJ mol}^{-1}$.

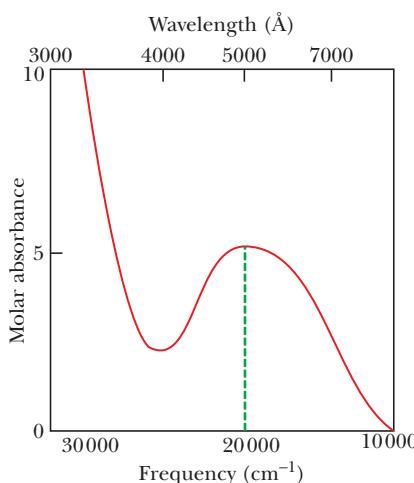


Figure 5.10 Ultraviolet and visible absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

Table 5.6 Colours absorbed and colours observed

Colour absorbed	Colour observed	Wavenumber observed (cm ⁻¹)
Yellow-green	Red-violet	24 000–26 000
Yellow	Indigo	23 000–24 000
Orange	Blue	21 000–23 000
Red	Blue-green	20 000–21 000
Purple	Green	18 000–20 000
Red-violet	Yellow-green	17 300–18 000
Indigo	Yellow	16 400–17 300
Blue	Orange	15 300–16 400
Blue-green	Red	12 800–15 300

The magnitude of Δ_o depends on three factors:

1. The nature of the ligands.
2. The charge on the metal ion.
3. Whether the metal is in the first, second or third row of transition elements.

Examination of the spectra of a series of complexes of the same metal with different ligands shows that the position of the absorption band (and hence the value of Δ_o) varies depending on the ligands which are attached (Table 5.7).

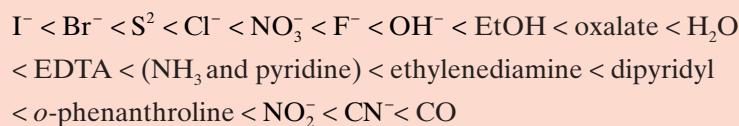
Table 5.7 Crystal field splittings by various ligands

Complex	Absorption peak	
	(cm ⁻¹)	(kJ mol ⁻¹)
[Cr ^{III} Cl ₆] ³⁻	13 640	163
[Cr ^{III} (H ₂ O) ₆] ³⁺	17 830	213
[Cr ^{III} (NH ₃) ₆] ³⁺	21 680	259
[Cr ^{III} (CN) ₆] ³⁻	26 280	314

Ligands which cause only a small degree of crystal field splitting are termed weak field ligands. Ligands which cause a large splitting are called strong field ligands. Most Δ values are in the range 7,000 cm⁻¹ to 30,000 cm⁻¹. The common ligands can be arranged in ascending order of crystal field splitting Δ . The order remains practically constant for different metals, and this series is called the spectrochemical series.

Spectrochemical series

weak field ligands



strong field ligands

The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effects of σ and π bonding. The halides are in the order expected from electrostatic effects. In other cases we must consider covalent bonding to explain the order. A pattern of increasing σ donation is followed:



The crystal field splitting produced by the strong field CN⁻ ligand is about double that for weak field ligands like the halide ions. This is attributed to π bonding in which the metal donates electrons from a filled t_{2g}

orbital into a vacant orbital on the ligand. In a similar way, many unsaturated N donors and C donors may also act as π acceptors.

The magnitude of Δ_o increases as the charge on the metal ion increases.

Table 5.8 Crystal field splittings for hexa-aqua complexes of M^{2+} and M^{3+}

Oxidation state	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
(+II)	Electronic configuration	d^2	d^3	d^4	d^5	d^6	d^7	d^8
	Δ_o in cm^{-1}	—	12 600	13 900	7 800	10 400	9 300	8500
(+ III)	Electronic configuration	d^1	d^2	d^3	d^4	d^5	d^6	d^7
	Δ_o in cm^{-1}	20 300	18 900	17 830	21 000	13 700	18 600	—
	Δ_o in kJ mol^{-1}	243	226	213	(251)	164	222	—

Note: Values in parenthesis for d^4 and d^9 are approximate because of tetragonal distortion.

Table 5.9 Δ_o crystal field splittings in one group

	cm^{-1}	kJ mol^{-1}
$[\text{Co}(\text{NH}_3)_6]^{3+}$	24 800	296
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34 000	406
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41 000	490

For first row transition metal ions, the values of Δ_o for M^{3+} complexes are roughly 50% larger than the values for M^{2+} complexes (Table 5.8).

The value of Δ_o also increases by about 30% between adjacent members down a group of transition elements (Table 5.9). The crystal field stabilization energy in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, which has a d^1 configuration, has previously been shown to be $-0.4\Delta_o$. In a similar way, complexes containing a metal ion with a d^2 configuration will have a CFSE of $2 \times -0.4\Delta_o = -0.8\Delta_o$, by singly filling two of the t_{2g} orbitals. (This is in agreement with Hund's rule that the arrangement with the maximum number of unpaired electrons is the most stable.) Complexes of d^3 metal ions have a CFSE of $3 \times -0.4\Delta_o = -1.2\Delta_o$.

Complexes with a metal ion with a d^4 configuration would be expected to have an electronic arrangement in accordance with Hund's rule (Figure 5.11a) with four unpaired electrons, and the CFSE will be $(3 \times -0.4\Delta_o) + (0.6\Delta_o) = -0.6\Delta_o$. An alternative arrangement of electrons which does not comply with Hund's rule is shown in Figure 5.11b. This arrangement has two unpaired electrons, and the CFSE is

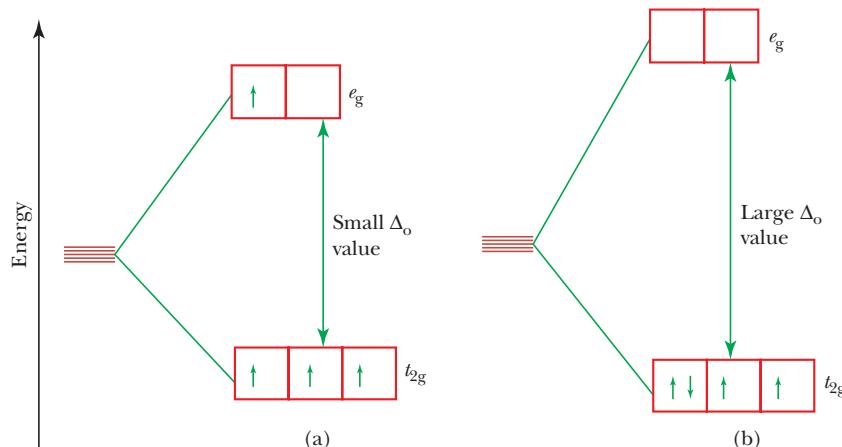


Figure 5.11 High- and low-spin complexes: (a) d^4 high-spin arrangement (weak ligand field); (b) d^4 low-spin arrangement (strong ligand field).

Table 5.10 CFSE and pairing energy for some complexes

Complex	Configuration	Δ_o (cm ⁻¹)	P (cm ⁻¹)	Predicted	Found
[Fe ^{II} (H ₂ O) ₆] ²⁺	d^6	10 400	17 600	high spin	High spin
[Fe ^{II} (CN) ₆] ⁴⁻	d^6	32 850	17 600	low spin	Low spin
[Co ^{III} F ₆] ³⁻	d^6	13 000	21 000	high spin	High spin
[Co ^{III} (NH ₃) ₆] ³⁺	d^6	23 000	21 000	low spin	Low spin

$(4 \times -0.4\Delta_o) = -1.6\Delta_o$. The CFSE is larger than in the previous case. However, the energy P used to pair the electrons must be allowed for, so the total stabilization energy is $-1.6\Delta_o + P$. These two arrangements differ in the number of unpaired electrons. The one with the most unpaired electrons is called 'high-spin' or 'spin-free', and the other one the 'low-spin' or 'spin-paired' arrangement. Both arrangements have been found to exist. Which arrangement occurs for any particular complex depends on whether the energy to promote an electron to the upper e_g level (that is the crystal field splitting Δ_o) is greater than the energy to pair electrons (that is P) in the lower t_{2g} level. For a given metal ion P is constant. Thus the amount of crystal field splitting is determined by the strength of the ligand field. A weak field ligand such as Cl⁻ will only cause a small splitting of energy levels Δ_o . Thus it will be more favourable energetically for electrons to occupy the upper e_g level and have a high-spin complex, rather than to pair electrons. In a similar way, strong field ligands such as CN⁻ cause a large splitting Δ_o . In this case it requires less energy to pair the electrons and form a low-spin complex. (see Table 5.10.).

Similar arguments apply to high- and low-spin complexes of metal ions with d^5 , d^6 and d^7 configurations. These are summarized in Table 5.11.

Table 5.11 CFSE and electronic arrangements in octahedral complexes

Number of d electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment $\mu_s(D)$	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment $\mu_s(D)$
d^1			-0.4	1.73			-0.4	1.73
d^2			-0.8	2.83			-0.8	2.83
d^3			-1.2	3.87			-1.2	3.87
d^4			-1.2 +0.6 = -0.6	4.90			-1.6	2.83
d^5			-1.2 +1.2 = -0.0	5.92			-2.0	1.73
d^6			-1.6 +1.2 = -0.4	4.90			-2.4	0.00
d^7			-2.0 +1.2 = -0.8	3.87			-2.4 +0.6 = -1.8	1.73
d^8			-2.4 +1.2 = -1.2	2.83			-2.4 +1.2 = -1.2	2.83
d^9			-2.4 +1.8 = -0.6	1.73			-2.4 +1.8 = -0.6	1.73
d^{10}			-2.4 +2.4 = -0.0	0.00			-2.4 +2.4 = -0.0	0.00

5.10 | EFFECTS OF CRYSTAL FIELD SPLITTING

In octahedral complexes, the filling of t_{2g} orbitals decreases the energy of a complex, that is makes it more stable by $-0.4 \Delta_o$ per electron. Filling e_g orbitals increases the energy by $+0.6\Delta_o$ per electron. The total crystal field stabilization energy is given by

$$\text{CFSE}_{\text{octahedral}} = -0.4n_{(t_{2g})} + 0.6n_{(e_g)}$$

where $n_{(t_{2g})}$ and $n_{(e_g)}$ are the number of electrons occupying the t_{2g} and e_g orbitals respectively. The CFSE is zero for ions with d^0 and d^{10} configurations in both strong and weak ligand fields. The CFSE is also zero for d^5 configurations in a weak field. All the other arrangements have some CFSE, which increases the thermodynamic stability of the complexes. Thus many transition metal compounds have a higher measured lattice energy (obtained by calculations using the terms in the Born–Haber cycle) than is calculated using the Born–Landé, Born–Meyer or Kapustinskii equations. In contrast, the measured (Born–Haber) and calculated values for compounds of the main groups (which have no CFSE) are in close agreement (Table 5.12). There is also close agreement in MnF_2 which has a d^5 configuration and a weak field ligand: hence there is no CFSE.

Table 5.12 Measured and calculated lattice energies

Compound	Structure	Measured lattice energy (kJ mol ⁻¹)	Calculated lattice energy (kJ mol ⁻¹)	Difference (measured – calculated) (kJ mol ⁻¹)
NaCl	Sodium chloride	-764	-764	0
AgCl	Sodium chloride	-916	-784	-132
AgBr	Sodium chloride	-908	-759	-149
MgF ₂	Rutile	-2908	-2915	+7
MnF ₂	Rutile	-2770	-2746	-24
FeF ₂	Rutile	-2912	-2752	-160
NiF ₂	Rutile	-3046	-2917	-129
CuF ₂	Rutile	-3042	-2885	-157

A plot of the lattice energies of the halides of the first row transition elements in the divalent state is given in Figure 5.12. In the solid, the coordination number of these metals is 6, and so the structures are analogous to octahedral complexes. The graphs for each halide show a minimum at Mn^{2+} , which has a d^5 configuration. In a weak field this has a high-spin arrangement with zero CFSE. The configurations d^0 and d^{10} also have zero CFSE. The broken line through Ca^{2+} , Mn^{2+} and Zn^{2+} represents zero stabilization. The heights of other points above this line are the crystal field stabilization energies.

The hydration energies of the M^{2+} ions of the first row transition elements are plotted in Figure 5.13a.



The ions Ca^{2+} , Mn^{2+} and Zn^{2+} have d^0 , d^5 and d^{10} configurations, and have zero CFSE. An almost straight line can be drawn through these points. The distance of the other points above this line corresponds to the CFSE. Values obtained in this way agree with those obtained spectroscopically. A similar graph of the M^{3+} ions is shown in Figure 5.13b: here the d^0 , d^5 and d^{10} species are Sc^{3+} , Fe^{3+} and Ga^{3+} .

The ionic radii for M^{2+} ions might be expected to decrease smoothly from Ca^{2+} to Zn^{2+} because of the increasing nuclear charge, and the poor shielding by d electrons. A plot of these radii is given in Figure 5.14. The change in size is not regular.

A smooth (broken) line is drawn through Ca^{2+} , Mn^{2+} and Zn^{2+} . These have d^0 , d^5 and d^{10} configurations as the d orbitals are empty, half full or full. These arrangements constitute an almost spherical field round the nucleus. In Ti^{2+} the d electrons occupy orbitals away from the ligands, providing little or no shielding of the nuclear charge. Thus the ligands are drawn closer to the nucleus. The increased nuclear charge has an even greater effect in the case of V^{2+} . At Cr^{2+} the e_g level contains one electron. This is concentrated

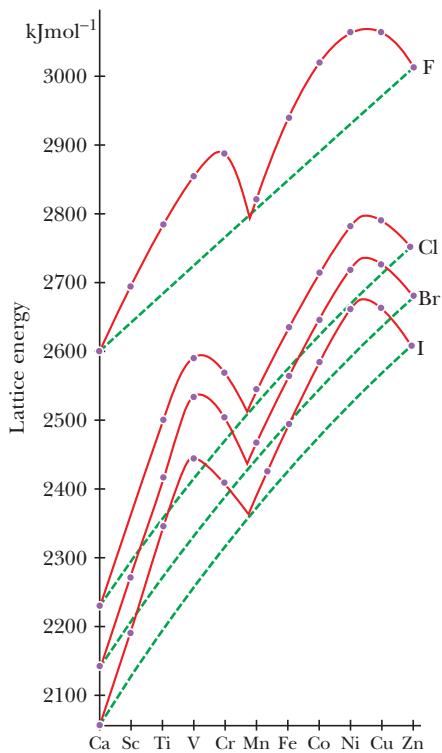
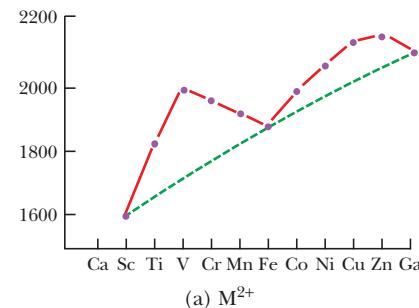
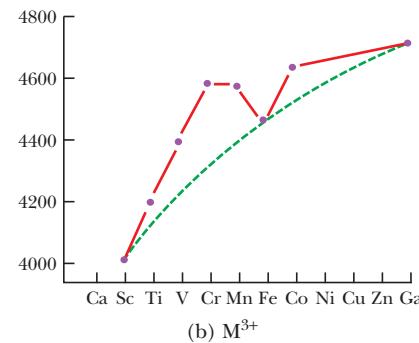


Figure 5.12 CFSE of dihalides of the first transition series. (After T.C. Waddington. Lattice energies and their significance in inorganic chemistry. *Advances in Inorganic Chemistry and Radiochemistry*, 1, Academic Press, New York, 1959.)



(a) M^{2+}



(b) M^{3+}

Figure 5.13 Enthalpies of hydration for M^{2+} and M^{3+} , in kJ mol^{-1} .

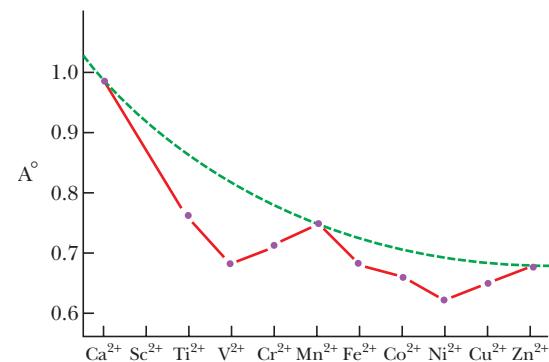


Figure 5.14 Octahedral ionic radii of M^{2+} for first row transition elements.

in the direction of the ligands, thus providing very good shielding. Thus the ligands can no longer approach so closely and the ionic radius increases. This increase in size is continued with the filling of the second e_g orbital at Mn^{2+} . The screening by the e_g orbitals is so good that the radius of Mn^{2+} is slightly smaller than it would be if it were in a truly spherical field. The same sequence of size changes is repeated in the second half of the series.

5.11 | TETRAGONAL DISTORTION OF OCTAHEDRAL COMPLEXES (JAHN-TELLER DISTORTION)

The shape of transition metal complexes is determined by the tendency of electron pairs to occupy positions as far away from each other as possible. This is the same as for the main group compounds and complexes. In addition, the shapes of transition metal complexes are affected by whether the d orbitals are symmetrically or asymmetrically filled.

Repulsion by six ligands in an octahedral complex splits the d orbitals on the central metal into t_{2g} and e_g levels. It follows that there is a corresponding repulsion between the d electrons and the ligands. If the d electrons are symmetrically arranged, they will repel all six ligands equally. Thus the structure will be a completely regular octahedron. The symmetrical arrangements of d electrons are shown in Table 5.13.

Table 5.13 Symmetrical electronic arrangements

Electronic configuration	t_{2g}	e_g	Nature of ligand field	Examples
d^0			Strong or weak	$Ti^{IV}O_2 \cdot [Ti^{IV}F_6]^{2-}$ $[Ti^{IV}Cl_6]^{2-}$
d^3			Strong or weak	$[Cr^{III}(oxalate)_3]^{3-}$ $[Cr^{III}(H_2O)_6]^{3+}$
d^5			Weak	$[Mn^{II}F_6]^{4-}$ $[Fe^{III}F_6]^{3-}$
d^6			Strong	$[Fe^{II}(CN)_6]^{4-}$ $[Co^{III}(NH_3)_6]^{3+}$
d^8			Weak	$[Ni^{II}F_6]^{4-}$ $[Ni^{II}(H_2O)_6]^{2+}$
d^{10}			Strong or weak	$[Zn^{II}(NH_3)_6]^{2+}$ $[Zn^{II}(H_2O)_6]^{2+}$

All other arrangements have an asymmetrical arrangement of d electrons. If the d electrons are asymmetrically arranged, they will repel some ligands in the complex more than others. Thus the structure is distorted because some ligands are prevented from approaching the metal as closely as others. The e_g orbitals point directly at the ligands. Thus asymmetric filling of the e_g orbitals results in some ligands being repelled more than others. This causes a significant distortion of the octahedral shape. In contrast the t_{2g} orbitals do not point directly at the ligands, but point in between the ligand directions. Thus asymmetric filling of the t_{2g} orbitals has only a very small effect on the stereochemistry. Distortion caused by asymmetric filling of the t_{2g} orbitals is usually too small to measure. The electronic arrangements which will produce a large distortion are shown in Table 5.14.

Table 5.14 Asymmetrical electronic arrangements

Electronic configuration	t_{2g}	e_g	Nature of ligand field	Examples
d^4			Weak field (high-spin complex)	Cr (+ II), Mn (+ III)
d^7			Strong field (low-spin complex)	Co (+ II), Ni (+ III)
d^9			Either strong or weak	Cu (+ II)

The two e_g orbitals $d_{x^2-y^2}$ and d_{z^2} are normally degenerate. However, if they are asymmetrically filled then this degeneracy is destroyed, and the two orbitals are no longer equal in energy. If the d_{z^2} orbital contains one more electron than the $d_{x^2-y^2}$ orbital then the ligands approaching along $+z$ and $-z$ will encounter greater repulsion than the other four ligands. The repulsion and distortion result in elongation of the octahedron along the z axis. This is called tetragonal distortion. Strictly it should be called tetragonal elongation. This form of distortion is commonly observed.

If the $d_{x^2-y^2}$ orbital contains the extra electron, then elongation will occur along the x and y axes. This means that the ligands approach more closely along the z axis. Thus there will be four long bonds and two short bonds. This is equivalent to compressing the octahedron along the z axis and is called tetragonal compression. Tetragonal elongation is much more common than tetragonal compression, and it is not possible to predict which will occur.

For example, the crystal structure of CrF_2 is a distorted rutile (TiO_2) structure. Cr^{2+} is octahedrally surrounded by six F^- , and there are four $Cr-F$ bonds of length 1.98–2.01 Å, and two longer bonds of length

2.43 Å. The octahedron is said to be tetragonally distorted. The electronic arrangement in Cr^{2+} is d^4 . F⁻ is a weak field ligand, and so the t_{2g} level contains three electrons and the e_g level contains one electron. The $d_{x^2-y^2}$ orbital has four lobes whilst the d_z orbital has only two lobes pointing at the ligands. To minimize repulsion with the ligands, the single e_g electron will occupy the d_z orbital. This is equivalent to splitting the degeneracy of the e_g level so that d_z is of lower energy, i.e. more stable, and $d_{x^2-y^2}$ is of higher energy, i.e. less stable. Thus the two ligands approaching along the $+z$ and $-z$ directions are subjected to greater repulsion than the four ligands along $+x$, $-x$, $+y$ and $-y$. This causes tetragonal distortion with four short bonds and two long bonds. In the same way MnF_3 contains Mn^{3+} with a d^4 configuration, and forms a tetragonally distorted octahedral structure.

Many Cu(II) salts and complexes also show tetragonally distorted octahedral structures. Cu²⁺ has a d^9 configuration:



To minimize repulsion with the ligands, two electrons occupy the d_z orbital and one electron occupies the $d_{x^2-y^2}$ orbital. Thus the two ligands along $-z$ and $-z$ are repelled more strongly than are the other four ligands.

The examples above show that whenever the d_z and $d_{x^2-y^2}$ orbitals are unequally occupied, distortion occurs. This is known as Jahn–Teller distortion. The Jahn–Teller theorem states that 'Any non-linear molecular system in a degenerate electronic state will be unstable, and will undergo some sort of distortion to lower its symmetry and remove the degeneracy.' More simply, molecules or complexes (of any shape except linear), which have an unequally filled set of orbitals (either t_{2g} or e_g), will be distorted. In octahedral complexes distortions from the t_{2g} level are too small to be detected. However, distortions resulting from uneven filling of the e_g orbitals are very important.

5.12 | SQUARE PLANAR ARRANGEMENTS

If the central metal ion in a complex has a d^8 configuration, six electrons will occupy the t_{2g} orbitals and two electrons will occupy the e_g orbitals. The arrangement is the same in a complex with weak field ligands. The electrons are arranged as shown in Figure 5.15. The orbitals are symmetrically filled, and a regular octahedral complex is formed, for example by $[\text{Ni}^{II}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}^{II}(\text{NH}_3)_6]^{2+}$.

The single electron in the $d_{x^2-y^2}$ orbital is being repelled by four ligands, whilst the electron in the d_z orbital is only being repelled by two ligands. Thus the energy of the $d_{x^2-y^2}$ increases relative to that of d_z . If the ligand field is sufficiently strong, the difference in energy between these two orbitals becomes larger than the energy needed to pair the electrons. Under these conditions, a more stable arrangement arises when both the e_g electrons pair up and occupy the lower energy d_z orbital. This leaves the $d_{x^2-y^2}$ orbital empty (Figure 5.16). Thus four ligands can now approach along the $+x$, $-x$, $+y$ and $-y$ directions without any difficulty, as the $d_{x^2-y^2}$ orbital is empty. However, ligands approaching along the $+z$ and $-z$ directions meet very strong repulsive forces from the filled d_z orbital (Figure 5.17). Thus only four ligands succeed in bonding to the metal. A square planar complex is formed, the attempt to form an octahedral complex being unsuccessful.

The amount of tetragonal distortion that occurs depends on the particular metal ion and ligands. Sometimes the tetragonal distortion may become so large that the d_z orbital is lower in energy than the d_{xy} orbital as shown in Figure 5.18. In square planar complexes of Co^{II} , Ni^{II} and Cu^{II} the d_z orbital has nearly the same energy as the d_{xz} and d_{yz} orbitals. In $[\text{PtCl}_4]^{2-}$ the d_z orbital is lower in energy than the d_{xz} and d_{yz} orbitals.

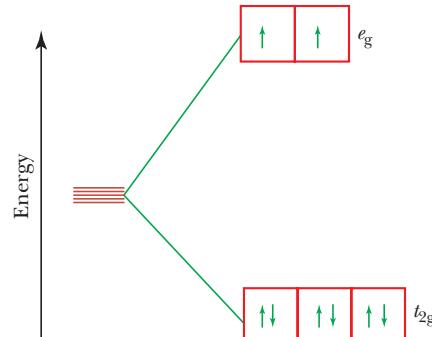


Figure 5.15 d^8 arrangement in weak octahedral field.

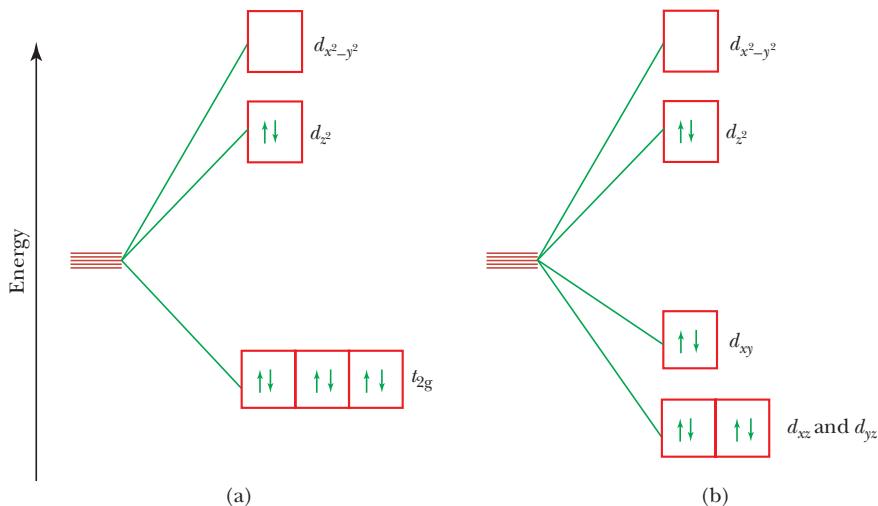


Figure 5.16 d^8 arrangement in very strong octahedral field. Tetragonal distortion splits (a) the e_g level; and (b) also splits the t_{2g} level. The d_{xy} orbital is higher in energy than the d_{xz} or d_{yz} . (For simplicity this is sometimes ignored.)

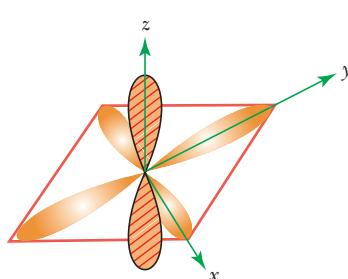


Figure 5.17 d^8 arrangement, strong field. (The d_{x^2} orbital is full, the $d_{x^2-y^2}$ empty.)

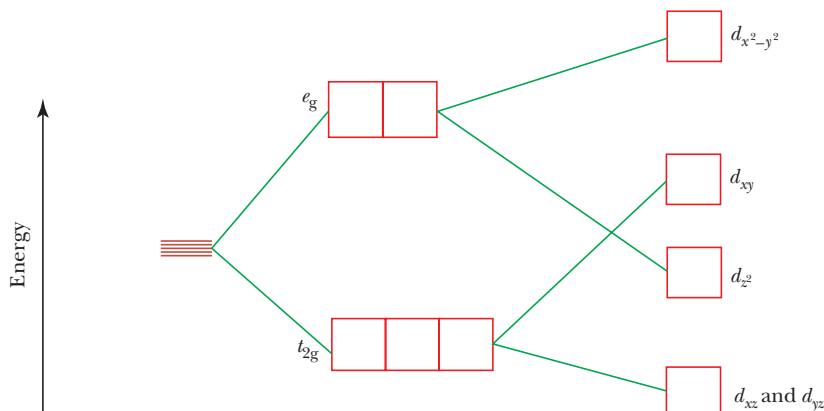


Figure 5.18 Tetragonal distortion.

Square planar complexes are formed by d^8 ions with strong field ligands, for example $[\text{Ni}^{II}(\text{CN})_4]^{2-}$. The crystal field splitting Δ_o is larger for second and third row transition elements, and for more highly charged species. All the complexes of $\text{Pt}^{(II)}$ and $\text{Au}^{(III)}$ are square planar – including those with weak field ligands such as halide ions.

Square planar structures can also arise from d^4 ions in a weak ligand field. In this case the d_z orbital only contains one electron. Some ions that form square planar complexes are given in Table 5.15.

Table 5.15 Ions that form square planar complexes

Electronic configuration	Ions	Type of field	Number of unpaired electrons
d^4	$\text{Cr}^{(II)}$	Weak	4
d^6	$\text{Fe}^{(II)}$	(Haem)	2
d^7	$\text{Co}^{(II)}$	Strong	1
d^8	$\text{Ni}^{(II)}, \text{Rh}^{(I)}, \text{Ir}^{(I)}$	Strong	0
	$\text{Pd}^{(II)}, \text{Pt}^{(II)}, \text{Au}^{(III)}$	Strong and weak	0
d^9	$\text{Cu}^{(II)}, \text{Ag}^{(II)}$	Strong and weak	1

5.13 | TETRAHEDRAL COMPLEXES

A regular tetrahedron is related to a cube. One atom is at the centre of the cube, and four of the eight corners of the cube are occupied by ligands as shown in Figure 5.19.

The directions x , y and z point to the centres of the faces of the cube. The e_g orbitals point along x , y and z (that is to the centres of the faces). The t_{2g} orbitals point between x , y and z (that is towards the centres of the edges of the cube) (Figure 5.20).

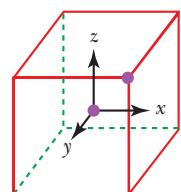
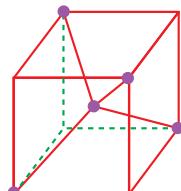


Figure 5.19 Relation of a tetrahedron to a cube.

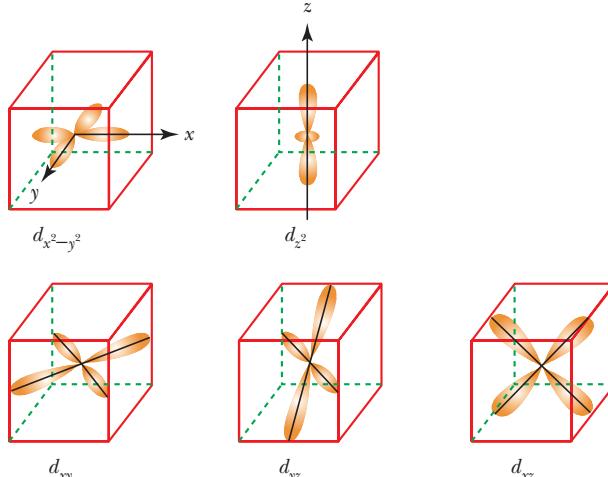


Figure 5.20 Orientation of d orbitals relative to a cube.

The direction of approach of the ligands does not coincide exactly with either the e_g or the t_{2g} orbitals. The angle between an e_g orbital, the central metal and the ligand is half the tetrahedral angle = $109^{\circ}28'/2=54^{\circ}44'$. The angle between a t_{2g} orbital, the central metal and the ligand is $35^{\circ}16'$. Thus the t_{2g} orbitals are nearer to the direction of the ligands than the e_g orbitals. (Alternatively the t_{2g} orbitals are half the side of the cube away from the approach of the ligands, whilst the e_g orbitals are half the diagonal of the cube away.) The approach of the ligands raises the energy of both sets of orbitals. The energy of the t_{2g} orbitals is raised most because they are closest to the ligands. This crystal field splitting is the opposite way round to that in octahedral complexes (Figure 5.21).

The t_{2g} orbitals are $0.4\Delta_t$ above the weighted average energy of the two groups (the Bari centre) and the e_g orbitals are $0.6\Delta_t$ below the average (Figure 5.22).

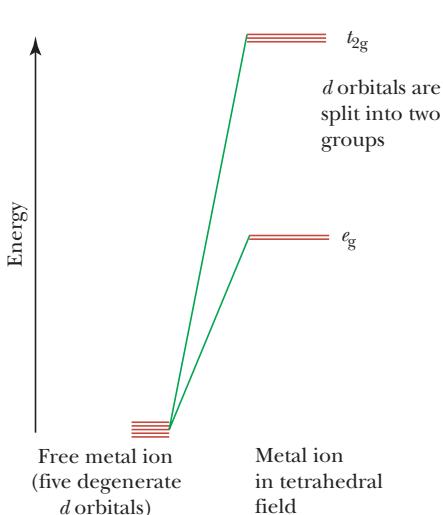


Figure 5.21 Crystal field splitting of energy levels in a tetrahedral field.

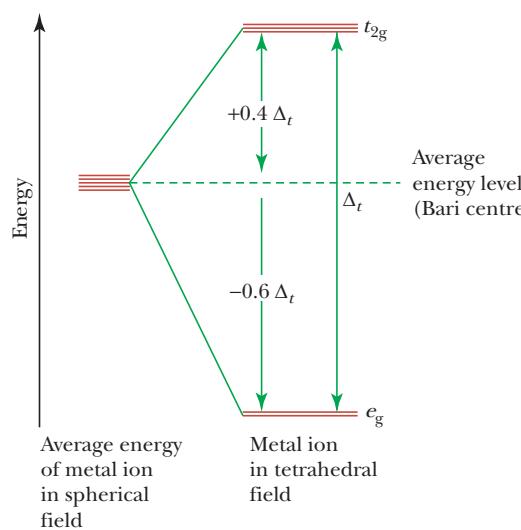


Figure 5.22 Energy levels for d orbitals in a tetrahedral field.

The magnitude of the crystal field splitting Δ in tetrahedral complexes is considerably less than in octahedral fields. There are two reasons for this:

1. There are only four ligands instead of six, so the ligand field is only two thirds the size: hence the ligand field splitting is also two thirds the size
2. The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly a further two thirds.

Thus the tetrahedral crystal field splitting Δ_t roughly $2/3 \times 2/3 = 4/9$ of the octahedral crystal field splitting Δ_0 . Strong field ligands cause a bigger energy difference between t_{2g} and e_g than weak field ligands. However, the tetrahedral splitting Δ_t is always much smaller than the octahedral splitting Δ_0 . Thus it is never energetically favourable to pair electrons, and all tetrahedral complexes are high-spin.

Table 5.16 CFSE and electronic arrangements in tetrahedral complexes

Number of d electrons	Arrangement of electrons		Spin only magnetic moment	Tetrahedral CFSE	Tetrahedral CFSE scaled for comparison with octahedral values, assuming $\Delta_t = \frac{4}{9} \Delta_0$	Octahedral CFSE Δ_0	
	e_g	t_{2g}				Weak field	Strong field
d^1			1.73	-0.6	-0.27	-0.4	-0.4
d^2			2.83	-1.2	-0.53	-0.8	-0.8
d^3			3.87	-1.2 + 0.4 = -0.8	-0.36	-1.2	-1.1
d^4			4.90	-1.2 + 0.8 = -0.4	-0.18	-0.6	-1.6
d^5			5.92	-1.2 + 1.2 = 0.0	-0.00	0.0	-2.0
d^6			4.90	-1.8 + 1.2 = -0.6	-0.27	-0.4	-2.4
d^7			3.87	-2.4 + 1.2 = -1.2	-0.53	-0.8	-1.8
d^8			2.83	-2.4 + 1.6 = -0.8	-0.36	-1.2	-1.2
d^9			1.73	-2.4 + 2.0 = -0.4	-0.18	-0.6	-0.6
d^{10}			0.00	-2.4 + 2.4 = 0.0	0.00	0.0	0.0

The CFSE in both octahedral and tetrahedral environments is given in Table 5.16. This shows that for d^0 , d^5 and d^{10} arrangements the CFSE is zero in both octahedral and tetrahedral complexes. For all other electronic arrangements there is some CFSE, and the octahedral CFSE is greater than the tetrahedral CFSE. It follows that octahedral complexes are generally more stable and more common than tetrahedral complexes. This is partly because there are six bond energy terms rather than four, and partly because there is a larger CFSE term. Despite this some tetrahedral complexes are formed, and are stable. Tetrahedral complexes are favoured:

1. Where the ligands are large and bulky and could cause crowding in an octahedral complex.
2. Where attainment of a regular shape is important. For tetrahedral structures d^0 , d^2 , d^5 , d^7 and d^{10} configurations are regular. Some tetrahedral complexes which are regular are: $\text{Ti}^{IV}\text{Cl}_4$ (e_g^0, t_{2g}^0), $[\text{Mn}^{VII}\text{O}_4]^-$ (e_g^0, t_{2g}^0), $[\text{Fe}^{VI}\text{O}_4]^{2-}$ (e_g^0, t_{2g}^0), $[\text{Fe}^{III}\text{Cl}_4]^-$ (e_g^2, t_{2g}^0), $[\text{Co}^{II}\text{Cl}_4]^{2-}$ (e_g^4, t_{2g}^3) and $[\text{Zn}^{II}\text{Cl}_4]^{2-}$ (e_g^4, t_{2g}^6).
3. When the ligands are weak field, and the loss in CFSE is thus less important.
4. Where the central metal has a low oxidation state. This reduces the magnitude of Δ .

- Where the electronic configuration of the central metal is d^0, d^5 or d^{10} as there is no CFSE.
- Where the loss of CFSE is small, e.g. d^1 and d^6 where the loss in CFSE is $0.13\Delta_o$ or d^2 and d^7 where the loss is $0.27\Delta_o$.

Many transition metal chlorides, bromides and iodides form tetrahedral structures.

5.14 | MAGNETISM

The magnetic moment can be measured using a Gouy balance. If we assume that the magnetic moment arises entirely from unpaired electron spins then the ‘spin only’ formula can be used to estimate n , the number of unpaired electrons. This gives reasonable agreement for complexes of the first row of transition metals.

$$\mu_s = \sqrt{n(n+2)}$$

Once the number of unpaired electrons is known, either the valence bond or the crystal field theory can be used to work out the shape of the complex, the oxidation state of the metal, and, for octahedral complexes, whether inner or outer d orbitals are used. For example, Co (+III) forms many complexes, all of which are octahedral. Most of them are diamagnetic, but $[\text{CoF}_6]^{3-}$ is paramagnetic with an observed magnetic moment of 5.3 BM. Crystal field theory explains this (Figure 5.23).

Co(+II) forms both tetrahedral and square planar four-coordinate complexes. These can be distinguished by magnetic measurements (Figure 5.24).

However, orbital angular momentum also contributes to a greater or lesser degree to the magnetic moment. For the second and third row transition elements not only is this contribution significant, but spin orbit coupling may occur. Because of this, the ‘spin only’ approximation is no longer valid, and there is extensive temperature-dependent paramagnetism. Thus the simple interpretation of magnetic moments in terms of the number of unpaired electrons cannot be extended from the first row of transition elements to the second and third rows. The temperature dependence is explained by the spin orbit coupling. This removes the degeneracy from the lowest energy level in the ground state. Thermal energy then allows a variety of levels to be populated.

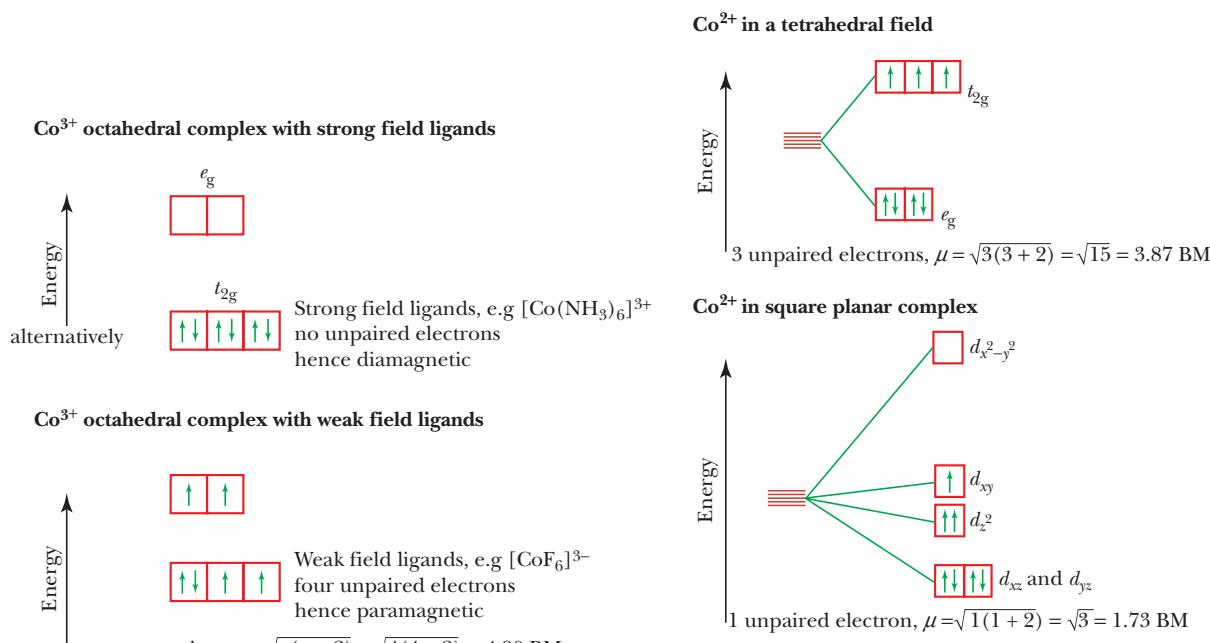


Figure 5.23 Co³⁺ in high-spin and low-spin complexes.

Figure 5.24 Co²⁺ in tetrahedral and square planar complexes.

5.15 | EXTENSION OF THE CRYSTAL FIELD THEORY TO ALLOW FOR SOME COVALENCY

The crystal field theory is based on purely electrostatic attraction. At first sight this seems to be a most improbable assumption. Nevertheless, the theory is remarkably successful in explaining the shapes of complexes, their spectra and their magnetic properties. Calculations can be carried out quite simply. The disadvantage of the theory is that it ignores evidence that some covalent bonding does occur in at least some transition metal complexes:

1. Compounds in the zero oxidation state such as nickel carbonyl $[\text{Ni}^0(\text{CO})_4]$ have no electrostatic attraction between the metal and the ligands. Thus the bonding must be covalent.
2. The order of ligands in the spectrochemical series cannot be explained solely on electrostatic grounds.
3. There is some evidence from nuclear magnetic resonance and electron spin resonance that there is some unpaired electron density on the ligands. This suggests the sharing of electrons, and hence some covalency.

The Racah interelectron repulsion parameter B is introduced into the interpretation of spectra. This makes allowance for covalency arising from the delocalization of d electrons from the metal onto the ligand. If B is reduced below the value for a free metal ion, the d electrons are delocalized onto the ligand. The more B is reduced the greater the delocalization and the greater the amount of covalency. In a similar way an electron delocalization factor k can be used in interpreting magnetic measurements.

5.16 | NOMENCLATURE OF COORDINATION COMPOUNDS

The rules for systematic naming of coordination compounds are discussed as follows:

1. The name of the cationic part is written first followed by the anionic part.
2. The name of the ligand is listed before the name(s) of the central atom(s).
3. No space is left between the names that refer to the same coordination entity.
4. Ligand names are listed in the alphabetical order (multiplicative prefixes indicating the number of ligands are not considered in determining that order).
5. a. When there are several ligands of the same kind, prefixes like di, tri, tetra, penta, hexa, etc. are used before the name of the ligand to indicate their number.
b. When the name of the ligand includes terms like di, tri, tetra, etc. then prefixes like bis, tris, tetrakis, pentakis, etc. are written before the name of the ligand, and the ligand name is kept within brackets to avoid ambiguity. For example,
 - (i) $(\text{NH}_3)_2$: diammine
 - (ii) Me_2NH : dimethylamine
 - (iii) $(\text{en})_2$: bis (ethylenediamine)
 - (iv) $(\text{NH}_2\text{Me})_2$: bis (methylamine)
(to make it distinct from dimethylamine)
- c. There is no deletion of vowels or use of a hyphen. For example,
 $(\text{NH}_3)_4$: tetr**a**mmine.
6. The names of cationic ligands are ended with 'ium'. For example,
 - (i) $\overset{+}{\text{NO}}$: nitrosylum
 - (ii) $\text{NH}_2 - \overset{+}{\text{NH}_3}$: hydrazinium
7. The neutral ligand names have no special endings. For example,
 - (i) H_2O : aqua
 - (ii) NH_3 : ammine
 - (iii) CO : carbonyl
 - (iv) NO : nitrosyl

- (iv) MeCONH_2 : acetamide
- (v) MeNH_2 : methanamine
- (vi) MePH_2 : methylphosphane
- (vii) MeO S(=O)OH : methyl hydrogen sulphite
- (ix) Me_2O : dimethyl ether
- (x) Me_2S : dimethyl thioether
- (xi) C_6H_6 : benzene

8. The names of anionic ligands are ended with 'o'. For example,

a. Ligand names ending with 'ate' are changed to 'ato'.

- (i) NO_3^- : nitrato
- (ii) CO_3^{2-} : carbonato
- (iii) MeCO_2^- : acetato or ethanoato
- (iv) acac^- : acetylacetato

b. Ligand names ending with 'ite' are changed to 'ito'.

- (i) SO_3^{2-} : sulphito
- (ii) ClO_2^- : chlorito
- (iii) OCl : hypochlorito
- (iv) NO_2^- : nitrito

c. Ligand names ending with 'ide' are changed to 'ido'.

- (i) F^- : fluorido
- (ii) Cl^- : chlorido
- (iii) CN^- : cyanido
- (iv) H^- : hidrido
- (v) OH^- : hydroxido
- (vi) NH_2^- : amido
- (vii) D^- : deuterido or $[^2\text{H}]$ hidrido

d. The anionic organic ligands where the C atom is the donor atom, are not ended with 'o'. For example,

- (i) CH_3^- : methyl (not methyo)
- (ii) $\text{CH}_2\text{CH}=\text{CH}_2$: allyl
- (iii) Ph^- : phenyl
- (iv) C_3H_5^- : cyclopropyl
- (v) $\text{CH}_2=\text{CH}$: vinyl

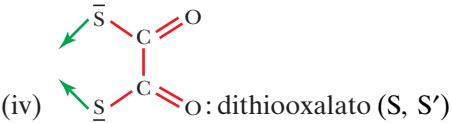
e. For the π - donors, the prefix like η^x is to be used, where η indicates π - electron donation and x is known as the hapticity of the ligand, i.e. the number of atoms involved in the π - donation. For example,

- (i) $\pi-\text{C}_5\text{H}_5^-$: η^5 - cyclopentadienyl or pentahaptocyclopentadienyl
- (ii) $\pi-\text{C}_6\text{H}_6$: η^6 - benzene or hexahaptobenzene
- (iii) $\pi-\text{C}_3\text{H}_5^-$: η^3 - allyl or trihaptoallyl

f. Ambidentate ligands are named as follows:

- (i) $\leftrightarrow:\bar{\text{C}}\text{N}$: cyanido or cyanido - C
 $\leftrightarrow:\text{N}\bar{\text{C}}$: isocyanido or cyanido - N
- (ii) $\leftrightarrow:\text{NO}_2^-$: nitro or nitrito - N
 $\leftrightarrow\text{ON}\bar{\text{O}}$: nitrito or nitrito - O
- (iii) $\leftrightarrow:\bar{\text{O}}\text{CN}$: cyanato or cyanato - O
 $\leftrightarrow:\text{NC}\bar{\text{O}}$: isocyanato or cyanato - N

- (iv) $\leftrightarrow \bar{S}CN^-$: thiocyanato or thiocyanato – S
 $\leftrightarrow NC\bar{S}^-$: isothiocyanato or thiocyanato – N



9. For anionic complexes, metal names are ended with ‘ate’, i.e. ‘ate’ is to replace ‘ium’, ‘um’, or ‘enum’ in the metal’s name. For example,

- (i) Aluminium : Aluminate
- (ii) Platinum : Platinate
- (iii) Molybdenum : Molybdate
- (iv) Zinc : Zincate
- (v) Nickel : Nickelate
- (vi) Cobalt : Cobaltate
- (vii) Iron : Ferrate
- (viii) Manganese : Manganate

10. The oxidation number of the central atom is written in Roman numerals within brackets, after the name of the central atom. For example, as. (II), (-I), (0), etc.

Alternatively, the charge on a coordination entity may be indicated. The net charge is written in Arabic numerals, with the number preceding the charge sign and enclosed in parenthesis. It follows the name of the central atom (including the ending ‘ate’ if applicable) without the intervention of a space. For example,

- (i) $K_4[Fe(CN)_6]$: potassium hexacyanidoferate (II)
or potassium hexacyanidoferate (4-)
or tetrapotassium hexacyanidoferate
- (ii) $K_2[OsCl_5N]$: potassium pentachloridonitridoosmate (2-)
or potassium pentachloridonitridoosmate (VI)
- (iii) $[CuCl_2\{O=C(NH_2)_2\}_2]^0$: dichloridobis (urea) copper (II)
- (iv) $[CoCl(NH_3)_5]Cl_2$: pentamminechloridocobalt (III) chloride
or pentaamminechloridocobalt (2+) chloride

11. If there is any water of crystallization, it is to included in the name. For example,



These rules are illustrated by the following examples:

$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
$[CoCl(NH_3)_5]^{2+}$	Pentaamminechloridocobalt(III) ion
$[CoSO_4(NH_3)_4]NO_3$	Tetraamminesulphatocobalt(III) nitrate
$[Co(NO_2)_3(NH_3)_3]$	Triaminetrinitrocobalt(III)
$[CoCl \cdot CN \cdot NO_2 \cdot (NH_3)_3]$	Triamminechloridocyanonitrocobalt(III)
$[Zn(NCS)_4]^{2-}$	Tetrathiocyanato-N-zincate(II) ion

$[\text{Cd}(\text{SCN})_4]^{2-}$	Tetrathiocyanato-S-cadmiate(II) ion
$\text{Li}[\text{AlH}_4]$	Lithium tetrahydridoaluminate(III) (<i>lithium aluminium hydride</i>)
$\text{Na}_2[\text{ZnCl}_4]$	Sodium tetrachloridozincate(II)
$\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)\text{NH}_3]$	Potassium amminedicyanodioxoperoxo chromate(VI)
$[\text{Pt}(\text{py})_4][\text{PtCl}_4]$	Tetrapyridineplatinum(II) tetrachloridoplatinate(II)
$[\text{Cr}(\text{en})_3]\text{Cl}_3$	<i>d</i> or <i>l</i> Tris(ethylenediamine)chromium(III) chloride
$[\text{CuCl}_2(\text{CH}_3\text{NH}_2)_2]$	Dichloridobis(methylamine)copper(II)

5.17 | ISOMERISM

Compounds that have the same chemical formula but different structural arrangements are called isomers. Because of the complicated formulae of many coordination compounds, the variety of bond types and the number of shapes possible, many different types of isomerism occur. Werner's classification into polymerization, ionization, hydrate linkage, coordination, coordination position, and geometric and optical isomerism is still generally accepted.

Polymerization isomerism

This is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights. Thus $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)\text{Cl}_3]_2$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}_2][\text{PtCl}_4]$

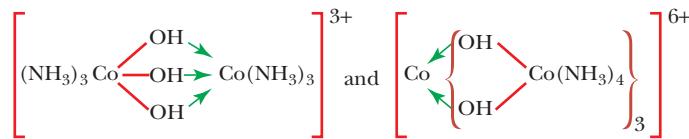


Figure 5.25 Polymerization isomers.

all have the same empirical formula. Polymerization isomerism may be due to a different number of nuclei in the complex, as shown in Figure 5.25.

Ionization isomerism

This type of isomerism is due to the exchange of groups between the complex ion and the ions outside it. $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ is red-violet. An aqueous solution gives a white precipitate of BaSO_4 with BaCl_2 solution, thus confirming the presence of free SO_4^{2-} ions. In contrast $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ is red. A solution of this complex does not give a positive sulphate test with BaCl_2 . It does give a cream-coloured precipitate of AgBr with AgNO_3 , thus confirming the presence of free Br^- ions. Note that the sulphate ion occupies only one coordination position even though it has two negative charges. Other examples of ionization isomerism are $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$, and $[\text{Co}(\text{en})_2\text{NO}_2 \cdot \text{Cl}]\text{SCN}$, $[\text{Co}(\text{en})_2\text{NO}_2 \cdot \text{SCN}]\text{Cl}$ and $[\text{Co}(\text{en})_2\text{Cl} \cdot \text{SCN}]\text{NO}_2$.

Hydrate isomerism

This type of isomerism is shown by compounds having the same formula but differing only in the number of water molecules of crystallization. More broadly, it can also be called solvent isomerism to include other solvents also (like NH_3 or other ligands) present in a similar manner. Some examples of hydrate isomerism are as follows

1. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ can exist in following forms:
 $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$; violet (three chloride ions)

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$: bright blue green (two chloride ions)

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$: dark green (one chloride ion)

$[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$: dark green (no chloride ion)

2. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Br}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl} \cdot \text{H}_2\text{O}$.

3. $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$.

Note that hydrate isomerism is also a kind of ionization isomerism.

Linkage isomerism

Certain ligands contain more than one atom which could donate an electron pair. Thus this type of isomerism is shown by ambidentate ligands. For example, in the NO_2^- ion, either N or O atoms can act as the electron pair donor. Thus there is the possibility of isomerism. Two different complexes $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ have been prepared, each containing the NO_2^- group in the complex ion. One is red and is easily decomposed by acids to give nitrous acid. It contains $\text{Co}-\text{ONO}$ and is a nitrito complex. The other complex is yellow and is stable to acids. It contains the $\text{Co}-\text{NO}_2$ group and is a nitro compound. The two materials are represented in Figure 5.26.

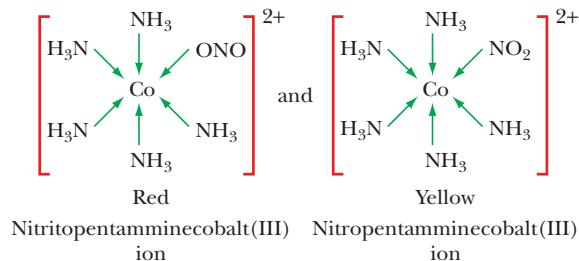
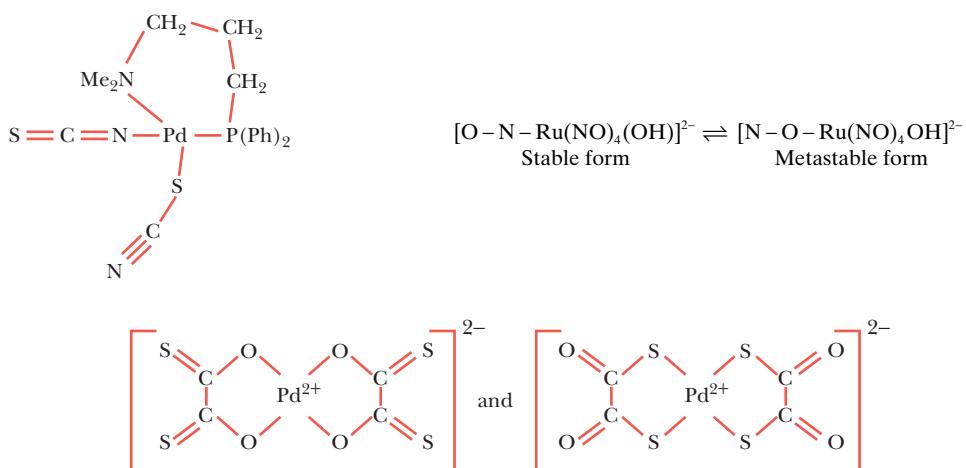


Figure 5.26 Nitrito and nitro complexes.

This type of isomerism also occurs with other ligands such as SCN^- , OCN^- , $\text{S}_2\text{O}_3^{2-}$, CN^- , NOS^- , NO and $\text{C}_2\text{O}_2\text{S}_2^{2-}$ (dithiooxalate ion). For example,



Coordination isomerism

When both the positive and negative ions are complex ions, isomerism may be caused by the interchange of ligands between the anion and cation, for example $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$. Intermediate types between these extremes are also possible. For example,

Formula	Possible number of isomers
$[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Cr}(\text{NO}_2)_6]^{3-}$	6
$[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{NO}_2)_6]^{3-}$	3
$[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{PtCl}_4]^{2-}$	2
$[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{CuCl}_4]^{2-}$	4
$[\text{Ni}(\text{NH}_3)_6]^{3+}[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$	4
$[\text{Ni}(\text{en})_3]^{3+}[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$	4

Coordination position isomerism

In polynuclear complexes an interchange of ligands between the different metal nuclei gives rise to positional isomerism. An example of this type of isomerism is given in Figure 5.27.

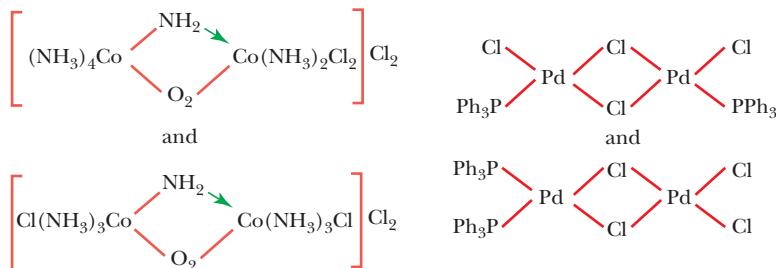


Figure 5.27 Coordination position isomers.

Geometrical isomerism and optical isomerism

In disubstituted complexes, the substituted groups may be adjacent or opposite to each other. This gives rise to geometric isomerism. This type of isomerism is observed in complexes with coordination number four, five and six.

If a molecule is asymmetric, it cannot be superimposed on its mirror image. The molecule and its mirror image have the type of symmetry as shown by the left and right hands and are called an enantiomeric pair. The two forms are optical isomers. They are called either *dextro* or *laevo* (often shortened to *d* or *l*), depending on the direction in which they rotate the plane of polarized light in a polarimeter. (*d* rotates to the right, *l* to the left.) Optical isomerism is common in octahedral complexes involving bidentate groups.

The geometrical and optical isomerism for complexes having coordination numbers four, five and six is discussed as follows.

1. For coordination number 6

The complexes with coordination number 6 can exist in octahedral geometry. The following cases may arise in complexes with octahedral geometry.

a. All ligands are monodentate, having no chiral centre: The various structures possible are listed below. Here M is the metal ion and a, b, c, d, e and f represent monodentate ligands.

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
Ma_6	1	0	1
Ma_5b	1	0	1

(Continued)

(Continued)

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$Ma_4 b_2$	2	0	2
$Ma_4 bc$	2	0	2
$Ma_3 b_3$	2	0	2
$Ma_3 b_2 c$	3	0	3
$Ma_3 bcd$	5	1	4
$Ma_2 b_2 c_2$	6	1	5
$Ma_2 b_2 cd$	8	2	6
$Ma_2 bcde$	15	6	9
$Mabcdef$	30	15	15

b. When ligands are bidentate symmetrical and monodentate type, having no chiral centre: The various structures possible are listed below. Here M is the metal ion, AA is a bidentate symmetrical ligand and a, b, c, and d represent monodentate ligands.

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$[M(AA)_3]$	2	1	1
$[M(AA)_2a_2]$	3	1	2
$[M(AA)_2ab]$	3	1	2
$[M(AA)a_4]$	1	0	1
$[M(AA)a_3b]$	2	0	2
$[M(AA)a_2b_2]$	4	1	3
$[M(AA)a_2bc]$	6	2	4
$[M(AA)abcd]$	12	6	6

c. When ligands are bidentate unsymmetrical and monodentate type having no chiral centre: The various structures possible are listed below. Here M is the metal ion, AB is a bidentate unsymmetrical ligand and a, b, c, and d represent monodentate ligands.

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$[M(AB)_3]$	4	2	2
$[M(AB)_2a_2]$	8	3	5
$[M(AB)_2ab]$	11	5	6
$[M(AB)a_4]$	1	0	1
$[M(AB)a_3b]$	4	1	3
$[M(AB)a_2b_2]$	6	2	4
$[M(AB)a_2bc]$	12	5	7
$[M(AB)abcd]$	24	12	12

Some examples of each kind are illustrated as follows:

(i) For $[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm}$: The various structures possible are shown in Figure 5.28.

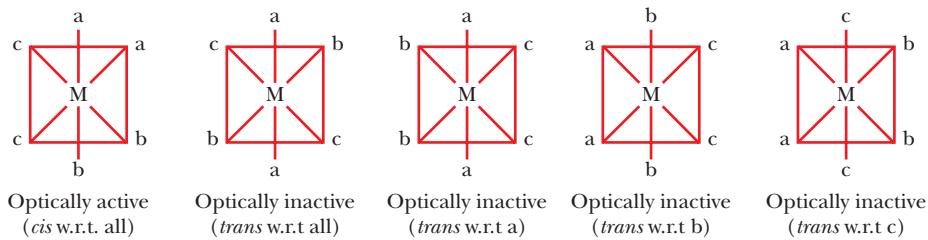


Figure 5.28 Possible structures for octahedral complexes of the type $[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm}$.

(ii) For $[\text{M}(\text{AA})\text{a}_2\text{bc}]^{n\pm}$: The various structures possible are shown in Figure 5.29.

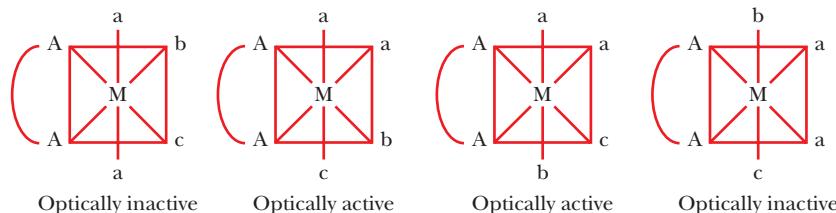


Figure 5.29 Possible structures for octahedral complexes of the type $[\text{M}(\text{AA})\text{a}_2\text{bc}]^{n\pm}$.

(iii) For $[\text{M}(\text{AB})\text{a}_2\text{b}_2]^{n\pm}$: The various structures possible are shown in Figure 5.30.

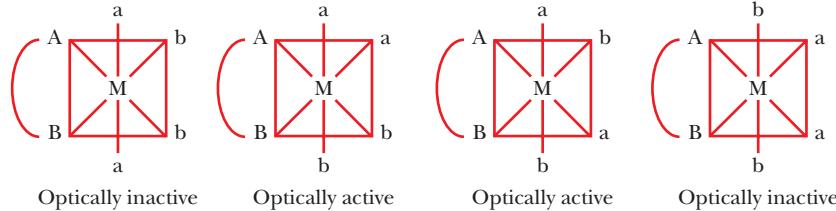


Figure 5.30 Possible structures for octahedral complexes of the type $[\text{M}(\text{AB})\text{a}_2\text{b}_2]^{n\pm}$.

(iv) For Ma_3b_3 : The various structures possible are shown in Figure 5.31.

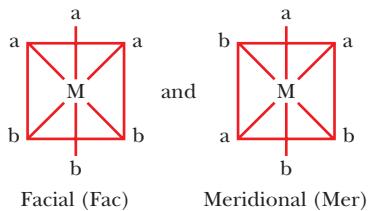


Figure 5.31 Possible structures for octahedral complexes of the type Ma_3b_3 .

2. For coordination number 5

- a. The formula Ma_5 can exist in two possible geometries, i.e. trigonal bipyramidal and square pyramidal. These two are also called allogen isomers (Figure 5.32).

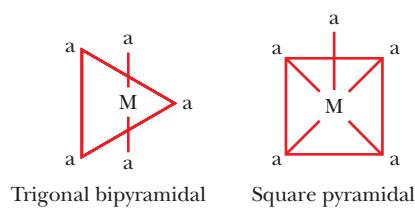


Figure 5.32 Possible structures for complexes of the type Ma_5 .

- b.** The formula Ma_2b_3 can exist in six possible geometries as shown in Figure 5.33.

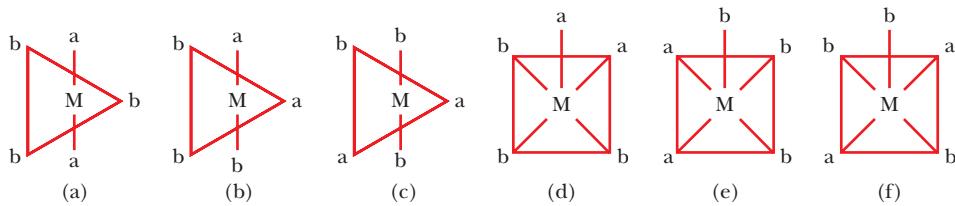


Figure 5.33 Possible structures for complexes of the type Ma_2b_3 . Here (a), (b), (c) are geometrical isomers of each other but any one of (a), (b), (c) and any one of (d), (e), (f) are allogon isomers of each other.

3. For coordination number 4

The complexes with coordination number four (e.g. Ma_4) can have two possible geometries, i.e. tetrahedral or square planar (Figure 5.34).

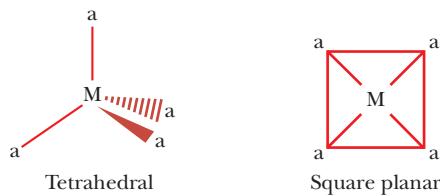


Figure 5.34 Possible structures for complexes with coordination number four.

a. For tetrahedral geometry:

- (i) If the ligands are different, then no geometrical isomerism is observed in tetrahedral geometry, i.e. complexes of the type Mabcd exist as two optical isomers only (Figure 5.35).

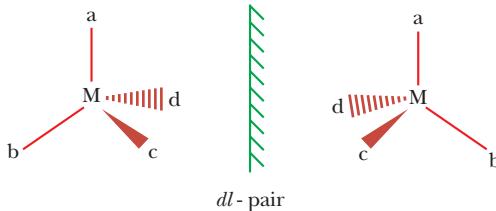
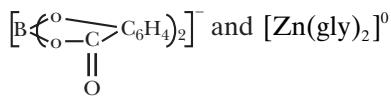


Figure 5.35 Possible structures for complexes of the type Mabcd .

- (ii) If symmetrical bidentate ligands having no chiral center are present, then the complexes are optically inactive. For example, the following compounds are optically inactive: $[\text{Zn}(\text{acac})_2]^0$, $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$ and $[\text{B}(\text{C}_6\text{H}_4)_2]^-$
- (iii) If unsymmetrical bidentate ligands are present, then the compound will be optically active. For example, the following compounds are optically active:



b. For square planar geometry:

- (i) The complexes with formula $[\text{Ma}_4]^{n\pm}$, $[\text{Ma}_3\text{b}]^{n\pm}$, $[\text{M}(\text{AA})_2]^{n\pm}$, $[\text{M}(\text{AA})\text{a}_2]^{n\pm}$ and $[\text{M}(\text{AB})\text{a}_2]^{n\pm}$ do not show geometrical isomerism since possible geometry is only one. Here, a, b are simple monodentate ligands; AA is a symmetrical bidentate ligand and AB is an unsymmetrical bidentate ligand, all having no chiral centre.
- (ii) The complexes with formulae $[\text{Ma}_2\text{b}_2]^{n\pm}$ and $[\text{Ma}_2\text{bc}]$ can have two geometrical isomers, as shown in Figure 5.36 a and 5.36 b respectively.

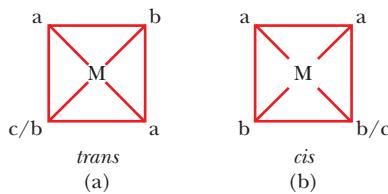


Figure 5.36 Geometrical isomers for complexes of the type $[Ma_2b_2]^{n\pm}$ and $[Ma_2bc]$.

- (iii) The complexes with formula $[Mabcd]^{n\pm}$ can have three geometrical isomers (Figure 5.37). For these isomers, *cis* and *trans* terminology is not applicable or it is to be mentioned with respect to a, b or b, c, etc.

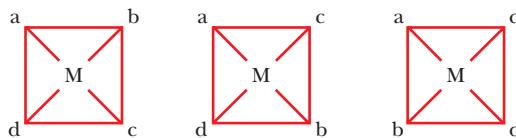


Figure 5.37 Geometrical isomers for complexes of the type $[Mabcd]^{n\pm}$.

- (iv) For complex with the type $[M(AB)_2]^{n\pm}$, two geometrical isomers are possible (Figure 5.38).



Figure 5.38 Geometrical isomers for complexes of the type $[M(AB)_2]^{n\pm}$.

- (v) In complexes of the type $[M(AB)ab]^{n\pm}$, two geometrical isomers are possible (Figure 5.39).

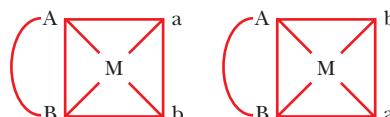


Figure 5.39 Geometrical isomers for complexes of the type $[M(AB)ab]^{n\pm}$.

- (vi) The complexes of the type $[M(AA)_2]^{n\pm}$ can show geometrical isomerism if the ligand AA has a chiral centre. For example, consider the geometrical isomers of $[\text{Pt}(\text{bn})_2]^{2+}$ (Figure 5.40), where $\text{bn} : \text{CH}_3 - \overset{*}{\text{CH}}(\text{NH}_2) - \overset{*}{\text{CH}}(\text{NH}_2) - \text{CH}_3$,

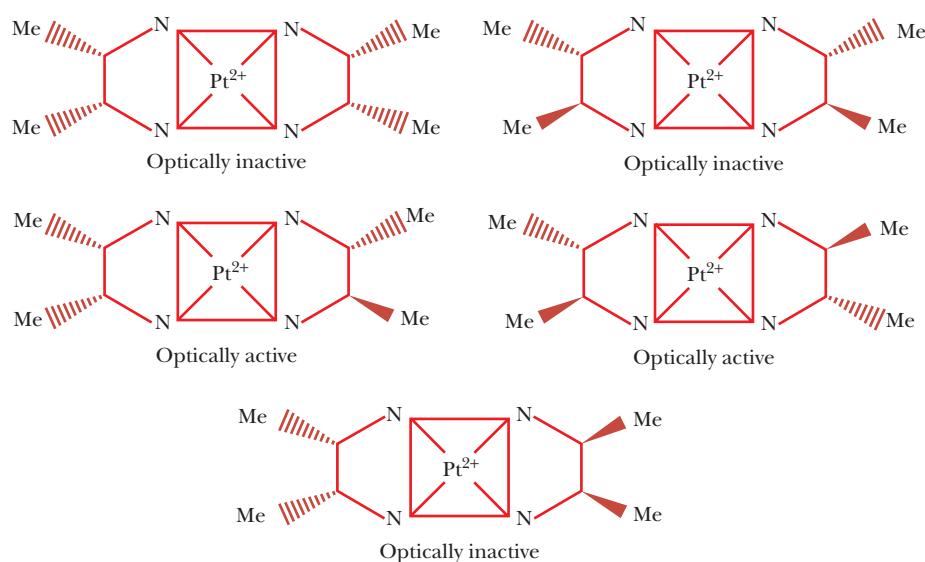


Figure 5.40 Geometrical isomers of $[\text{Pt}(\text{bn})_2]^{2+}$.

- (vii) The complexes of the type $[M(AB)_2]^{n\pm}$ can show geometrical as well as optical isomerism if the ligand AB has a chiral centre. For example, the compound $[Pd(NH_2 - CH(CH_3) - CO_2)_2]^0$ can have four geometrical isomers (Figure 5.41).

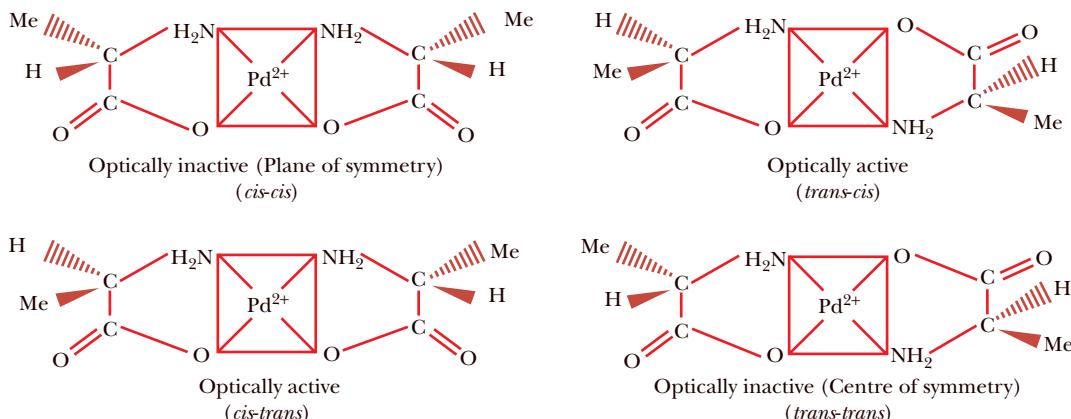


Figure 5.41 Geometrical isomers of $[\text{Pd}(\text{NH}_2 - \text{CH}(\text{CH}_3) - \text{CO}_2^-)_2]^0$:

- (viii) Geometrical isomers are possible for square planar binuclear complexes of the type, $[\text{Pd}_2\text{Cl}_4(\text{PPh}_3)_2]$ (Figure 5.42)

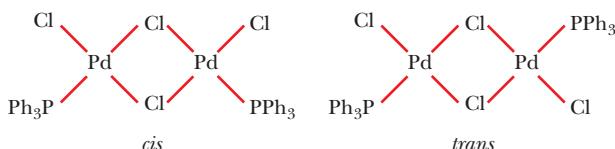


Figure 5.42 Geometrical isomers of $[\text{Pd}_2\text{Cl}_4(\text{PPh}_3)_2]$.

SINGLE CORRECT CHOICE TYPE QUESTIONS

8. Which of the following complex has low spin?
 (A) $K_2[Fe(CN)_6]$
 (B) $K_3[Fe(CN)_6]$
 (C) $K_3[Co(OX)_3]$
 (D) All of these

9. Which of the following complex is optically inactive but its other geometrical isomer is optically active?
 (A) *trans*-tetraquaquadichloridocobalt (III) nitrate
 (B) *mer*-triaquaquatrifluoridocobalt (III)
 (C) *trans*-diamminebis (ethane 1, 2 diamine) cobalt (III) chloride
 (D) *trans*-diamminedichloridoplatinum (II)

10. Which of the following complexes is colourless?
 (A) MnO_4^-
 (B) $[Ni(H_2O)_6]^{2+}$
 (C) $[Cu(CH_3CN)_4]^+$
 (D) $[Cr(H_2O)_6]^{3+}$

11. The correct statement is
 (A) $[NiCl_4]^{2-}$ is sp^3 hybridized and paramagnetic in nature.
 (B) $[PtCl_4]^{2-}$ is dsp^2 hybridized and paramagnetic in nature.
 (C) $[Ni(CO)_4]$ is dsp^2 hybridized and diamagnetic in nature.
 (D) $[Co(H_2O)_6]^{3+}$ is sp^3d^2 hybridized and diamagnetic in nature.

12. Which of the following complex is most stable?
 (A) $[Co(H_2O)_6]Cl_3$
 (B) $K_3[Co(CN)_6]$
 (C) $K_3[Co(OX)_3]$
 (D) $K_3[CoF_6]$

13. The geometries of $[Co(CO)_4]^-$ and $[Cd(CN)_4]^{2-}$ are
 (A) both square planar.
 (B) both tetrahedral.
 (C) tetrahedral and square planar, respectively.
 (D) square planar and tetrahedral, respectively.

14. Which of the following species exists as optically inactive form?
 (A) $[Fe(en)_3]Cl_3$
 (B) $[RhCl(PPh_3)(CO)(H_2O)]$
 (C) $[Pd(en)_2Cl_2]$
 (D)

15. Which of the following ligands can act as chelating agent but does not have a chiral centre?
 (A) nta³⁻ (B) bn
 (C) pn (D) None of these

16. Which type of isomerism may be shown by the complex $[Ru(NH_3)_4(H_2O)(S_2O_3)]NO_3$?
 (A) Ionization isomerism
 (B) Linkage isomerism
 (C) Geometrical isomersim
 (D) All of these

17. Select correct statement about this complex $[Pt(OX)(py)_2(O_2)(H_2O)]$
 (A) Oxidation state of O_2 is -1.
 (B) EAN of Pt is 86.
 (C) Complex will show geometrical as well as optical isomerism.
 (D) Both (B) and (C).

18. Select the incorrect statement about metal carbonyl complex compounds.
 (A) Metal-carbon bonds in metal carbonyls possess both σ and π character.
 (B) Due to synergic bonding metal-carbon bond becomes weak.
 (C) Due to synergic bonding carbon-oxygen bond strength decreases.
 (D) In metal carbonyls the extent of synergic bonding will increase with increase in negative charge on central metal ion.

19. In which of the following complexes, spin only magnetic moment is independent of the nature of ligand?
 (L = monodentate ligand)
 (A) $[NiL_4]^{II}$ (B) $[CoL_6]^{II}$
 (C) $[FeL_6]^{III}$ (D) $[CrL_6]^{III}$

20. Match the complexes with their characteristics.

Column-I	Column-II
(P) $[Ni(CN)_4]^{2-}$	(1) Spin magnetic moment $= \sqrt{8} BM$
(Q) $Fe(CO)_5$	(2) sp^3 hybridized state of central metal
(R) $[MnBr_4]^{2-}$	(3) dsp^2 hybridized state of central metal
(S) $[Ni(NH_3)_6]^{2+}$	(4) Trigonal bipyramidal complex

Code:
 P Q R S
 (A) 3 4 1 2
 (B) 3 4 2 1
 (C) 1 4 3 2
 (D) 2 4 3 1

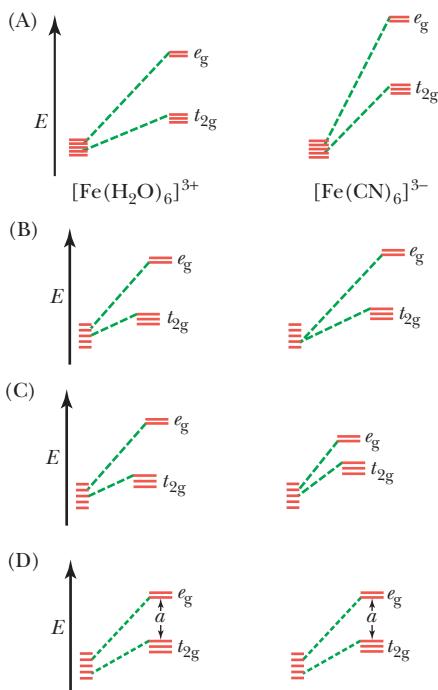
21. Which of the following statements is correct for the complex $[Fe(H_2O)_5NO]SO_4$?
 (A) The EAN value of Fe in this complex depends on the charge of NO ligand.
 (B) The EAN value of Fe in this complex does not depend on the charge of NO ligand.
 (C) The hybridization of the central atom is d^2sp^3 .
 (D) It is paramagnetic with $\mu = 1.73$ B.M.

22. The EAN value of $[Ti(\sigma-C_5H_5)_2(\pi-C_5H_5)_2]^0$ is
 (A) 32
 (B) 33
 (C) 34
 (D) 35

23. Which of the following ligands can show linkage isomerism?

- (A) NO
(B) NH₃
(C) NO₃
(D) None of these.

24. Which of the splitting patterns is correct for $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ respectively?



25. In [isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane) palladium (II)], the Pd–NCS combination is linear while the Pd–SCN combination is bent with the $\angle \text{Pd}–\text{S}–\text{C}$ of 107.3° . Predict the structure adopted for SCN[−] group in this complex.

- (A) $\bar{\text{S}}–\text{C}\equiv\text{N}:$
(B) $\text{S}=\text{C}=\bar{\text{N}}$
(C) Hybrid of (A) and (B).
(D) Cannot be predicted.

26. Choose the correct order for Δ_o for the following complexes.

- I: $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ II: $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
III: $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ IV: $[\text{Fe}(\text{CN})_6]^{3-}$

- (A) I < II < III < IV
(B) I < III < II < IV
(C) I < II = III < IV
(D) I < II < IV < III

27. $[\text{Fe}(\text{H}_2\text{O})_4(\text{CN})_2]$ is the empirical formula of a compound which has a magnetic moment corresponding to $2\frac{2}{3}$ unpaired electrons per iron. The best possible formula of the compound is

- (A) $[\text{Fe}(\text{H}_2\text{O})_4(\text{CN})_2]_2[\text{Fe}(\text{H}_2\text{O})_4(\text{CN})_2]$
(B) $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{H}_2\text{O})_2(\text{CN})_4]$

- (C) $[\text{Fe}(\text{H}_2\text{O})_6]_2[\text{Fe}(\text{CN})_6]$
(D) None of these.

28. Which of the following statements is true for the compounds: $[\text{CoF}_6]^{3-}$ (I) and $[\text{NiF}_6]^{3-}$ (II)?

- (A) Both I and II are paramagnetic.
(B) Both I and II are diamagnetic.
(C) I is paramagnetic while II is diamagnetic.
(D) I is diamagnetic while II is paramagnetic.

29. The correct order of C–C bond length in the following compounds is:

- (I) C_2F_4 (II) C_2H_4 (III) $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$
(A) I > II > III
(B) I < II < III
(C) I > III > II
(D) I > II = III

30. Which of the following statements is incorrect?

- (A) CN[−] is a weaker π -acceptor than CO
(B) The Fe–C bond length is more in $[\text{Fe}(\text{CN})_6]^{4-}$ as compared to that in $[\text{Fe}(\text{CN})_6]^{3-}$
(C) The Fe–C bond length is less in $[\text{Fe}(\text{CN})_6]^{4-}$ as compared to that in $[\text{Fe}(\text{CN})_6]^{3-}$
(D) The $d_{\text{Fe}-\text{O}}$ {in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ } < $d_{\text{Fe}-\text{O}}$ {in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ }

31. The V–C distances in $\text{V}(\text{CO})_6$ and $[\text{V}(\text{CO})_6]^-$ are respectively (in pm)

- (A) 200, 200 (B) 193, 200
(C) 200, 193 (D) 193, 193

32. Which of the following complexes contains a cationic ligand?

- (A) $[\text{Ni}(\eta^5-\text{C}_5\text{H}_5)_2]^+$
(B) $[\text{V}(\eta^6-\text{C}_7\text{H}_8)(\eta^7-\text{C}_7\text{H}_7)]^+$
(C) $[\text{Fe}(\text{CO})_2(\text{NO})_2]^0$
(D) None of these.

33. Which of the following compounds can show *cis-trans* isomerism?

- (A) $[\text{Ni}(\eta^3-\text{C}_3\text{H}_5)_2]^0$ (B) $[\text{Zn}(\text{gly})_2]^0$
(C) $[\text{Pd}(\text{acac})_2]^0$ (D) None of these.

34. Which among the following statements is correct regarding the bonding of Pt and C_2H_4 in Zeise's salt?

- (I) It involves σ -donation from the π -orbital of alkene into vacant metal hybrid orbital.
(II) It involves π -donation from the π -orbital of alkene into vacant metal hybrid orbital.
(III) It involves π -back donation from the filled metal d -orbital (or hybrid) into the vacant antibonding orbital of alkene.
(A) I, II and III (B) I and III
(C) II and III (D) III only

35. Which of the following compounds is resolvable into *d* or *l* forms?

- (A) $[\text{Zn}(\text{acac})_2]^0$ (B) $[\text{B}(\text{C}_6\text{H}_4)_2]^0$
(C) $[\text{B}(\text{C}_6\text{H}_3-\text{CH}_3)_2]^0$ (D) $[\text{PdCl}_2(\text{en})]^0$.

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. Which of the following bidentate ligand(s) has similar donor atoms?

(A) py (B) bn
(C) en (D) gly^-

2. Consider the formation of the following metal carbonyl complex.

$$\text{Ni} + 4\text{CO} \rightarrow [\text{Ni}(\text{CO})_4]$$

carbon monoxide (Y)

Select the correct statement(s) about compound Y.

(A) Compound Y has no counter ion.
(B) Four monodentate uninegative ligands are connected with central metal ion.
(C) This compound produces two ions in its aqueous solution.
(D) Total number of electrons remains the same during the formation of compound Y.

3. Which of the following statement(s) is/are correct?

(A) $\text{Ni}(\text{CO})_4$ is diamagnetic and sp^3 hybridized.
(B) Complex $[\text{Cu}(\text{CN})_4]^{3-}$ is paramagnetic and Cu^{2+} ion is dsp^2 hybridized.
(C) $[\text{MnBr}_4]^{2-}$ ion is paramagnetic and sp^3 hybridized.
(D) Vaska's catalyst, that is, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ is diamagnetic and Ir^+ ion is dsp^2 hybridized.

4. Which of the following chemical species can act as a non-classical ligand(s)?

(A) CO (B) C_2H_4
(C) NO^+ (D) PR_3

5. Which of the following is/are characteristic of ferrocene?

(A) Cyclopentadienyl act as a π -donor ligand.
(B) Fe is in (+2) oxidation state.
(C) It is organometallic compound.
(D) It has a metal–carbon bond.

6. Which of the following chemical species is/are diamagnetic as well as coloured?

(A) Hexafluoridoferate(III) ion
(B) Permangate ion
(C) Brown ring complex
(D) Chromate ion

7. In case of $[\text{Mn}(\text{NH}_3)_6]^{2+}$

(A) relation in between Δ_0 and P is $\Delta_0 < P$.
(B) two unpaired electrons are present in axial d -orbital of Mn^{2+} .
(C) hybridization of central metal atom of complex is d^2sp^3 .
(D) d -orbitals involved in hybridization of central atom are d_x^2 and d_{xy} .

8. $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_3(\text{NH}_3)]_2$ is the polymerization isomer of which of the following compounds?

(A) *cis* - $[\text{PtCl}_2(\text{NH}_3)_2]$
(B) *trans* - $[\text{PtCl}_2(\text{NH}_3)_2]$
(C) $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{PtCl}_4]$
(D) None of these.

9. Which of the following types of isomerism is/are possible for the compound $[\text{Co}(\text{Cl})(\text{en})_2(\text{NH}_2 - \text{C}_6\text{H}_4 - \text{Me})\text{Cl}_2]$?

(A) Geometrical isomerism
(B) Linkage isomerism
(C) Optical isomerism
(D) Ligand isomerism

10. Which of the following pairs of compounds has the same EAN value but does not obey Sidgwick EAN rule?

(A) $\text{Fe}(\text{CO})_5$, $\text{Ni}(\text{CO})_4$
(B) $[\text{Fe}(\text{NH}_3)_6]^{2+}$, $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$
(C) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$, $[\text{Mn}(\text{CO})_6]$
(D) $[\text{Ti}(\text{CO})_6]$, $[\text{Mn}(\text{C}_2\text{O}_4)_3]^{3-}$

11. Which of the following statements is/are correct for ferrocene?

(A) The dipole moment of the eclipsed form of ferrocene is zero.
(B) The dipole moment of the staggered form of ferrocene is non-zero.
(C) All C atoms are equidistant from Fe^{2+} ion.
(D) Synergic bonding takes place in the π^* orbital of C atoms.

12. Which of following IUPAC names is/are correct for the complex $[\text{CO}(\text{NH}_3)_2(\text{tn})(\sigma-\text{C}_3\text{H}_5)_2]\text{NO}_3$?

(A) Diallyldiamminetrimethylenediaminecobalt (III) nitrate.
(B) 1,3-Diaminopropanediamminediallycobalt (III) nitrate
(C) Diammine-1,3-diaminopropanedicyclopropyl cobalt (III) nitrate.
(D) Diallyldiammine-1,3-diaminopropane cobalt (III) nitrate.

13. A complex compound consists of 1 mole of Co^{3+} ion, 6 moles of NH_3 , 6 moles of NO_2^- and 1 mole of Cr^{3+} ion. The complex has neither the highest value nor the lowest value of electrical conductivity. The possible formulae for the complex is/are

(A) $[\text{Cr}(\text{NH}_3)_5(\text{NO}_2)][\text{Co}(\text{NH}_3)(\text{NO}_2)_5]$
(B) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$
(C) $[\text{Cr}(\text{NH}_3)_4(\text{NO}_2)_2][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
(D) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)][\text{Cr}(\text{NH}_3)(\text{NO}_2)_5]$

14. Which of the following complexes is/are square planar?

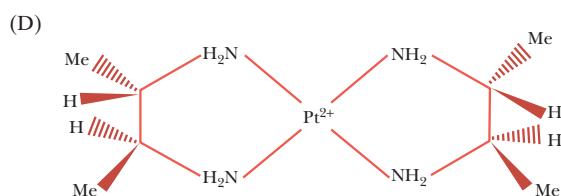
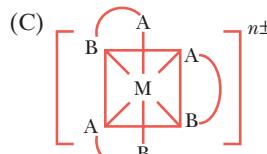
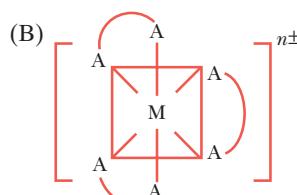
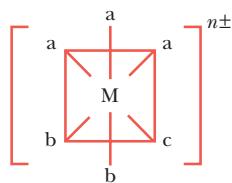
(A) $[\text{AgF}_4]^-$
(B) $[\text{AuCl}_4]^-$
(C) $[\text{NiCl}_2(\text{PPh}_3)_2]$
(D) $[\text{NiCl}_2(\text{PMe}_3)_2]$

15. Choose the correct statement(s) from the following:

(A) Monovalent silver complexes (coordination number 2) are diamagnetic.
(B) Bivalent silver complexes (coordination number 4 and 6) are paramagnetic with $\mu = 1.73 \text{ BM}$.

- (C) Trivalent silver complexes (coordination number 4) are diamagnetic.
 (D) AgO is diamagnetic.
16. Which of the following complexes have geometrical isomers that are optically inactive due to the presence of centre of symmetry?
 (A) $[\text{Pt}(\text{bn})_2]^{2+}$
 (B) $[\text{Fe}(\text{gly})_3]^0$
 (C) $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]^0$
 (D) $[\text{Pd}(\text{NH}_2 - \text{CH}(\text{CH}_3) - \text{CO}_2)_2]^0$

17. Which of the following complexes is/are optically inactive due to the presence of plane of symmetry?
 (A)



COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1–2

Isomers in coordination chemistry include many types. In structural isomers hydrate or solvent isomers, ionization isomers and coordination isomers have same overall formula but have different ligands attached to the central atom or ion.

The terms linkage isomerism or ambidentate isomerism are used for cases of bonding through different atoms of the same ligand.

- Which of the following is not correctly matched against indicated isomerism?
 (A) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Br}_2$: Ionization isomerism
 (B) $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{NCS})]$: Linkage isomerism
 (C) $[\text{Pt}(\text{NH}_3)_4][(\text{PtCl}_4)]$: Coordination isomersim
 (D) $[\text{Zn}(\text{gly})_2]$ tetrahedral : Geometrical isomerism
- Ma_3b_3 complex has two geometrical forms: facial and meridional. Then which of the following statement is incorrect?
 (A) In facial isomers, three same ligands occupy adjacent positions on octahedron face.
 (B) In meridional isomers, same ligands are present at 90° and 180° angles.
 (C) In facial isomers, same ligands are present only at 90° angle.
 (D) Both isomers (facial and meridional) are optically active.

Passage 2: For Questions 3–5

The magnetic moment for two complexes of empirical formula $\text{Ni}(\text{NH}_3)_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ is zero and 2.84 BM respectively. The second complex is not a neutral complex.

- The number of water molecules of crystallization are respectively
 (A) zero, two.
 (B) zero, zero.
 (C) two, zero.
 (D) two, two.

- The correct formula and geometry of the first complex is
 (A) $[\text{Ni}(\text{H}_2\text{O})_2(\text{NO}_3)_2] \cdot 4\text{NH}_3$; tetrahedral.
 (B) $[\text{Ni}(\text{NH}_3)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; tetrahedral.
 (C) $[\text{Ni}(\text{NH}_3)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; square planar.
 (D) $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$; octahedral.

- Which of the following statements are true for the second complex?
 (A) It has the EAN value of 36.
 (B) It can show optical isomerism.
 (C) It cannot show geometrical isomerism.
 (D) It produces three-fold freezing point depression.

Passage 3: For Questions 6–8

Some ligands not only donate their lone pair to the central metal atom but also accept the electron cloud from the central metal atom. This is known as synergic bonding.

- In which of the following cases is the bond energy of C – O bond minimum?
 (A) Free CO molecule.
 (B) Terminal CO group in a complex.
 (C) Doubly bridging CO in a complex.
 (D) Triply bridging CO in a complex.
- Select the correct order for the stretching frequencies of C – O bond the following compounds.

- (I) fac-Mo(CO)₃(PF₃)₃ (II) fac-Mo(CO)₃(PCl₃)₃
 (III) fac-Mo(CO)₃(PMe₃)₃
- (A) I < II < III. (B) I > II > III.
 (C) I = II = III. (D) II > I > III.
8. In which of the following complexes is the bond order of C – O bond minimum?
 (A) [Mn(CO)₆]⁺ (B) [Cr(CO)₆]
 (C) [Ti(CO)₆]²⁻ (D) [V(CO)₆]⁻

Passage 4: For Questions 9–11

The series $[\text{CoCl}_n(\text{NH}_3)_{6-n}]\text{Cl}_{3-n}$ gives rise to 4, 3, 2, and zero ions in solution respectively, for $n = 0, 1, 2$, and 3.

9. For which value of n is the electrical conductivity of the complex maximum?
 (A) 0 (B) 1
 (C) 2 (D) 3
10. For which value of n will the complex not show optical isomerism?
 (A) 1 (B) 2
 (C) 3 (D) All of these
11. For which value of n , the complex will show minimum freezing point depression?
 (A) 0 (B) 3
 (C) 2 (D) 1

Passage 5: For Questions 12–13

Synergic bond is a type of back bonding.

12. Which of the following has higher stretching frequency for C–O bond?
 (A) [Ni(CO)₃PF₃]
 (B) [Ni(CO)₃(PMe₃)]
 (C) Both have equal stretching frequency.
 (D) None of these.

13. Which of the following has higher multiple bond character in M–C bond?
 (A) [Ni(CO)₄]
 (B) [Co(CO)₄]⁻
 (C) [Fe(CO)₄]²⁻
 (D) (B) and (C) both have equal bond character in M–C bond.

Passage 6: For Questions 14–16

Coordination number of a central atom is its inherent property and has no role on its isomerism.

14. $[\text{CoCl}_2(\text{NH}_3)_4]^+ + \text{Cl}^- \rightarrow [\text{CoCl}_3(\text{NH}_3)_3] + \text{NH}_3$
 If in the above reaction two isomers of the product are obtained, which is true for the initial (reactant) complex?
 (A) compound is in *cis* form.
 (B) compound is in *trans* form.
 (C) compound is in both (*cis* and *trans*) forms.
 (D) cannot be predicted.
15. When 0.1 mol of $\text{CoCl}_3(\text{NH}_3)_5$ is treated with excess of AgNO_3 , 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to (cation : anion)
 (A) 1 : 3 electrolyte
 (B) 1 : 2 electrolyte
 (C) 1 : 1 electrolyte
 (D) 3 : 1 electrolyte
16. Due to the presence of ambidentate ligands coordination compounds show isomerism, palladium complexes of the type $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{SCN})_2]$ and $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{NCS})_2]$ are
 (A) linkage isomers.
 (B) coordination isomers.
 (C) ionisation isomers.
 (D) geometrical isomers.

ASSERTION–REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
 (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
 (C) If Statement I is true but Statement II is false.
 (D) If Statement I is false but Statement II is true.

1. **Statement I:** Only *cis* $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ reacts with oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) to form $[\text{PtCl}_2(\text{ox})]^{2-}$ not the *trans* isomer.

Statement II: The oxalate ion is a bidentate ligand which occupies adjacent positions only.

2. **Statement I:** Under the strong field ligand only, the degeneracy of the d -orbital is lost.

Statement II: After splitting of the d -orbitals also, Hunds rule is not violated anywhere.

3. **Statement I:** NO is $3e$ -donor.

Statement II: The antibonding electron of NO is very much susceptible to donate apart from its lone pair.

4. **Statement I:** Dithiooxalate is bidentate ambidentate ligand.

Statement II: At a time either two S atoms or two O atoms act as donor atoms.

5. **Statement I:** PF₃ is weakest donor as well as weakest acceptor compared to PMe₃ in synergic bonding.

Statement II: Me group is having $+I$ effect while F atom is having $-I$ effect.

6. **Statement I:** SnCl_2 does not act as ligand but SnCl_3^- acts as good ligand.

Statement II: On addition of Cl^- to SnCl_2 , the orbital containing the lone pair acquires less *s*-character.

7. **Statement I:** $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is more acidic compared to $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

Statement II: Both are inner orbital complexes.

8. **Statement I:** Under the influence of a strong field ligand, d^7 -system will have only one unpaired electron either in coordination number six or four.

Statement II: $t_{2g}^6 e_g^1$ is the electronic configuration for both cases.

9. **Statement I:** CdS is yellow coloured.

Statement II: The $d - d$ transition does not take place in this compound.

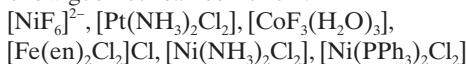
10. **Statement I:** $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Br}]\text{SO}_4$ has lower electrical conductivity as compared to $[\text{Co}(\text{en})_2(\text{NH}_3)\text{SO}_4]$ Br.

Statement II: Both the ions produce the same number of ions in solution.

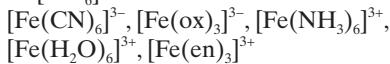
INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. Find the number of diamagnetic complexes which show geometrical isomerism.



2. Find the number of complexes in which stability constant value is greater than the stability constant value of $[\text{FeF}_6]^{3-}$.



3. Suppose we replace all the fluoride and water ligands from $[\text{CoF}_3(\text{H}_2\text{O})_3]$ by oxalate ligand without changing the oxidation state and coordination number of central metal atom or ion. Predict the number of parameters among following which increase in the newly formed complex.

- (I) Δ_0
- (II) Number of t_{2g} electrons
- (III) Number of e_g electrons
- (IV) Number of stereoisomers
- (V) Number of geometrical isomers
- (VI) EAN value

4. The number of coordination isomers possible for:

- (a) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$ is _____.
- (b) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{Pt}(\text{CN})_4]$ is _____.
- (c) $[\text{Fe}(\text{NH}_3)_6]^{3+}[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ is _____.
- (d) $[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{CuCl}_4]^{2-}$ is _____.
- (e) $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{Pt}(\text{SCN})_4]$ is _____.

5. The possible number of stereoisomers for the formula $[\text{Ma}_3\text{b}_2]^{n\pm}$ is _____.

6. The number of stereoisomers, optically active isomers and geometrical isomers for the complex $[\text{Co}(\text{en})(\text{pn})(\text{NO}_2)_2]^+$ is _____, _____ and _____ respectively.

7. If CFSE increases by 30% and 40% respectively for Co^{3+} to Rh^{3+} and for Rh^{3+} to Ir^{3+} , then the total increase in CFSE for Ir^{3+} with respect to Co^{3+} is _____ %.

8. The hapticity of the organic ligand in the following complex is _____.



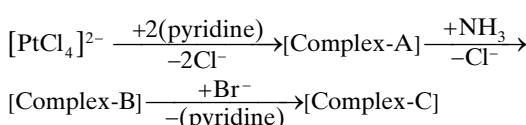
9. The coordination number of the central atom in $[\text{Co}(\text{NH}_3)_4\text{SO}_4]\text{NO}_3$ is _____.

10. The number of optically active isomers for the complex of formula $[\text{Ma}_2\text{b}_2\text{cd}]$ is _____.

11. The number of unpaired electrons in the t_{2g} set of *d* orbitals in the complex $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]$ is _____.

12. The number of unpaired electrons present in $[\text{NiF}_6]^{2-}$ is _____.

13. The sum of stereoisomers of complex-A, complex-B and complex-C in following reaction is _____.



MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D),

while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the processes with their respective characteristics.

Column-I	Column-II
(A) $[\text{CoCl}_6]^{3-} \rightarrow [\text{Co}(\text{en})_2\text{Cl}_2]^+$	(P) Change in number of geometrical isomers
(B) $[\text{Fe}(\text{EDTA})]^- \rightarrow [\text{Fe}(\text{en})_3]^{+3}$	(Q) Change in number of stereoisomers
(C) $[\text{Pt}(\text{NH}_3)_4]^{+2} \rightarrow [\text{Pt}(\text{ONO})_4]^{2-}$	(R) EAN value does not change
(D) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3 \rightarrow [\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3]\cdot 3\text{H}_2\text{O}$	(S) Change in number of structural isomers (T) Change in magnitude of Δ

2. Match the metal complex type with the properties.

Column I	Column II
(A) $[\text{M}(\text{AA})\text{abcd}]^{n\pm}$	(P) All geometrical isomers are optically active.
(B) $[\text{M}(\text{AB})\text{a}_2\text{b}_2]^{n\pm}$	(Q) The number of stereoisomers is four.

4. Match the processes carried out with the changes observed.

Column I	Column II
(A) $[\text{M}(\text{AB})\text{a}_3\text{b}]^{n\pm} \xrightarrow{-\text{a}/+\text{b}} [\text{M}(\text{AB})\text{a}_2\text{b}_2]^{n\pm}$	(P) The number of pairs of enantiomers is increased by one.
(B) $[\text{M}(\text{AB})\text{a}_2\text{bc}]^{n\pm} \xrightarrow{-\text{c}/+\text{b}} [\text{M}(\text{AB})\text{a}_2\text{b}_2]^{n\pm}$	(Q) The number of geometrical isomers in the final product is four.
(C) $[\text{Ma}_3\text{b}_2\text{c}]^{n\pm} \xrightarrow{-\text{b}/+\text{d}} [\text{Ma}_3\text{bcd}]^{n\pm}$	(R) The number of stereoisomers is increased to double of the original or decreased to half of the original.
(D) $[\text{M}(\text{AA})\text{a}_3\text{b}]^{n\pm} \xrightarrow{-\text{a}/+\text{b}} [\text{M}(\text{AA})\text{a}_2\text{b}_2]^{n\pm}$	

5. Match the complex compounds with the properties not depicted by them.

Column I	Column II
(A) $[\text{Fe}(\text{CO})_4]^{2-}$	(P) Hybridization is dsp^2 .
(B) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	(Q) Hybridization is sp^3 .
(C) $[\text{Pt}(\text{bn})_2]^{2+}$	(R) Exhibits geometrical isomerism.
(D) $[\text{Zn}(\text{gly})_2]^0$	(S) Low spin complex. (T) Exhibits optical isomerism.

6. Match the pair of complex compounds with the properties that are different in them.

Column I	Column II
(A) $[\text{Mn}(\text{NH}_3)_6]\text{SO}_4$ and $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$	(P) Hybridization.
(B) $(\text{NH}_4)_2[\text{PtCl}_4]$ and $\text{K}_2[\text{NiCl}_4]$	(Q) Magnetic moment value.
(C) $\text{K}_4[\text{Fe}(\text{CN})_5\text{O}_2]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$	(R) Magnetic behaviour.
	(S) Electrical conductivity with significant change.

Column I	Column II
(C) $[\text{M}(\text{AB})_3]^{n\pm}$	(R) The number of geometrical isomers is four.
(D) $[\text{Ma}_2\text{b}_2\text{cd}]^{n\pm}$	(S) The number of optically active isomers is four.

3. Match the complex compounds with their properties.

Column I	Column II
(A) $[\text{CoF}_3(\text{H}_2\text{O})_3]^0$	(P) Diamagnetic and low spin complex.
(B) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$	(Q) Paramagnetic and outer orbital complex.
(C) $[\text{AuCl}_4]^-$	(R) Paramagnetic but inner orbital complex.
(D) $[\text{Fe}(\text{CN})_6]^{3-}$	(S) Diamagnetic and high spin complex.
	(T) Paramagnetic and low spin complex.

7. Match the pair of complex compounds with the properties that are same in them.

Column I	Column II
(A) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Mn}(\text{NH}_3)_6]^{2+}$	(P) Hybridization.
(B) $[\text{AuCl}_4]^-$ and $[\text{PdCl}_4]^{2-}$	(Q) Magnetic moment value.
(C) $[\text{Fe}(\text{DMG})_2]^0$ and $[\text{Ni}(\text{DMG})_2]^0$	(R) EAN value.
(D) $[\text{Fe}(\text{CO})_5]^0$ and $[\text{Ni}(\text{CO})_4]^0$	(S) Shape.

8. Match the coordination complex with the number of isomers formed.

Column I	Column II
(A) $[\text{M}(\text{AB})_3]^{n\pm}$	(P) Complex having two optically active isomers.
(B) $[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm}$	(Q) Complex having four stereoisomers.

8. Match the coordination complex with the number of isomers formed.

Column I	Column II
(A) $[M(AB)_3]^{n\pm}$	(P) Complex having two optically active isomers.
(B) $[Ma_2b_2c_2]^{n\pm}$	(Q) Complex having four stereoisomers.
(C) $[M(AA)a_2b_2]^{n\pm}$	(R) Complex having odd number of geometrical isomers.
(D) $[Ma_3bcd]^{n\pm}$	(S) Complex having even number of geometrical isomers. (T) All geometrical isomerism are not optically active.

9. Match the complex with its property.

Column I	Column II
(A) $[Co(C_2O_4)_3]^{3-}$	(P) High-spin complex.
(B) $[CoF_6]^{3-}$	(Q) Low-spin complex.
(C) $[Ni(NH_3)_6]^{2+}$	(R) Zero electron in e_g set of orbital.
(D) $[Cr(CN)_6]^{3-}$	(S) Paramagnetic behaviour. (T) d^2sp^3 hybridization.

ANSWERS

Single Correct Choice Type Questions

- | | | | | |
|--------|---------|---------|---------|---------|
| 1. (A) | 8. (D) | 15. (A) | 22. (C) | 29. (B) |
| 2. (B) | 9. (C) | 16. (D) | 23. (A) | 30. (B) |
| 3. (D) | 10. (C) | 17. (D) | 24. (A) | 31. (C) |
| 4. (A) | 11. (A) | 18. (B) | 25. (A) | 32. (B) |
| 5. (A) | 12. (B) | 19. (D) | 26. (B) | 33. (A) |
| 6. (D) | 13. (B) | 20. (B) | 27. (C) | 34. (B) |
| 7. (A) | 14. (B) | 21. (B) | 28. (C) | 35. (C) |

Multiple Correct Choice Type Questions

- | | | | | |
|-----------------------|-----------------------|-------------------|------------------------|--------------|
| 1. (B), (C) | 5. (A), (B), (C), (D) | 9. (A), (C), (D) | 13. (A), (D) | 17. (A), (D) |
| 2. (A), (D) | 6. (B), (D) | 10. (C), (D) | 14. (A), (B), (D) | |
| 3. (A), (C), (D) | 7. (A), (B) | 11. (A), (C), (D) | 15. (A), (B), (C), (D) | |
| 4. (A), (B), (C), (D) | 8. (A), (B), (C) | 12. (A), (C), (D) | 16. (A), (D) | |

Comprehension Type Questions

- | | | | |
|--------|--------|---------|---------|
| 1. (D) | 5. (D) | 9. (A) | 13. (C) |
| 2. (D) | 6. (D) | 10. (D) | 14. (A) |
| 3. (C) | 7. (B) | 11. (B) | 15. (B) |
| 4. (C) | 8. (C) | 12. (A) | 16. (A) |

Assertion–Reasoning Type Questions

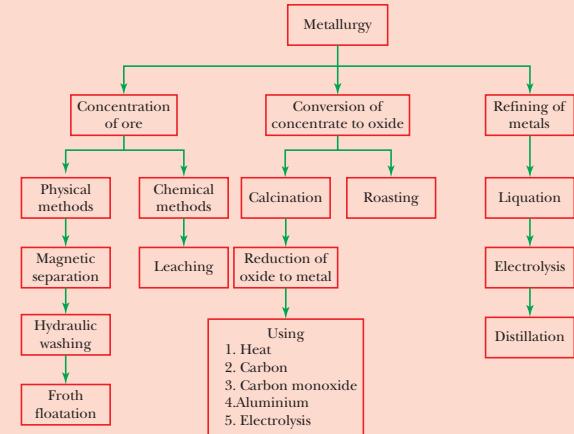
- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (A) | 3. (A) | 5. (D) | 7. (C) | 9. (B) |
| 2. (D) | 4. (A) | 6. (A) | 8. (C) | 10. (D) |

Matrix-Match Type Questions

- | | | | |
|--|--|--|---|
| 1. (A) \rightarrow (P), (Q), (R), (T) | (C) \rightarrow (P) | 6. (A) \rightarrow (P), (Q), (R), (S) | (D) \rightarrow (P), (S), (T) |
| (B) \rightarrow (R), (T) | (D) \rightarrow (T), (R) | (B) \rightarrow (P), (Q), (R) | 9. (A) \rightarrow (Q), (R), (T) |
| (C) \rightarrow (R), (S), (T) | 4. (A) \rightarrow (P), (Q) | (C) \rightarrow (Q), (R) | (B) \rightarrow (P), (S) |
| (D) \rightarrow (P), (Q), (R), (T) | (B) \rightarrow (Q), (R) | 7. (A) \rightarrow (S) | (C) \rightarrow (S) |
| 2. (A) \rightarrow (P) | (C) \rightarrow (P), (Q) | (B) \rightarrow (P), (Q), (S) | (D) \rightarrow (R), (S), (T) |
| (B) \rightarrow (R), (S) | (D) \rightarrow (P), (R) | (C) \rightarrow (P), (Q), (S) | |
| (C) \rightarrow (P), (Q), (S) | 5. (A) \rightarrow (P), (R), (S), (T) | (D) \rightarrow (Q), (R) | |
| (D) \rightarrow (S) | (B) \rightarrow (Q), (T) | 8. (A) \rightarrow (Q), (S) | |
| 3. (A) \rightarrow (Q) | (C) \rightarrow (Q) | (B) \rightarrow (P), (R), (T) | |
| (B) \rightarrow (R) | (D) \rightarrow (P), (R), (S) | (C) \rightarrow (P), (Q), (R), (T) | |

6

Metallurgy



Metallurgical processes.

Contents

- 6.1 Types of Ores
- 6.2 Principal Steps in the Recovery of a Metal from its Ore
- 6.3 Concentration or Dressing of Ore
- 6.4 Conversion of Concentrated Ore into its Oxide
- 6.5 Different Reduction Processes
- 6.6 Purification or Refining of Metal
- 6.7 Thermodynamics of Reduction Process
- 6.8 Alloys and Amalgams
- 6.9 Different types of Furnaces used in Metallurgy
- 6.10 Extraction of Silver
- 6.11 Extraction of Gold by Cyanide Process
- 6.12 Extraction of Tin
- 6.13 Extraction of Magnesium
- 6.14 Extraction of Aluminium
- 6.15 Extraction of Lead
- 6.16 Extraction of Copper
- 6.17 Extraction of Zinc
- 6.18 Extraction of Iron

Metallurgy is the subject which deals with the science and technology applied for the extraction of metals economically on a large scale from their respective ores. Another aspect of metallurgy deals with making of alloys which are metallic solutions composed of two or more elements.

To begin with we must understand the difference between a mineral and an ore.

1. Mineral: The compounds of a metal which are naturally available in the earth's crust and can be obtained by mining are called minerals. A mineral may consist of one or more metallic compounds, having almost fixed chemical composition.

2. Ore: The minerals from which a metal can be extracted economically and conveniently are called ores.

Hence *all ores are minerals but all minerals are not ores*. For example, FeS_2 (iron pyrite) is abundantly available in the Earth's crust but cannot be used as ore of iron. The chemical reactions involved in conversion of iron pyrite to iron are:



The removal of S from FeS_2 to obtain iron involves high cost of production and presence of high percentage of sulphur in iron makes it brittle and thus of no use.

The impurities present in the ore are known as **gangue**. For example, silica (SiO_2) is a common impurity present in most of the ores.

6.1 | TYPES OF ORES

The different types of ores are depicted in Figure 6.1.

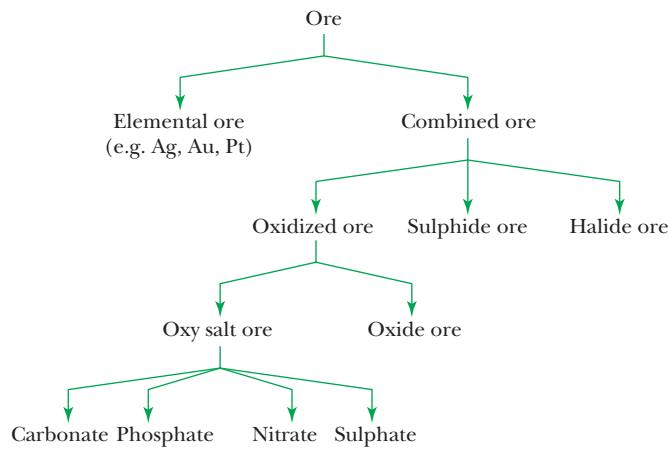


Figure 6.1 Different types of ores.

Some important ores of different types and their formulas are listed as follows.

1. Oxide ores

ZnO	Zincite	CaMg ₃ (SiO ₃) ₄	Asbestos
Fe ₂ O ₃	Haematite	MgO · Al ₂ O ₃	Spinel
Fe ₃ O ₄	Magnetite	Al ₂ O ₃ · 3H ₂ O	Gibbsite
Al ₂ O ₃ · 2H ₂ O	Bauxite	Al ₂ O ₃ · H ₂ O	Diaspore
Fe ₂ O ₃ · 3H ₂ O	Limonite	Al ₂ O ₃	Corundum
Cu ₂ O	Cuprite or Ruby copper	PbCrO ₄	Crocoisite
MnO ₂	Pyrolusite	ZnO · Fe ₂ O ₃	Franklinite
SnO ₂	Tinstone or Casseterite	ZnSiO ₃	Willemite
TiO ₂	Rutile	ZnSiO ₃ · ZnO · H ₂ O	Electric calamine
FeCr ₂ O ₄ (FeO + Cr ₂ O ₃)	Chromite ore	K ₂ O · Al ₂ O ₃ · 6SiO ₂	Feldspar
Na ₂ B ₄ O ₇ · 10H ₂ O	Borax or Tincal	Al ₂ O ₃ · 2SiO ₂ · 2H ₂ O	China clay or Kaolin
Ca ₂ B ₆ O ₁₁ · 5H ₂ O	Colemanite		
U ₃ O ₈	Pitch blende		
FeO · TiO ₂	Ilmenite		

2. Sulphide ores

PbS	Galena	Ag ₂ S	Argentite or silver glance
HgS	Cinnabar	3Ag ₂ S · Sb ₂ S ₃	Ruby silver
ZnS	Zinc blende or Sphalerite		
Cu ₂ S	Copper glance or Chalcocite		
CuFeS ₂	Copper pyrite or Chalcopyrite		
FeS ₂	Iron pyrite or Fool's gold		
Ag ₂ S	Silver glance or Argentite		

3. Halide ores

NaCl	Rock Salt
KCl	Sylvine
CaF ₂	Fluorspar

Na_3AlF_6	Cryolite
AgCl	Horn silver
$\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$	Carnalite
$\text{Cu}_2\text{Cl}(\text{OH})_3$	Atacamite

4. Oxy salt ores

a. Carbonate ores

CaCO_3	Limestone
MgCO_3	Magnesite
$\text{CaCO}_3\cdot\text{MgCO}_3$	Dolomite
FeCO_3	Siderite
ZnCO_3	Calamine
$\text{Cu}(\text{OH})_2\cdot\text{CuCO}_3/\text{Cu}_2(\text{OH})_2\text{CO}_3$	Malachite or Basic copper carbonate
$\text{Cu}(\text{OH})_2\cdot 2\text{CuCO}_3$	Azurite
PbCO_3	Cerrusite

b. Sulphate ores

$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	Gypsum	$\text{K}_2\text{SO}_4\cdot \text{MgSO}_4\cdot \text{MgCl}_2\cdot 6\text{H}_2\text{O}$	Kainite
$\text{MgSO}_4\cdot 7\text{H}_2\text{O}$	Epsom salt	$\text{MgSO}_4\cdot \text{H}_2\text{O}$	Kieserite
PbSO_4	Anglesite	$\text{K}_2\text{SO}_4\cdot \text{Al}_2(\text{SO}_4)_3\cdot 4\text{Al}(\text{OH})_3$	Alunite
BaSO_4	Baryte	$\text{PbO}\cdot \text{PbSO}_4$	Lanarkite
$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$	Glauber Salt		
$\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	Chalcanthite		

c. Nitrate ores

KNO_3	Indian saltpeter
NaNO_3	Chile saltpeter

6.2 | PRINCIPAL STEPS IN THE RECOVERY OF A METAL FROM ITS ORE

The various steps involved in the recovery of a metal from its ore are listed as follows:

1. Concentration of ore or dressing of ore.
2. Conversion of concentrated ore into a suitable form for reduction, mostly into an oxide depending on the nature and chemical characteristics of ore, i.e. *calcination* and *roasting*.
3. Production of metal by reduction.
4. Purification and refining of metal.
5. Process of pollution control for treating waste gases/materials.

These steps are discussed in detail in the following sections.

6.3 | CONCENTRATION OR DRESSING OF ORE

This process can be carried out by two methods of separation — physical and chemical.

1. Physical methods of separation:
 - Gravity separation or levigation.
 - Magnetic separation.
 - Froth floatation.
2. Chemical methods of separation, i.e. leaching.

Gravity separation or levigation

This technique utilizes the density difference between the ore and impurity to concentrate the ore. It is mainly applicable to oxide ores. For example, SnO_2 , Fe_2O_3 and FeCr_2O_4 are concentrated by this method from siliceous impurities.

In gravity separation the crushed ore is washed by a current of water on a sloping table fitted with a series of corrugated boards known as Wilfley table (Figure 6.2). The table is continuously vibrating as a result of which the lighter particles move downwards and the heavier particles are left behind the corrugations (as barriers).

A suitable arrangement is made to remove the heavier particles continuously, otherwise the separation process will become ineffective after some time as heavier and lighter particles will start passing the barrier together.

Magnetic separation

Generally this method is used to separate the magnetic impurities from the non-magnetic ore. For example, tin stone (SnO_2) is separated from magnetic impurity wolframite ($\text{FeWO}_4 + \text{MnWO}_4$ (minor)) by this method. In magnetic separation powdered ore is allowed to move towards magnetic roller and fall downwards. The magnetic material makes a new heap because it is held to the roller for a longer time (Figure 6.3).

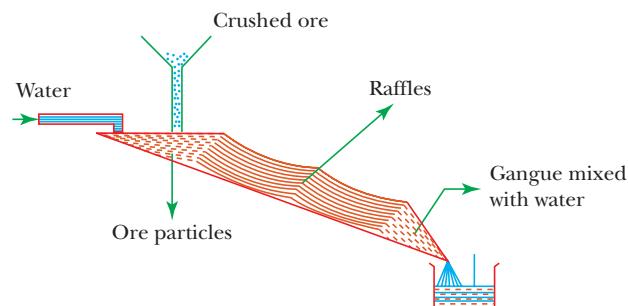


Figure 6.2 Representation of gravity separation using Wilfley table.

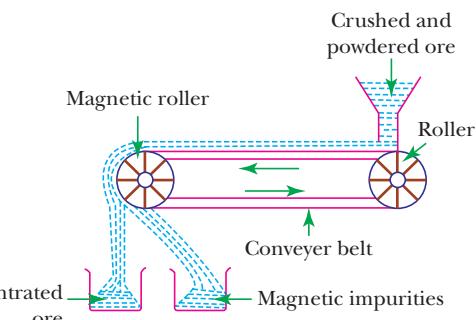


Figure 6.3 Representation of magnetic separator.

Froth floatation or oil floatation

This process is used to separate the sulphide ore from impurity in the ore. It is based upon the differential wetting of the ore by oil and the impurity by water.

In this process, the ore is ground to fine powder and mixed with water to form a slurry. Any one of the oily components such as pine oil, eucalyptus oil, crude coal tar, cresols, etc. is added to it together with sodium ethyl xanthate as collector. Air is bubbled through the mixture which acts as an agitator and creates bubbles. Finally, the ore is floated to the froth and siliceous impurities are settled at the bottom of the tank. Then the froth is collected into a separate container and washed thoroughly and dried.

The oil added acts as frothing agent. It reduces the surface tension of water and helps to produce a stable froth. Reagents such as aniline or cresol are used to stabilize the froth. The formation of bubble involves an increase in air–water surface that means doing work against surface tension. The energy

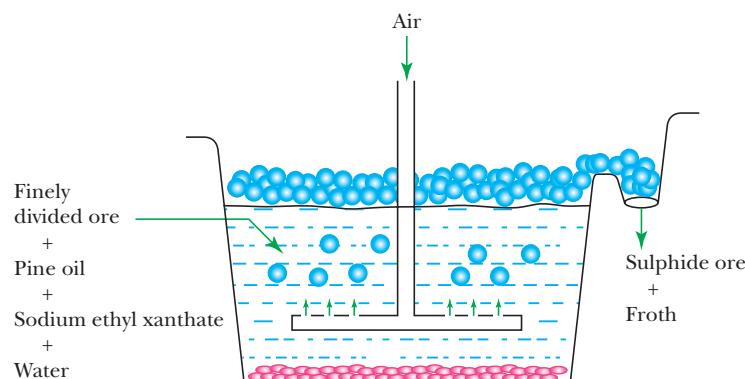
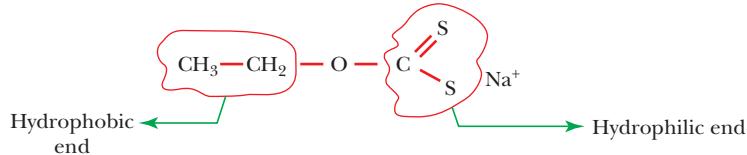


Figure 6.4 Froth floatation process for sulphide ore.

required to create a bubble of radius r is $2 \times 4\pi r^2 \times E$, where E is the energy required to create unit surface area and, is directly proportional to surface tension.

The froth floatation process is usually applied for sulphide ores and the schematic representation is shown in Figure 6.4. Sodium ethyl xanthate acts as a collector of sulphide ore.



The hydrophobic end prefers to stay in air and hydrophilic end prefers to stay in water. Since the molecule has both hydrophobic and hydrophilic part, the best place for it to stay is the air–water interface and hence it shows floating characteristics. The hydrophilic end attracts the sulphide particles and forms surface coated particles as shown Figure 6.5.

Finally, the collected sulphide particles are floated to the froth and transferred to a separate container, washed with huge amounts of water, dried and sent for next step of extraction.

1. The other alkyl groups in xanthate may be amyl ($\text{C}_5\text{H}_{11}-$), octyl ($\text{C}_8\text{H}_{17}-$), etc. instead of the ethyl group.
2. The other collectors that may be used are

- a. Sodium lauryl sulphate: $\text{C}_{12}\text{H}_{25}\text{O}-\text{SO}_3^-\text{Na}^+$
- b. Trimethyl cetyl ammonium bromide: $\text{C}_{16}\text{H}_{33}\text{N}^+(\text{Me})_3\text{Br}^-$

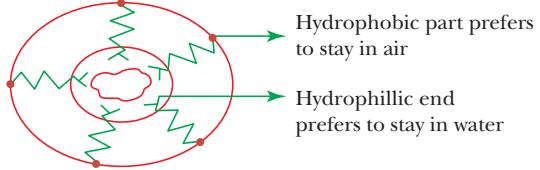
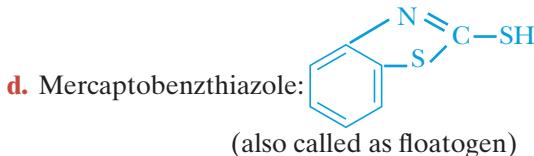
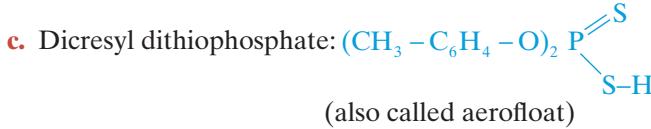
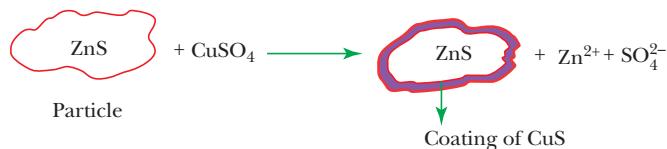


Figure 6.5 Sodium ethyl xanthate at the air–water interface.

The overall ore collecting process occurs through adsorption and depends upon the unbalanced forces on the solid surface.

Activator is a substance that is added to help the collector stay attached to the particles to be floated and hence improve the floating characteristics of the ore. For example, the floating characteristic of ZnS is poor as compared to that of CuS . Hence CuSO_4 is used as activator to form a coating of CuS on the ZnS surface and improve its floating characteristics.



Accordingly using suitable activators, the froth floatation process can also be applied for non-sulphide ore. For example, Na_2S is suitable activator for malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) and anglesite (PbSO_4) in which the coatings of CuS and PbS are formed by the activator, respectively.

Depressant is a substance that is added to suppress the floating characteristic of the ore particles. For example, galena (PbS) is associated with another sulphide impurity ZnS which also rises to the surface with the froth. The reagent NaCN/KCN is used to suppress the floating characteristics of ZnS by forming a soluble complex with KCN .



Chemical method of separation: Leaching

It is the process by which the required substance (may be the metal component or impurities) is dissolved out from the ore by using a suitable reagent. For example,

1. Al_2O_3 is dissolved from red bauxite by using 40% NaOH.



2. Ag_2S is dissolved out from silver glance (Ag_2S + impurity) by using NaCN solution in the presence of air.



3. In Sn extraction, the removal of impurities like FeS_2 and Cu_2S also involves application of the leaching process. These two sulphides are roasted carefully to produce soluble sulphates that are washed out with hot water.

6.4 | CONVERSION OF CONCENTRATED ORE INTO ITS OXIDE

This is generally carried out by two methods—calcination and roasting.

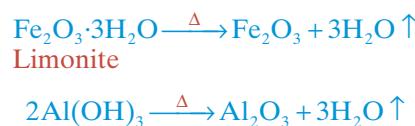
Calcination

It is the process in which the concentrated ore is heated to a high temperature (just below its fusion temperature) in the absence of air (or limited supply of air).

1. This process is mainly used for a carbonate ore to get its oxide



2. Hydrated ores or hydroxides become anhydrous by calcination. For example,



3. Impurities like S, As and Sb are removed in the form of their elemental vapours by calcination.
4. The products formed by calcination are always porous.

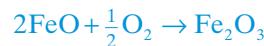
Roasting

It is the process in which the concentrated ore is heated to a high temperature (just below its fusion temperature) in presence of excess of air.

1. This process is mainly applicable for sulphide ores to get the corresponding metal oxides.



2. Sometimes the lower oxidation state oxide gets converted into higher oxidation state oxide. For example,



3. Hydrated ores become anhydrous through roasting.
4. The impurities like organic matter, S and As are removed by roasting in the form of their volatile oxides, i.e. $(\text{CO}_2 + \text{H}_2\text{O})$, SO_2 and As_2O_3 respectively.
5. The products formed by roasting are always porous.

6.5 | DIFFERENT REDUCTION PROCESSES

Carbon reduction

This process is used for commercial extraction of Fe, Sn, Zn, Pb.



This process is also known as smelting, but smelting does not always require that the reduction has to take place in that step. For example, in extraction of Cu, smelting is done without any reduction of ore. The roasted or calcined ore must be porous because the porous mass makes larger surface area available for reduction and improves the rate of reduction.

Flux is an impurity added externally to remove the impurity already present within the ore.



The choice of flux depends upon the nature of impurity/gangue present within the ore.

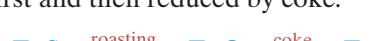
1. If the impurity is acidic (such as SiO_2), flux must be basic, e.g. CaO , MnO , etc.
2. If the impurity is basic (such as MnO , FeO), flux must be acidic, e.g. SiO_2 or P_2O_5 .

The slag formation in carbon reduction is a kind of acid–base reaction according to the Lux–Flood acid–base concept which defines acids and bases as oxide/anion acceptors and oxide/anion donors respectively. For example,

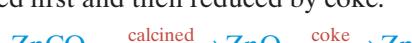
1. $\text{CaO} + \text{SiO}_2 \rightarrow \text{Ca}^{2+} \text{SiO}_3^{2-}$
oxide donor oxide acceptor slag
(base) (acid)
2. $\text{LiCl} + \text{AlCl}_3 \rightarrow \text{Li}^+ [\text{AlCl}_4]^-$
base acid

The carbon reduction process is applicable for

1. Direct reduction of oxide ore. For example,
 - a. $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO} \uparrow$
 $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2 \uparrow$
 - b. $\text{SnO}_2 + 2\text{C} \rightarrow \text{Sn} + 2\text{CO} \uparrow$
 $\text{SnO}_2 + 2\text{CO} \rightarrow \text{Sn} + 2\text{CO}_2 \uparrow$
2. Indirect reduction of sulphide, carbonate and sulphate ores. For example,
 - a. Sulphide ores are roasted first and then reduced by coke.



- b. Carbonate ores are calcined first and then reduced by coke.



- c. Sulphate ores are initially reduced to sulphides, e.g.



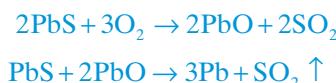
and then different possibilities are there to get molten metal.

1. $\text{PbS} + \text{PbSO}_4 \rightarrow 2\text{Pb} + 2\text{SO}_2 \uparrow$
 $\text{PbS} + \frac{3}{2}\text{O}_2 \rightarrow \text{PbO} + \text{SO}_2 \uparrow$
 $\text{PbS} + 2\text{PbO} \rightarrow 3\text{Pb} + \text{SO}_2 \uparrow$
2. $\text{PbO} + \text{C} \rightarrow \text{Pb} + \text{CO}$
 $\text{PbO} + \text{CO} \rightarrow \text{Pb} + \text{CO}_2$

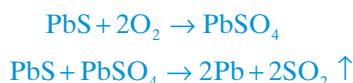
Note: The chief reducing agent for carbon reduction process is CO(g) and not C(s) because the interaction between solid oxide ore and gaseous CO is much higher as compared to that between the solid oxide ore and solid C .

Self reduction

This method is applicable to some of the sulphides, e.g. PbS , Cu_2S and HgS . It does not involve use of reducing agent from an external source. Here the sulphide ore is partially roasted into its oxide, which in turn reacts with unreacted sulphide to produce molten metal. For example,

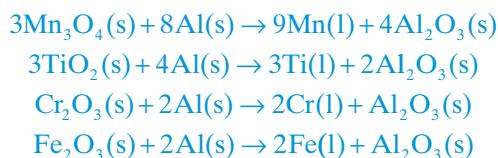


Another side reaction takes place, which is as follows



Thermite reduction (or Goldschmidt-Thermite process)

The metal oxides having very high melting points, e.g. the oxides of Cr, Mn, Ti, Mo, Fe, etc., are very difficult to reduce by carbon reduction method. These can be reduced by thermite reduction method using Al powder as reducing agent. For example,



All these reactions are highly exothermic in nature. Here Al is chosen as reducing agent due to its very high oxygen affinity. Since the formation of Al_2O_3 is exothermic in nature, it helps keep the temperature very high and thus the metal produced comes out in molten state.

The reaction of Fe_2O_3 is not used for commercial production of Fe. Primarily it is used in thermite-welding for rail road joining all over the world due to flexibility of its use anywhere. In this process, magnesium ribbon/tape is ignited and it carries the fire up to the ignition mixture, which burns together to provide

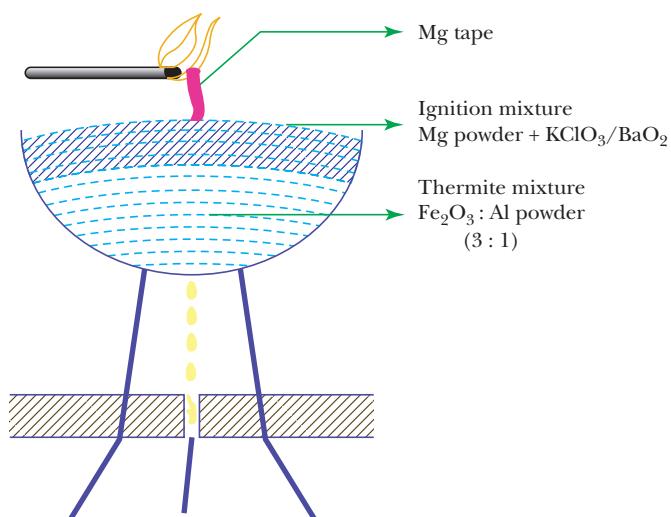
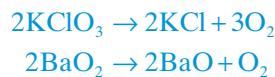


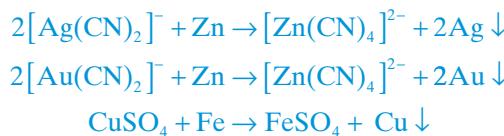
Figure 6.6 Diagrammatic representation of thermite welding.

the activation energy required for the reaction (Figure 6.6). KClO_3 or BaO_2 provides O_2 from each and every part of mixture and helps the ignition mixture to burn together.



Metal replacement method (Hydrometallurgy)

In this process, the desired metal is extracted from its solution by the addition of a more electropositive metal. The fuel cost is nil in this process because the reduction process takes place at room temperature or slightly higher temperature. Using this process, Ag, Au and Cu are precipitated from their respective solutions as follows:



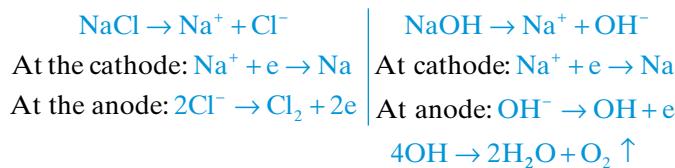
Electrolytic reduction

The oxides of strong electropositive metals such as K, Ca, Na, Al and Mg are very stable. It is difficult to reduce them into metallic state by carbon reduction process because of the following reasons.

1. The temperature requirement is very high so the fuel cost is high.
2. The collection of metals is to be done very carefully under inert environment, otherwise the metals react with air to form their respective oxides again.
3. At high temperatures, the metals being extracted may also form carbides in the presence of excess carbon taken for carbon reduction.

Such metals are extracted by passing electricity through their fused chlorides or oxides or hydroxides. For example,

1. Na is extracted from molten NaCl or molten NaOH .



2. Al is extracted from molten Al_2O_3 (details will be discussed in the individual extraction).

Note: Aqueous solution cannot be used as electrolyte here because then these electropositive metals will react again with H_2O to liberate H_2 at the cathode.

3. The metals which come below Al in the electrochemical series can be extracted by the electrolysis of the aqueous solutions of their salts. This process is applicable for Cu, Zn, Sn, Pb, etc. For example, ZnSO_4 solution can be used to get Zn



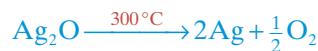
The electrode used is Zn or Al (as cathode) and the reaction at the cathode is



Similarly, CuSO_4 and SnSO_4 solutions are used to get Cu and Sn respectively.

Thermal decomposition method

Some of the metal oxides are thermally unstable and thermal decomposition is utilized to get metals from these oxides. For example,



6.6 | PURIFICATION OR REFINING OF METAL

Metals obtained by any of the above mentioned reduction processes are not pure and require further refining. There are two methods for the refining of crude metals—thermal refining and electrorefining.

Thermal refining

Oxidation by air and poling

This process is applicable for refining of Cu and Sn. In this process, the crude metal is melted and air is blasted through the melt. After air is blown, the melt is stirred with a raw wooden pole and its unburnt condition produces sufficient amount of carbon and CO to reduce the metallic oxide formed and yield refined metal. A coke powder layer is maintained at the top of the surface to prevent reoxidation of the metal formed (Figure 6.7). A small amount of metal to be refined, however, may get oxidized in this process.

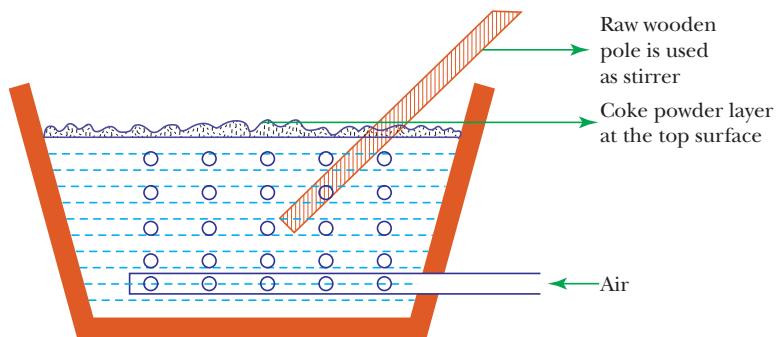
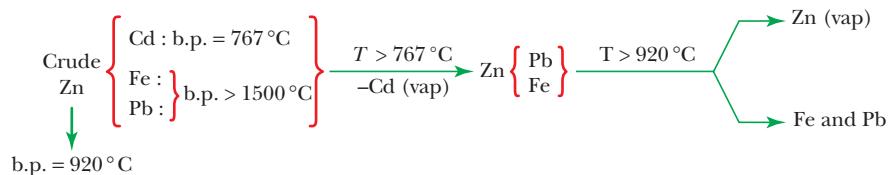


Figure 6.7 Diagrammatic representation of oxidation by air and poling.

The more basic metallic impurities are preferably oxidized by oxygen of air forming volatile or nonvolatile oxides (i.e. scum). The less basic impurities (if any) are not removed by oxidation, because under this situation metal to be refined will be oxidized in preference.

Fractional distillation

This refining process utilizes the boiling point difference between the metal and that of the impurity. Using this process, crude zinc containing Cd, Fe and Pb as impurities can be refined as follows:



At temperature $>767\text{ }^{\circ}\text{C}$, Cd separates as vapours; and at temperature $>920\text{ }^{\circ}\text{C}$, pure Zn separates as vapours leaving behind Fe and Pb impurities in the melt.

Liquation or Sweating

This method is applicable for metals, such as Sn, Pb and Bi, which have low melting points as compared to their impurities. In this method, the block of crude metal is kept at the top of the sloping furnace and heated just above the melting point of the metal to be refined. The pure metal melts and flows down the sloping hearth and gets collected in a receiver at the bottom of the slope (Figure 6.8). The perforated block of impurity is thrown later.

The impurity content has to be high enough in the crude metal, otherwise the impurities also flow down with the molten metal.

Zone refining

Metals like Si, Ge and Ga of high purity (which are used in semiconductors) are purified by this method. This process is known as ultrapurification because it results in impurity level decreasing to ppm level.

Zone refining is based upon fractional crystallization as the impurity prefers to stay in the melt and on solidification only the pure metal solidifies on the top surface of the melt. In this process, a ring furnace is heated to a suitable temperature for melting the metal rod (Figure 6.9) and producing a thin zone throughout the cross-sectional area as shown in Figure 6.10.

It is desirable that the diameter of the rod, d is small enough to give a uniform melt.

When the melted zone in the metal rod is ready, the furnace is allowed to move downwards very slowly together with the melted zone (Figure 6.11). The furnace is then switched off, cooled down and taken to the top again for repetition of the process. Almost all impurity sweeps out to the bottom after several repetitions of the process.

Vapour phase refining

The two essential criteria for the vapour phase refining process are listed as follows:

1. The intermediate compound formed has to be volatile.
2. The intermediate compound formed has to be relatively unstable, i.e. it should decompose on heating at practically achievable temperature.

This refining technique is used in the following purification processes.

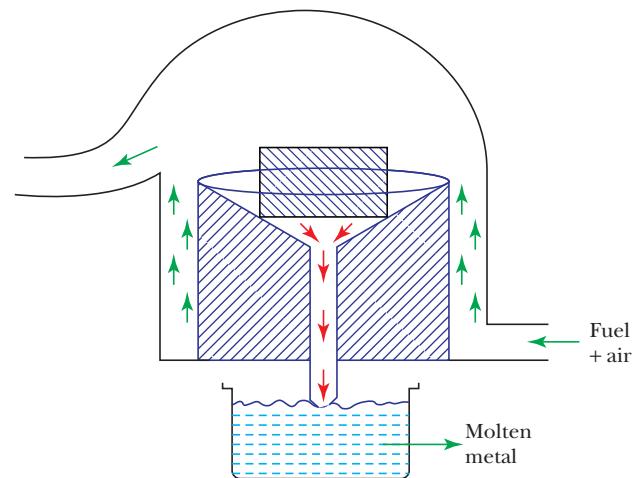


Figure 6.8 Diagrammatic representation for liquation.

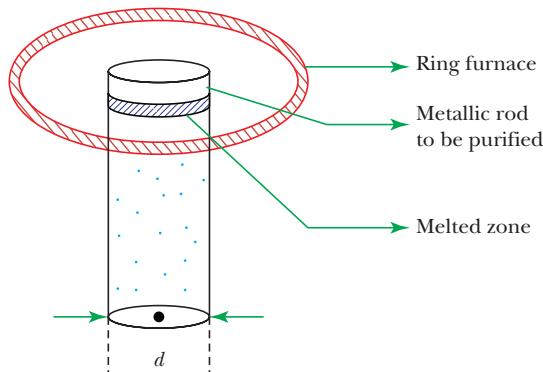


Figure 6.9 Metal rod heated by ring furnace.



Figure 6.10 Cross-sectional view of the metal rod.

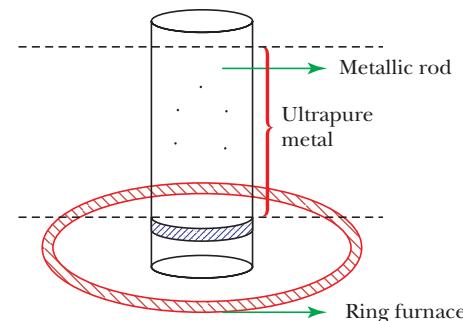


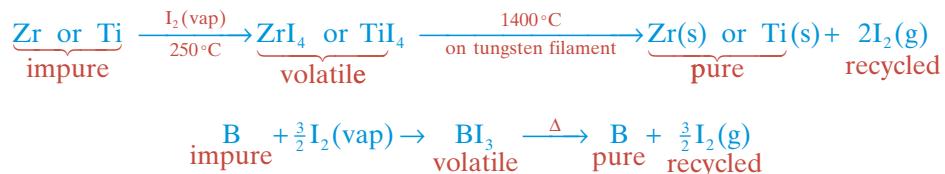
Figure 6.11 Ring furnace moving down the metal rod.

a. Mond's process for purification of nickel



If Ni(CO)_4 is not volatile, it cannot be separated from impurities, so its volatile nature helps to free it from impurities. Also Ni(CO)_4 needs to undergo thermal decomposition easily, otherwise it cannot produce pure metal.

b. Van-Arkel-de Boer process for purification of zirconium, boron and titanium



Electrorefining

This method is applicable for purification of Cu, Zn, Sn, Ag, Au, Ni, Pb and Al. The cathode is made of thin strip of pure metal (same as that to be refined) and the anode is made of large slab of impure metal (to be refined). The electrolyte is the aqueous solution of suitable salt of the metal (to be refined) or the melt of oxide/salt sometimes (Figure 6.12).

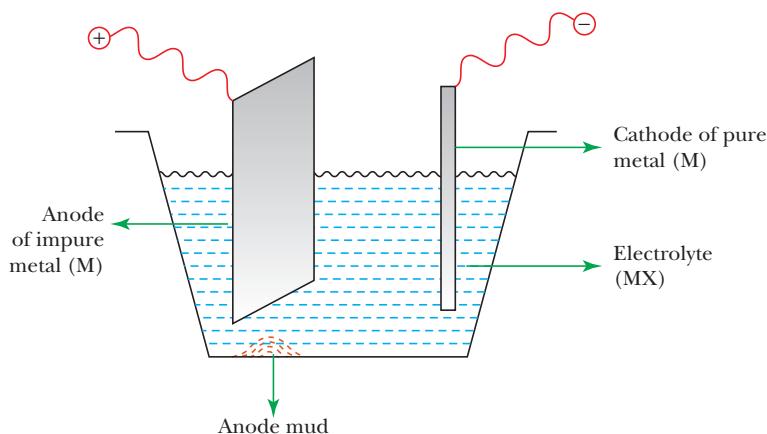


Figure 6.12 Diagrammatic representation of electrorefining.

The metal gets corroded from the anode. Pure metal gets deposited at the cathode and is purified in this way.

Reactions at the electrodes:

At cathode : $\text{M}^{n+} + ne \rightarrow \text{M}$

At anode : (i) $\text{M} \rightarrow \text{M}^{n+} + ne$ (wanted)

(ii) $\text{X}^{n-} \rightarrow \frac{1}{2}\text{X}_2 + ne$ (unwanted)

There are two reactions competing at the anode. So the anionic part of the electrolyte is to be chosen in such way that the reaction (ii) does not take place at the anode.

Hence at a particular moment, the number of moles of metal dissolved in the electrolyte is equal to the number of moles of metal ions deposited at the cathode. The concentration of metal ion in the electrolyte remains the same at a particular time.

The metallic impurities having lower oxidation potential than that of the metal to be refined are separated in the form of anode mud at the bottom.

The suitable electrolytes used in general for respective metals are:

Cu: CuSO ₄ solution	Sn: SnSO ₄ solution	Ni: Ni(NO ₃) ₂ solution
Zn: ZnSO ₄ solution	Ag: AgNO ₃ solution	Pb: PbSiF ₆ solution
	Au: AuCl ₃ solution	Al: (Al ₂ O ₃ + Na ₃ AlF ₆) melt + BaF ₂

6.7 | THERMODYNAMICS OF REDUCTION PROCESS

The extraction of metals from their oxides using carbon or other metals, and by thermal decomposition (Table 6.1), involves a number of points which merit detailed discussion.

Table 6.1 Reduction potentials and extraction methods

Element	E° (V)	Materials	Extraction method
Lithium	Li ⁺ Li	-3.05	LiCl KCl, [KCl, MgCl ₂ , 6H ₂ O] CaCl ₂ NaCl MgCl ₂ , MgO
Potassium	K ⁺ K	-2.93	
Calcium	Ca ²⁺ Ca	-2.84	
Sodium	Na ⁺ Na	-2.71	
Magnesium	Mg ²⁺ Mg	-2.37	
Aluminium	Al ³⁺ Al	-1.66	Al ₂ O ₃
Manganese	Mn ²⁺ Mn	-1.08	Mn ₃ O ₄ , MnO ₂
Chromium	Cr ³⁺ Cr	-0.74	FeCr ₂ O ₄
Zinc	Zn ²⁺ Zn	-0.76	ZnS
Iron	Fe ²⁺ Fe	-0.44	Fe ₂ O ₃ , Fe ₃ O ₄
Cobalt	Co ²⁺ Co	-0.27	CoS
Nickel	Ni ²⁺ Ni	-0.23	NiS, NiAs ₂
Tin	Sn ²⁺ Sn	-0.14	SnO ₂
Lead	Pb ²⁺ Pb	-0.13	PbS
Copper	Cu ²⁺ Cu	+0.35	Cu(metal), CuS
Silver	Ag ⁺ Ag	+0.80	Ag(metal), Ag ₂ S, AgCl
Mercury	Hg ²⁺ Hg	+0.85	HgS
Gold	Au ³⁺ Au	+1.38	Au(metal)

For a spontaneous reaction, the free energy change ΔG must be negative.

$$\Delta G = \Delta H - T\Delta S$$

ΔH is the enthalpy change during the reaction, T is the absolute temperature, and ΔS is the change in entropy during the reaction. Consider a reaction such as the formation of an oxide:



Dioxygen is used up in the course of this reaction. Gases have a more random structure (less ordered) than liquids or solids. Consequently, gases have a higher entropy than liquids or solids. In this reaction S the entropy or randomness decreases, and hence ΔS is negative. Thus if the temperature is raised then $T\Delta S$ becomes more negative. Since $T\Delta S$ is subtracted in the equation, then ΔG becomes less negative. *Thus the free energy change increases with an increase of temperature.*

The free energy changes that occur when one gram molecule of a common reactant (in this case dioxygen) is used may be plotted graphically against temperature for a number of reactions of metals to their oxides. This graph is shown in Figure 6.13 and is called an Ellingham diagram (for oxides). Similar diagrams can be produced for one gram molecule of sulphur, giving an Ellingham diagram for sulphides, and similarly for halides.

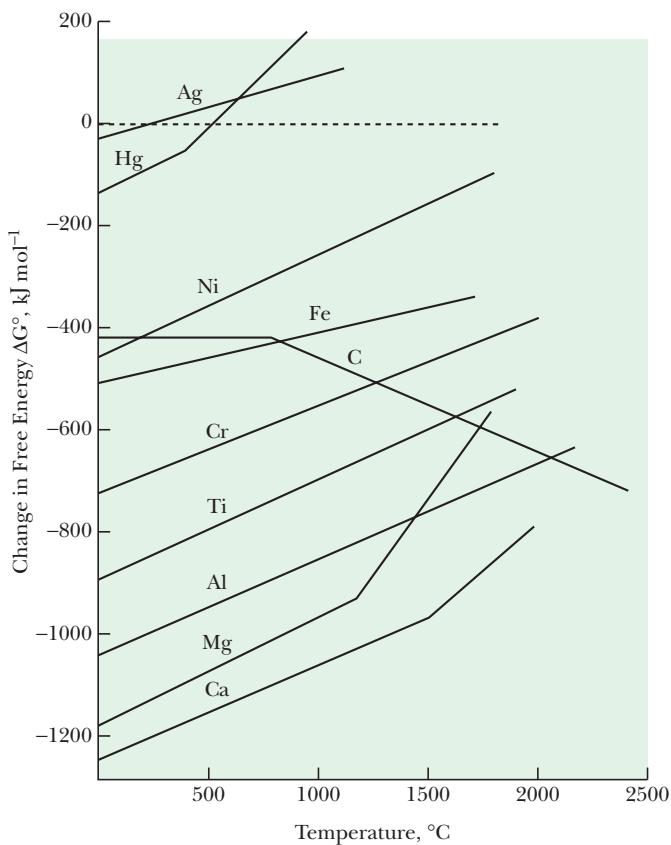


Figure 6.13 Ellingham diagram showing the change in free energy ΔG with temperature for oxides (based on 1 g mol of dioxygen in each case).

The Ellingham diagram for oxides shows several important features:

1. The graphs for metal to metal oxide all slope upwards, because the free energy change increases with an increase of temperature as discussed above.
2. All the free energy changes follow a straight line unless the materials melt or vaporize, when there is a large change in entropy associated with the change of state, which changes the slope of the line (for example, the Hg–HgO line changes slope at 356 °C when Hg boils, and similarly Mg–MgO changes at 1120 °C when Mg boils).
3. When the temperature is raised, a point will be reached where the graph crosses the $\Delta G = 0$ line. Below this temperature the free energy of formation of the oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, the oxide becomes unstable, and should decompose into the metal and dioxygen.

Theoretically all oxides can be decomposed to give the metal and dioxygen if a sufficiently high temperature can be attained. In practice the oxides of Ag, Au and Hg are the only oxides which can be decomposed at temperatures which are easily attainable, and these metals can therefore be extracted by thermal decomposition of their oxides.

4. In a number of processes, one metal is used to reduce the oxide of another metal. Any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram because the free energy will become more negative by an amount equal to the difference between the two graphs at that particular temperature. Thus Al reduces oxides of Fe, Cr, Ti in the well known thermite reaction, but Al will not reduce MgO at temperatures below 1500 °C.

In the case of carbon reacting with dioxygen, two reactions are possible:



In the first reaction, the volume of CO_2 produced is the same as the volume of O_2 used, so the change in entropy is very small, and ΔG hardly changes with temperature. Thus the graph of ΔG against T is almost horizontal.

The second reaction produces two volumes of CO for every one volume of dioxygen used. Thus ΔS is positive, and hence ΔG becomes increasingly negative as T increases. Consequently, the line on the Ellingham diagram slopes downwards (Figure 6.14). The two lines for $\text{C} \rightarrow \text{CO}_2$ and $\text{C} \rightarrow \text{CO}$ cross at about 710°C . Below this temperature, the reaction to form CO_2 is energetically more favourable, but above 710°C the formation of CO is preferred.

Carbon is extensively used to reduce iron oxide in the extraction of iron, but it may also be used to reduce any of the other oxides above it on the Ellingham diagram. Since the ΔG line slopes downwards it will eventually cross and lie below all the other graphs for metal/metal oxide. Thus in principle carbon could be used to reduce any metal oxide if a sufficiently high temperature were used. At one time MgO was reduced by C at 2000°C , followed by shock (i.e. rapid) cooling, though this process is now obsolete. Similarly the reduction of very stable oxides like TiO_2 , Al_2O_3 and MgO is theoretically possible, but is not attempted because of the high cost and practical difficulties of using extremely high temperatures. A further limitation on the use of carbon for extracting metals is that at high temperatures many metals react with carbon, forming carbides.

Many metals occur as sulphide ores. Though carbon is a good reducing agent for oxides, it is a poor reducing agent for sulphides. The reason why carbon reduces so many oxides at elevated temperatures is that the $\Delta G^\circ/T$ line for CO has a negative slope. There is no compound CS analogous to CO with a steep negative $\Delta G^\circ/T$ line. Thus sulphides are normally roasted in air to form oxides before reducing with carbon.



In a similar way hydrogen is of limited use as a reducing agent for extracting metals from their oxides since the $\Delta G^\circ/T$ line has a positive slope, and runs parallel to many metal oxide lines.



Thus only those metals with metal \rightarrow metal oxide lines above the hydrogen line will be reduced, and this does not change with temperature. A further problem with H_2 is that many metals react with hydrogen, forming hydrides, and if hydrogen remains dissolved in the metal (interstitial hydrides) it significantly affects the properties of the metal.

Thermodynamic arguments about what will reduce a given compound have two limitations. They assume that the reactants and products are in equilibrium, which is often untrue, and they indicate whether a reaction is possible but do not predict the rate of reaction, or if some alternative reaction is even more favourable.

6.8 | ALLOYS AND AMALGAMS

In general an alloy is a homogeneous metallic material which contains two or more metals as a solid solution, and if one of the constituents of the alloy is mercury, it is called amalgam.

Classification of alloys

Alloys are classified as

- 1. Ferrous alloys:** If the alloy has iron as one of its constituents, it is called a ferrous alloy, e.g. stainless steel ($\text{Cr} + \text{Fe} + \text{Ni}$), ferrosilicon ($\text{Fe} + \text{Si}$), etc.
- 2. Non-ferrous alloys:** The alloy which does not contain iron is called a non-ferrous alloy, e.g. brass ($\text{Cu} + \text{Zn}$), bell metal ($\text{Cu} + \text{Sn}$), solder ($\text{Sn} + \text{Pb}$), etc.

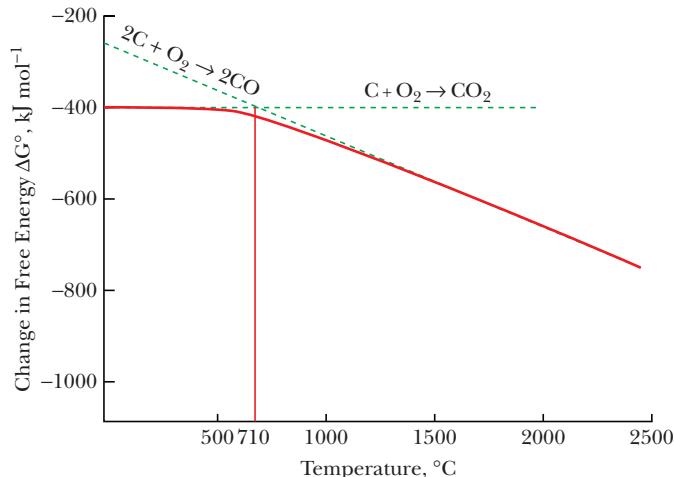


Figure 6.14 Ellingham diagram for carbon.
(The composite curve is the solid line.)

Characteristics of alloys

Alloys are prepared to develop some specific properties which are not found in the constituent elements. Both physical and chemical properties of an alloy differ considerably from those of its constituents. Some properties of metals that can be improved by preparing alloys are as follows:

- 1. Superior casting:** Formation of alloys increases the casting property of the metal. For example, Type metal (Pb-80% + Sb-16% + Sn-4%) contains Sb which expands on solidification and consequently it takes a sharp impression of the mould. Hence it improves the casting property of lead.
- 2. Hardness:** Alloys are harder than non-metals and metals from which they are made. For example, steel is harder than cast iron.
- 3. Resistance to corrosion:** Alloys are more resistant towards corrosion, e.g. stainless steel is more resistant towards corrosion than iron.
- 4. Melting point:** Alloys have low melting points as compared to their constituent elements.
- 5. Tenacity:** The tenacity of copper is doubled on addition of 5% silicon to it.

Preparation of alloys

The methods utilized for preparation of alloys are described as follows:

- 1. By fusion:** Brass (90% Cu + 10% Zn) and bronze (90% Cu + 10% Sn) are prepared by this method.
- 2. By reduction:** Aluminium bronze is prepared by heating aluminium oxide and carbon in presence of the required amount of Cu.



- 3. By compression:** The required metals are first converted into thin sheets and then rolled together and hammered under high pressure to give the alloy. Alloys like solder (50% Pb + 50% Sn) are prepared by this method.
- 4. By simultaneous electrodeposition:** An aqueous solution of the salts of the component metals is taken in an electrolytic cell and electric current is passed. The desired metals are deposited simultaneously on the cathode to give the desired alloy. For example, brass is obtained by electrolysis of a solution containing Cu and Zn cyanides in KCN solution.

Some important alloys with their compositions and uses are listed in Table 6.2.

Table 6.2 Composition and uses of some important alloys

	Alloy	Composition	Products manufactured
1	Magnelium	Al : 98%, Mg : 2%	Chemical balances
2	Duralumin	Al : 95%, Cu : 4% Mg : 0.5%, Mn : 0.5%	Air craft parts, boat machinery
3	Aluminium bronze	Al : 10%, Cu : 90%	Coins, photo frames, utensils, golden paints
4	Alnico	Al : 20%, Ni : 20% Co : 10%, Steel : 50%	Permanent magnets
5	γ -Alloy	Al : 92%, Cu : 4% Mg : 1.5%, Ni : 2.5%	Pistons and machine parts
6	Nickeloy	Al : 95%, Cu : 2%, Ni : 1%	Aircraft parts
7	Pewter	Pb : 20, Sn : 50	Utensils
8	Solder	Pb : 75, Sn : 20	Soldering
9	Type metal	Pb : 20, Sn : 5, Sb : 20	Printing type

(continued)

Table 6.2 (continued)

Alloy	Composition	Products manufactured
10 Bell metal	Cu : 80%, Sn : 20%	Bells making
11 Babbit metal	Sn : 90%, Sb : 7%, Cu : 3%	Bearing of machinery
12 Frary metal	Pb : 97%, Ba : 2%, Ca : 1%	Bearing of machine
13 Lino type metal	Pb : 83%, Sn : 3%, Sb : 14%	Printing type
14 Brass	Cu : 70%, Zn : 30%	Utensils
15 Bronze	Cu : 88-96%, Sn : 4-12%	Utensils, coins, statues
16 Monel metal	Cu : 27%, Ni : 68%, Fe : 5%	Pumps, turbines of ships, boilers
17 German silver	Cu : 50%, Zn : 30%, Ni : 20%	Flower vases and ornaments
18 Electron	Mg : 95%, Zn : 4.5, Cu : 0.5%	Parts of aeroplane and motor cars
19 Dutch metal	Cu : 80%, Zn : 20%	Golden yellow colour used for decorative purpose
20 Nichrome	Ni : 78%, Cr : 20%, Fe : 2%	
21 Gun metal	Cu : 87%, Zn : 3%, Sn : 10%	
22 Con Stanan	Cu : 60%, Ni : 40%	
23 Artificial gold	Cu : 90%, Al : 10%	
24 14 Carat gold	Au : 58%, Ag : 14% to 30%, Cu : 12-28%	
25 24 Carat gold	Au : 100%	
Alloys of steel		
1 Vanadium	V : 0.2-1%	
2 Chromium	Cr : 2-4%	
3 Nickel	Ni : 3-5%	
4 Manganese steel	Mn : 10-18%	
5 Stainless steel	Cr : 12-14% and Ni : 2-4%	
6 Tungsten	W : 10-20%	
7 Invar	Ni : 36%	

Amalgam

Treating different metals like Sn, Zn, Au, Na, Ag, etc. with mercury produces amalgams. Some uses of amalgam are

1. Ag–Hg or Au–Hg amalgams are used in filling dental cavities.
2. Tin amalgam is used for silvering mirrors.
3. Na–Hg amalgam is utilized to have decreased reactivity of Na.

6.9 | DIFFERENT TYPES OF FURNACES USED IN METALLURGY

Various types of furnaces used in metallurgical processes are listed below:

1. **Blast furnace:** Mainly the smelting of the roasted ore is carried out in this furnace (discussed under extraction of Fe).
2. **Reverberatory furnace:** Mainly roasting and calcination are done in this kind of furnace (Figure 6.15).

3. **Muffle furnace:** It is basically a closed chamber which is heated using an external heating arrangement so that the material to be heated does not come in direct contact with the fuel. This is used in small-scale metallurgical processes.
4. **Electric furnace:** This is used where very high temperature is necessary and the high temperature is achieved by an electric arc struck between two graphite electrodes.

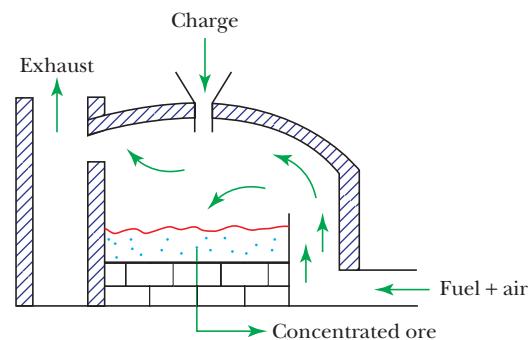


Figure 6.15 Reverberatory furnace.

6.10 | EXTRACTION OF SILVER

Important ores of silver are

1. Argentite or silver glance : Ag_2S
2. Ruby silver : $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$
3. Stromeeyerite or silver copper glance : $\text{Ag}_2\text{S} \cdot \text{Cu}_2\text{S}$
4. Horn silver : AgCl

There are three processes commonly used for extraction of Ag. The cyanide process is described below. The other two processes, i.e. Parke's process and Pattinson's process are beyond the scope of discussion.

Cyanide process or Mc-Arthur Forest process: This process is depicted in the flow diagram given in Figure 6.16.

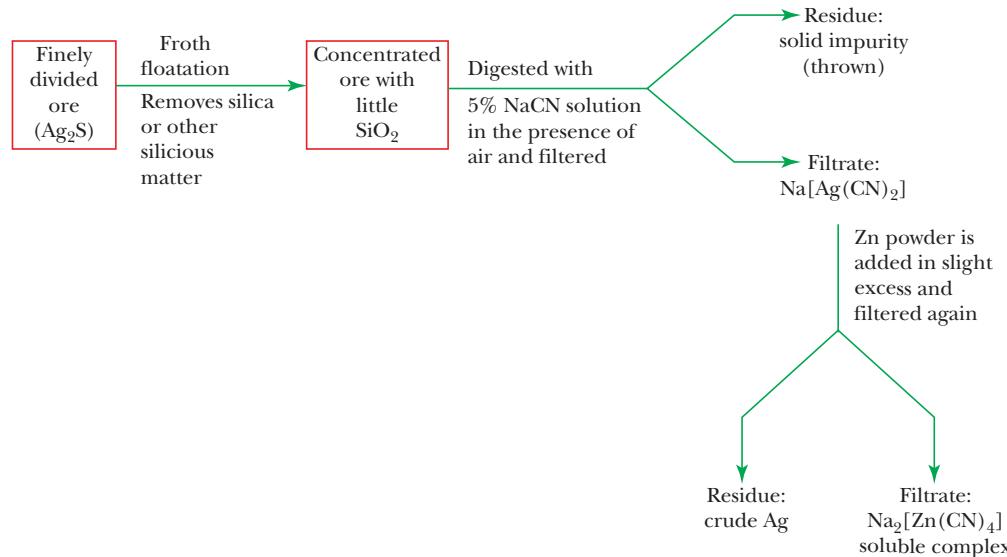


Figure 6.16 Flow chart for Mc-Arthur Forest process for extraction of silver.

Reactions taking place at the different stages in the cyanide process are as follows:



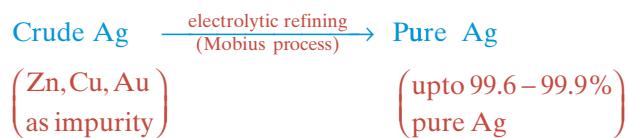
Since the above reaction is reversible, the conversion ratio is not good. Hence the process is carried out in the presence of air which converts the Na_2S produced into Na_2SO_4 and S and the overall reaction becomes unidirectional.

2. In the step involving precipitation of Ag, a little excess of Zn powder is added by which $\text{Na}[\text{Ag}(\text{CN})_2]$ becomes the limiting reagent, otherwise the loss of Ag will be more. Here Zn is chosen because it is more electropositive as compared to Ag and the replacement reaction occurs very easily.



Refining of Ag

Refining of silver is carried by electrolytic process.



Electrolyte : AgNO_3 solution + 10% HNO_3

Cathode : Pure Ag strip

Anode : Impure Ag slab

Reactions at the electrodes:

At cathode : $\text{Ag}^+ + \text{e} \rightarrow \text{Ag}$

At anode : $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}$

6.11 | EXTRACTION OF GOLD BY CYANIDE PROCESS

The flow diagram for different stages involved in the cyanide process for extraction of gold is shown in Figure 6.17.

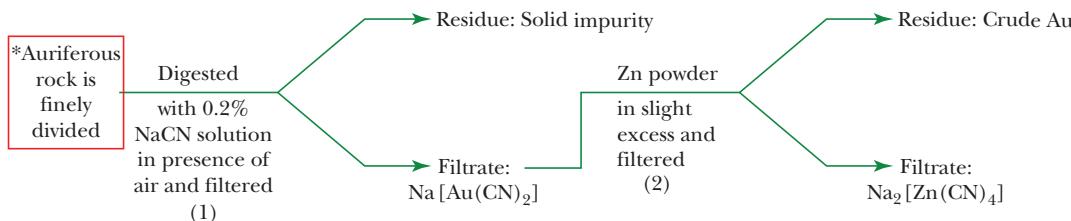


Figure 6.17 Flow chart for cyanide process for extraction of gold.

*Auriferous rock is rock of quartz contaminated with gold linings.

Reactions taking place in different steps are:

1. In step 1:



Here oxidation of Au is not possible without the presence of air and NaCN acts as a complexing agent.

2. In step 2:



Refining of Au

The steps involved in the refining of Au are given in Figure 6.18. In the third step, on heating with borax, the soluble metaborate of Cu, i.e. $\text{Cu}(\text{BO}_2)_2$, is formed and washed out with water. Similarly, in the fourth step also Ag dissolves out as Ag_2SO_4 leaving behind pure Au.

Note: 1. The removal of Ag can also be carried out using chlorine or by electrolysis.

2. Cupellation is a process, where crude gold is taken in a small bowl called cupell and melted in the presence of air. Due to high oxygen affinity of Pb, it is converted into PbO (volatile) and escapes from the system.

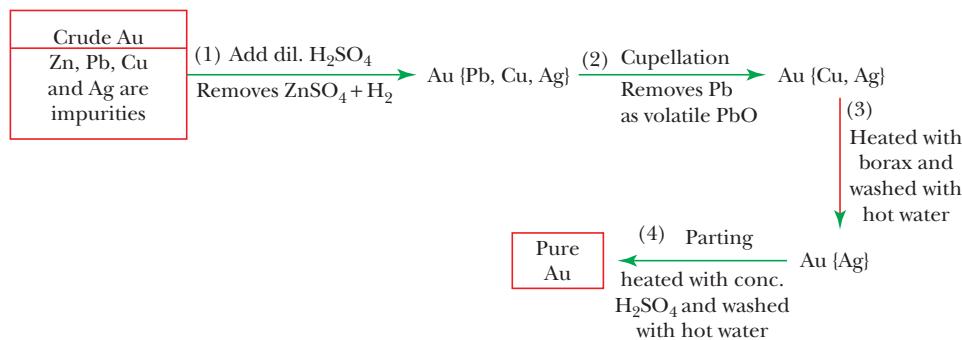


Figure 6.18 Flow chart for refining gold.

6.12 | EXTRACTION OF TIN

An important ore of tin is cassiterite or tin stone (1–5% SnO_2 present in it). The main impurities present in the ore are sand (SiO_2), pyrite of Cu and Fe, and wolframite $[\text{FeWO}_4 + \text{MnWO}_4]$. The flow chart for extraction of Sn is depicted in flow chart in Figure 6.19.

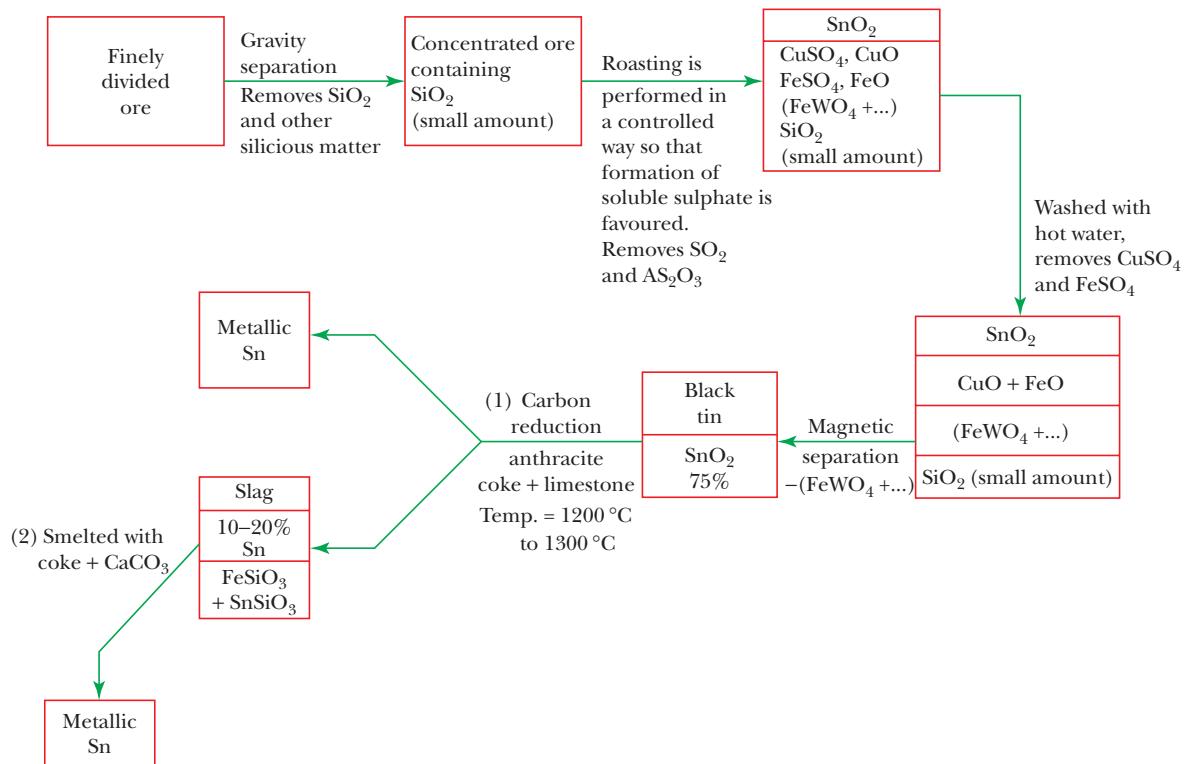


Figure 6.19 Flow chart for extraction of tin.

The reactions taking place in the extraction of Sn are:

1. In step 1:



2. In step 2:



Refining of Sn

The steps involved in the refining of Sn are shown in Figure 6.20.

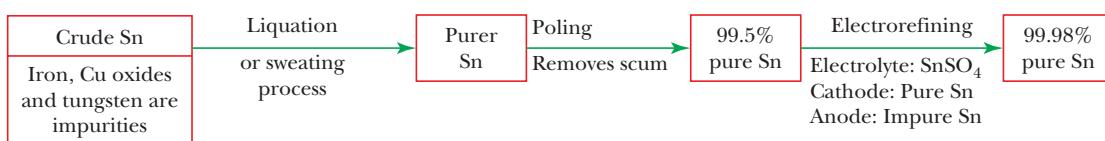


Figure 6.20 Flow chart for refining tin.

6.13 | EXTRACTION OF MAGNESIUM

The important ores of magnesium are:

1. Magnesite : $MgCO_3$
2. Dolomite : $MgCO_3 \cdot CaCO_3$
3. Carnalite : $KCl \cdot MgCl_2 \cdot 6H_2O$
4. Kainite : $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$
5. Kieserite : $MgSO_4 \cdot H_2O$
6. Asbestos : $CaMg_3(SiO_3)_4$
7. Spinel : $MgO \cdot Al_2O_3$

Two processes recommended for extraction of Mg are electrolytic reduction and carbon reduction. The latter is a very costly process due to very high temperature requirement.

Electrolytic reduction

The process for extraction of magnesium consists of the following three steps.

1. Preparation of hydrated $MgCl_2$

- a. **From carnalite ($KCl \cdot MgCl_2 \cdot 6H_2O$):** The steps involved in the preparation of hydrated $MgCl_2$ from carnalite are depicted in Figure 6.21.

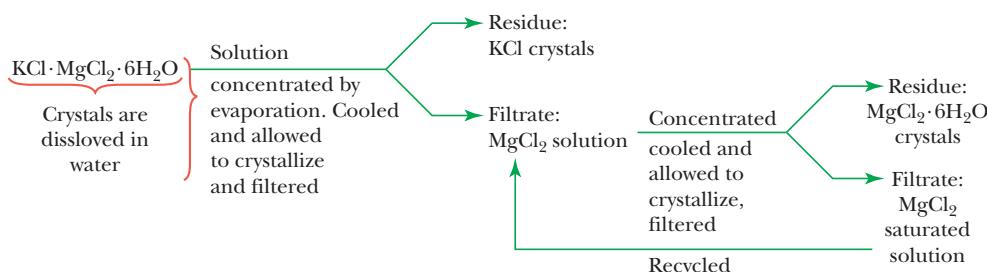


Figure 6.21 Flow chart for preparation of hydrated $MgCl_2$ from carnalite.

The principle behind this process is that KCl is less soluble as compared to $MgCl_2$ and crystallizes first.

- b. **From sea water:** Sea water consists of a lot of $MgCl_2$. The process for extraction of $MgCl_2$ from sea water is known as Dow sea water process. The steps involved in the process are depicted in Figure 6.22.

The principle behind this process is that $Ca(OH)_2$ is soluble in water while $Mg(OH)_2$ is sparingly soluble in water.

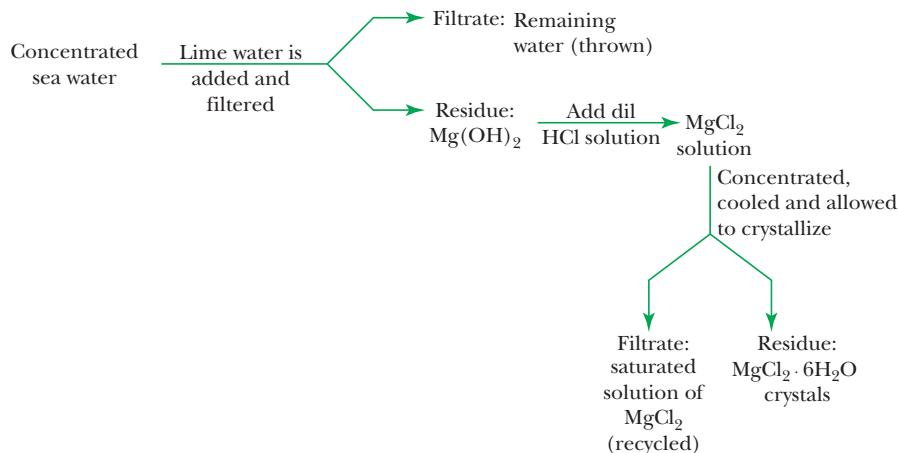
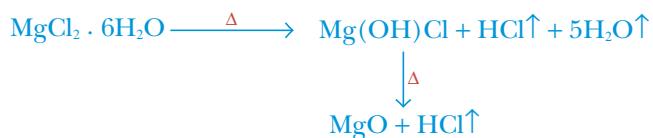


Figure 6.22 Flow chart for preparation of hydrated MgCl_2 from sea water.

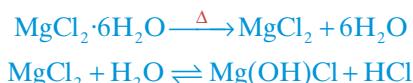
2. Conversion of hydrated MgCl_2 to anhydrous MgCl_2

On direct heating of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, anhydrous MgCl_2 cannot be obtained due to its hydrolysis.



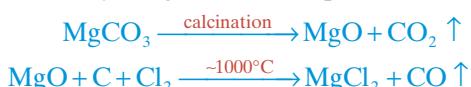
Also, MgO formed is an unwanted substance in the electrolytic reduction step due to its very high melting point (i.e. 2850°C).

Hence hydrated MgCl_2 is heated to 175°C in vacuum in a current of dry HCl gas and MgCl_2 (anhydrous) is formed.



When dry HCl is present in the system, the hydrolysis equilibrium shifts towards left but due to increase in thermal energy of the system, the decomposition reaction continues and results in anhydrous MgCl_2 .

An alternative method for preparation of anhydrous MgCl_2 involves heating calcined magnesite (MgO) to 1000°C in a current of dry Cl_2 gas with coke powder.



3. Electrolytic reduction of anhydrous MgCl_2

The schematic representation of electrolytic reduction of anhydrous MgCl_2 is shown in Figure 6.23.

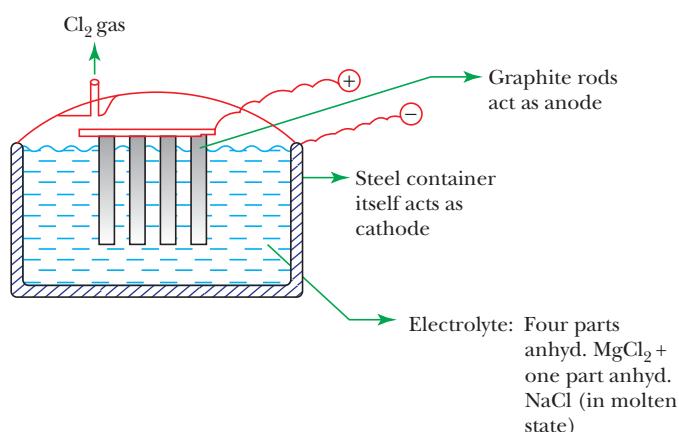


Figure 6.23 Electrolytic reduction of anhydrous MgCl_2 .

Reactions at the electrodes:



The container for electrolytic cell has to be covered and the air present inside is removed by passing the coal gas through an opening (not shown in the diagram) to prevent the oxidation of Mg formed which is floating on the top surface of the molten electrolyte.

The electrolyte in the molten state consists of four parts anhydrous MgCl_2 and one part anhydrous NaCl . One part of NaCl is added to reduce the melting temperature of the electrolyte from 1200°C (m.p. of pure MgCl_2) to 700°C and at the same time electrical conductivity of the melt is also increased.

Fused carnalite may also be used as electrolyte because both Na and K are more electropositive as compared to Mg and hence Mg^{2+} is preferably discharged at the cathode.

Carbon reduction process

In this process for extraction of magnesium, initially MgO is produced from calcination of MgCO_3 which is then directly heated with coke powder at around 2000°C in a closed electric furnace.



Mg thus obtained comes out in the vapour form and cooled suddenly to about 200°C by dilution with a large volume of H_2 gas to prevent reoxidation of Mg.

Note: b.p. of Mg is $\sim 1100^\circ\text{C}$.

Other processes

Some other processes used for extraction of magnesium are:

1. **Thermal reduction of MgCl_2 :** The mixture of anhydrous MgCl_2 and CaC_2 is heated at 1500°C and the vapours of Mg are collected in the same way as in carbon reduction process.



2. **Pidgeon process:** Here the calcined mixture of dolomite and powder of ferro-silicon (80% Si) is heated to 1200°C in a closed container. Mg is vaporized and collected in a condenser.



6.14 | EXTRACTION OF ALUMINIUM

The important minerals of Al are:

1. Hydrated oxides : Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)
Gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)
Diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$)
2. Oxide : Corundum (Al_2O_3)
3. Sulphate : Alunite [$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$]
4. Fluoride : Cryolite ($3\text{NaF} \cdot \text{AlF}_3$)
5. Aluminate : Spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$)

6. Silicate : Feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$)
China clay or Kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)

Bauxite is the ore most commonly used for extraction of aluminium. Bauxite is of two types

1. Red bauxite: $Al_2O_3 \cdot 2H_2O + Fe_2O_3$ (major impurity) + $SiO_2 + TiO_2$
2. White bauxite: $Al_2O_3 \cdot 2H_2O + SiO_2$ (major impurity) + $Fe_2O_3 + TiO_2$

The main steps involved in the extraction of Al from bauxite are:

1. Beneficiation of bauxite and preparation of pure alumina.
2. Electrolytic reduction of pure alumina.
3. Electrorefining of aluminium.

Beneficiation of bauxite

Different processes adopted for beneficiation of red and white bauxite are described below.

Bayer's process

This is used for beneficiation of red bauxite. Various stages of the process are depicted in the flow chart (Figure 6.24).

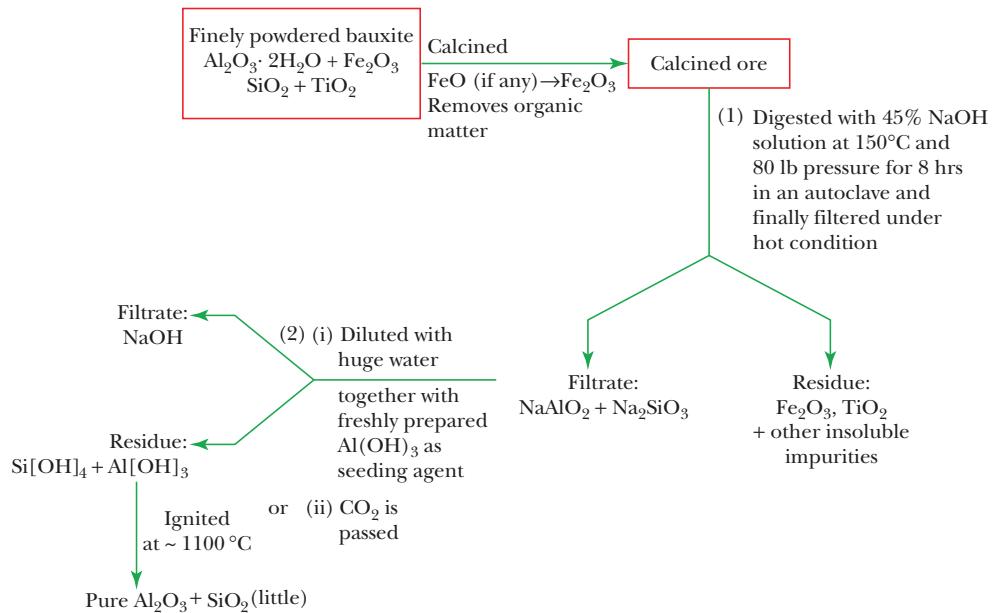


Figure 6.24 Flow chart for Bayer's process for beneficiation of bauxite.

The reactions involved in the above process are:

1. In step 1:



2. In step 2:



Since Al(OH)_3 is amphoteric in nature, it gets dissolved in alkali as well as in acid as shown in reactions above. Hence to get Al(OH)_3 from $[\text{Al(OH)}_4]^-$, the pH of the medium is to be reduced but it is to be taken care that the pH is not low enough to dissolve it further in the form of Al^{3+} . The decrease in pH can be done by

1. adding large amount of water which increases the volume and decreases the pH. But without the seeding agent (which provides the nucleus of the precipitate) the precipitation is delayed.
2. acidification which reduces the pH of the medium. But here a strong acid is not recommended to avoid any further dissolution of Al(OH)_3 in the form of Al^{3+} . Hence weak acid like CO_2 gas is passed which reacts as follows:



OH^- ions are consumed in the above reaction and the formation of Al(OH)_3 is favoured.

Note: The Bayer's process cannot be adopted for white bauxite because the major impurity SiO_2 is also separated out along with Al_2O_3 and finally Al_2O_3 of inferior quality is formed.

Hall's process

This process is adopted for beneficiation of low grade red bauxite. Various stages of the process are depicted in the flow diagram in Figure 6.25.

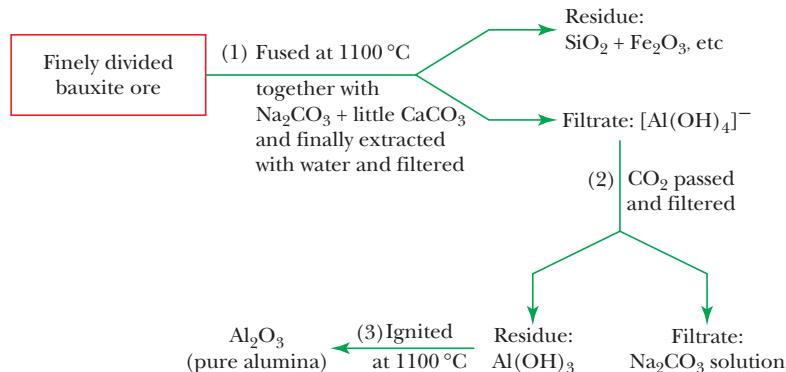
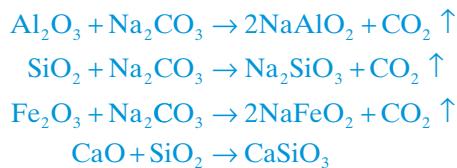


Figure 6.25 Flow chart for Hall's process for beneficiation of low grade red bauxite.

The reactions involved in the above process are:

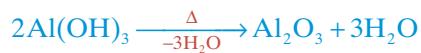
1. In step 1:



2. In step 2:



3. In step 3:



Serpeck's process

This process is used for beneficiation of white bauxite. Various steps of this process are depicted in the flow diagram in Figure 6.26.

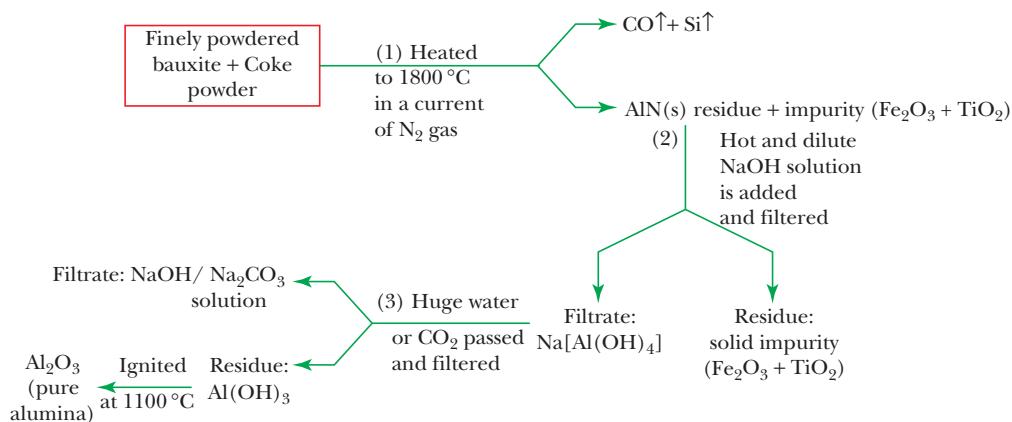
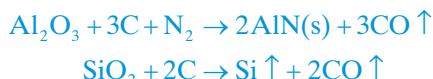


Figure 6.26 Flow chart for Serpeck's process for beneficiation of white bauxite.

The reactions involved in the above process are:

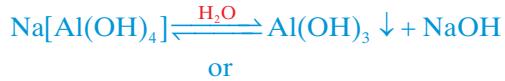
1. In step 1:



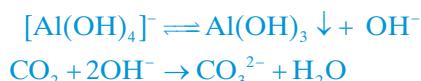
2. In step 2:



3. In step 3:



or

**Electrolytic reduction of pure Al_2O_3**

In electrolytic reduction of Al_2O_3 , i.e. molten alumina (20 %) mixed with cryolite (60%) and fluorspar (20 %) is taken in an iron tank with carbon lining that acts as the cathode. A graphite rod hanging from the top acts as the anode. A powdered coke layer is maintained at the top (Figure 6.27).

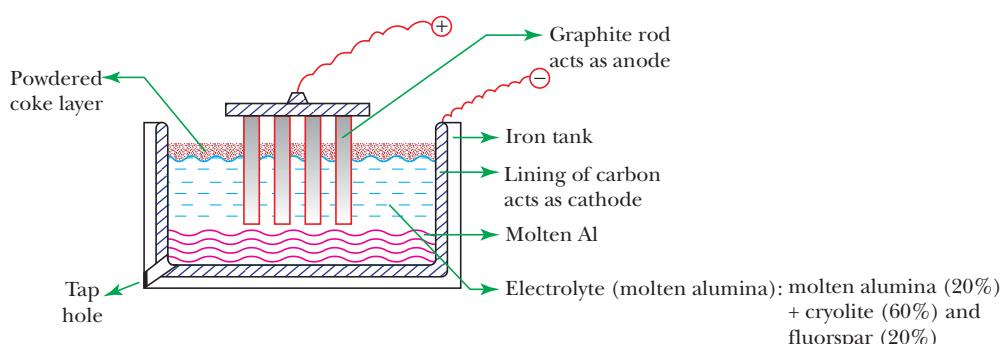


Figure 6.27 Electrolytic reduction of alumina.

On electrolysis molten Al is deposited at the cathode and since Al is heavier as compared to the electrolyte, it gets deposited at the bottom, while oxygen gas is liberated at the anode.

1. Reactions: $\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+} + 3\text{O}^{2-}$

At the cathode: $\text{Al}^{3+} + 3\text{e} \rightarrow \text{Al}$

Since Na and Ca are more electropositive than to Al, only Al^{3+} gets deposited at the cathode.

At the anode: $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}$

2. Functions of fluorspar (CaF_2)

a. It reduces the melting temperature of the mixture to 900°C from 2050°C (m.p. of pure Al_2O_3) and saves on the fuel cost.

b. It also improves the electrical conductivity of the melt as compared to molten Al_2O_3 .

3. Functions of cryolite

a. It also helps reduce the melting temperature of the mixture.

b. It acts as solvent and helps dissolve Al_2O_3 .

Alternative theory for electrolytic reaction at the anode can explain the dissolution of Al_2O_3 .



Since the $[\text{F}^-] \gg [\text{O}^{2-}]$, F^- ions gets discharged at the anode first which in turn react with Al_2O_3 and liberate O_2 at the anode.



4. Function of the coke powder layer at the top:

a. The oxygen liberated at the anode corrodes the anode surface reacting with graphite to produce CO and CO_2 and finally the anode cuts down at the bottom and electrical connectivity is lost (Figure 6.28).

At the junction of liquid–solid–air interface, the energy available is maximum (this can be proved thermodynamically) and corrosion is maximum at this point. To prevent this corrosion, the coke powder (having large surface area for reaction) layer is kept at the top which reacts with liberated oxygen or oxygen from the air.

b. The surface becomes rough unlike the shiny mirror like molten electrolyte; and the radiation loss of heat is also prevented.

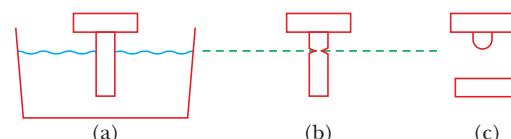


Figure 6.28 Corrosion of graphite anode.

Electrorefining of aluminium

Impure aluminium mixed with copper melt is taken in an iron tank with graphite lining. The layer of pure Al acts as the cathode. The graphite rods at the top are essential for electrical connection (Figure 6.29).

Here the electrolyte is the molten mixture of cryolite and BaF_2 saturated with Al_2O_3 . BaF_2 is added instead of CaF_2 to adjust the density in such way that it exists as a separate middle layer. Similarly in impure Al, the Cu melt is deliberately added to increase the density in such a way that it exists as a separate bottom layer.

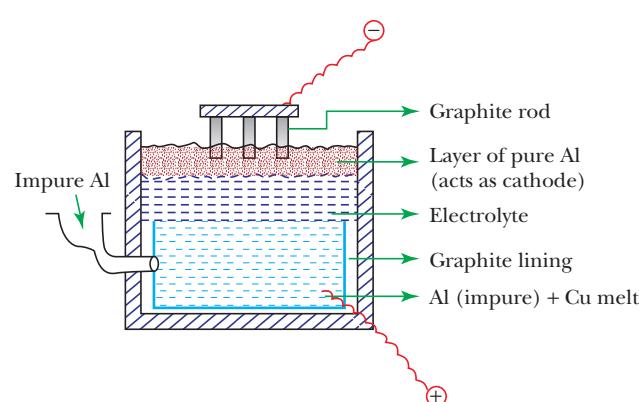


Figure 6.29 Electrorefining of aluminium.

The reactions involved in the process are:



Here the top surface of bottom layer acts as the anode and Al only enters into the electrolyte as Al^{3+} because $E_{\text{Al}/\text{Al}^{3+}}^{\circ} > E_{\text{Cu}/\text{Cu}^{2+}}^{\circ}$



Here the bottom surface of the top layer (the pure Al melt) acts as the cathode and Al^{3+} enters as Al from the electrolyte.

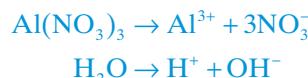
Note: (i) Impurities like Fe, Si and Cu remain intact in the bottom layer.

(ii) When the thickness of the top layer is increased to certain limit, it is drained out into a separate container.

1. Pure Al_2O_3 is not used as the electrolyte because:

- The m.p. of Al_2O_3 is 2050°C , hence the power consumption is very high.
- Al obtained at this temperature gets volatilized and the loss is very high.
- Aluminium is lighter than Al_2O_3 , and floats at the top surface and volatilizes easily, as well as attacked by the oxygen liberated at the anode.

2. The aqueous solution of Al salt cannot be used as electrolyte because hydrogen is discharged at the cathode in preference to Al as the discharge potential of H^+ is smaller compared to Al^{3+} . For example, if $\text{Al}(\text{NO}_3)_3$ is used, then the reactions involved are



3. Molten AlCl_3 is not chosen as electrolyte because being covalent in nature, it is a poor conductor of electricity. It also sublimes easily.

6.15 | EXTRACTION OF LEAD

The important ores of lead are:

1. Galena : (PbS)
2. Cerrusite : PbCO_3
3. Anglesite : PbSO_4
4. Crocoisite : PbCrO_4
5. Lanarkite : $(\text{PbO} \cdot \text{PbSO}_4)$

The ore used commercially for extraction of lead is galena. Depending upon the impurity content, lead can be extracted from galena by one of the following two processes.

1. Carbon reduction (when the impurity content is high enough).
2. Self reduction (when the impurity content is low).

Carbon reduction

The various stages involved in the carbon reduction process for extraction of lead are depicted in the flow diagram in Figure 6.30.

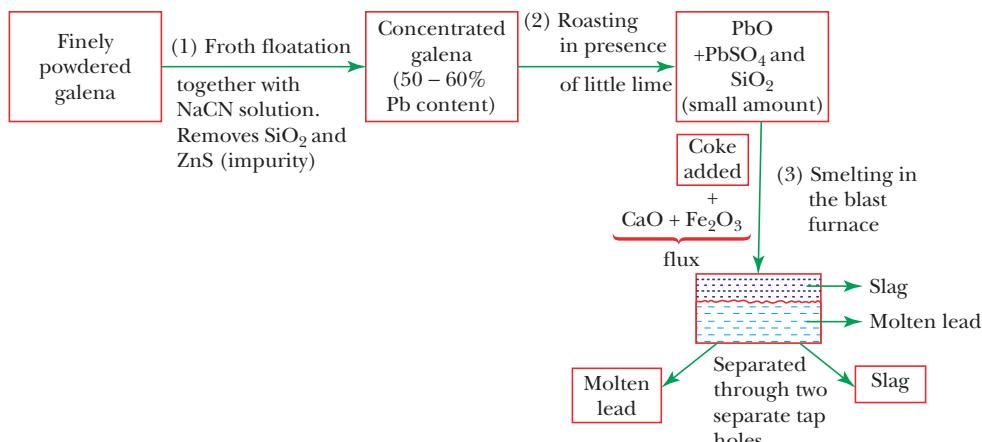
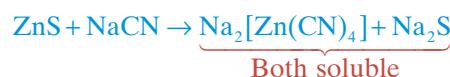


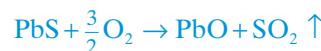
Figure 6.30 Carbon reduction process for extraction of lead.

The reactions involved at various stages of the process are:

- 1. In the froth floatation step:** PbS does not react with NaCN solution while ZnS gets dissolved in NaCN solution and its floating characteristics are completely lost.



- 2. In the roasting step:**



Function of lime: Since lime is more basic compared to PbO, the CaO reacts preferably with SiO₂ and its presence acts as negative catalyst towards the formation of PbSiO₃ and PbSO₄. It also helps to keep the mass porous and helps to complete reaction.

- 3. In the smelting step:** Initially coke is burnt in a blast of air to produce CO and CO₂



Pb formation reactions:



Slag formation reactions:



Self reduction process

The steps involved in the self reduction process are shown in the flow diagram in Figure 6.31. The reactions involved in the process are:

1. In the roasting step:



2. In the self reduction step:



Note: After partial roasting, air blasting is stopped and heating is continued for self reduction reactions.

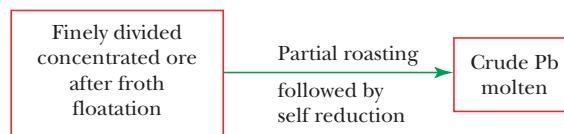
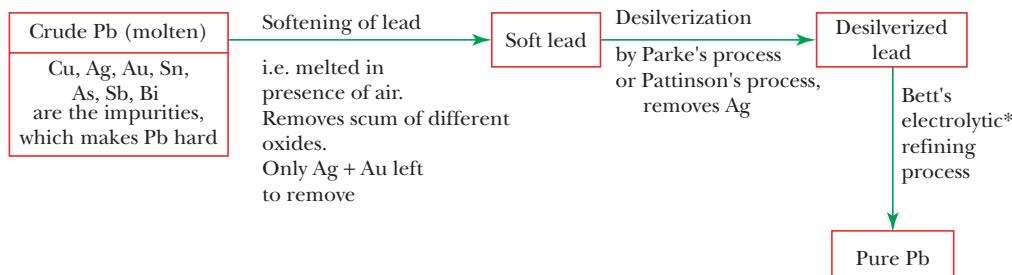


Figure 6.31 Flow chart for self reduction process for extraction of lead.

Refining of lead

The steps for refining of lead are given in the flow chart in Figure 6.32.



*Electrolyte: $\text{PbSiF}_6 + \text{H}_2\text{SiF}_6 + \text{gelatine}$
Gelatine is added to electrolyte to adjust the viscosity of electrolyte.
Anode: Impure Pb.
Cathode: Pure Pb strip.

Figure 6.32 Flow chart for refining of lead.

6.16 | EXTRACTION OF COPPER

The important ores of Cu are:

1. Chalcocite or copper glance : Cu_2S
2. Copper pyrite or chalcopyrites : CuFeS_2
3. Cuprite or ruby copper : Cu_2O
4. Malachite : $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$
5. Azurite : $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$

Less important ores of copper are chrysocolla ($\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$) and malonite (CuO).

The chief ore used for extraction of copper is copper pyrite ($\text{Cu}_2\text{S} \cdot \text{FeS} \cdot \text{FeS}_2$). The flow diagram for extraction of copper from copper pyrite is depicted in Figure 6.33.

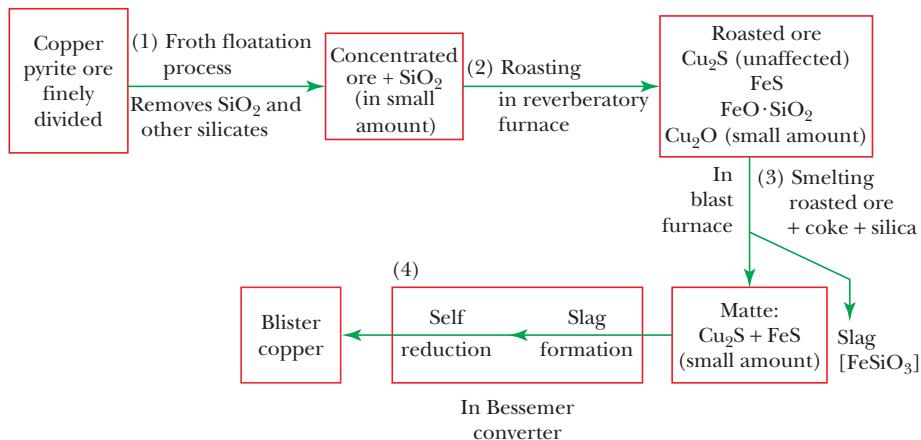
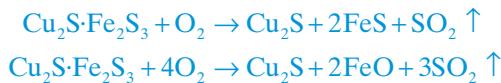


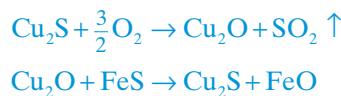
Figure 6.33 Flow chart for extraction of copper from copper pyrite.

The changes and reactions involved in the above process are:

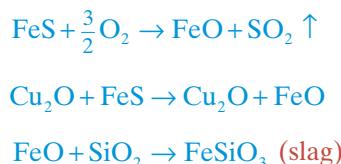
- 1. In the roasting step:** Roasting is done with excess of air and at temperature below the fusion temperature of the ore.



Since iron is more electropositive as compared to copper, its sulphide is preferentially oxidized and Cu₂S remains unaffected. If any Cu₂O (little amount) is formed, it also reacts with unreacted FeS to give back Cu₂S.

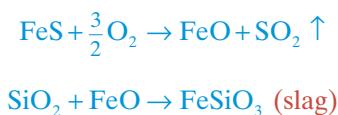


- 2. In the smelting step:** Coke is used here as fuel to maintain such temperature that keeps the mixture remains in the molten state.



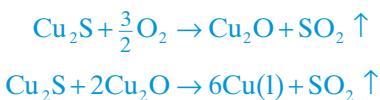
Slag being lighter floats as an immiscible layer on the top surface of Cu₂S (matte) and is removed through a separate hole.

- 3. In the Bessemer converter:** The raw material for the Bessemer converter is matte, i.e. Cu₂S + FeS (little). Here air blasting is initially done for slag formation and SiO₂ is added from external source.

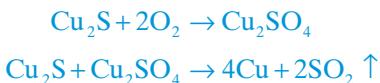


During slag formation, the characteristic green flame is observed at the mouth of the Bessemer converter which indicates the presence of iron in the form of FeO. Disappearance of this green flame indicates that the slag formation is complete. Then air blasting is stopped and slag is removed.

Again air blasting is restarted for partial roasting before self reduction, until two-thirds of Cu₂S is converted into Cu₂O. After this, only heating is continued for the self reduction process.



and



Thus the molten Cu obtained is poured into large container and allowed to cool and during cooling the dissolved SO_2 comes up to the surface and forms blisters. It is known as blister copper.

Refining of blister copper

Blister Cu contains 2–3% impurity (mainly Fe, S and As). The steps involved in its refining are depicted in the flow diagram in Figure 6.34.

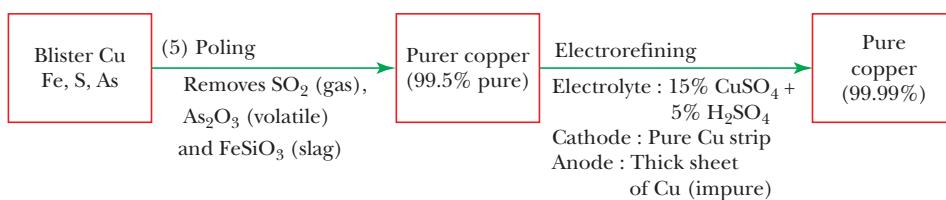


Figure 6.34 Refining of blister copper.

In the poling step, little Cu_2O formed is reduced to metallic Cu by the reducing gases produced from charring of green wooden pole. The powdered anthracite (coke) spread on the top surface of the molten mass also helps produce a reducing environment.

In the electrorefining step, the impurities like Fe, Ni, Zn get dissolved in the solution while Au, Ag and Pt are deposited as anode mud below the anode.

6.17 | EXTRACTION OF ZINC

The various ores of zinc are:

1. Zinc blende : ZnS
2. Zincite : ZnO
3. Franklinite : $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$
4. Calamine : ZnCO_3
5. Willemite : ZnSiO_3
6. Electric calamine : $\text{ZnSiO}_3 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$

The chief ore used for extraction of zinc is zinc blende, which is also known as 'Black Jack' due to the invariable association of galena (PbS) that is black in colour. Sometimes, calamine is also used to extract Zn by carbon reduction process.

The flow diagram for extraction and refining of zinc from zinc blende is depicted in Figure 6.35. The changes and reactions involved at various stages of zinc extraction are:

1. **In the froth floatation step:** This is done in two steps to separate out PbS and ZnS depending upon their different floating characteristics. On addition of pine oil, PbS floats first and is removed. Then more pine oil is added and ZnS floats on the top.

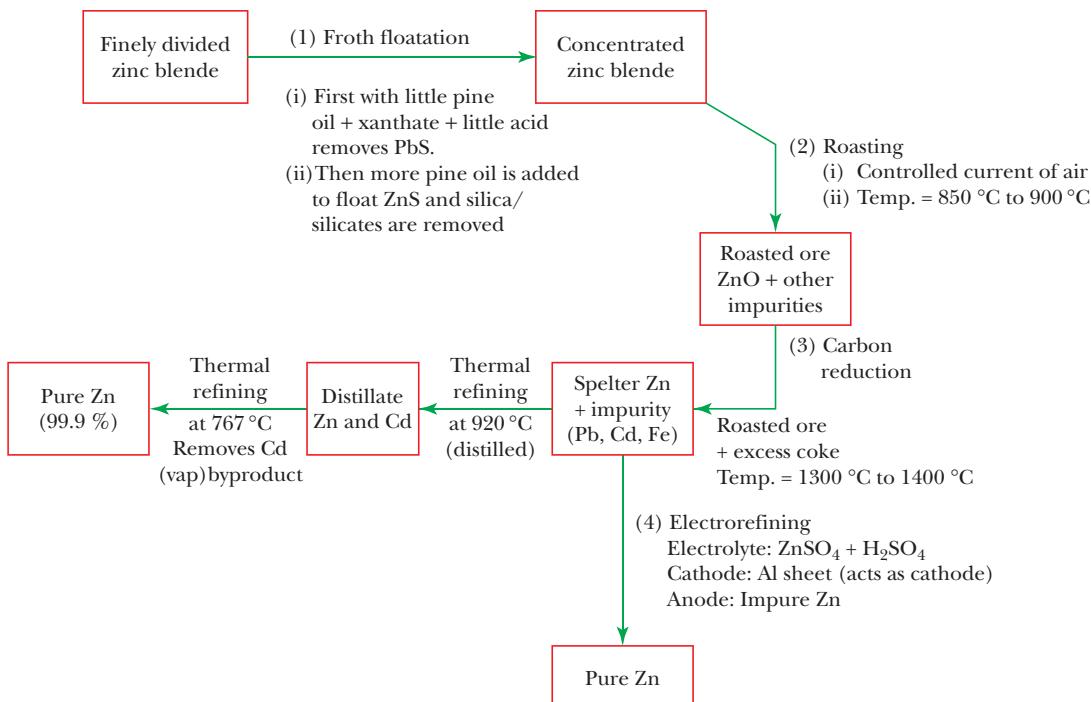
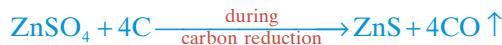
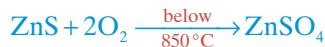
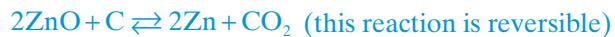


Figure 6.35 Flow chart for extraction and refining of zinc from zinc blende.

2. **In the roasting step:** During roasting, the temperature has to be above 850 °C and the air current must be controlled because below 850 °C and in excess of air, ZnS is converted into ZnSO₄ which converts back to ZnS during carbon reduction of roasted ore.

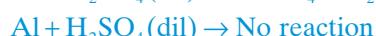
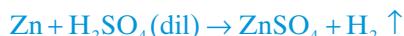


3. **In the smelting step:** During smelting, excess coke is used to stop the production of CO₂. Otherwise, Zn produced will be converted back to ZnO. Hence if any CO₂ is produced, it is allowed to convert into CO by the reaction with coke.



Temperature during smelting is kept above 1300 °C though the b.p. of Zn is 920 °C. The temperature is kept much higher as compared to that required for vapourizing zinc from the furnace. This is done because the reaction of carbon dioxide with coke is highly endothermic and brings down the temperature to below 920 °C and the evaporation of Zn is affected. Hence the temperature is maintained at 1300 °C–1400 °C.

4. **In the electrorefining step:** For electrorefining of Zn (crude), Al sheet is used as cathode instead of pure Zn strip. This is because the electrolyte used is ZnSO₄ + H₂SO₄(dil.), and in dil. H₂SO₄, Zn gets dissolved while Al does not.



Reactions at the electrode:



Note: The H_2SO_4 is added in the electrolyte together with ZnSO_4 to increase the over voltage of H^+ . This helps in the deposition of only Zn^{2+} at the cathode, otherwise H_2 will be evolved at the cathode.

6.18 | EXTRACTION OF IRON

The various ores of iron are:

1. Haematite : Fe_2O_3
2. Magnetite : Fe_3O_4
3. Brown haematite or limonite : $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
4. Siderite or spathic iron ore : FeCO_3
5. Iron pyrite : FeS_2

The chief ore used for extraction of iron is haematite, while FeS_2 is never used because iron obtained from this ore contains a lot of sulphur which makes it brittle and of no use. The flow diagram for extraction of iron from different ores is depicted in Figure 6.36

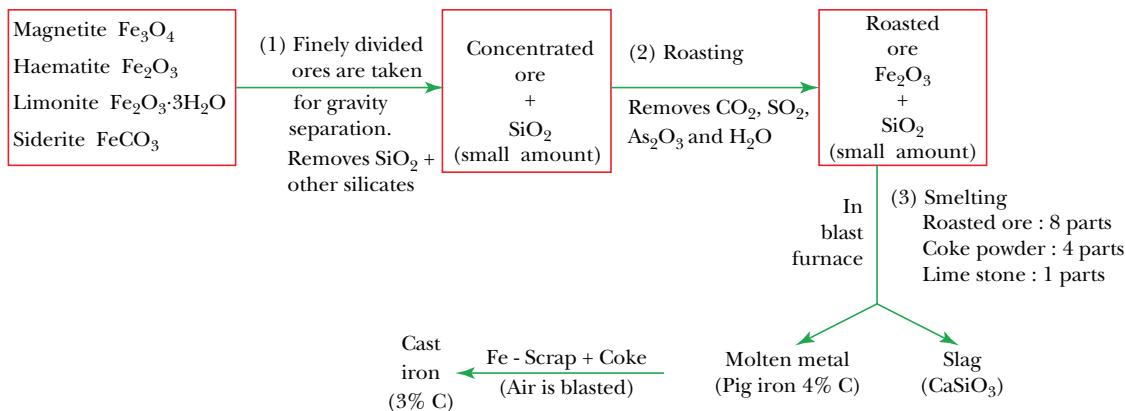
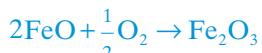


Figure 6.36 Flow chart for extraction of iron from haematite.

The reactions at various steps of the iron extraction process are :

1. In the roasting step:



Hence the final product of roasting is Fe_2O_3 .

Though there is no sulphide ore yet roasting is adopted here to convert all FeO present into Fe_2O_3 . As Fe_2O_3 does not form slag, this prevents the loss of FeO as slag (FeSiO_3).

2. In the smelting step:

The various changes taking place during smelting in the blast furnace are shown in Figure 6.37. The reactions involved are:

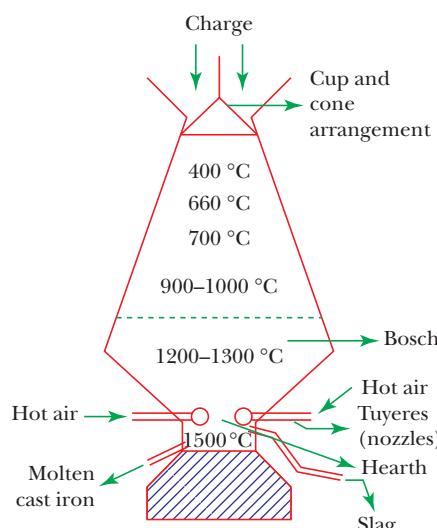
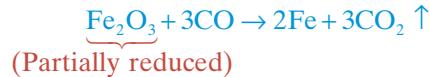
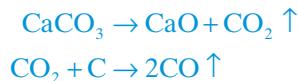


Figure 6.37 Smelting in the blast furnace.

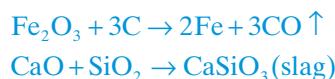
At 600–900°C:



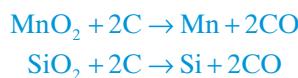
At 900–1000°C:



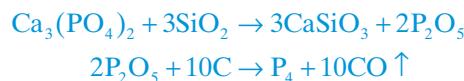
At 1000–1300°C:



At 1500°C (i.e. at the hearth): The coke powder crossing the line of tuyers does not have the scope of burning any more and reacts with MnO_2 and SiO_2 to produce impurities like Mn and Si as follows:



$\text{Ca}_3(\text{PO}_4)_2$ present in the limestone reacts with SiO_2 to produce slag and P_2O_5 is reduced by coke to produce P_4 as impurity.



Finally the cast iron produced consists of impurities like Mn, Si, P, C and S.

Purification of iron or preparation of wrought iron

Wrought iron is the purest form of iron which contains the total impurity less than 0.5%. The carbon content is 0.1 – 0.15% and other impurities (Mn, P, S, Si) are less than 0.3%. The steps involved in preparation of wrought iron are shown in the flow diagram given in Figure 6.38.

The haematite lining has a special significance as it removes the impurity as well as produces iron at that place.

The various reactions taking place in the process are:

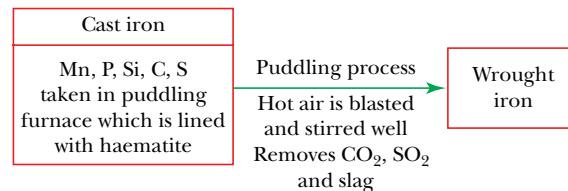
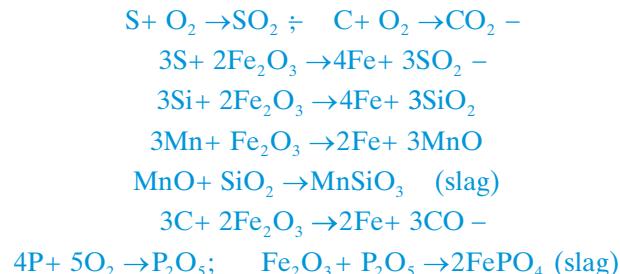


Figure 6.38 Flow chart for preparation of wrought iron from cast iron.

Byproducts of iron extraction

- Slag:** It consists of huge amount of CaSiO_3 and little $\text{Al}_2(\text{SiO}_3)_3$. These days it is used for making cement and now is known as slag cement.
- Blast furnace gas:** The composition of the blast furnace gas is 58% N_2 , 25% CO , 10.5% CO_2 and 6.5% H_2 and the rest are hydrocarbons. It contains a very large quantity of CO and the H_2 which constitutes a good fuel. It is used for preheating the air used and for cooking purpose also.

Steel making

Steel is made by removing most of the carbon and other impurities from pig iron. Composition of various steels depending upon percentage of carbon is given as follows

% C	Type of steel
0.15 – 0.3	Mild steel
0.3 – 0.6	Medium steel
0.6 – 0.8	High carbon steel
0.8 – 1.4	Tool steel

The steel making process involves melting and oxidizing C, Si, Mn, S and P present in the pig iron so that these impurities are removed as gases or converted into slag. This is followed by addition of required additives (i.e. different elements) to iron to impart desired properties to steel.

Different elements present in steel provide different properties as described below

Element	Properties imparted
P above 0.05%	Imparts low tensile strength and cold brittleness.
Mn	Imparts high hardness and increases tensile strength, e.g. rail road contains 13% Mn.
Cr and Ni	Imparts stainless characteristic by producing impervious coating of their oxides on the surface.
N (above 0.01%)	Makes steel brittle as well as difficult to weld
C	Improves hardness and strength.

The addition of mixture of C and Mn into produced steel is known as 'spiegeleisen'. C and Mn act as deoxidizers, remove any dissolved O₂ and reduce FeO (if any). The excess carbon (if any) supplies the desired quality. Mn makes the steel hard and improves its tensile strength also. Various processes used for preparation of good quality steel are:



1. Puddling process: This process involves stirring of molten iron in reverberatory furnace by rods which are consumed in the process.
2. Bessemer and Thomas process
3. Siemens open hearth process
4. Basic oxygen process (also called Linz-Donawitz (L.D.) process).

All these processes are developed to economize the production of steel from iron. In the Bessemer and Thomas process or Siemens open hearth process, impurities are oxidized by air; while in the L.D. process, pure O₂ is used for the oxidation of impurities. This is because in the first two processes the molten metal takes up small amount of nitrogen from the air. In concentrations above 0.01%, nitrogen makes steel brittle and nitriding the surface makes the metal more difficult to weld. The use of O₂ not only helps overcome these problems but also has the following advantages:

1. There is faster conversion, so a given plant can produce more in a day i.e. larger quantities can be handled in lesser time. For example, a 300 tonnes charge can be converted in 40 minutes compared to 6 tonnes in 20 minutes by the Bessemer process.
2. It gives a purer product and the surface is free from nitrides.

The lining of the furnace is designed based on the impurities present in the cast iron:

1. If the cast iron contains Mn, but not P, S, Si, then the lining used is silica brick and the process is known as acid Bessemer process.
2. If the cast iron contains acidic impurities such as Si, S, P, a lining of calcined dolomite (CaO·MgO) or magnesia (MgO) is used and the process is called basic Bessemer process. In this process, the P₂O₅ formed from P combines with lime and forms basic slag [Ca₃(PO₄)₂·CaO] which is known as Thomas slag. It is a valuable byproduct and sold as phosphate fertilizer.

Some heat treatment processes related to steel

- Annealing:** The hard steel is heated to bright redness ($700\text{--}800^\circ\text{C}$) and then allowed to cool to the room temperature very slowly by which the hard steel becomes soft. This process is known as annealing.
- Quenching or hardening:** The soft steel is heated to bright redness and then cooled suddenly to the room temperature immersing it into water or oil by which the steel becomes hard and brittle. This process is known as quenching.
- Tempering:** The hard and brittle steel is heated to $200\text{--}300^\circ\text{C}$ temperature range and cooled very slowly to the room temperature by which the brittleness of the steel disappears while the hardness remains same. This process is called as tempering.
- Case-hardening:** For this process the mild steel or wrought iron is heated to bright redness in the presence of hydrocarbons or $\text{K}_4[\text{Fe}(\text{CN})_6]$ or heated to bright redness followed by dipping into NaCN/KCN solution. This makes the surface layer hard due to the formation of carbide of Fe (called cementite). This kind of steel is used for making armour plates, cutting tools and machinery parts which are in constant wear and tear.
- Nitriding:** The mild steel containing 1% Al is heated to 550°C in the presence of NH_3 . This makes the surface layer hard due to formation of the nitrides of Fe and Al. This kind of steel is used for making borewell drilling equipment.

SINGLE CORRECT CHOICE TYPE QUESTIONS

- Which form of iron has the highest carbon content?
 - Steel
 - Pig iron
 - Cast iron
 - Wrought iron
 - Which of the following statements is incorrect?
 - Combination of tin stone and wolframite is non-magnetic.
 - No external reducing agent is required for the extraction of Hg from HgO .
 - For extraction of copper in Bessemer converter, the process like slag formation, oxidation, and reduction take place.
 - Poling method is mainly used when impure metal has its oxide as impurity.
 - Which of the following is not correctly matched?

Method	Used for refining
(A) Van Arkel	Zr and Ti
(B) Zone refining	Ge, Si, Ga, In
(C) Liquation	Zn and Hg
(D) Mond's	Ni
 - If formula of muscovite (white mica) is $\text{KAl}_2(\text{OH})_2 \text{Si}_3\text{AlO}_{10}$ and formula of pyrophyllite is $\text{Al}_2(\text{OH})_2 \text{Si}_4\text{O}_{10}$, then select the correct statement.
 - Mica is formed when one quarter of the Si^{IV} in pyrophyllite are replaced by Al^{3+} and the resulting negative charge is balanced by K.
 - Mica is formed when half of the Si^{IV} in pyrophyllite are replaced by Al^{3+} and the resulting negative charge is balanced by K.
 - Mica is formed when one third of the Si^{IV} in pyrophyllite are replaced by Al^{3+} and the resulting negative charge is balanced by K.
 - None of the above
 - Read the following statements:
 - Al has greater affinity than Fe, for oxygen.
 - Cast iron has impurity of zinc and lead.
 - Refining of nickel is done by vapour phase refining.
 - In cyanide process, oxygen and zinc dust are used as oxidizing agent and reducing agent, respectively.
- Choose the correct set of statements.
- I, III
 - II, III, IV
 - I, III, IV
 - I, IV
- Spiegel (or spiegeleisen) used in the manufacture of steel by the Bessemer process is an alloy of
 - iron, nickel and carbon.
 - iron, manganese and carbon.
 - iron, tungsten and carbon.
 - iron, chromium and carbon.
 - ACl_2 (excess) + $\text{BCl}_2 \rightarrow \text{ACl}_4 + \text{B} \downarrow$
- $$\text{BO} \xrightarrow[400^\circ\text{C}]{\Delta} \frac{1}{2} \text{O}_2 + \text{B}$$
- If A and B are metals, then ore of B would be
- Siderite.
 - Cinnabar.
 - Malachite.
 - Horn silver.
- In bauxite $\text{AlO}_x(\text{OH})_{3-2x}$ the value of x is
 - $0 < x < 1$
 - $x = 1$
 - $x = 0$
 - $1 < x < 0$
 - From the Ellingham graphs of carbon, which of the following statements is false?
 - CO_2 is more stable than CO at less than 983 K.

- (B) CO reduces Fe_2O_3 to Fe at less than 983 K.
 (C) CO is less stable than CO_2 at more than 983 K.
 (D) CO reduces Fe_2O_3 to Fe in the reduction zone of blast furnace.

10. Before introducing FeO in blast furnace, it is converted to Fe_2O_3 by roasting so that
 (A) it may not be removed as slag with silica.
 (B) it may not evaporate in the furnace.
 (C) presence of it may increase the melting point of charge.
 (D) None of these.

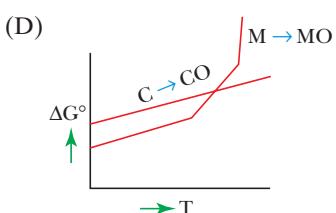
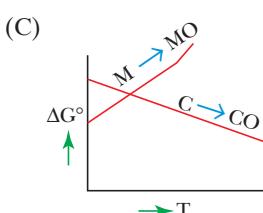
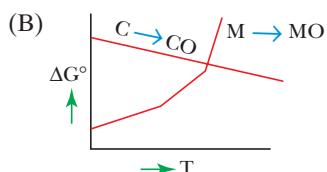
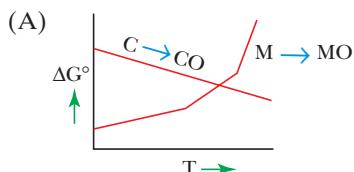
11. Match the processes with the element for which they are used.

Column-I	Column-II
(P) Bessemerisation	(1) Ti
(Q) Van Arkel Method	(2) Cast iron
(R) Carbon reduction	(3) Sn
(S) Cupellation	(4) Ag

Code:

	P	Q	R	S
(A)	2	1	3	4
(B)	3	1	2	4
(C)	2	4	3	1
(D)	1	2	3	4

12. Which of the following statements is correct?
 (A) Anthracite and chalcocite are both ores of copper.
 (B) Anthracite and chalcocite are both sulphide ores.
 (C) Both German silver and horn silver have zero percent silver content.
 (D) Malachite and azurite are both basic copper carbonates.
13. Which of the following statements is correct regarding self reduction?
 (A) Partial roasting and self reduction occur together.
 (B) First self reduction occurs followed by partial roasting.
 (C) First partial roasting occurs followed by self reduction.
 (D) Partial roasting is done in the reverberatory furnace first, and then self reduction is done in the blast furnace.
14. Which is not an ore of copper?
 (A) Atacamite
 (B) Copper glance
 (C) Chalcopyrite
 (D) Cerrusite
15. Which of the following curves assures that the metal obtained by carbon reduction is in the vapour state?



16. In the froth floatation process, pine oil
 (A) increases the surface tension of the solution.
 (B) decreases the surface tension of the solution.
 (C) does not affect the surface tension of the solution.
 (D) acts as a collector.
17. Which of the following activities is not related to poling?
 (A) Metallic impurities having higher oxidation potential than the metal to be refined are oxidized first.
 (B) Non-volatile oxides are removed in the form of scum.
 (C) Metallic impurities having lower oxidation potential than the metal to be refined settle down at the bottom of the furnace.
 (D) Green poles of wood are used as stirrers.
18. Which of the following options is incorrectly matched?

Column I	Column II
(Metal)	(Electrolyte used for electrorefining)
(A) Al	$\text{Al}_2(\text{SO}_4)_3$ aqueous solution
(B) Cu	$(\text{CuSO}_4 + \text{H}_2\text{SO}_4)$ aqueous solution
(C) Zn	$(\text{ZnSO}_4 + \text{H}_2\text{SO}_4)$ aqueous solution
(D) Sn	$(\text{SnSO}_4 + \text{H}_2\text{SO}_4)$ aqueous solution

19. Fe cannot be extracted commercially by thermite reduction process because

- (A) very high temperature is associated.
 (B) Fe is more electropositive than Al.
 (C) Al has very high affinity towards oxygen.
 (D) it is very expensive.

20. Which of the following ores can be considered as an ore of both Ca and Mg?
 (A) Dolomite
 (B) Calcite
 (C) Magnesite
 (D) Magnetite

21. Identify M and N in the following reaction.

Copper glance $\xrightarrow[\text{M} \xrightarrow{\text{N}} \text{Cu} + \text{SO}_2 \uparrow]{\text{controlled heating in presence of air}}$ M + SO₂

(A) M = Cu₂O; N = Self reduction
 (B) M = Cu₂O + Cu₂S; N = only heating
 (C) M = Cu₂O; N = carbon reduction
 (D) M = Cu₂O; N = Electrolytic reduction

22. Which of the following reactions does not take place during smelting step in carbon reduction process for extraction of Pb?
 (A) PbO + CO → Pb + CO₂
 (B) PbO + C → Pb + CO
 (C) 3PbO + $\frac{1}{2}$ O₂ → Pb₃O₄
 (D) CaO + SiO₂ → CaSiO₃

23. There are different categories of lead pencil like 4B, 3B, 2B, HB, H, 2H, 3H and 4H (where B indicates softness and H indicates hardness). Which of the following statements is correct if all these varieties of lead pencil are made of different kinds of lead?
 (A) Impurity content increases from 4B to 4H.

(B) Impurity content decreases from 4B to 4H.
 (C) Impurities have no impact on hardness.
 (D) All are incorrect.

24. Which of the following substances is used for making mirrors?
 (A) Pure Sn
 (B) Pure Hg
 (C) Zinc amalgam
 (D) Tin amalgam

25. Choose the reaction which does not indicate slag formation?
 (A) 3MgO + P₂O₅ → Mg₃(PO₄)₂
 (B) SiO₂ + PbO → PbSiO₃
 (C) Fe₂O₃ + P₂O₅ → FePO₄
 (D) None of these

26. In which of the following metal extraction processes, there is no reduction of respective ore of metal in the smelting step?
 (A) Extraction of Fe.
 (B) Extraction of Cu.
 (C) Extraction of Pb.
 (D) Extraction of Sn.

27. Which of the following characteristics of steel are developed by the tempering process?
 (A) Steel becomes hard and brittle.
 (B) Steel becomes soft.
 (C) Steel remains hard but brittleness disappears.
 (D) Only the surface layer becomes hard.

28. The purest variety of iron is called
 (A) cementite.
 (B) wrought iron.
 (C) pig iron.
 (D) steel.

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

6. Carbon reduction cannot be employed for the extraction of Al from Al_2O_3 because
 (A) the temperature requirement is very high ($\sim 2000^\circ\text{C}$).
 (B) the Ellingham diagram says Al_2O_3 is impossible to reduce by the carbon reduction process.
 (C) Al obtained in the vapour state is very difficult to handle.
 (D) Al forms its carbide (Al_4C_3) and a lot of it gets wasted.
7. Electrorefining may be employed for refining of metals like
 (A) Al and Ni.
 (B) Cu and Zn.
 (C) Sn and Au.
 (D) Pb and Ag.
8. In the Al extraction, the coke powder is used at the top of the electrolyte melt because
 (A) it makes the surface rough by which the radiation loss is minimized.
 (B) it prevents oxidation of the electrolyte by air.
 (C) it reacts with evolved oxygen at the anode and prevents the corrosion of the anode.
 (D) it increases the electrical conductivity of the melt.
9. The magnesium oxide can be reduced to Mg by which of the following reducing agents?
 (A) CaC_2
 (B) Coke powder
 (C) Cr powder
 (D) Si powder
10. In general which of the following substances are used as an electrolyte to extract Mg by electrolytic reduction?
 (A) Aqueous solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
 (B) Molten carnalite
 (C) Molten anhydrous MgCl_2
- (D) Molten (anhydrous MgCl_2 + anhydrous NaCl)
11. Which of the following reaction(s) takes place in the Bessemer converter for the extraction of Cu?
 (A) $2\text{CuFeS}_2 + 4\text{O}_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeO} + 3\text{SO}_2$
 (B) $\text{Cu}_2\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \text{Cu}_2\text{O} + \text{SO}_2$
 (C) $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$
 (D) $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$
12. Which of the following are the byproducts obtained in the extraction of copper?
 (A) SO_2 , which is further used in the manufacture H_2SO_4 by the contact process.
 (B) Gold, silver and platinum obtained as anode mud.
 (C) FeSO_4 , which is used to prepare green vitriol.
 (D) FeSiO_3 , obtained as slag, used in road making.
13. Which of the following terms is related to galvanization?
 (A) Pickling
 (B) Sherardizing
 (C) Metallizing
 (D) Hot galvanizing
14. Which of the following statements are correct regarding roasting?
 (A) Impurities are removed in the form of their elemental vapours.
 (B) Lower oxidation state oxides are oxidized further.
 (C) Sulphide ores are converted into their oxides.
 (D) The temperature of the process is maintained just above the melting point of the mixture.
15. Which are the byproducts of the extraction of iron?
 (A) Pig iron
 (B) Slag
 (C) Wrought iron
 (D) Blast furnace gas

COMPREHENSION TYPE QUESTIONS

Passage *1: For Questions 1–2

Ellingham diagram (Figure 6.39) is the graph between ΔG° and temperature for the metal oxidation reaction. It simply indicates whether a reaction is possible or not, that is, the tendency of reduction with a particular reducing agent. This is so because it is based only on the thermodynamic concepts. It does not say anything about the kinetics of the reduction process.

1. Which of the following methods of extraction is/are correctly matched?
 (A) Zn from ZnS: Roasting followed by reduction with coke.
 (B) Al from $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$: Electrolysis of Al_2O_3 dissolved in molten $\text{Na}_2\text{AlF}_6/\text{CaF}_2$.
 (C) Fe from haematite: Reduction of the oxide with CO in blast furnace.

(D) Cu from copper pyrite or copper glance: Roasting of sulphide partially and self-reduction.

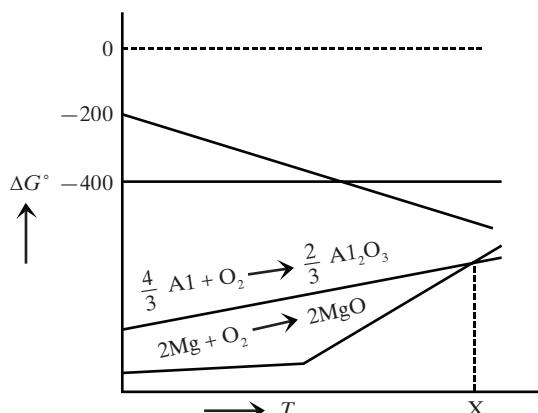
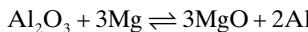


Figure 6.39 Passage 1.

2. Which of the following characteristics is/are not correctly matched at given temperature in the following options?

(A) At temperature X, $\Delta G = 0$ for



(B) Below temperature X, Mg can reduce Al_2O_3 .

(C) Mg is not used for the reduction of alumina above temperature X, although is thermodynamically feasible because the process is uneconomical.

(D) Below temperature X, Al can reduce MgO .

*One or more than one correct answers.

Passage 2: For Questions 3–5

Consider the flow chart in Figure 6.40.

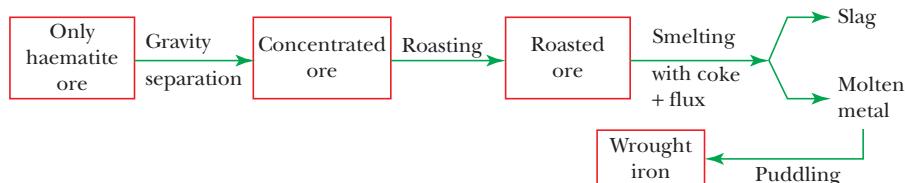


Figure 6.40 Passage 2.

3. Which of the following steps is unnecessary in the extraction of Fe as shown in the above flow diagram?

(A) Gravity separation
(B) Roasting
(C) Smelting
(D) Puddling

4. Majority of reduction reaction occurs through which of the following reactions?

(A) $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$
(B) $\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}$
(C) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2 \uparrow$
(D) $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$

5. Which of following flux is more convenient to use in the smelting process?

(A) Lime
(B) Limestone
(C) Mixture of (A) and (B)
(D) None of these

Passage 3: For Questions 6–8

In the froth floatation process, finely divided ore, water, pine oil and sodium ethyl xanthate are taken together and air is blown from the bottom of the container. Froth is formed, ore particles float on the top of the froth and are collected into a separate container. These are washed with water to remove sticking impurities. Finally, the ore is separated from impurities.

6. This process is applicable mainly for

(A) sulphate ores.
(B) sulphite ores.
(C) non-sulphide ores.
(D) sulphide ores.

7. Sometimes for other kinds of ores also, this process can be employed using a suitable reagent which is called

(A) collector.
(B) activator.
(C) frother.
(D) depressant.

8. The overall floatation of the ore occurs due to
(A) absorption process between ore particle and collector.
(B) only adsorption between ore particles and collector.
(C) adsorption and lyophilic-lyophobic aptitude of collector.
(D) only lyophilic-lyophobic aptitude of collector.

Passage 4: For Questions 9–11

The Ellingham diagram (Figure 6.41) represents the formation of oxides of several metals together with oxides of C (i.e. CO and CO_2). The diagram is not to scale yet it can help in making a lot of predictions.

9. Which is the chief reducing agent if the carbon reduction of iron oxides is carried out below 710 °C?

(A) CO
(B) C
(C) Either C or CO
(D) Cannot be predicted on the basis of given information.

10. At ~ 1100 °C, which of the following reactions is thermodynamically most favourable?

(A) $\text{TiO}_2 + \text{C} \rightarrow \text{Ti} + \text{CO}_2$
(B) $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$
(C) $\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Al} + 3\text{CO}$
(D) $\text{Cr}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Cr} + 3\text{C}$

11. Which of following statements is incorrect?

(A) Si cannot reduce MgO at all.
(B) Al can reduce MgO at above 1500 °C.
(C) Al can reduce Cr_2O_3 as well as TiO_2 .
(D) Al cannot reduce ZrO_2 but Mg can reduce ZrO_2 .

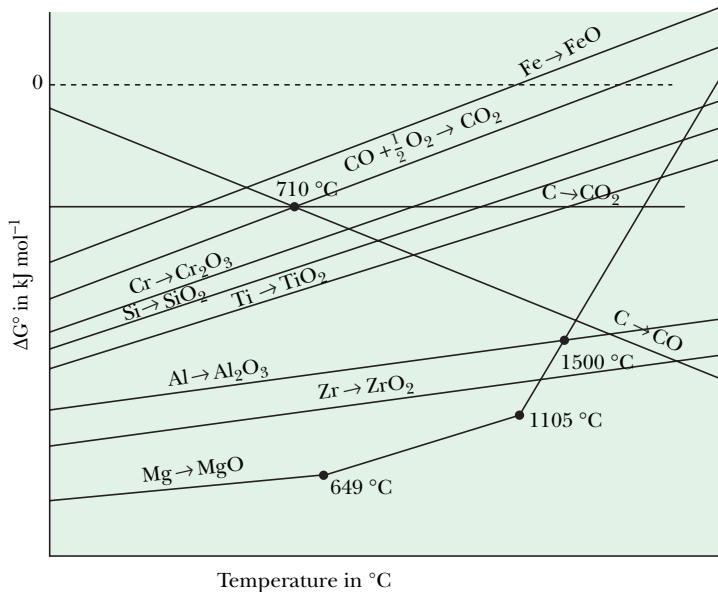


Figure 6.41 Passage 4.

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
- (C) If Statement I is true but Statement II is false.
- (D) If Statement I is false but Statement II is true.

1. Statement I: All ores are minerals.

Statement II: All minerals are ores.

2. Statement I: Dressing of the ore is an essential step in metal extraction.

Statement II: Dressing is done to improve the physical appearance of the ore.

3. Statement I: In the thermite reduction, Al powder is chosen as reducing agent.

Statement II: $2\text{Al} + \frac{3}{2}\text{O}_2 \rightarrow \text{Al}_2\text{O}_3$; ΔH for this reaction is highly negative.

4. Statement I: Al cannot reduce MgO below 1500°C while Al can reduce MgO above 1500°C.

Statement II: Mg is a liquid at less than 1500°C and gas at above 1500°C.

5. Statement I: Elements present in the anode mud of an electrolytic refining process have higher oxidation potential as compared to that of the metal to be refined.

Statement II: Impurities having higher oxidation potential as compared to the metal to be refined get dissolved in the electrolyte during electrorefining.

6. Statement I: If pure haematite is used as an ore for iron extraction, there is no need of the roasting step.

Statement II: Final product of the roasting step is Fe_2O_3 in the extraction of Fe.

7. Statement I: Choice of flux depends upon the nature of impurities within the ore.

Statement II: Flux is an impurity which is added from an external source.

8. Statement I: Both calamine and siderite are carbonate ores.

Statement II: Both calamine and siderite are the ores of lead.

9. Statement I: Sintering is the partial fusion at the contact point of grain boundaries between two grains.

Statement II: Sintering helps keep the mass porous.

10. Statement I: In the self reduction process, there is no use of reducing agent from external source, rather part of the sulphide ore acts as the reducing agent.

Statement II: The true reducing agent in the self reduction process is S^{2-} ion.

11. Statement I: Anhydrous MgCl_2 cannot be prepared by direct heating of hydrated MgCl_2 .

Statement II: During heating, hydrolysis of MgCl_2 takes place producing MgO .

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. Among the following, total number of metals from which metal is extracted by self-reduction method is _____.

Pb, Zn, Cu, Mg, Hg, Fe, Al, Au

2. Find the number of type of metals present in a mixture of ore containing sylvite, Indian saltpetre, colemanite, dolomite and anglesite.

3. Find the number of ores from the following which can be concentrated by magnetic separation method.

Fe_2O_3 , Fe_3O_4 , FeCO_3 , FeS_2 , CuFeS_2 , Cu_2O , ZnS , ZnCO_3 , ZnO

4. Among the following, number of compounds that would require electrolysis process to get their respective metal is _____.

NaCl , Cr_2O_3 , MgCl_2 , Al_2O_3 , CaCl_2 , Fe_2O_3

5. The oxidation state of Cu in chalcopyrite is _____.

6. In the smelting process of Fe, the ratio of roasting ore to coke used is approximately _____.

7. Among the following elements, number of elements for which zone refining can be used is _____.

Zr, Ga, Ti, Ge, B, Si

8. The value of n in $\text{Be}_3\text{Al}_n(\text{Si}_6\text{O}_{18})$ is _____.

9. The number of steps involved in the extraction of Zn from zinc blende is _____.

Smelting, froth floatation, distillation, electro-refining, electrolytic reduction, magnetic separation

10. The number of ores in which Pb is present is

Galena, limonite, chalcolite, azurite _____.

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the name of processes with corresponding commercial extraction of metals.

Column-I	Column-II
(A) Bessarmerisation	(P) Pb
(B) Electrolytic reduction/ refining method	(Q) Cu
(C) Carbon reduction	(R) Zn
(D) Roasting	(S) Mg
	(T) Ag

2. Match the ores with their extraction characteristics.

Column-I	Column-II
(A) Siderite	(P) Carbonate ore.
(B) Galena (with large impurity)	(Q) Ore of Fe.
(C) Calamine	(R) Carbon reduction is used for commercial extraction of metal.
(D) Magnetite	(S) Electrorefining may be used for refining of respective metal.

3. Match the reactions with the nature of process involved.

Column-I	Column-II
(A) $\text{Cu}_2\text{S} \rightarrow \text{Cu}$	(P) Calcination
(B) $\text{CaCO}_3 \rightarrow \text{CaO}$	(Q) Carbon reduction
(C) $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$	(R) Roasting
(D) Red	(S) Leaching
$\text{Bauxite} \rightarrow [\text{Al}(\text{OH})_4]^-$	(T) Self reduction

4. Match the metals/elements with the refining process employed for their purification.

Column-I	Column-II
(A) Ni	(P) Electrorefining
(B) B	(Q) Distillation
(C) Zn	(R) Vapour phase refining
(D) Sn	(S) Poling

5. Match the ore with its constituting elements.

Column-I	Column-II
(A) Chalcopyrite	(P) Fe or Ca.
(B) Dolomite	(Q) Mg or Cu.
(C) Chromite	(R) O atom.
(D) Carnalite	(S) K or Cr.
	(T) S or Cl.

6. The constituting element of ore in Column I is a component of alloy in Column II.

Column-I	Column-II
(A) Chalcocite	(P) Bronze (Cu or Sn)
(B) Bauxite	(Q) Solder (Pb, Sn)
(C) Cassiterite	(R) Duralumin (Al, Cu, Mg, Mn)
(D) Carnalite	(S) Magnelium (Mg, Al)
	(T) German silver (Cu, Zn, Ni)

ANSWERS

Single Correct Choice Type Questions

- | | | | |
|--------|---------|---------|---------|
| 1. (B) | 8. (A) | 15. (B) | 22. (C) |
| 2. (A) | 9. (C) | 16. (B) | 23. (A) |
| 3. (C) | 10. (A) | 17. (C) | 24. (D) |
| 4. (A) | 11. (A) | 18. (A) | 25. (D) |
| 5. (C) | 12. (D) | 19. (D) | 26. (B) |
| 6. (B) | 13. (C) | 20. (A) | 27. (C) |
| 7. (B) | 14. (D) | 21. (B) | 28. (B) |

Multiple Correct Choice Type Questions

- | | | | |
|------------------|-----------------------|-------------------|------------------------|
| 1. (A), (C), (D) | 5. (A), (C), (D) | 9. (A), (B), (D) | 13. (A), (B), (C), (D) |
| 2. (A), (C), (D) | 6. (A), (C), (D) | 10. (B), (D) | 14. (B), (C) |
| 3. (B), (C) | 7. (A), (B), (C), (D) | 11. (B), (C), (D) | 15. (B), (D) |
| 4. (A), (B) | 8. (A), (C) | 12. (A), (B), (D) | |

Comprehension Type Questions

- | | | | |
|-----------------------|--------|--------|---------|
| 1. (A), (B), (C), (D) | 4. (C) | 7. (B) | 10. (B) |
| 2. (C), (D) | 5. (B) | 8. (C) | 11. (A) |
| 3. (B) | 6. (D) | 9. (A) | |

Assertion–Reasoning Type Questions

- | | | | |
|--------|--------|--------|---------|
| 1. (C) | 4. (C) | 7. (B) | 10. (A) |
| 2. (C) | 5. (D) | 8. (C) | 11. (A) |
| 3. (A) | 6. (A) | 9. (B) | |

Integer Answer Type Questions

- | | | | |
|------|------|------|-------|
| 1. 3 | 4. 4 | 7. 4 | 10. 1 |
| 2. 5 | 5. 1 | 8. 2 | |
| 3. 4 | 6. 2 | 9. 4 | |

Matrix-Match Type Questions

- | | | |
|---|---|---|
| 1. (A) → (Q)
(B) → (P), (Q), (R), (S), (T)
(C) → (P), (R)
(D) → (P), (Q), (R) | 3. (A) → (R), (T)
(B) → (P)
(C) → (Q)
(D) → (S) | 5. (A) → (P), (Q), (T)
(B) → (P), (Q), (R)
(C) → (P), (R), (S)
(D) → (Q), (R), (S), (T) |
| 2. (A) → (P), (Q), (R)
(B) → (R), (S)
(C) → (P), (R), (S)
(D) → (Q), (R) | 4. (A) → (P), (R)
(B) → (R)
(C) → (P), Q
(D) → (P), (S) | 6. (A) → (P), (R), (T)
(B) → (R), (S)
(C) → (P), (Q)
(D) → (R), (S) |

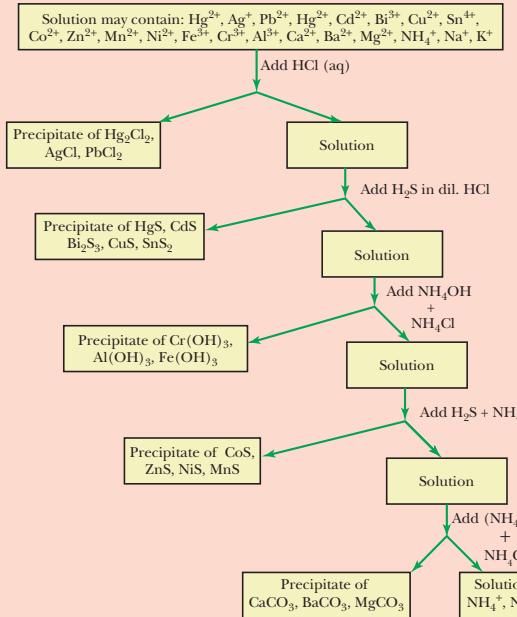
Qualitative Salt Analysis

A salt consists of:

1. cationic part, known as the basic radical.
2. anionic part, known as the acid radical.

In qualitative analysis of salts, tests are carried out for both acid and basic radicals. In general, the tests for acid radicals are done before tests for basic radicals. Acid radicals such as PO_4^{3-} , F^- , borate, silicate and arsenate interfere in the detection of metal ions during the group separation of basic radicals in an alkaline medium and are called interfering radicals. In the separation of Group 3 elements, as the solution is made ammonical, metal ions of the subsequent group may precipitate as phosphate, borate, etc. along with metal hydroxides of Group 3. Such precipitation may also occur in the absence of metal ions of Group 3. This will be misleading in the detection of metal ions. Hence, in the acid radicals test, if these radicals are detected, they should be first removed according to the standard procedure (not in the syllabus) and then the group separation of basic radicals should be carried out.

Aqueous solutions of salts are generally used for tests of acid and basic radicals. When the salt sample is insoluble in water, **soda extract** is used to prepare solution of the salt. For preparation of soda extract, a mixture of 0.5 g of sample and 1.5–2.0 g of Na_2CO_3 powder are taken with 20 cm^3 of distilled water in a 100 cm^3 beaker. The mixture is heated strongly for 10–15 minutes, filtered and the filtrate is called soda extract. The flow diagram depicting steps involved in preparation of neutralized soda extract from soda extract are given in Figure 7.1.



The classic method for separation of common cations.

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- 7.2 Tests for $\text{CO}_3^{2-}/\text{HCO}_3^-$ and $\text{SO}_3^{2-}/\text{HSO}_3^-$ Radicals
- 7.3 Tests for Sulphide (S^{2-}) Radical
- 7.4 Tests for Thiosulphate ($\text{S}_2\text{O}_3^{2-}$) Radical
- 7.5 Tests for Nitrite (NO_2^-) Radical
- 7.6 Tests for Acetate, Formate and Oxalate Radicals
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Tests for Basic Radicals

- 7.14 Dry Tests for Basic Radicals
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Heating Effects

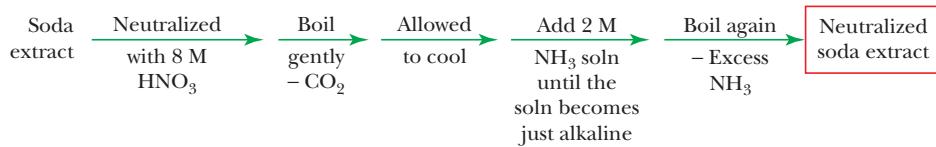


Figure 7.1 Flow chart for neutralized soda extract preparation.

Some important points regarding soda extract preparation are listed as follows:

- Instead of Na_2CO_3 , no other carbonate can be used for this purpose because all sodium salts are soluble in water and are passed into the filtrate.



- HNO_3 is used for neutralization, because *no nitrate salt is insoluble in water* and the test of nitrate is never done from soda extract.
- In the above process, NH_3 is used to make the solution alkaline because it is soluble in cold water but not in hot water. Hence excess NH_3 can be removed easily.

TESTS FOR ACID RADICALS

There is no systematic method to separate common anions into major groups and subsequently test the individual anions. However, a simple classification is suggested which is described below but it is not very rigid because some anions belong to more than one subgroup.

Class I: This class consists of radicals which are identified by volatile products obtained on treatment of radical with acid. This class is divided into two subgroups:

I A: Gases are evolved when radicals of this subgroup are treated with dil. HCl or dil. H_2SO_4 . For example, CO_3^{2-} , HCO_3^- , SO_3^{2-} , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, S^{2-} , NO_2^- , CH_3CO_2^- .

I B: Gases or acid vapours are evolved when radicals of this subgroup are treated with conc. H_2SO_4 . For example, all anions in I A + Cl^- , Br^- , I^- , NO_3^- , borate, $\text{C}_2\text{O}_4^{2-}$. However, test with conc. H_2SO_4 is not preferred for detection of radicals of subgroup IA.

Note: HCO_3^- evolves gas with both dilute as well as conc. H_2SO_4 and the latter is preferred for its test.

Class II: This consists of radicals that are dependent upon reactions in solutions for their identification. This class is divided into two subgroups:

II A: Identified on the basis of precipitation reactions. For example, SO_4^{2-} , PO_4^{3-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$.

II B: Identified on the basis of oxidation/reduction reactions. For example, MnO_4^- , MnO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$.

7.1 | ACTION OF DILUTE ACIDS

This is the first test carried out for identification of Class IA radicals. On addition of dil. HCl or dil. H_2SO_4 to the salt solution:

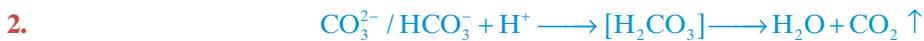
- If brown coloured fumes are formed, the presence of NO_2^- is confirmed.
- If colourless fumes are obtained, any of the remaining Class IA radicals, i.e. CO_3^{2-} , HCO_3^- , SO_3^{2-} , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, S^{2-} , CH_3CO_2^- , may be present.

Reactions involved

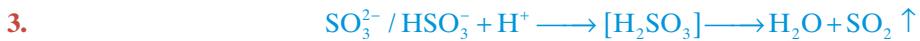
The addition of dilute acids to the salt solutions involves the following reactions with the acid radicals:

1.





Observation: Colourless, odourless gas comes out with brisk effervescence.



Observation: Colourless gas comes out with burning smell of sulphur.



Observation: Colourless gas with rotten egg smell (offensive smell).



Observation: White turbidity is observed first which finally produces a white precipitate due to the presence of free acid. H_2SO_3 formed is present in the solution and produces SO_2 gas on warming.



Observation: Vinegar smell is observed on warming.

7.2 | TESTS FOR $\text{CO}_3^{2-}/\text{HCO}_3^-$ AND $\text{SO}_3^{2-}/\text{HSO}_3^-$ RADICALS

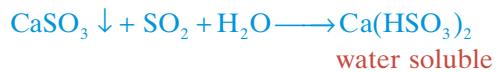
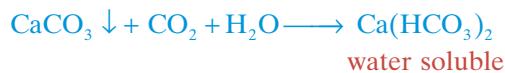
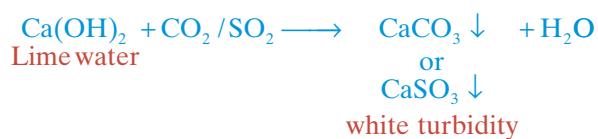
The gases evolved by addition of dilute acids to salt solutions containing radicals $\text{CO}_3^{2-}/\text{HCO}_3^-$ and $\text{SO}_3^{2-}/\text{HSO}_3^-$ are CO_2 and SO_2 respectively. The two gases can be distinguished on the basis of following two tests.

1. **Smell of the evolved gas:** If the evolved gas is odourless, it implies that the gas is CO_2 and the radicals responsible for its formation are $\text{CO}_3^{2-}/\text{HCO}_3^-$.

If the evolved gas has burning smell of sulphur, it implies that the gas is SO_2 and the radicals responsible for its formation are $\text{SO}_3^{2-}/\text{HSO}_3^-$.

2. **Lime water test:** The unknown colourless gas obtained on addition of dilute acid to the salt solution is passed through lime water. If lime water turns milky, the gas is passed in excess to obtain a clear solution. These observations imply that the gas may be (i) CO_2 or (ii) SO_2 or (iii) $\text{CO}_2 + \text{SO}_2$

Reactions involved:



Note: (i) Instead of lime water $\text{Ca}(\text{OH})_2$, baryta water $\text{Ba}(\text{OH})_2$ can also be used.

(ii) In case of CaSO_3 , the turbidity dissolves slowly.

3. **Test with oxidizing agents:** The lime water test confirms the presence of CO_2 and/or SO_2 ruling out presence of other colourless gases. Further test with oxidizing agents (O.A.) is carried out to confirm the identity as SO_2 or CO_2 .



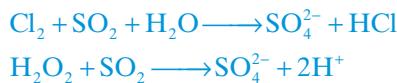
This is because carbon is already present in maximum oxidation state.



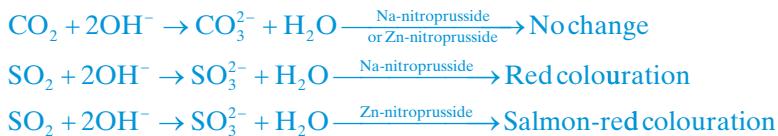
The oxidizing agents that can be used for detection of CO_2 and/or SO_2 and their relevant reactions are as follows:

- a. $\text{MnO}_4^- + \text{SO}_2 \xrightarrow{\text{H}^+} \text{Mn}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O}$
purple colourless/light pink
- b. $\text{Cr}_2\text{O}_7^{2-} + \text{SO}_2 \xrightarrow{\text{H}^+} \text{Cr}^{3+} + \text{SO}_4^{2-} + \text{H}_2\text{O}$
orange green
- c. $\underbrace{\text{IO}_3^- + \text{starch}}_{\text{starch iodate}} + \text{SO}_2 \xrightarrow{\text{H}^+} (\text{I}_2 + \text{starch}) + \text{SO}_4^{2-}$
colourless deep blue solution
- d. $\underbrace{\text{FeCl}_3}_{\text{yellow solution}} + \text{SO}_2 + \text{H}_2\text{O} \longrightarrow \text{FeCl}_2 + \text{SO}_4^{2-} + \text{H}^+$
colourless/light green
- e. $\text{Br}_2 - \text{water} + \text{SO}_2 + \text{H}_2\text{O} \longrightarrow \text{SO}_4^{2-} + \text{HBr}$
red colourless
- f. $\text{I}_2 - \text{water} + \text{SO}_2 + \text{H}_2\text{O} \longrightarrow \text{SO}_4^{2-} + \text{HI}$
violet colourless

Note: Other oxidizing agents can also oxidize SO_2 but no colour changes are observed. Hence they are not used for purpose of detection of SO_2 . For example, Cl_2 -water and H_2O_2 give colourless products.



4. Test with alkaline Na-nitroprusside and alkaline Zn-nitroprusside:



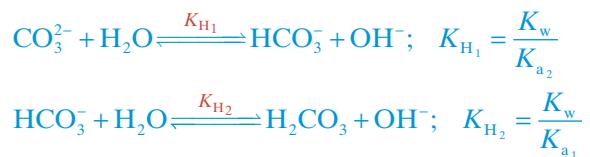
Distinction between carbonate and bicarbonate

Once the presence of CO_3^{2-} / HCO_3^- radicals is established by identification of the evolved gas CO_2 , the next step is to determine whether carbonate or bicarbonate is present. The methods used for this purpose are described as follows.

1. Using phenolphthalein: On addition of phenolphthalein to the salt solution:

- a. if no colour change is observed, it indicates the presence of HCO_3^- radical.
- b. if pink colouration is obtained, it indicates the presence of CO_3^{2-} radical.

Phenolphthalein is colourless in the pH range of 8 to 10 and above pH = 10, it changes its colour to pink.



As $K_{\text{a}_1} \gg K_{\text{a}_2} \Rightarrow K_{\text{H}_1} \gg K_{\text{H}_2}$, so the $[\text{OH}^-]$ obtained on hydrolysis of CO_3^{2-} ion is much larger as compared to $[\text{OH}^-]$ obtained from the hydrolysis of HCO_3^- . Hence pink colouration is formed in the presence of CO_3^{2-} ions.

- 2. Using precipitating reagents:** These selectively form coloured precipitates with CO_3^{2-} ions but not with HCO_3^- ions.



The reagents commonly used for detection of CO_3^{2-} radical and the formula and colour of precipitates formed are listed as follows.

	Reagent	Formula of the precipitate	Colour
I	CaCl_2	CaCO_3	White
	SrCl_2	SrCO_3	White
	BaCl_2	BaCO_3	White
	AgNO_3	Ag_2CO_3	White (very light yellow)
	$\text{Hg}_2(\text{NO}_3)_2$	Hg_2CO_3	Yellow
II	HgCl_2	$\text{HgCO}_3 \cdot 3\text{HgO}$	Reddish brown
	ZnCl_2	$\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$	White
	$\text{Pb}(\text{OAc})_2$	$\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$	White
	MgCl_2	$\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$	White
	CuCl_2	$\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$	Green

- Note:** (i) Reagents in set I produce simple carbonates of their metals while reagents in set II produce the basic carbonates of their metals.
- (ii) The bicarbonates of all the metals listed above are soluble in water, hence no precipitates are formed.
- (iii) NaCl cannot be used as reagent here though NaHCO_3 is sparingly soluble in water but its solubility is relatively high. It gives ppt. of NaHCO_3 from its concentrated solution only.

Detection of carbonate and bicarbonate when both are present together

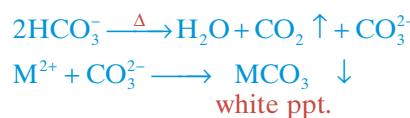
The different methods and reagents used for detection of carbonate and bicarbonate when present together are discussed as follows.

- 1. Using MCl_2 , where $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{and Ba}^{2+}$**

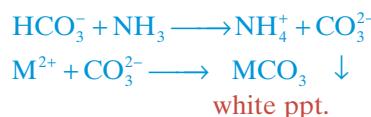
The steps involved in the process are depicted in the flow chart given in Figure 7.2.

Reactions involved:

(i)



(ii)



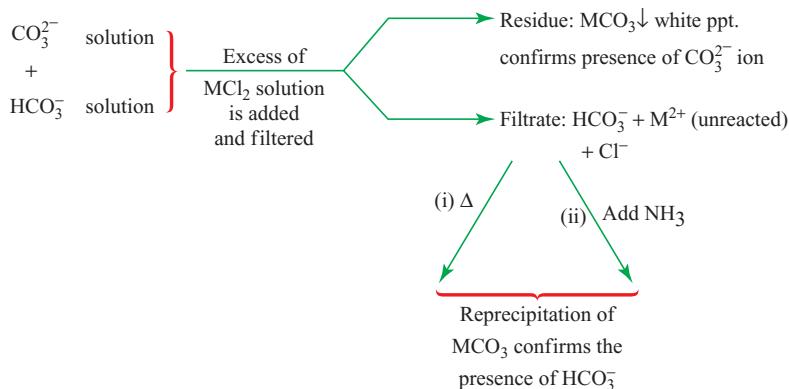


Figure 7.2 Flow chart for detection of carbonate and bicarbonate present together, using MCl₂.

2. Using AgNO₃ in excess: The steps involved in the process are depicted in the flow diagram shown in Figure 7.3.

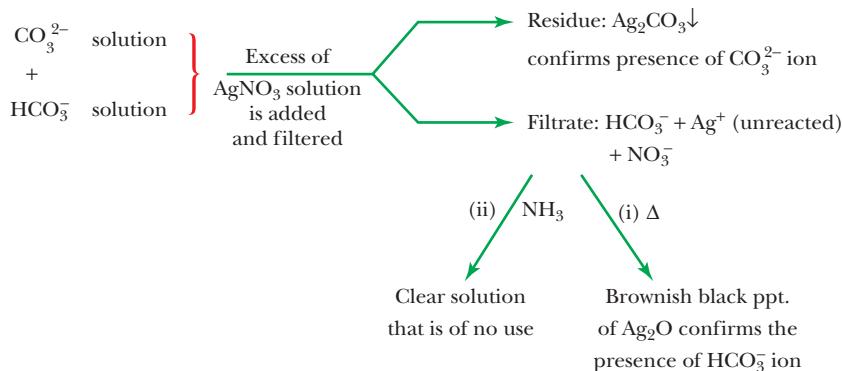
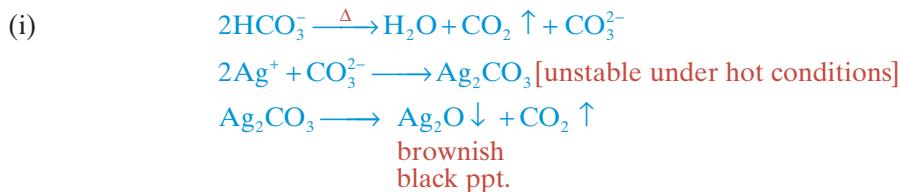


Figure 7.3 Flow chart for detection of carbonate and bicarbonate when present together, using AgNO₃.

Reactions involved:



Here the formation of Ag₂CO₃ is due to decomposition of HCO₃⁻ on heating and confirms the presence of HCO₃⁻.

(ii) In NH₃ solution, Ag₂CO₃ as well as Ag₂O are soluble and form [Ag(NH₃)₂]⁺ complex. Hence a clear solution is obtained and no change is observed. Thus NH₃ cannot be used for this purpose.

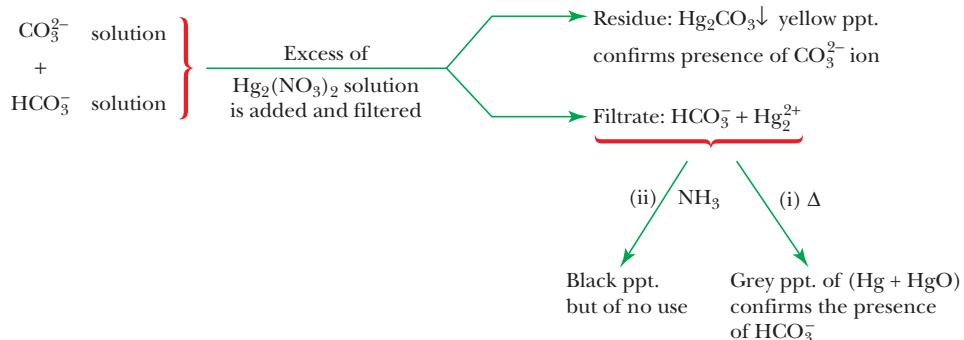
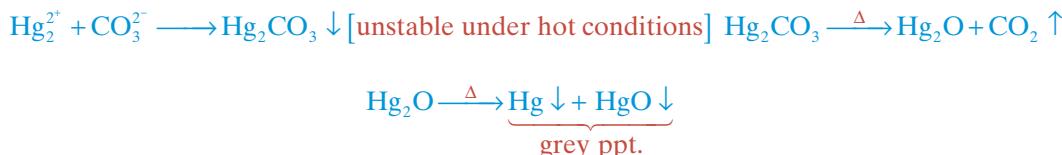


Figure 7.4 Flow chart for detection of carbonate and bicarbonate present together, using Hg₂(NO₃)₂.

- 3. Using $\text{Hg}_2(\text{NO}_3)_2$ in excess:** The steps involved in the process are depicted in the flow diagram in Figure 7.4.

Reactions involved:

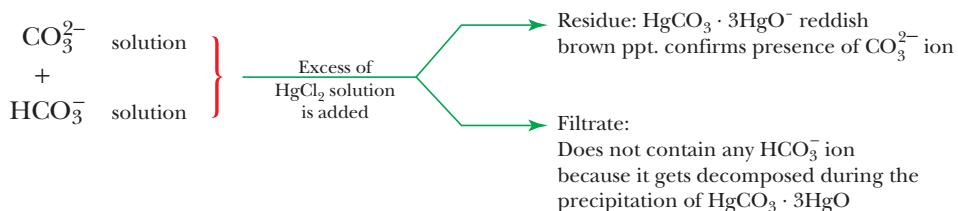


- (ii) In NH_3 solution, black ppt. of the complex is obtained irrespective of the presence or absence of HCO_3^- . Hence presence of HCO_3^- cannot be confirmed by this method.



The following reagents cannot be used for distinction of HCO_3^- and CO_3^{2-} when present together.

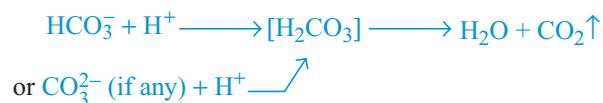
- 1. HgCl_2 in excess:** The changes taking place when HgCl_2 is used in excess are



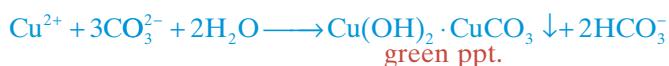
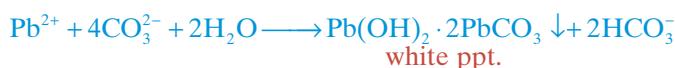
Reaction involved:



On precipitation of 1 mole of CO₃²⁻, 6 moles of H⁺ are formed and pH of the medium is drastically decreased. This combines with HCO₃⁻ and CO₃²⁻ (if any) and finally releases CO₂ gas. Even then the evolution of CO₂ does not confirm the presence of HCO₃⁻ because CO₃²⁻ also can release CO₂.



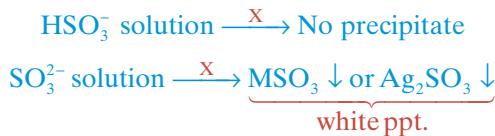
- 2. $\text{MgCl}_2, \text{Pb(OAc)}_2, \text{ZnCl}_2, \text{CuCl}_2$:** In reactions with all these reagents, during the precipitation of basic carbonates of the respective metals, some HCO₃⁻ ions are formed and passed into the filtrate. Hence it cannot be confirmed whether HCO₃⁻ was present in the original sample or generated during the reaction. For example,



Distinction between sulphite and bisulphite

Once the presence of $\text{SO}_3^{2-}/\text{HSO}_3^-$ radicals is established by identifying the evolved gas as SO_2 , the next step is to distinguish whether sulphite or bisulphite is present. The methods used for this purpose are described as follows.

- 1. Using precipitating reagents:** These selectively form coloured precipitates with SO_3^{2-} ions but not with HSO_3^- ions.



$X = \text{CaCl}_2, \text{SrCl}_2, \text{BaCl}_2, \text{Pb(OAc)}_2, \text{ and AgNO}_3$ solution.

- 2. Using litmus paper:** HSO_3^- solution is neutral towards litmus paper while SO_3^{2-} solution is alkaline towards it.



The reaction produces sufficient amount of OH^- ions to show alkaline behaviour towards litmus paper.



The OH^- ions formed are not sufficient to show alkaline nature with litmus paper and are considered neutral.

- 3. Using oxidizing agents:** Reagents such as H_2O_2 act as an oxidizing agent for both HSO_3^- and SO_3^{2-} ions. However, on oxidation the behaviour towards litmus paper undergoes a change as depicted in the following reactions.



Some other tests for SO_3^{2-} ions

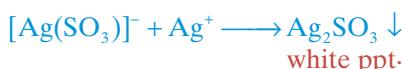
- 1. Test with AgNO_3 solution:** When AgNO_3 is gradually added to solution of SO_3^{2-} , initially there is no precipitation. However, when more reagent is added, white precipitate of Ag_2SO_3 is obtained. White precipitate is dissolved on addition of excess reagent and grey precipitate of metallic silver is obtained on boiling the complex solution or the aqueous suspension of white precipitate.

Reactions involved:

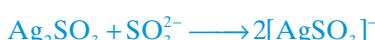
- (i) When $[\text{SO}_3^{2-}] >> [\text{Ag}^+]$



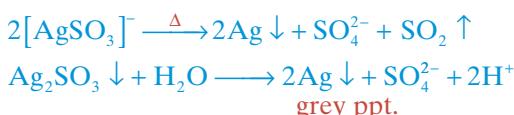
- (ii) When $[\text{Ag}^+] > [\text{SO}_3^{2-}]$



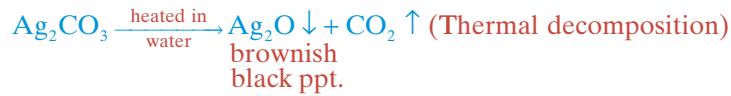
On further addition of sulphite solution, the precipitate gets dissolved



- (iii) On boiling

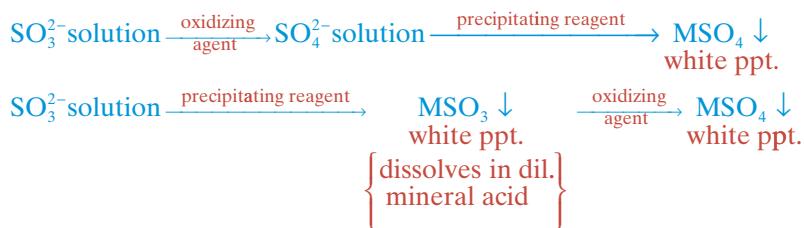


- Note:** (i) All silver compounds, except AgI and Ag_2S , are soluble in NH_3 , forming a complex $[\text{Ag}(\text{NH}_3)_2]^+$.
(ii) Heating of aqueous suspension of Ag_2SO_3 and Ag_2CO_3 produces different types of products.



Ag^+ has mild oxidizing properties which can oxidize SO_2 into H_2SO_4 while it cannot oxidize SO_2 anymore.

2. SO_3^{2-} can be easily oxidized either in solution or in solid state:



The precipitate MSO_4 formed does not dissolve in dilute mineral acids.

Various oxidizing agents that can be used for oxidizing SO_3^{2-} are:

- (i) Br_2 – water
- (ii) H_2O_2
- (iii) boiling in presence of air
- (iv) dil. HNO_3

The precipitating reagents that can be used include:

- (i) CaCl_2
- (ii) SrCl_2
- (iii) BaCl_2
- (iv) $\text{Pb}(\text{OAc})_2$

3. Test with dil. H_2SO_4 + Zn powder:

On addition of dil. H_2SO_4 and zinc powder to SO_3^{2-} solution, a colourless gas is evolved.



The gas evolved can be identified by the following properties:

- a. It has rotten eggs smell.
- b. It can turn the moist $\text{Pb}(\text{OAc})_2$ paper black due to the formation of PbS (black).
- c. It can turn the moist $\text{Cd}(\text{OAc})_2$ paper yellow due to the formation of CdS (yellow).

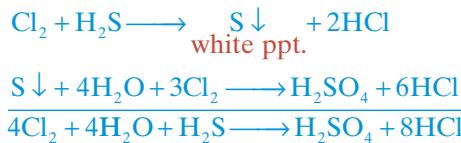
Note: If the paper is not moist, the above observations are not noted because



H_2S may also be identified by utilizing its reducing properties. For example,



In all these reducing reaction, sulphur is precipitated and other oxidizing agents like Cl_2 –water (dilute), H_2O_2 , conc. H_2SO_4 , conc. HNO_3 , H_2SO_3 may also be used to get sulphur precipitate. However, if Cl_2 –water is concentrated, then finally it will be again colourless.

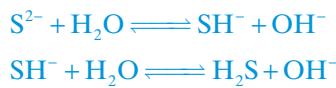


7.3 | TESTS FOR SULPHIDE (S^{2-}) RADICAL

Various tests carried out for identification of sulphide radicals are listed as follows.

1. Solubility

- a. Alkali metals sulphides are soluble in water; their aqueous solution exhibits alkaline characteristics due to hydrolysis.



- b. Alkaline earth metal sulphides are sparingly soluble in water but pass into the solution with time and hence do not give precipitates from their aqueous solution. For example,



2. Test with dil. HCl/dil. H_2SO_4



Observation: Colourless gas with rotten eggs smell is obtained. Other methods for its identification have already been discussed in Section 7.2.

This is a confirmatory test for sulphides.

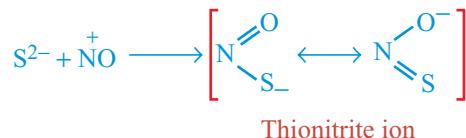
Note: Here dil. HNO_3 cannot be used because S^{2-} ions get oxidized to sulphur by dil. HNO_3 .

3. Test with sodium nitroprusside solution



Observation: Purple colouration is observed when sodium nitroprusside is added to solution of sulphide ions, e.g. Na_2S , $(\text{NH}_4)_2\text{S}$ solution.

The actual reaction is:



This is a confirmatory test for sulphides.

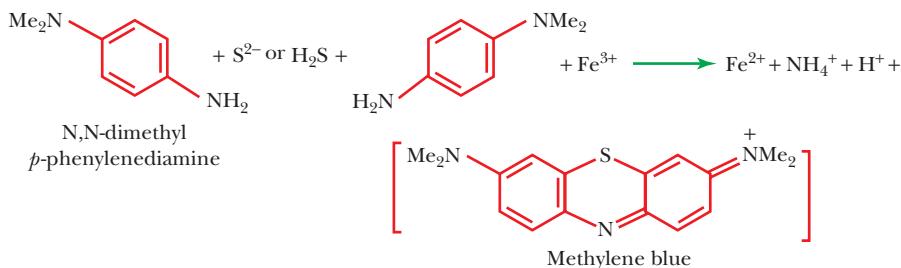
Note: When H_2S gas is passed through sodium nitroprusside solution, no colour change is observed. However, when the solution is made alkaline, purple colouration is obtained.



This is because H_2S is a weak acid, therefore $[\text{S}^{2-}]$ formed is not sufficient to give the above observation. However, on addition of alkali $[\text{OH}^-]$, concentration of S^{2-} ions increases and gives this test.

4. Test with $AgNO_3$ solution**5. Test with $Pb(OAc)_2$ solution****6. Test with $Cd(OAc)_2$ solution****7. Test with silver foil**

When S^{2-} solution is added to silver foil, a black spot is observed due to the formation of Ag_2S stain.

8. Methylene blue test

This reaction is very sensitive and confirmative test for soluble sulphides as well as for H_2S .

9. Iodine-azide test

But



Observation: Colourless gas is evolved which is N_2 and S^{2-} ion acts as a catalyst here.

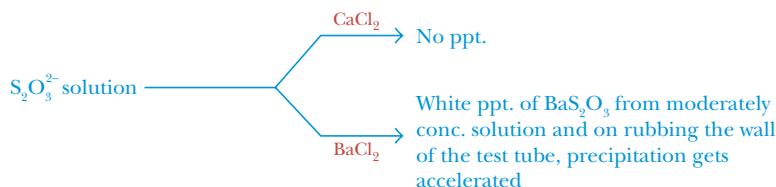
Note: This test has to be performed in the absence of SCN^- or $S_2O_3^{2-}$ because they also give similar observation. Hence it is not a confirmative test of S^{2-} ion.

7.4 | TESTS FOR THIOSULPHATE ($S_2O_3^{2-}$) RADICAL

Various tests carried out for identification of $S_2O_3^{2-}$ radical are listed as follows.

1. Solubility

- a. Alkali metal thiosulphates are soluble in water.
- b. MgS_2O_3 and CaS_2O_3 are soluble in water while BaS_2O_3 is sparingly soluble in water.

2. Test with $CaCl_2$ and $BaCl_2$ **3. Test with dil. HCl or dil. H_2SO_4** 

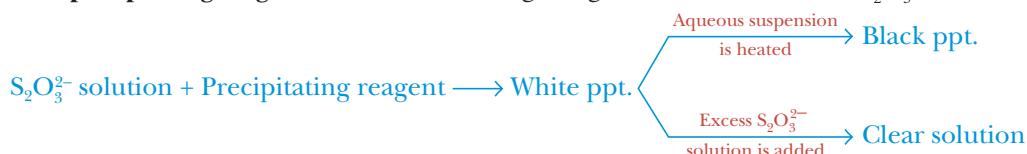
Observation: White turbidity appears and on warming burning smell of sulphur is obtained.

4. Test with I, solution



Observation: The colour of iodine solution is discharged.

5. Test with precipitating reagents: Five different reagents give similar results with $\text{S}_2\text{O}_3^{2-}$ radical as shown:

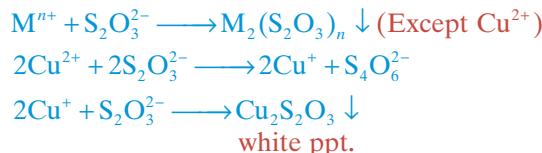


The various precipitating reagents used, formulae of precipitate and clear solution formed are listed below:

Reagent	Formula of precipitate	Formula of clear solution	
	White	Black	
$\text{Ag}^+(\text{AgNO}_3)$	$\text{Ag}_2\text{S}_2\text{O}_3 \downarrow$	$\text{Ag}_2\text{S} \downarrow$	$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$
$\text{Pb}^{2+}(\text{Pb}(\text{OAc})_2)$	$\text{PbS}_2\text{O}_3 \downarrow$	$\text{PbS} \downarrow$	$[\text{Pb}(\text{S}_2\text{O}_3)_2]^{2-}$
$\text{Hg}^{2+}(\text{Hg}(\text{NO}_3)_2)$	$\text{HgS}_2\text{O}_3 \downarrow$	$\text{HgS} \downarrow$	$[\text{Hg}(\text{S}_2\text{O}_3)_2]^{2-}$
$\text{Bi}^{3+}(\text{BiCl}_3)$	$\text{Bi}_2(\text{S}_2\text{O}_3)_3 \downarrow$	$\text{Bi}_2\text{S}_3 \downarrow$	$[\text{Bi}(\text{S}_2\text{O}_3)_3]^{3-}$
$\text{Cu}^{2+}(\text{CuSO}_4)$	$\text{Cu}_2\text{S}_2\text{O}_3 \downarrow$	$\text{Cu}_2\text{S} \downarrow$	$[\text{Cu}_6(\text{S}_2\text{O}_3)_5]^{4-}$

Reactions involved:

a. During precipitate formation



b. During conversion of white ppt. into black ppt.



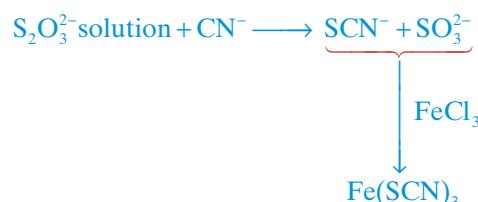
6. Test with FeCl_3 solution



Reactions involved:

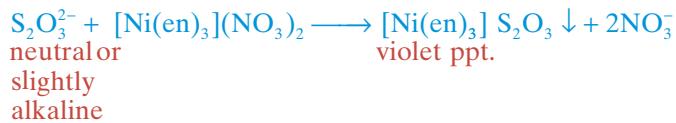


7. Test with KCN solution followed by FeCl_3 solution: This test is a specific test for $\text{S}_2\text{O}_3^{2-}$ radical and involves the following reaction



Observation: Blood red colouration due to the formation of $\text{Fe}(\text{SCN})_3$.

8. Test with $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ solution



However, in the presence of H_2S or $(\text{NH}_4)_2\text{S}$, the precipitation of NiS takes place.

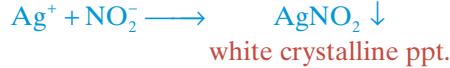
- 9. Blue ring test:** In this test conc. H_2SO_4 is taken in a test tube and a mixture of $\text{S}_2\text{O}_3^{2-}$ and $(\text{NH}_4)_2\text{MoO}_4$ solution is poured slowly down the side of the tube. A blue ring is temporarily formed at the contact zone due to the formation of molybdenum blue Mo_2O_5 .

Note: $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is the only thiosulphate having water of crystallization.

7.5 | TESTS FOR NITRITE (NO_2^-) RADICAL

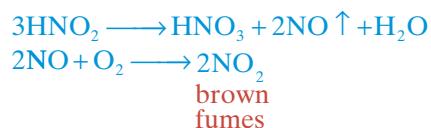
Various tests carried out for the identification of NO_2^- radical are listed as follows.

- 1. Solubility:** Except AgNO_2 , all other nitrites are soluble in water.
- 2. Test with AgNO_3 solution:** In this test, a white crystalline precipitate is obtained with concentrated AgNO_3 solution.



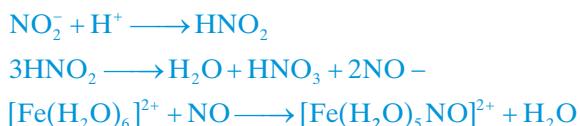
- 3. Test with BaCl_2 solution:** No precipitation is observed.
- 4. Test with dil. HCl:** In this test, dil. HCl is added carefully to solid nitrite solution (under cold conditions) to obtain a transient, pale blue liquid; brown fumes of NO_2 are evolved.

Reactions involved:



- 5. Brown ring test:** In this test, when nitrite solution is slowly added to freshly prepared FeSO_4 solution acidified with dil. AcOH or dil. H_2SO_4 , a brown ring is formed at the junction of the two liquids due to the formation of $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$.

Reactions involved:



Some important points related to the brown ring test are:

- FeSO_4 solution must be freshly prepared because Fe^{2+} ion is very prone to aerial oxidation and gets converted to Fe^{3+} , which does not give this test.
- Concentrated H_2SO_4 cannot be used in this test instead of dil. H_2SO_4 because it produces intense brown fumes with NO_2^- and under these conditions no ring can be observed.
- Shaking and warming are not allowed for this test because $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ formed is unstable and liberates NO easily.

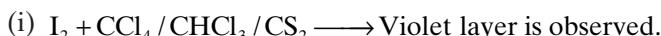
6. Test with KI solution:



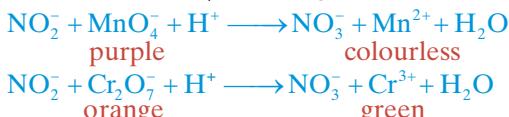
Reactions involved:



Note: The observation depends upon co-reagent taken, for example



7. Test with acidified KMnO_4 : In this test NO_2^- acts as reducing agent and decolorizes the acidified KMnO_4 solution and turns acidified KMnO_4 solution green.



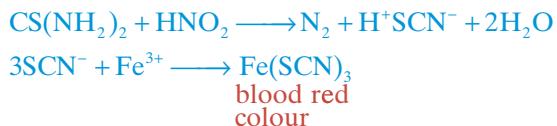
8. Test with NH_4Cl solution: When NH_4Cl solution is added in excess to nitrite solution and boiled, colourless and odourless N_2 gas is evolved.



9. Test with urea [$\text{CO}(\text{NH}_2)_2$]: When nitrite solution acidified with dil. HCl is added to solid urea, $\text{N}_2 + \text{CO}_2$ gases are evolved.



10. Test with thiourea [$\text{CS}(\text{NH}_2)_2$]: When nitrite solution acidified with dil. AcOH is added to solid thiourea, N_2 gas is evolved and thiocyanic acid is formed, which is identified by addition of FeCl_3 solution acidified with dil. HCl.



11. Test with sulphamic acid ($\text{HO} \cdot \text{SO}_2 \cdot \text{NH}_2$): With this reagent, nitrite solution is completely decomposed.

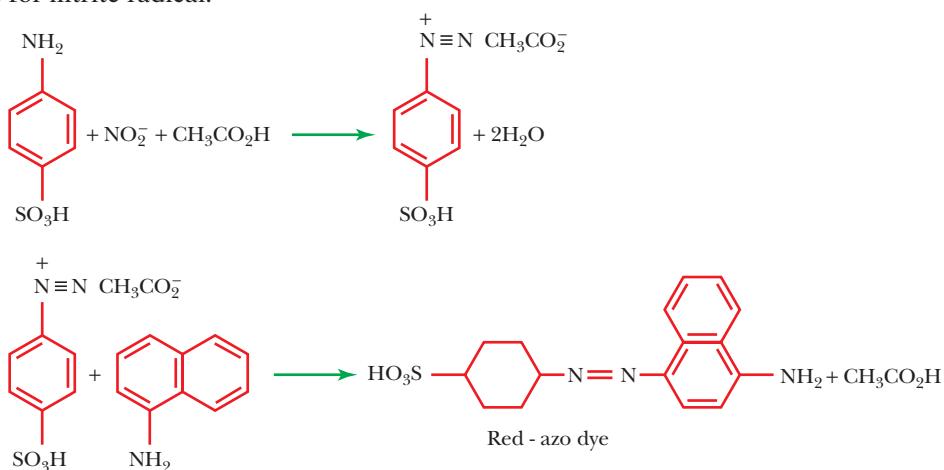


It is the best method to destroy nitrite whenever it is required, because no nitrate is formed during the reaction, whereas traces of nitrates are formed with NH_4Cl , urea and thiourea used in reactions 8, 9 and 10 respectively.

NO_2^- radical can also be removed by use of NaN_3 which however, is an expensive reagent.



12. Gries–Illosvay test: This test is based upon the diazo-coupling reaction of sulphanilic acid. This test is specific for nitrite radical.



- Note:** (i) Fe^{3+} should not be present in the solution and if present, it must be masked by tartaric acid.
(ii) The test solution should be very dilute, otherwise the reaction will stop at the diazotization stage.

- 13. Test with indole reagent:** The acidified solution of nitrite reacts with indole to produce red coloured nitroso indole.

7.6 | TESTS FOR ACETATE, FORMATE AND OXALATE RADICALS

Various tests carried out for identification of acetate, formate and oxalate radicals are listed as follows.

1. Solubility

Acetate: Most of the acetates are soluble in water except



Formate: Most of the formates are soluble in water except



Oxalate:

- Alkali metal oxalates are soluble in water.
- Alkaline earth metal oxalates are sparingly soluble in water except BeC_2O_4 .

2. Test with dil. H_2SO_4 :

These three radicals can be distinguished easily using dil. H_2SO_4 .



Note: (i) In an unknown sample, only acetate can be confirmed by its characteristic smell.

(ii) In case of $\text{C}_2\text{O}_4^{2-}$, the evolution of CO_2 is observed when MnO_2 is added with dil. H_2SO_4 .



3. Test with conc. H_2SO_4 :

The three radicals can also be easily distinguished using this reagent.

Acetate: On reaction with conc. H_2SO_4 , $\text{CH}_3\text{CO}_2\text{H}$ is evolved together with SO_2 (due to partial oxidation of $\text{CH}_3\text{CO}_2\text{H}$ by conc. H_2SO_4) which suppresses the vinegar smell of acetic acid. Hence conc. H_2SO_4 is not preferred for the test of acetate radical.

Formate: Initially, HCO_2H is formed which is dehydrated by conc. H_2SO_4 to produce CO gas.



Observation: A colourless gas evolves which

- burns with blue flame.
- turns PdCl_2 solution into black metallic deposit of Pd.



Note: These two reactions are methods for detection of CO .

Oxalate



and



strong
dehydrating agent

Observation: A colourless gas evolves which

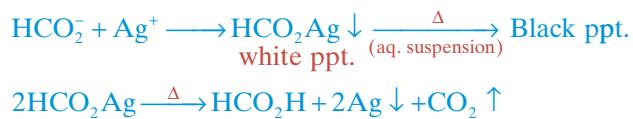
- burns with blue flame.
- can turn the lime water milky.

- 4. Test with AgNO_3 solution:** Addition of AgNO_3 cannot distinguish these three radicals, but addition of AgNO_3 followed by heating can distinguish one from the other.

Acetate



Formate

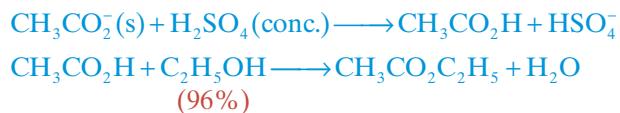


Oxalate



- 5. Esterification test:** The reagent used for this test is $\text{C}_2\text{H}_5\text{OH} + \text{conc. H}_2\text{SO}_4$.

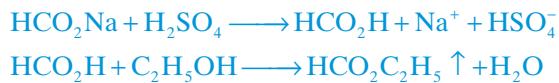
Acetate



Observation: Pleasant, odour is obtained.

Note: In the second reaction, conc. H_2SO_4 acts as dehydrating agent and drives the reaction in the forward direction.

Formate



Observation: Pleasant odour is observed.

Note: Here also conc. H_2SO_4 acts as dehydrating agent in the second reaction.

Oxalate



Note: This reagent is not effective to distinguish these radicals.

- 6. Test with CaCl_2 , BaCl_2 and HgCl_2 (separately):** The response of acetate; formate and oxalate radicals to these reagents is listed below:

Radical \ Reagent	CaCl_2	BaCl_2	HgCl_2
CH ₃ CO ₂ ⁻	✗	✗	✗
HCO ₂ ⁻	✗	✗	✓
C ₂ O ₄ ²⁻	✓	✓	✗

✗ ⇒ Does not respond to the test.

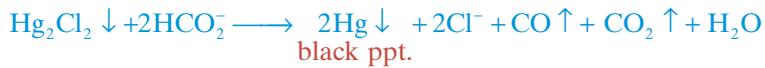
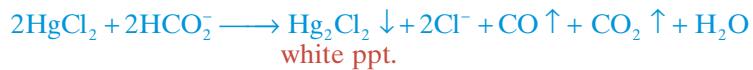
✓ ⇒ Responds to the test.

As the three radicals respond differently to these reagents, they can be distinguished using them.

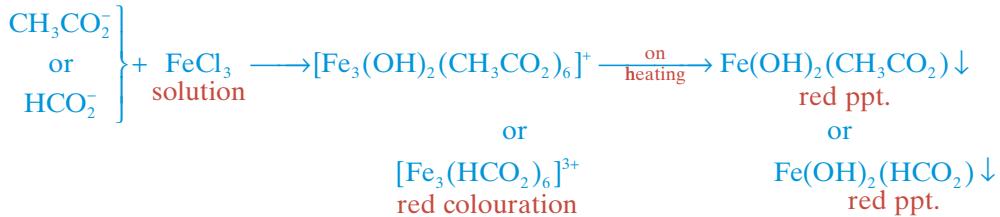
Oxalate



Formate

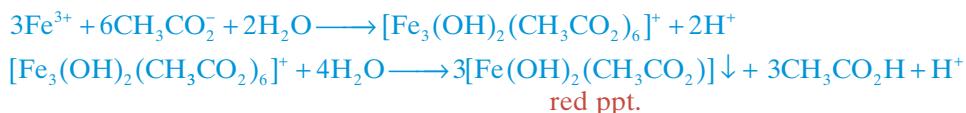


7. Test with FeCl_3 solution

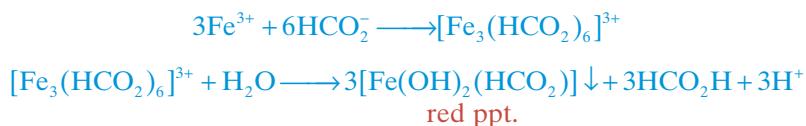


Reactions involved:

Acetate:

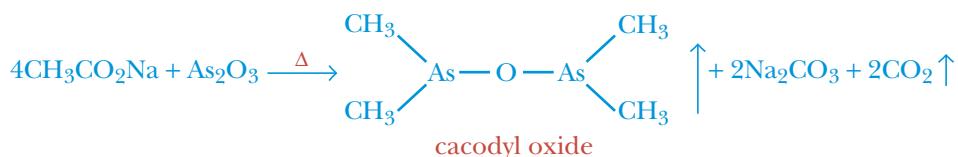


Formate



Specific test for acetate (cacodyl oxide test)

In this test acetate salt in solid form is mixed with As_2O_3 and heated.

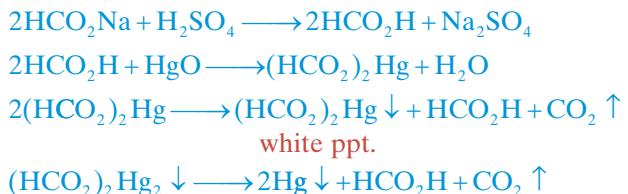


Observation: The nauseating smell of cacodyl oxide which is extremely poisonous.

Specific test for formate (mercury (II) formate test)

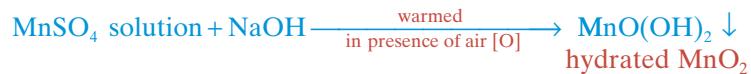
Free formic acid is necessary for this test. Initially, the solution of HCO_2Na is acidified with dil. H_2SO_4 and shaken vigorously with little HgO . Then the solution is filtered and the filtrate is boiled. A white precipitate of $\text{Hg}(\text{I})$ formate is momentarily produced which rapidly changes into a grey precipitate of metallic Hg .

Reactions involved:



Specific tests for oxalate

Test with MnSO_4 solution:



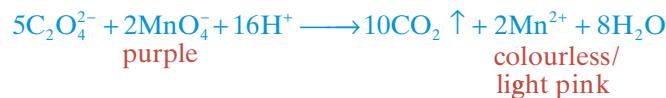
Hydrated MnO_2 is acidified and the oxalate solution is added slowly to it to obtain red coloured solution.

Reaction involved:



Another test for oxalate

Test with KMnO_4 solution: In this test, the colour of KMnO_4 is discharged by $\text{C}_2\text{O}_4^{2-}$ solution.



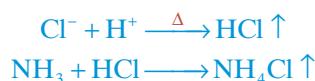
7.7 | TESTS FOR HALIDE (Cl^- , Br^- , I^-) RADICALS

Various tests used for identification of halides are listed as follows.

1. Solubility: Except Cl^- , Br^- , I^- of Ag^+ , Hg_2^{2+} , Pb^{2+} , Cu^+ ; HgI_2 and BiI_3 , most of the salts of Cl^- , Br^- , I^- are soluble in water.

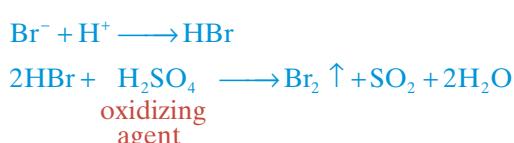
2. Test with conc. H_2SO_4

Chloride



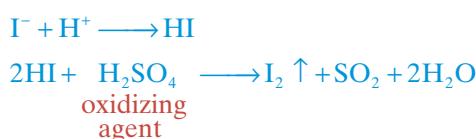
Observation: White fumes of HCl are obtained which intensify on contact with the glass rod dipped in NH_3 .

Bromide



Observation: Reddish-brown vapours of bromine are observed.

Iodide



Observation: Violet vapours of iodine are observed.

Thus the three radicals can be distinguished easily using conc. H_2SO_4 :

3. Test with $(\text{MnO}_2 + \text{conc. H}_2\text{SO}_4)$



Observation:

When $X_2 = Cl_2$, greenish yellow gas is evolved.

When $X_2 = Br_2$, reddish brown vapours are evolved.

When $\text{X}_2 = \text{I}_2$, violet vapours are evolved.

Hence these three radicals can be distinguished easily using ($\text{MnO}_2 + \text{conc. H}_2\text{SO}_4$).

4. Test with AgNO_3 :

Chloride $\text{Cl}^- + \text{Ag}^+ \longrightarrow \text{AgCl} \downarrow$ (white ppt.)

Bromide $\text{Br}^- + \text{Ag}^+ \longrightarrow \text{AgBr} \downarrow$ (pale yellow ppt.)

Iodide $\text{I}^- + \text{Ag}^+ \longrightarrow \text{AgI} \downarrow$ (yellow ppt.)

The solubility of these precipitates in different solvents is listed below.

Solvent \ Precipitate	NH_3	HNO_3	$\text{Na}_2\text{S}_2\text{O}_3$	NaCN/KCN
AgCl	Completely soluble	Insoluble	Soluble	Soluble
AgBr	Partially soluble	Insoluble	Soluble	Soluble
AgI	Insoluble	Insoluble	Soluble	Soluble

Note: (i) In NH_3 , Ag^+ forms soluble complex of $[\text{Ag}(\text{NH}_3)_2]^+$

In $\text{Na}_2\text{S}_2\text{O}_3$, Ag^+ forms soluble complex of $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$

In NaCN , Ag^+ forms soluble complex of $[\text{Ag}(\text{CN})_2]^-$

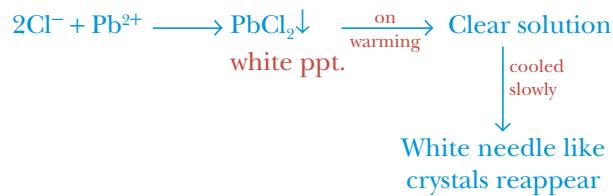
(ii) AgCl when shaken with Na_3AsO_3 solution gives rise to yellow precipitate of Ag_3AsO_3 and this can be used to distinguish AgCl from AgBr and AgI , which remain unaffected by this treatment. This test may be used as confirmatory test for chloride.



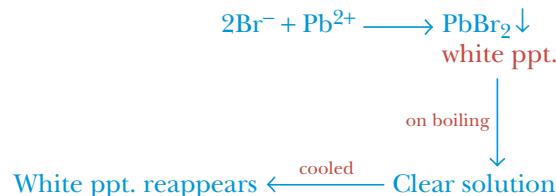
5. Test with Pb(OAc)_2 solution:

The three halide radicals can be distinguished by addition of Pb(OAc)_2 , followed by heating and cooling.

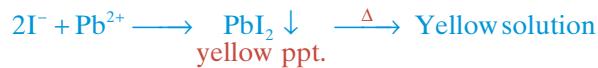
Chloride



Bromide



Iodide



Specific test for Cl^- (chromyl chloride test)

The steps involved in this test are shown in Figure 7.5.

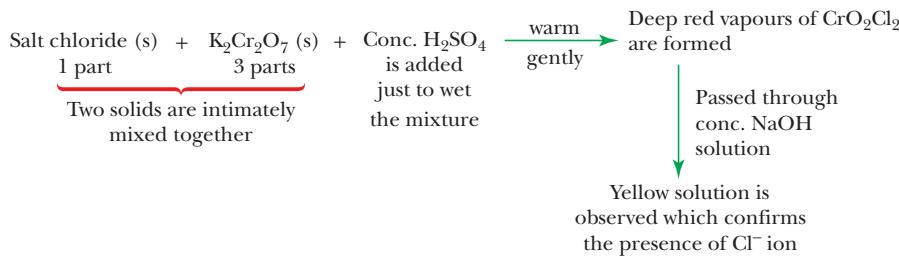
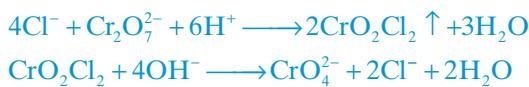
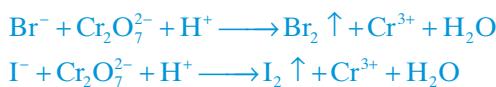


Figure 7.5 Chromyl chloride test.

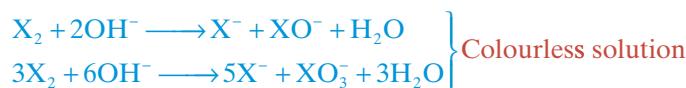
Reactions involved:



Note: (i) Br^- and I^- must be absent for this test because they are oxidized by $\text{Cr}_2\text{O}_7^{2-}$ into Br_2 (red vapours) and I_2 (violet vapours) respectively.



Both Br_2 and I_2 produce colourless solution with NaOH solution.



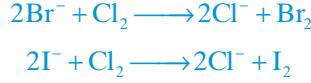
where $\text{X}_2 = \text{Br}_2$ or I_2

- (ii) F^- also produces volatile red-coloured CrO_2F_2 . Hence F^- should also be absent.
- (iii) NO_2^- , NO_3^- and ClO_2^- radicals also interfere with this test and so should be absent.
- (iv) AgCl , HgCl_2 , Hg_2Cl_2 , PbCl_4 , SnCl_4 do not respond to this test due to their high covalent character as a result of which sufficient free Cl^- ions are not available.

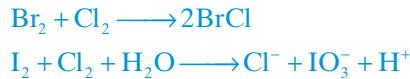
Specific test for Br^- and I^- (layer test)

In this test, chlorine water is added to the bromide or iodide salt solution dropwise and shaken well in the presence of an organic layer like CS_2 , CHCl_3 or CCl_4 . The presence of bromine is indicated by red colour in the organic layer and the presence of iodine by violet colour in organic layer.

Reactions involved:



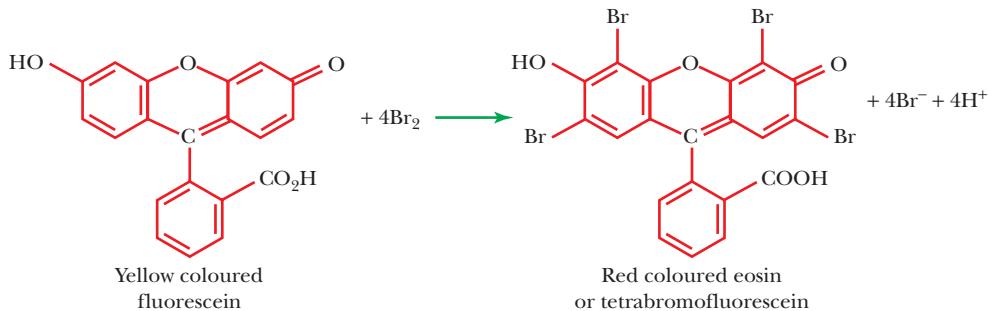
Note: On addition of excess of Cl_2 –water, red layer of Br_2 changes into pale yellow layer of BrCl in organic solvent while the violet layer of I_2 changes into colourless solution.



Other test for Br^-

Test with conc. HNO_3 : Hot and fairly conc. HNO_3 (8 M) oxidizes Br^- to Br_2 which can be recognized by (i) its irritating odour; (ii) its bleaching action on litmus paper; (iii) its staining of starch paper orange-red; and (iv) the red colouration produced on filter paper impregnated with fluorescein.





Note: (i) Chlorine bleaches the reagent and iodine forms red-violet coloured iodoeosin and hence these radicals must be absent for the test. But if Br^- radical is oxidized to free bromine by heating with PbO_2 and acetic acid, practically no chlorine is simultaneously evolved from chlorides and hence the test may be performed in the presence of chlorides.



(ii) Only free Br_2 converts the decolorized fuchsin into a blue or violet brominated dyestuff and the reaction is not shown by free Cl_2 or I_2 . Hence Br^- can be detected in presence of Cl^- and I^- .

Other tests for I^-

1. Test with CuSO_4 solution



Reactions involved:



Note: The dark brown colour of I_3^- is so dark that the white precipitate of CuI becomes invisible and becomes visible only when $\text{Na}_2\text{S}_2\text{O}_3$ converts the I_3^- ion into iodide.



2. Test with HgCl_2 solution: Scarlet red precipitate of HgI_2 is obtained which dissolves in excess of KI solution forming soluble complex of $[\text{HgI}_4]^{2-}$.

Reactions involved:



3. Test with oxidizing agents: Iodide solution is readily oxidized in acidic medium to free iodine by a number of oxidizing agents like $\text{K}_2\text{Cr}_2\text{O}_7$, KNO_3 and FeCl_3 solution.



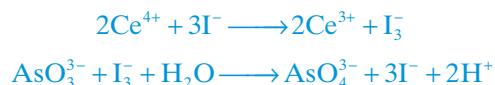
The observations depend upon the other reagents associated. For example,

- When starch is present, a deep blue solution is obtained.
- When excess KI is present, a dark brown solution is obtained.
- When $\text{CCl}_4/\text{CHCl}_3/\text{CS}_2$ is present, a violet layer is observed.

- Catalytic reduction of cerium (IV) salt test:** The reduction of cerium (IV) salts in acid solution by arsenites takes place very slowly:



Iodide accelerates this reaction and acts as catalyst



Finally the yellow colour of Ce (IV) solution disappears.

7.8 | TESTS FOR NITRATE (NO_3^-) RADICAL

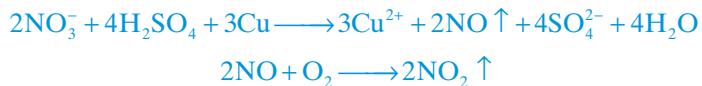
Various tests carried out for identification of NO_3^- radical are listed as follows.

- Solubility:** All nitrates are soluble in water.
- Test with dil. H_2SO_4 :** No action is observed. This property helps in distinction between NO_2^- and NO_3^- .
- Test with conc. H_2SO_4 :** Addition of conc. H_2SO_4 to solid nitrate salt gives brown vapours of NO_2 , which are further intensified in the presence of copper turnings or pieces of filter paper.

Reactions involved:

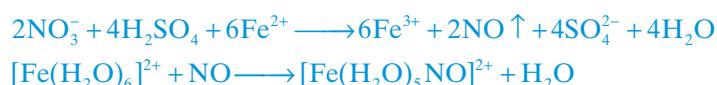


and



- Brown ring test:** In this test, when conc. H_2SO_4 is poured slowly in a mixture of nitrate salt solution and freshly prepared FeSO_4 solution, a brown ring is observed at the junction of two liquids. This is the **only** confirmatory test for nitrate radical.

Reactions involved:



Note: (i) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ is the compound responsible for the brown colour of the ring.

(ii) On shaking or warming, the brown colour disappears and NO gas is evolved.



- Radicals such as Br^- , I^- and NO_2^- must be absent because these produce coloured gases with conc. H_2SO_4 like Br_2 , I_2 and NO_2 respectively and no ring is observed.
- $\text{Ca}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ do not respond to the test due to precipitation of their corresponding metal sulphates.

- Reduction of nitrate to NH_3 :** When the nitrate salt solution is treated with metals like Zn or Al in the presence of conc. NaOH , it gets reduced and ammonia gas is evolved.

Reactions involved:

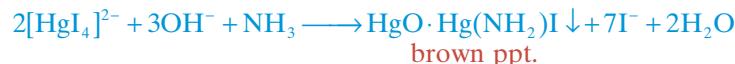


Deverda's alloy (Cu + Al + Zn) can also be used in place of these metals and shows better performance.

Note: NO_2^- radical can also be reduced to ammonia by the same reagents and gives same observations.

Ammonia gas evolved can be detected by the following methods:

- It has a characteristic pungent smell.
- It turns the moist litmus paper blue.
- It produces white fumes when it comes in contact with a glass rod dipped in HCl.
- It turns brown the filter paper dipped into Nessler's reagent.



- It turns black the filter paper dipped in $(\text{MnSO}_4 + \text{H}_2\text{O}_2)$ solution.



But



and this OH^- comes from the reaction,



- Reduction to nitrite test:** In this test, the nitrate solution is reduced to nitrite radical in the presence of Zn powder and acetic acid. The nitrite ion formed is further identified using Gries–Ilosvay test.

Reaction involved:



Note: Nitrite radical interferes with this test and should best be removed by sulphanilic acid.

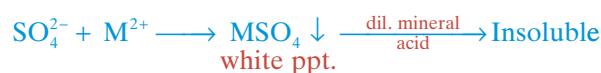
7.9 | TESTS FOR SULPHATE (SO_4^{2-}) RADICAL

Various tests carried out for identification of sulphate radical are listed as follows.

1. Solubility

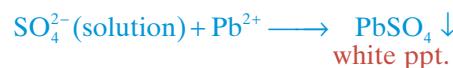
- Alkali metal sulphates are soluble in water.
- CaSO_4 , SrSO_4 and BaSO_4 are insoluble in water while BeSO_4 and MgSO_4 are soluble in water.

2. Test with MCl_2 solution (where M^{2+} : Ca^{2+} , Sr^{2+} , Ba^{2+})



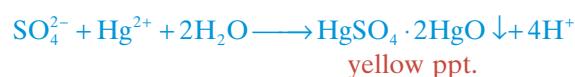
This is a confirmatory test for SO_4^{2-} ion.

3. Test with lead acetate solution



The white precipitate obtained is insoluble in dilute mineral acids and also confirms the presence of SO_4^{2-} .

4. Test with $\text{Hg}(\text{NO}_3)_2$ solution



This precipitate is obtained even from the suspension of BaSO_4 and PbSO_4 and hence the test is very sensitive. It is also confirmatory test for SO_4^{2-} .

5. $\text{KMnO}_4 - \text{BaSO}_4$ test: In this test, when BaCl_2 is added to a mixture of KMnO_4 + sulphate salt solution, the BaSO_4 formed is pink coloured (violet) due to adsorption of KMnO_4 . The adsorbed permagnate cannot be reduced by the common reducing agent (including H_2O_2).



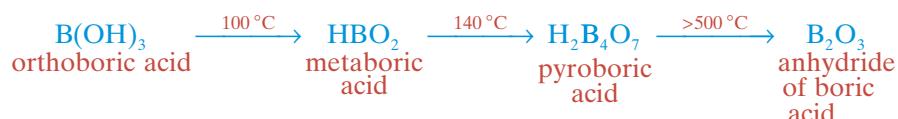
7.10 | TESTS FOR BORATE (BO_3^{3-}) RADICAL

Various tests carried out for identification of borate radical are listed as follows.

1. Solubility

- a. The borates of alkali metals are soluble in water.
- b. The borates of other metals are sparingly soluble in water.

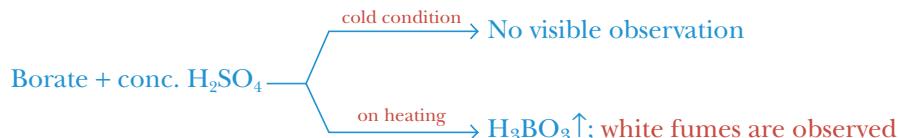
2. Heating effects



Note: All kinds of borate solutions are alkaline in nature due to their hydrolysis.



3. Test with conc. H_2SO_4 and conc. HCl : In this test, when conc. H_2SO_4 is added to the solution of borate in cold conditions, no visible change is observed. On heating, white fumes of H_3BO_3 are observed.



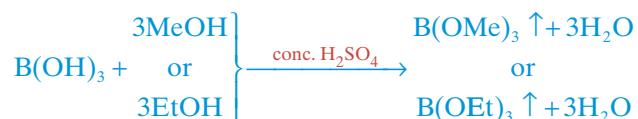
However, the addition of conc. HCl to borate ions in cold conditions leads to the formation of white crystals of H_3BO_3 , but conc. HCl in hot condition cannot be used because it fumes a lot (even at room temperature).



Reason: The B(OH)_3 produced forms hydrogen bonds with conc. H_2SO_4 and does not aggregate together to be precipitated out. In case of HCl , no hydrogen bonding takes place and B(OH)_3 formed aggregates to form white crystals.

4. Test with conc. H_2SO_4 and alcohol (green flame test): When conc. H_2SO_4 is added to solution of borate ions in presence of methanol or ethanol, colourless fumes are evolved which burn with a green flame.

Reaction involved:



Note: (i) Use of methyl alcohol is preferred due to high volatility of the product formed, i.e. B(OMe)_3 .

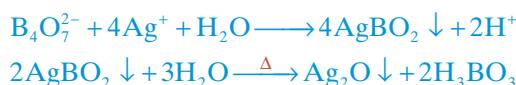
(ii) Copper and barium salts also give similar green flame. To avoid their interference in the test, the following modification to the test is helpful to identify borate radical in presence of Cu and Ba salts. It is based upon the greater volatility of BF_3 .

Thoroughly mix the borate with powdered CaF_2 and a little conc. H_2SO_4 , and bring a little paste formed with the help of glass rod very close to the edge of the base of Bunsen flame without actually touching it. Volatile BF_3 is formed and produces green flame.



5. Test with AgNO_3 solution: White precipitate of AgBO_2 is formed from fairly concentrated borax solution, and on boiling, it turns brownish black due to the formation of Ag_2O .

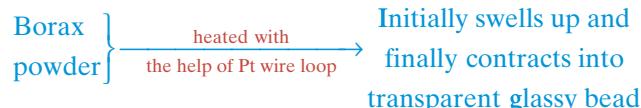
Reactions involved:



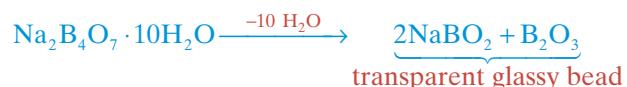
6. Test with $\text{BaCl}_2/\text{CaCl}_2/\text{SrCl}_2$ solution: White precipitate of $\text{M}(\text{BO}_2)_2$ is obtained on addition of these salts to borate radical.



7. Action of heat

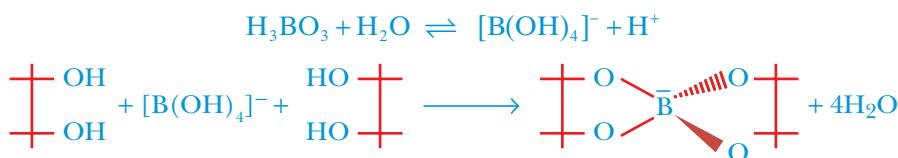


Reaction involved:



The glass possesses the property of dissolving many oxides on heating, forming metaborates, which often have characteristic colours; and this is the basis of borax bead test for various metals.

8. Bromothymol blue test: Boric acid is a weak monobasic acid ($K_a = 5.8 \times 10^{-10}$) but on addition of certain organic polyhydroxy compounds, such as mannitol, glycerol, dextrose or invert sugar, it is transformed into a relatively strong acid, as shown in the following reactions.



The formation of chelated complex in the second reaction helps shift the first reaction more towards right and boric acid becomes more strongly acidic.

Note: Ethylene glycol cannot give this test (reason is uncertain).

7.11 | TESTS FOR PHOSPHATE (PO_4^{3-}) RADICAL

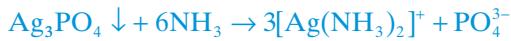
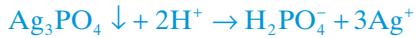
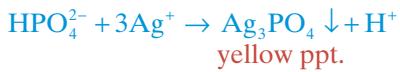
Various tests carried out for identification of phosphate radical are listed as follows.

1. Solubility

- Alkali metal phosphates are soluble in water except Li_3PO_4 and primary phosphates of alkaline earth metals are also soluble.
- All the phosphates of other metals and also the secondary and tertiary phosphates of alkaline earth metals are sparingly soluble in water.

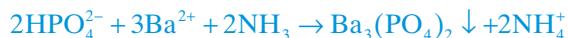
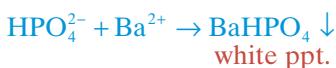
- 2. Test with AgNO_3 solution:** In this test, yellow precipitate of Ag_3PO_4 is obtained which is soluble in dil. HNO_3 and dil. NH_3 solution.

Reactions involved:



- 3. Test with BaCl_2 solution:** In this test, white precipitate of BaHPO_4 is obtained from neutral solution while tertiary phosphate $\text{Ba}_3(\text{PO}_4)_2$ is precipitated in the presence of NH_3 solution.

Reactions involved:



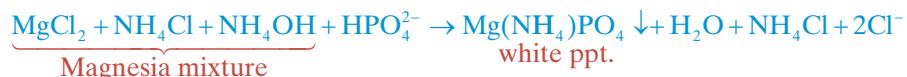
- 4. Test with FeCl_3 solution:** In this test yellowish white precipitate of FePO_4 is obtained.

Reaction involved:



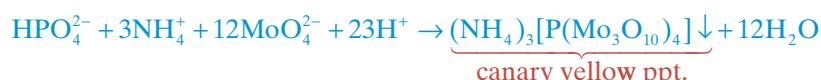
- 5. Test with magnesia mixture:** In this test, white precipitate of $\text{Mg}(\text{NH}_4)\text{PO}_4$ is obtained.

Reaction involved:



- 6. Canary yellow precipitate test:** In this test, the reagent used is $(\text{NH}_4)_2\text{MoO}_4$ in the presence of strongly acidic solution of HNO_3 , which reacts with HPO_4^{2-} to produce a canary yellow precipitate.

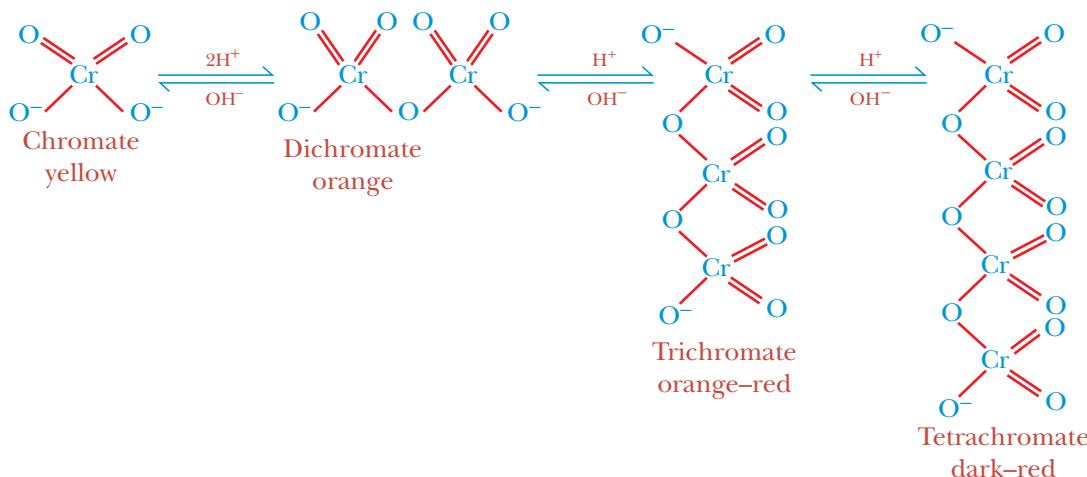
Reaction involved:



Note: Arsenate gives similar observation only under boiling conditions.

7.12 | TESTS FOR CHROMATE (CrO_4^{2-}) AND DICHROMATE ($\text{Cr}_2\text{O}_7^{2-}$) RADICALS

The chromates of different metals are coloured in solids and produce yellow solutions when dissolved in water. This yellow colour is due to charge transfer spectra. When pH of the solution is decreased by addition of acid, this yellow colour changes into orange or orange-red or dark-red depending upon the pH of the medium.



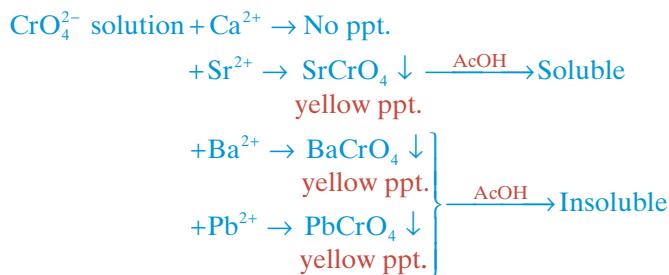
Various tests carried out for identification of chromate and dichromate radicals are listed as follows.

1. Solubility

- a. Alkali metal chromates and dichromates are soluble in water.
- b. $(\text{NH}_4)_2\text{CrO}_4$ and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ are soluble in water.
- c. MgCrO_4 and CaCrO_4 are soluble in water, whereas SrCrO_4 and BaCrO_4 are sparingly soluble in water.
- d. PbCrO_4 , Ag_2CrO_4 and $\text{Ag}_2\text{Cr}_2\text{O}_7$ are sparingly soluble in water.

2. Test with CaCl_2 , SrCl_2 , BaCl_2 and Pb(OAc)_2 solutions.

Chromate



In all these cases, the corresponding cation has no contribution to the colour, and the yellow colour is due to charge transfer within CrO_4^{2-} ion.

- Note:** (i) The addition of K_2CrO_4 can distinguish between Ca^{2+} and Sr^{2+} or Ca^{2+} and Ba^{2+} .
(ii) The addition of K_2CrO_4 followed by acetic acid can distinguish between these three cations. However, the addition of $(\text{K}_2\text{CrO}_4 + \text{AcOH})$ solution cannot distinguish between these three cations.

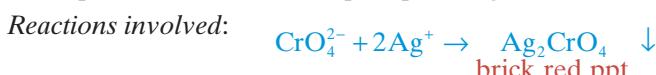
Dichromate

$\text{Cr}_2\text{O}_7^{2-}$ solution also produces the precipitate of BaCrO_4 with BaCl_2 solution, but the precipitation remains incomplete and becomes complete only on addition of NaOH or $\text{CH}_3\text{CO}_2\text{Na}$.

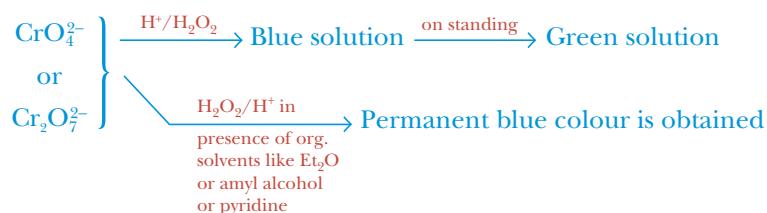


On addition of NaOH or $\text{CH}_3\text{CO}_2\text{Na}$, the H^+ ions produced are consumed to produce H_2O or $\text{CH}_3\text{CO}_2\text{H}$ by which the precipitation becomes complete.

- 3. Test with AgNO_3 :** The precipitates of Ag_2CrO_4 (brick red) and $\text{Ag}_2\text{Cr}_2\text{O}_7$ (reddish brown) are obtained from CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ solutions respectively. The precipitate from dichromate on heating in water produces the brick red precipitate again.



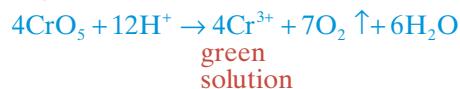
- 4. Test with acidified H_2O_2 solution:** Both chromate and dichromate radicals on reaction with acidified H_2O_2 give blue solution which turns green on standing. In the presence of organic solvents, such as diethyl ether, amyl alcohol or pyridine, permanent blue colour is obtained.



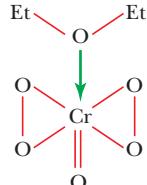
Reaction involved:



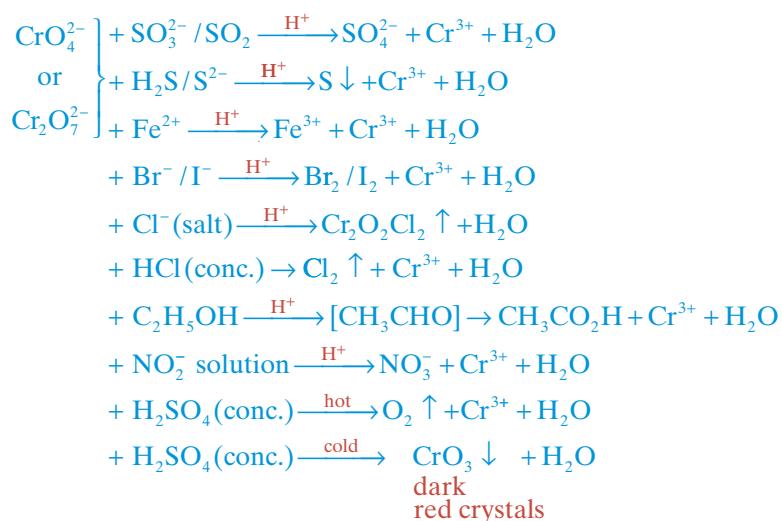
The blue solution is due to CrO_5 which undergoes decomposition on standing in acid solution.



In the presence of an organic solvent, CrO_5 is stabilized by complex formation which has permanent blue colour, as for example.



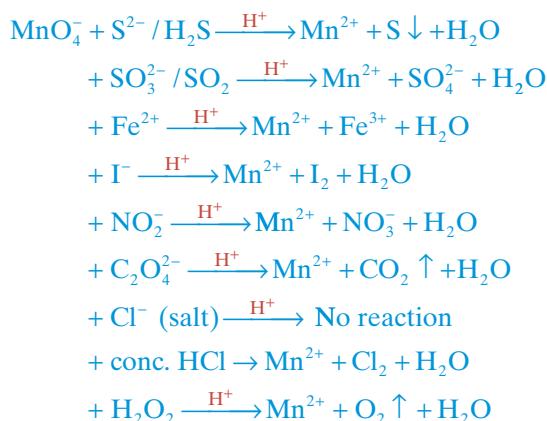
5. Tests utilizing the oxidizing property of CrO_4^{2-} / $\text{Cr}_2\text{O}_7^{2-}$ radicals: There are several tests in which the colour of CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ is decolorized due to its oxidizing property. Some such tests are:



7.13 | TESTS FOR PERMANGANATE (MnO_4^-) AND MANGANATE (MnO_4^{2-}) RADICALS

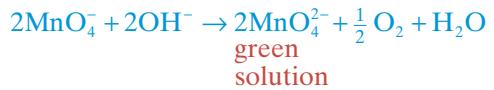
Various tests carried out for identification of manganate and permanganate radicals are listed as follows.

- 1. Solubility:** All available manganate and permanganate salts are soluble in water.
- 2. Tests using the oxidizing property of MnO_4^- :** There are several tests of MnO_4^- which are not shown by MnO_4^{2-} , because MnO_4^{2-} is stable in solution only above $\text{pH} = 12$. For example, the purple colour of MnO_4^- is discharged by several reducing agents as is evident in the following reactions:



- 3. Test with hot conc. NaOH:** In this test, permanganate radical gives green solution on treatment with hot and concentrated NaOH. The purple colour of permanganate solution is restored by acidification or by dilution with large amount of water.

Reactions involved:



- 4. Heating effect of KMnO_4 :** Heating of dry crystals of KMnO_4 (almost black in colour) gives a black residue. Addition of little water to this residue, followed by filtration, gives green filtrate and black residue.

Reaction involved:



K_2MnO_4 is water soluble and so is leached out as green filtrate. MnO_2 is insoluble in water and gives rise to black residue.

TESTS FOR BASIC RADICALS

There are two kinds of tests carried out for basic radicals, dry tests and wet tests. These are discussed in detail in the following sections.

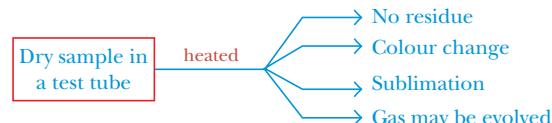
7.14 | DRY TESTS FOR BASIC RADICALS

All dry tests are preliminary tests because in most cases the proper oxidation state of the metal ion cannot be predicted in the original sample. The important dry tests carried out for identification of basic radicals in an unknown salt are described as follows.

Heating effects on the dry sample

The sample powder is taken in a dry test tube and heated slowly with Bunsen burner. The following observations are recorded with respect to

1. Residue
2. Colour change
3. Sublimation
4. Gas evolved

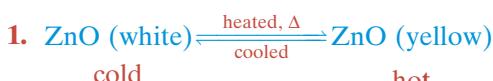


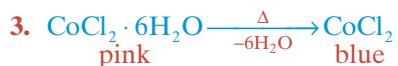
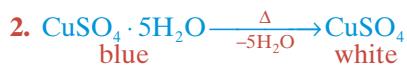
Residue

If no residue is obtained, then the cation present in the salt is not a metal ion. In general, salts of non-metallic cations such as NH_4^+ or PH_4^+ may be present.

Colour change

Most of the colour changes on heating are associated with the removal of water of crystallization or with the formation of f-centres under hot conditions. For example,



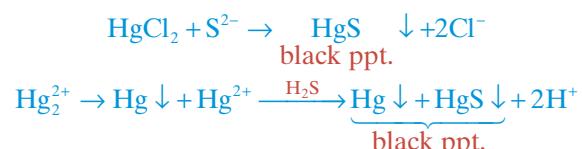


Sublimation

1. White sublimates are given by HgCl_2 , Hg_2Cl_2 , As_2O_3 , Sb_2O_3 and NH_4X (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$). These white sublimates are distinguished by the following procedure. Dilute HCl is added to the white sublimate and H_2S gas is passed through the solution to obtain a precipitate. The different colours of the precipitates obtained correspond to different basic radicals which are described below.

Salt	Colour of the precipitate	Formula of the precipitate
HgCl_2	Black	HgS
Hg_2Cl_2	Black	$\text{Hg} + \text{HgS}$
As_2O_3	Yellow	As_2S_3
Sb_2O_3	Orange	Sb_2S_3
NH_4X	No reaction	

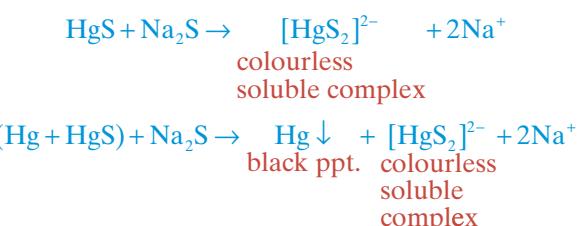
Reactions involved:



For $\text{M} = \text{As}, \text{Sb}$



The above two black precipitates are also well distinguished when they are treated with Na_2S solution.



2. Coloured sublimates are indicative of the nature of basic radical described as follows.

- If black: HgS (known as vermillion) or Hg_2S .
- If yellow: HgI_2 and As_2S_3 .

We can further distinguish between HgI_2 and As_2S_3 by the following procedure. On application of mechanical stress:

- If the yellow sublimate turns red, it indicates the presence of HgI_2 .
- No change in the sublimate shows the presence of As_2S_3 .

This behaviour can be explained on the basis of changes shown in Figure 7.6.

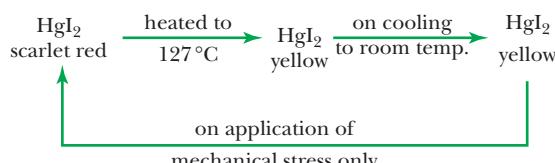


Figure 7.6 Changes during application of mechanical stress on the yellow sublimate.

Gas evolved

The evolved gas can be recognized based on its characteristic properties and is indicative of the nature of the acid radical present in the salt.

1. $\text{CO}_2 \Rightarrow$ Certain carbonates or organic materials are present.
2. $\text{SO}_2 \Rightarrow$ Sulphite, thiosulphates or sulphides may be present.
3. $\text{Cl}_2 \Rightarrow$ Certain chlorides may undergo thermal decomposition.
4. $\text{Br}_2 \Rightarrow$ Certain bromides may undergo thermal decomposition.
5. $\text{I}_2 \Rightarrow$ Certain iodides may undergo thermal decomposition.
6. $\text{NO}_2 \Rightarrow$ Decomposition of nitrates.
7. $\text{CO} \Rightarrow$ Decomposition of formates or oxalates.

Flame test

In the flame test, a platinum wire or glass rod is first dipped into concentrated HCl and then into a little of substance to be tested. It is then introduced into the lower oxidizing zone of the flame, and the imparted colour to the flame is observed. The different colours of the flame corresponding to different basic radicals are described below.

Metal	Colour observed
Na^+	Golden yellow flame
K^+	Violet (lilac) flame
Li^+	Carmine red flame
Ca^{2+}	Brick red flame
Sr^{2+}	Crimson red flame
Ba^{2+}	Apple green flame
$\text{Cu}^{2+}/\text{borate}$	Green flame

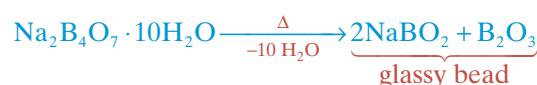
When Na^+ and K^+ are present together, the yellow colouration of sodium flame masks that of potassium. To confirm the presence of potassium under this condition, repeat the test through double blue glass and observe the flame colour again. The colours observed are described below.

Metal	Colour of the flame with naked eye	Colour of the flame through double blue (cobalt) glass
Na^+	Golden yellow	Flame disappears
K^+	Violet (lilac)	Crimson red flame
$\text{Na}^+ + \text{K}^+$	Golden yellow	Crimson red flame

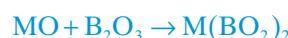
Note: Be^{2+} and Mg^{2+} do not impart any colour to the flame due to their high ionization energy.

Borax bead test

Borax powder is taken in a hot platinum wire loop and held in the hottest part of the flame; the borax powder swells up due to the loss of water of crystallization and shrinks upon the loop forming a transparent, colourless glassy bead which consists of sodium metaborate and boric anhydride.



Hot bead is touched on the salt sample, heated again and the colour of the bead is observed.



The different colours observed with different metals are given in Table 7.1

Table 7.1 Colour of borax beads for different metals

Metal	Oxidizing flame		Reducing flame	
	Hot	Cold	Hot	Cold
Cr	Yellow	Green	Green	Green
Mn	Violet	Violet	Colourless	Colourless
Fe	Yellowish brown	Yellow	Green	Green
Co	Blue	Blue	Blue	Blue
Ni	Violet	Reddish brown	Grey	Grey
Cu	Green	Blue	Colourless	Opaque*

*This opacity is due to red colour metallic copper deposition.

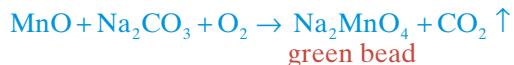
- Note:**
- Borax bead test is performed only for coloured salt samples.
 - The swelling characteristic is due to the loss of water of crystallization, but it is not mandatory that all compounds having water of crystallization will show swelling characteristic.
 - Alums also show swelling characteristic, but on strong heating they are converted into amorphous powder unlike the glassy bead in case of borax.

Sodium carbonate bead test

Small quantity of Na_2CO_3 powder is heated in platinum wire loop in the Bunsen flame, and a white, opaque bead is formed. Hot bead is dipped into a little KNO_3 powder and then into a sample powder and heated again.

Observation:

- If green bead is formed, presence of manganese compound is confirmed.



- If yellow bead is formed, presence of chromium compound is confirmed.



For all kinds of bead tests, the oxidation state of the metal ion in the original sample cannot be predicted.

7.15 | WET TESTS FOR BASIC RADICALS

Classification of cations (group analysis)

This classification based upon the differences of solubilities of the chlorides, sulphides, hydroxides and carbonates of metal ions. Basic radicals are divided into six groups based on their solubility and group reagent (Table 7.2).

Table 7.2 Classification of cations into groups

Group No.	Metal ion present	Group reagent	Precipitate obtained	Filtrate
I	Ag^+ , Hg_2^{2+} , Pb^{2+}	Dil. HCl	AgCl , PbCl_2 , Hg_2Cl_2 (all are white)	Filtrate is ready for Group II tests
II	Cu^{2+} , Sn^{2+} , Pb^{2+} Cd^{2+} , Hg^{2+} , As^{3+} , Sb^{3+} , Bi^{3+} As^{5+} , Sb^{5+} , Sn^{4+}	Dil. HCl + H_2S	MS MS_2 M_2S_3 M_2S_5	Colours will be discussed later **Filtrate is ready for Group III tests

(continued)

Table 7.2 (continued)

Group No.	Metal ion present	Group reagent	Precipitate obtained	Filtrate
III	Al ³⁺ , Cr ³⁺ , Fe ³⁺	NH ₄ Cl + NH ₄ OH	Al(OH) ₃ : white ppt. Cr(OH) ₃ : green ppt. Fe(OH) ₃ : Reddish brown ppt.	Filtrate is ready for Group IV tests
IV	Ni ²⁺ , Co ²⁺ , Mn ²⁺ , Zn ²⁺	NH ₄ OH + H ₂ S	NiS } black ppt. CoS } MnS: buff or flesh coloured ppt. ZnS: white	Filtrate is ready for Group V tests
V	Ca ²⁺ , Sr ²⁺ , Ba ²⁺	NH ₄ Cl + (NH ₄) ₂ CO ₃	CaCO ₃ } white ppt. SrCO ₃ } BaCO ₃ }	Filtrate is ready for Group VI tests
VI	The filtrate from Group V is divided into two parts	First part +Na ₂ HPO ₄ + NH ₄ Cl +NH ₄ OH Second part is evaporated to dryness and taking the solid residue (if any), flame test is performed	If white ppt. appears \Rightarrow Mg ²⁺ is confirmed. If no ppt. \Rightarrow Mg ²⁺ is absent. Na ⁺ or K ⁺ or (Na ⁺ + K ⁺) can be confirmed if present.	

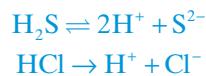
**Explained on page 258.

'Zero' group \Rightarrow NH₄⁺ : The test for NH₄⁺ is done from the original sample separately.

Some important points regarding group analysis:

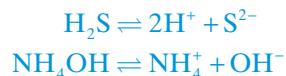
1. Among the cations in Table 7.2, only the chlorides of Ag⁺, Hg²⁺ and Pb²⁺ are sparingly soluble in water.
2. Pb²⁺ appears in two groups, Group I and Group II. This is because PbCl₂ is sparingly soluble in water and the concentration of Pb²⁺ ions passed into the filtrate is sufficient to give the precipitate of PbS with Group II reagents.
3. Dilute HCl and NH₄OH act as auxiliary reagents with Group II and Group IV reagents respectively. This is because we want to achieve the separation of cations in maximum possible groups. To do so, we take the help of the fact that 'K_{sp} of Group II sulphides is less than the K_{sp} of Group IV sulphides'. Hence Group II sulphides will be precipitated out even under low concentration of sulphides, while Group IV sulphides require higher concentration of sulphides. To fulfill this reaction condition, dil. HCl is chosen in Group II reagents and NH₄OH is chosen in Group IV reagents.

In Group II



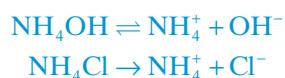
Due to common ion effect of H⁺, the first reaction shifts to left and [S²⁻] decreases.

In Group IV



NH₄OH consumes H⁺ from first reaction, so the first reaction shifts to right and [S²⁻] increases.

4. The function of NH₄Cl in Group III reagent is as follows:

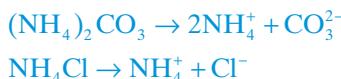


Due to the common ion effect of NH_4^+ , the concentration of OH^- ions decreases. If NH_4Cl is not added, then the following precipitates could be obtained together:

- All M(OH)_3 from Group III.
- All M(OH)_2 from Group IV.
- Mg(OH)_2 only from Group VI.

But when NH_4Cl is added, the $[\text{OH}^-]$ decreases to such an extent that only M(OH)_3 from Group III are precipitated due to their very low K_{sp} (in the range of $\sim 10^{-38}$) as compared to that of others.

- The function of NH_4Cl in the Group V reagent is discussed as follows



If NH_4Cl is not added, then the precipitates obtained are:

- MCO_3 from Group V.
- $\text{Mg(OH)}_2 \cdot 4 \text{MgCO}_3 \cdot 6\text{H}_2\text{O}$ from Group VI.

But when NH_4Cl is added, the concentration of CO_3^{2-} decreases to such an extent that only MCO_3 of Group V cations are precipitated.

Here the decrease in the concentration of CO_3^{2-} is not due to common ion effect. Rather on reaction with NH_4^+ ion, the concentration of CO_3^{2-} decreases as follows:



- Before adding the Group III reagent into the Group II filtrate, the following steps need to be taken care of:

- The dissolved H_2S is to be boiled off. If not done, then the dissolved H_2S reacts with NH_4OH of the Group III reagent and the produced $[\text{S}^{2-}]$ is sufficient to cause precipitation of some of the Group IV cations which is unwanted.



- Then add 2–3 drops of dil. HNO_3 and boil again to convert all Fe^{2+} (if any) into Fe^{3+} . If this is not done, then Fe^{2+} does not give precipitate with the Group I, Group II and Group III reagents and gives black precipitate of sulphide only with the Group IV reagent, which is difficult to separate from rest of the precipitates of the group.

Hence all Fe^{2+} ions (Fe^{2+} and Fe^{3+} in the original sample) are precipitated in the form of Fe(OH)_3 and observing this reddish-brown precipitate of Fe(OH)_3 , we cannot predict the oxidation state of iron in the original sample.

7.16 | SOME GENERAL TESTS FOR CATIONS

Here we will study the tests for cations in terms of reagents by which the comparison of observation can be done easily. Specific tests for cations will be covered in the next section. The various general tests used for identification of basic radicals are listed as follows.

- Test with dil. HCl:** Only three cations among all the cations listed in Table 7.2 form precipitate with dil. HCl. These are:

- Ag^+ : AgCl ; white ppt.
- Pb^{2+} : PbCl_2 ; white ppt.
- Hg_2^{2+} : Hg_2Cl_2 ; white ppt.

2. Reaction with NaOH: Different coloured precipitates are obtained with different cations and the behaviour of these precipitates in excess NaOH are listed below.

a. White precipitates obtained from reaction between M^{n+} and OH^- are shown in Figure 7.7

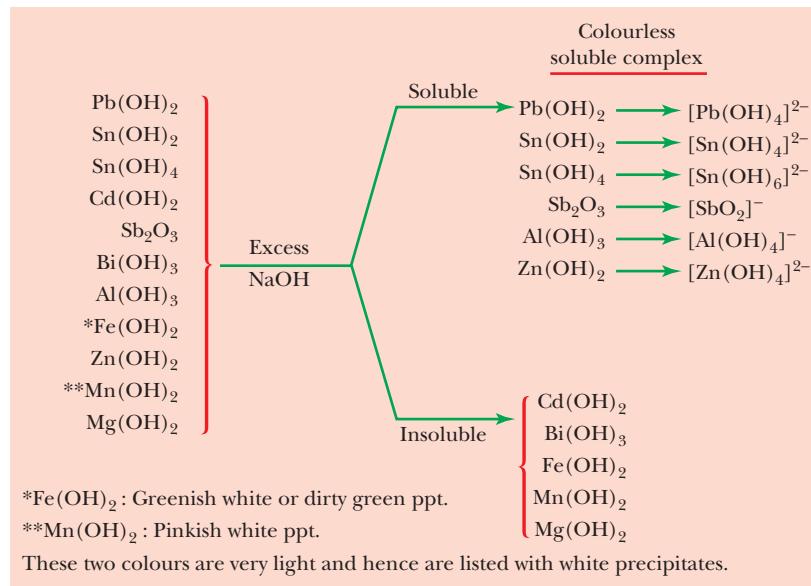
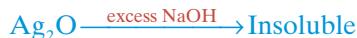


Figure 7.7 Flow chart for reaction of cations with NaOH

b. Brownish black precipitate:



c. Yellow precipitate:



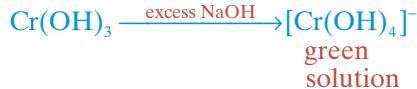
d. Blue precipitate:



If $X^- = Cl^-, NO_3^-$, then



e. Green precipitate:



f. Reddish-brown precipitate:



Note: (i) Cations like As^{3+} , As^{5+} , Sb^{5+} produce soluble species like AsO_3^{3-} , AsO_4^{3-} and SbO_4^{3-} , respectively, hence no precipitation is observed.
(ii) Hydroxides of Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} are soluble in water and hence no precipitation is observed.

3. Reaction with NH_4OH : In this test also different coloured precipitates are obtained from different cations and the behaviour of these precipitates in excess NaOH are listed below.

a. White precipitates obtained from reaction between M^{n+} and OH^- are shown in Figure 7.8.

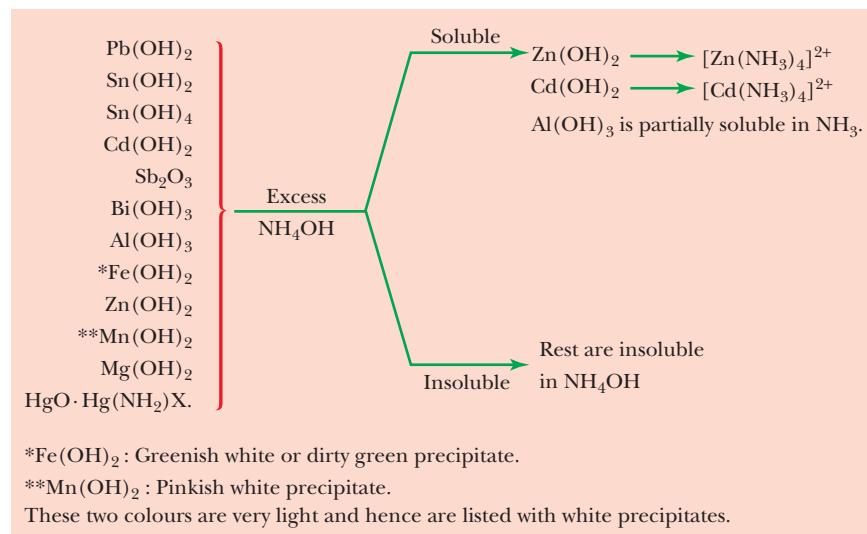
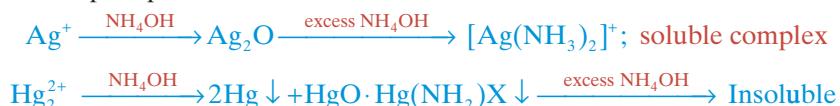


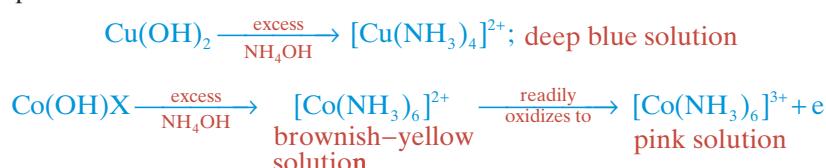
Figure 7.8 Flow chart for reaction with NH_4OH .

b. Brownish-black precipitate:

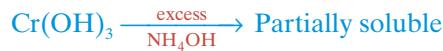


c. Yellow precipitate: No such precipitate is obtained from Hg^{2+} .

d. Blue precipitate:



e. Green precipitate:



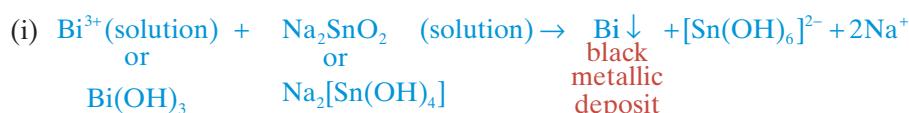
f. Reddish-brown precipitate:

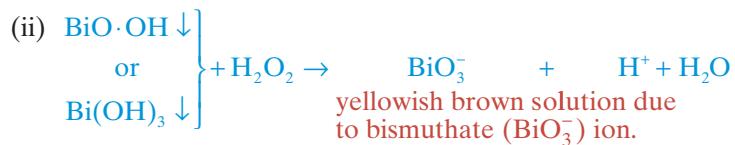


Note: (i) Cations like As^{3+} , As^{5+} , Sb^{5+} produce soluble species like AsO_3^{3-} , AsO_4^{3-} and SbO_4^{3-} respectively, hence no precipitation is observed.

(ii) Hydroxides of Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} are soluble in water and hence no precipitation is observed.

Some specific behaviour:





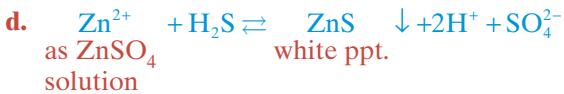
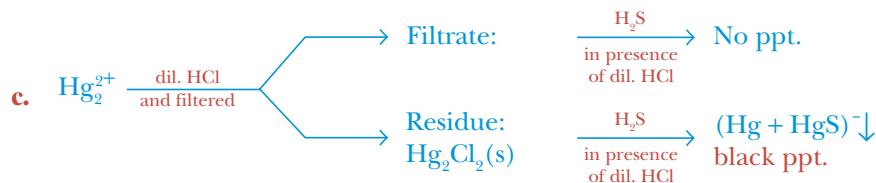
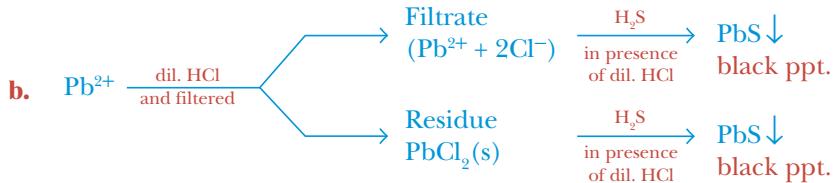
4. Reaction with $\text{H}_2\text{S}/\text{S}^{2-}$: The reagents used for this reaction are as follows:

- (i) dil. $\text{HCl} + \text{H}_2\text{S}$.
- (ii) H_2S gas is directly passed through the sample solution.
- (iii) $(\text{NH}_4)_2\text{S}$ or Na_2S .

The concentration order of $[\text{S}^{2-}]$ is: (i) < (ii) < (iii). The precipitates formed by different cations are their sulphides, that is, MS , M_2S , M_2S_3 , ... etc. depending on the charge of cation. The reagents used and different cations forming precipitate with them are listed as below.

Reagent	Cations forming their sulphide precipitate
Dil. $\text{HCl} + \text{H}_2\text{S}$	Group II and Group I cations except Ag^+ .
H_2S is directly passed	Group II and Group I cations plus Zn^{2+} .
$(\text{NH}_4)_2\text{S}$ or Na_2S	Group II, Group I and Group IV cations plus Fe^{2+} .

Reactions involved



Here the precipitation is partial because ZnS is soluble in acid below $\text{pH} = 6$ and the precipitation can be made complete in the presence of $\text{CH}_3\text{CO}_2\text{Na}$



4a. Reactions of Group III cations with $\text{H}_2\text{S}/\text{S}^{2-}$

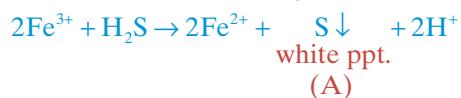
For Fe^{3+}



While

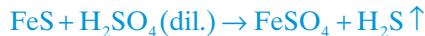
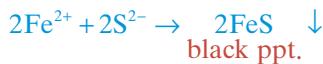
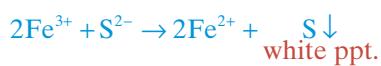


This can be explained on the basis of the following reactions:



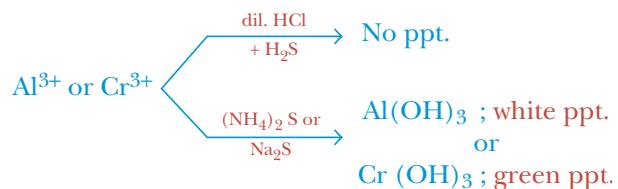


While



Hence the black precipitate (B) is (2 FeS + S) and FeS dissolves in dilute mineral acid and the white precipitate of S is obtained. The dissolution reaction of FeS with H_2SO_4 is utilized for the preparation of H_2S in the laboratory using Kipp's apparatus.

For Al^{3+} and Cr^{3+}



On addition of S^{2-} reagent, we get the precipitates of the hydroxide of these two metal ions. This happens due to the hydrolysis of S^{2-} ion in water as follows:



This $[\text{OH}^-]$ is sufficient to exceed the K_{sp} of Al(OH)_3 and Cr(OH)_3 , and yield the above precipitates because of their very low K_{sp} ($\sim 10^{-38}$).

4b. Classification of sulphides based on their colours with different cations

The sulphides of various cations are classified on the basis of their colour as follows:

Black: Ag_2S , PbS , $(\text{Hg} + \text{HgS})$, HgS , CuS , Bi_2S_3 (brownish black) NiS , CoS , FeS

Yellow: As_2S_3 , As_2S_5 , SnS_2 , CdS

Orange: Sb_2S_3 , Sb_2S_5

Buff: MnS

White: ZnS

Brown: SnS

4c. Classification of Group II sulphides based on their solubility in yellow ammonium sulphide (YAS)

$(\text{NH}_4)_2\text{S}_2$: These are classified as:

a. Group II A or 'Cu-group' which is insoluble in YAS: CuS , HgS , Bi_2S_3 , PbS , CdS .

b. Group II B or 'As-group' which is soluble in YAS: As_2S_3 , As_2S_5 , Sb_2S_3 , Sb_2S_5 , SnS , and SnS_2 .

Note: (i) CdS is the only yellow coloured sulphide precipitate which does not dissolve in YAS.

(ii) MnS is the only sulphide precipitate which dissolves in acetic acid.

(iii) Solubility of Group I, Group IIA and Group IV sulphides in different solvents are important information for use and given below:

- In HNO_3 (1:1), all are soluble except HgS and $(\text{Hg} + \text{HgS})$.

The generalized reaction is



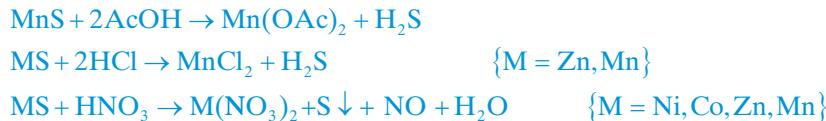
- In aqua regia ($3\text{HCl} + \text{HNO}_3$), all are soluble and the reactions is:



□ Solubility of Group IV sulphides

	AcOH	dil.HCl	dil.HNO ₃
NiS	✗	✗	✓
CoS	✗	✗	✓
ZnS	✗	✓	✓
MnS	✓	✓	✓

Reactions:



5. Reaction with KI: The following cations give this test and the presence of all these cations can be confirmed using KI.

- a. $\text{Ag}^+ \xrightarrow{\text{KI}} \text{AgI} \downarrow \xrightarrow{\text{excess KI}} \text{No change}$
yellow ppt.
- b. $\text{Pb}^{2+} \xrightarrow{\text{KI}} \text{PbI}_2 \downarrow \xrightarrow{\text{excess KI}} [\text{PbI}_4]^{2-}$
yellow ppt. colourless soluble complex
- c. $\text{Hg}_2^{2+} \xrightarrow{\text{KI}} \text{Hg}_2\text{I}_2 \downarrow \xrightarrow{\text{excess KI}} \text{Hg} \downarrow + [\text{Hg I}_4]^{2-}$
green ppt. black ppt. colourless soluble complex

Note: Using KI, Group I cations are well distinguished.

- d. $\text{Hg}^{2+} \xrightarrow{\text{KI}} \text{HgI}_2 \downarrow \xrightarrow{\text{excess KI}} [\text{HgI}_4]^{2-}$
scarlet red ppt. colourless soluble complex
- e. $\text{Bi}^{3+} \xrightarrow{\text{KI}} \text{BiI}_3 \downarrow \xrightarrow{\text{excess KI}} [\text{BiI}_4]^-$
brownish-black ppt. orange to yellow solution depending upon concentration.

Note: The above five cations give only precipitation reaction with KI.

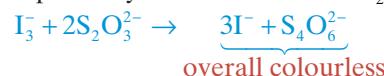
- f. Fe^{3+} gives only redox reaction with KI: $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$

Observations:

- If excess KI is used \Rightarrow dark brown appearance due to the formation of KI_3
 - If KI + starch is used \Rightarrow deep blue complex of (I_2 + starch)
 - If KI + organic layer like CCl_4 , CHCl_3 or CS_2 is used \Rightarrow violet organic layer is observed
- g. Cu^{2+} undergoes redox reaction first followed by precipitation



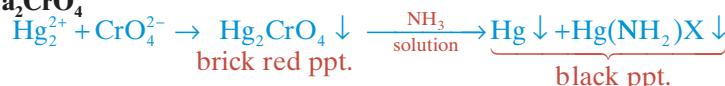
The colour of I_3^- is so dark that white precipitate of Cu_2I_2 or CuI becomes invisible. It becomes visible only when I_3^- is decomposed by the treatment of $\text{Na}_2\text{S}_2\text{O}_3$ (hypo) solution.



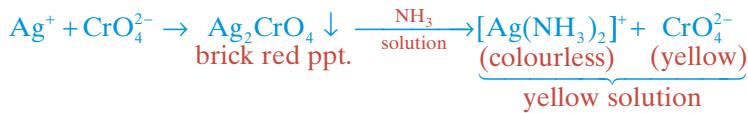
Note: There are other cations that give this test but these are beyond the scope of coverage.

6. Reaction with Na_2CO_3 : Already discussed in Section 7.2.

7. Reaction with Na_2CrO_4



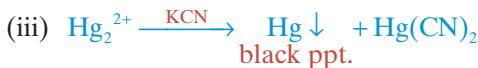
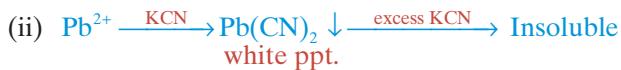
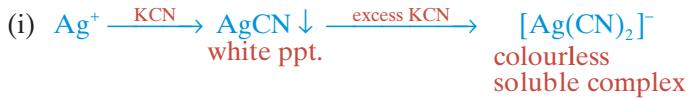
While



Here these two ions can be distinguished from each other using Na_2CrO_4 solution.

The reactions for other cations like Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} have already been discussed in Section 7.12.

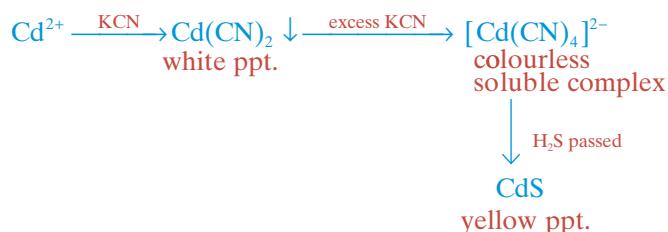
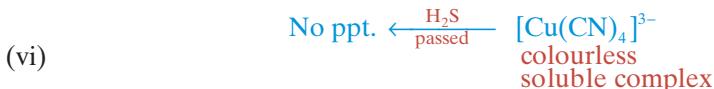
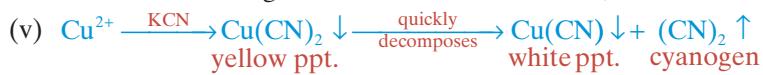
8. Reaction with KCN solution



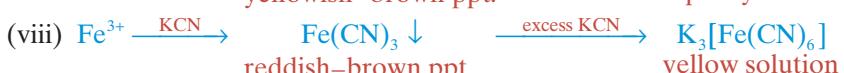
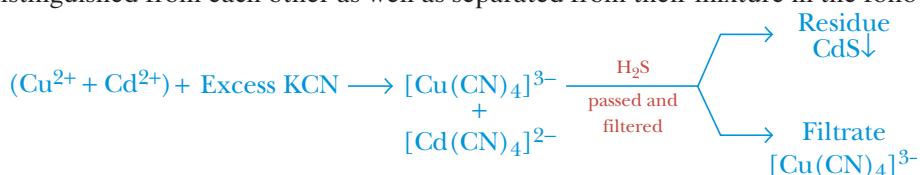
Note: Using KCN, Group I cations can be distinguished easily.



No observational changes because the water soluble, colourless compound is formed.



Note: From the sequential reactions of Cu^{2+} and Cd^{2+} towards KCN it is clear that these two cations can be distinguished from each other as well as separated from their mixture in the following way:

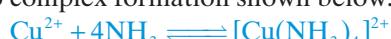


9. Reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$

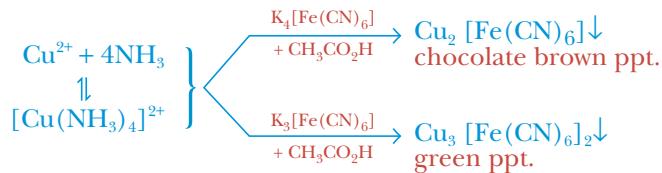
With Cu^{2+}



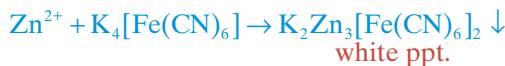
However, in the presence of NH_3 solution no such precipitates are obtained because free Cu^{2+} ions are not sufficiently available due to complex formation shown below:



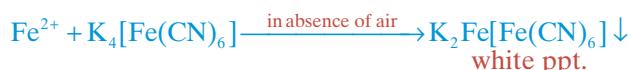
However, from this solution the same precipitates can be obtained when the above reagents are added with acetic acid.



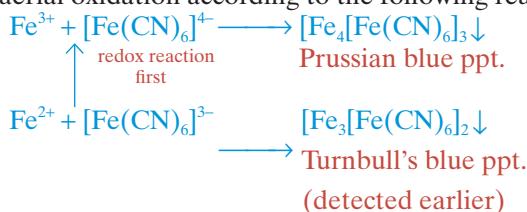
With Zn^{2+}



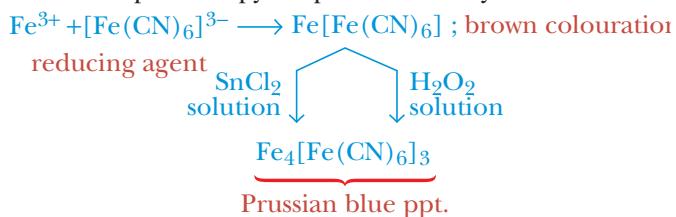
With Fe^{2+}



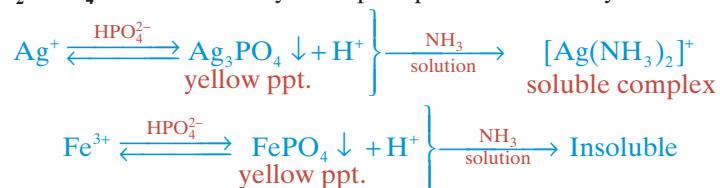
Under ordinary atmospheric conditions, a pale blue precipitate is obtained due to the partial conversion of Fe^{2+} into Fe^{3+} by aerial oxidation according to the following reaction.



Initially it was suggested that Prussian blue and Turnbull's blue are two different precipitates. But now with a detailed study by Mössbauer spectroscopy it is proved that they are of identical composition and structure.

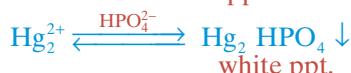
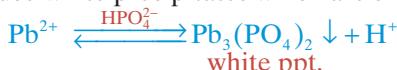


10. Reaction with Na_2HPO_4 : There are two yellow precipitates formed by the following reactions:

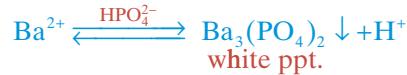
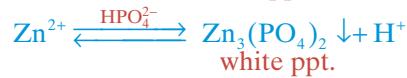
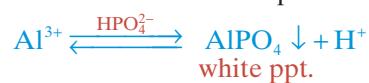


Hence using Na_2HPO_4 followed by addition of ammonia these two cations can be well distinguished.

There are six cations that produce white precipitates which are shown in the following reactions.



(This is the only case where no decrease in the pH of the medium is observed.)



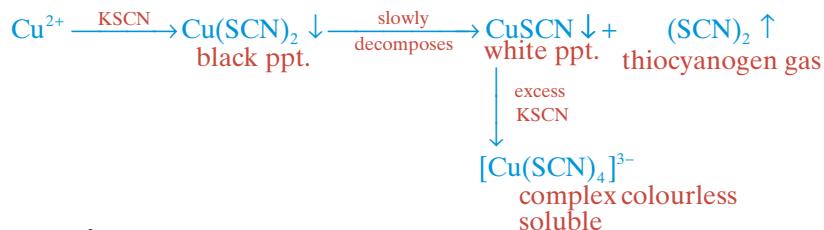
Only Mn^{2+} produces pink precipitate



11. Reaction with $NH_4SCN/KSCN$

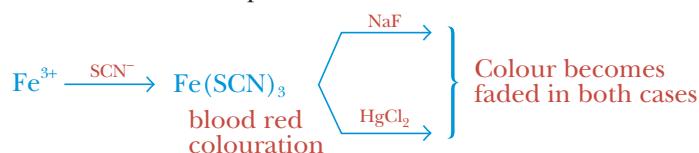
For Cu^{2+} :

It shows exactly similar behaviour towards both KSCN and KCN.

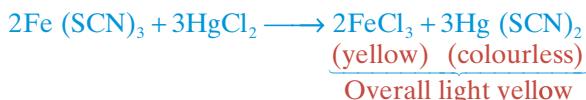


For Fe^{3+}

This test is specific for Fe^{3+} even in the presence of Fe^{2+} .



The reason is that:

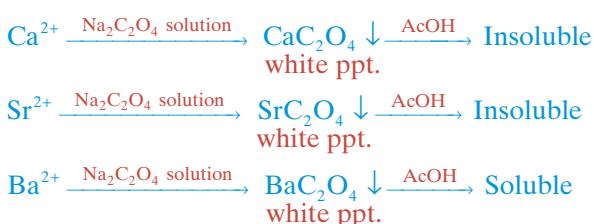


Tests for group V cations

1. Test with Na_2CO_3 or K_2CO_3 solution

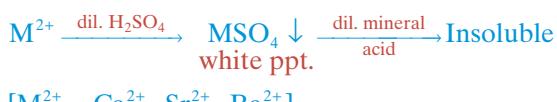


2. Test with $Na_2C_2O_4$ solution

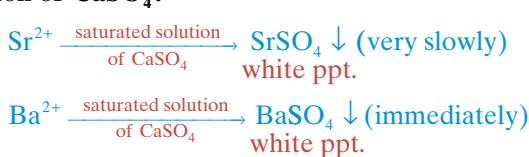


3. Test with Na_2CrO_4 solution: Discussed in Section 7.12.

4. Test with dil. H_2SO_4 solution

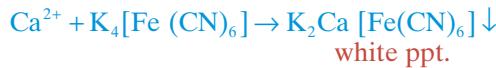


5. Test with saturated solution of $CaSO_4$:



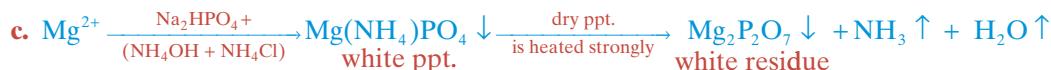
Reason: The solubility order is $\text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$ and the least soluble compound will be precipitated first.

6. **Test with $\text{K}_4[\text{Fe}(\text{CN})_6]$:** Among the three cations, only Ca^{2+} gives white precipitate with $\text{K}_4[\text{Fe}(\text{CN})_6]$.



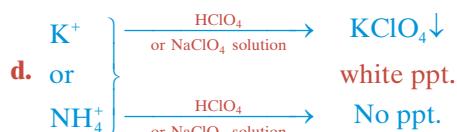
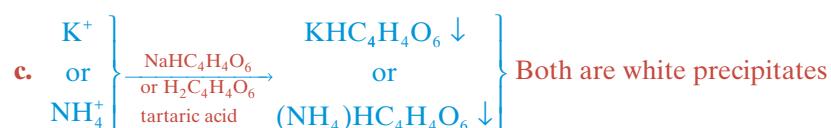
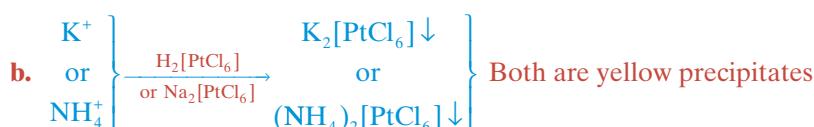
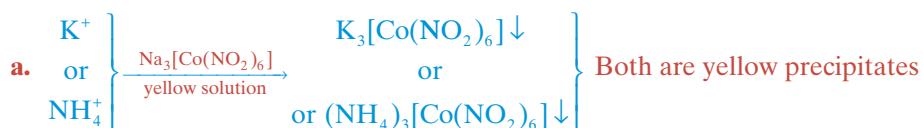
Tests for group VI and zero group cations

1. **For Mg^{2+} :** The tests for Mg^{2+} are listed together below:



2. **Test for Na^+ :** Flame test is done for its confirmation.

3. **Test for K^+ and NH_4^+ :** Most of the wet tests for K^+ and NH_4^+ are very similar in observations due to similarity in their radii, i.e. $r_{\text{K}^+} \approx r_{\text{NH}_4^+}$. The tests for both these cations are listed below:



This reagent is used to distinguish between K^+ and NH_4^+ .

- e. These two cations can also be distinguished by another gas evolution reaction

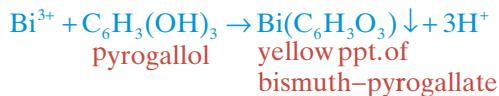


The colourless gas NH_3 evolved can be identified by several methods discussed in Section 7.8. No such gas is obtained with K^+ .

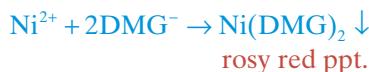
7.17 | SPECIFIC TESTS FOR SOME CATIONS

Apart from the reactions with common reagents, some specific tests are carried out for identification of some specific cations. Some specific tests for important cations are described as follows.

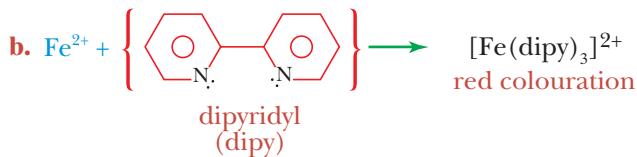
1. For Bi^{3+}



2. For Ni^{2+}



3. For Fe^{2+} : These tests are specific to Fe^{2+} even in the presence of Fe^{3+}



4. For Zn^{2+}

a. Rinmann's green test:

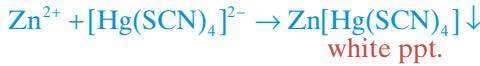


This green residue is known as Rinmann's green.

b. Test with $\{\text{CuSO}_4 + (\text{NH}_4)_2[\text{Hg}(\text{SCN})_4]\}$ solution:



While

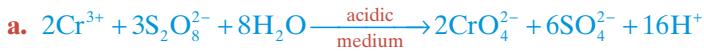


But in the presence of Zn^{2+} , Cu^{2+} also reacts through induced reaction giving rise to a violet precipitate due to complex formation with both the ions.



5. For Cr^{3+} :

The presence of Cr^{3+} is shown by chromate test where Cr^{3+} is converted into CrO_4^{2-} using different reagents. In all cases, the green colour due to Cr^{3+} is changed into the yellow colour of CrO_4^{2-} . Reagents used for conversion of Cr^{3+} to CrO_4^{2-} are listed as follows.



b. Cr^{3+} in alkaline medium exist as $[\text{Cr}(\text{OH})_4]^-$.



Here another very good reagent sodium perborate (NaBO_3) can be used instead of H_2O_2 . It produces H_2O_2 on hydrolysis *in situ*.



c. NaOBr solution also can be used for the same purpose.



6. For Mn^{2+} : Similarly, the presence of Mn^{2+} is confirmed by conversion to MnO_4^- and the observation is changed from colourless to purple. The various methods for this conversion are listed as follows:

a. Using $\text{K}_2\text{S}_2\text{O}_8$ or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution in acidic medium.



b. Using $(\text{PbO}_2 + \text{conc. HNO}_3)$.



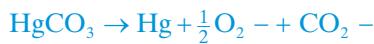
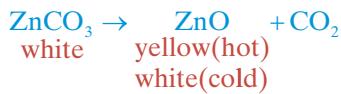
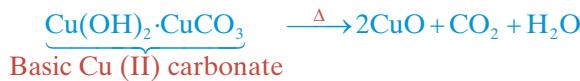
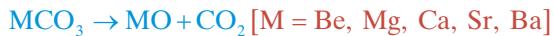
c. Using sodium bismuthate (NaBiO_3) solution.



HEATING EFFECTS

The effect of heating on various salts, oxides and acids can also be used for detection of radicals and identification of unknown salts. The characteristic products obtained on heating of different salts are listed as follows.

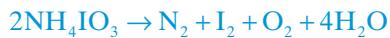
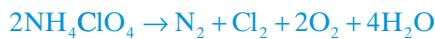
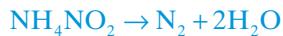
1. **Heating effect on carbonate and bicarbonate salts:** All carbonates except (Na, K, Rb, Cs) decompose on heating giving CO_2 . For example,



All bicarbonates decompose to give carbonates and CO_2 . For example,



General reaction: $2\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} + \text{CO}_2$

2. Heating effect on ammonium salts

Note: If the anionic part is oxidizing in nature, then N_2 will be the product (sometimes N_2O).



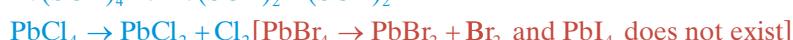
Note: If the anionic part is weakly oxidizing or non-oxidizing in nature then NH_3 will be the product.

3. Heating effect on nitrate salts

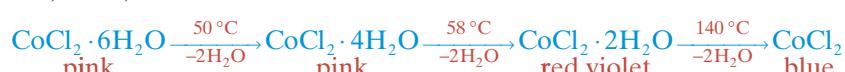
Where $\text{M} = \text{Na, K, Rb, Cs}$.



Where $\text{M} = \text{all bivalent metals such as Zn}^{2+}, \text{Mg}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Cu}^{2+}, \text{Pb}^{2+}$.

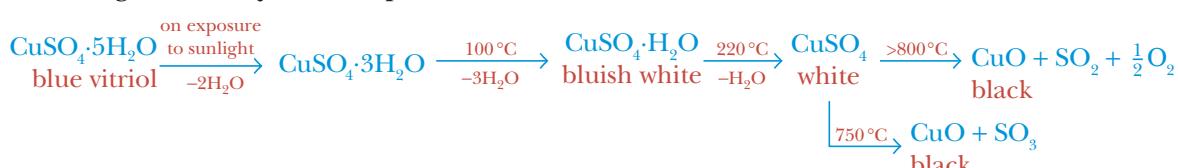
**4. Heating effect on halide salts****5. Heating effect on hydrated chloride salts**

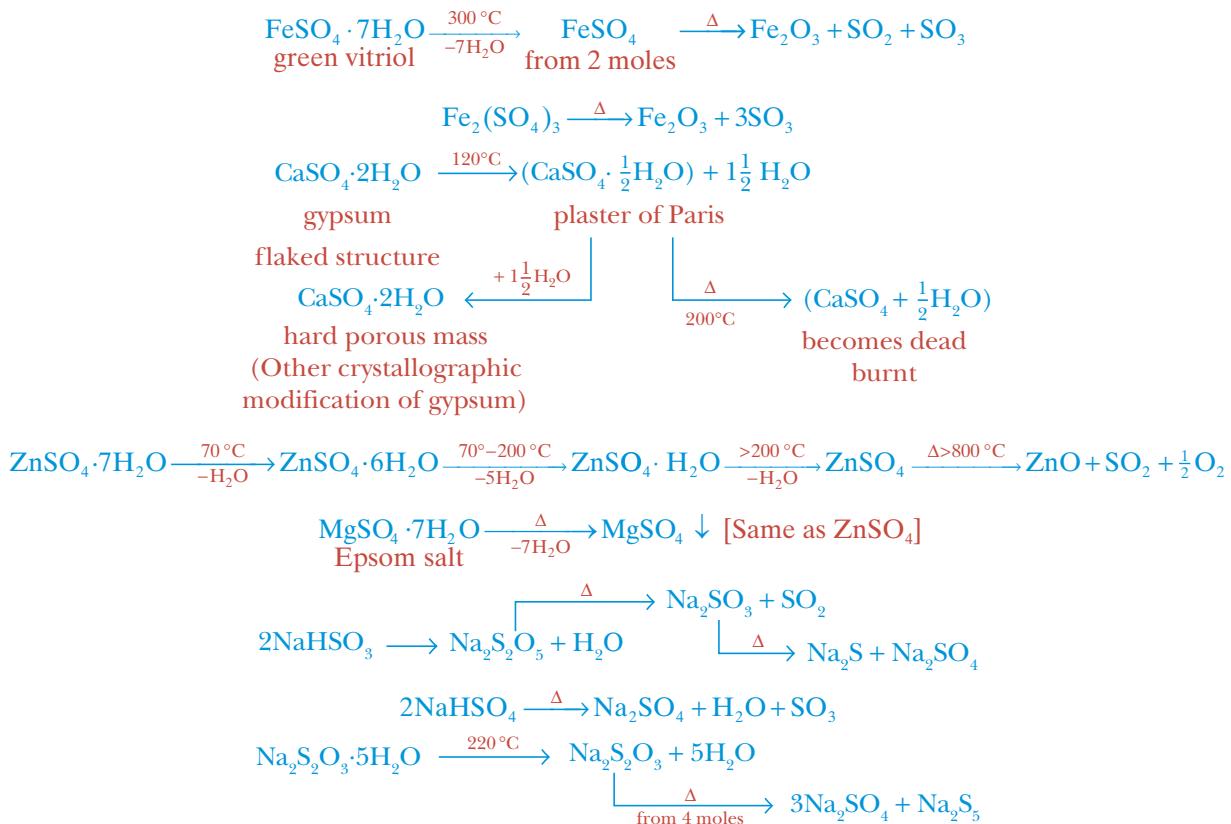
Where $\text{M}^{2+} = \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Sn}^{2+}$.



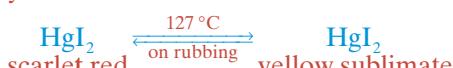
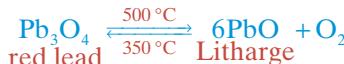
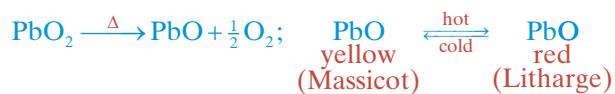
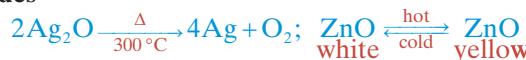
Hydrated Co^{2+} salt is pink.

Anhydrous Co^{2+} salt is blue.

6. Heating effect on hydrated sulphate salts



7. Heating effect on oxides

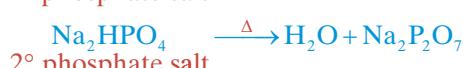


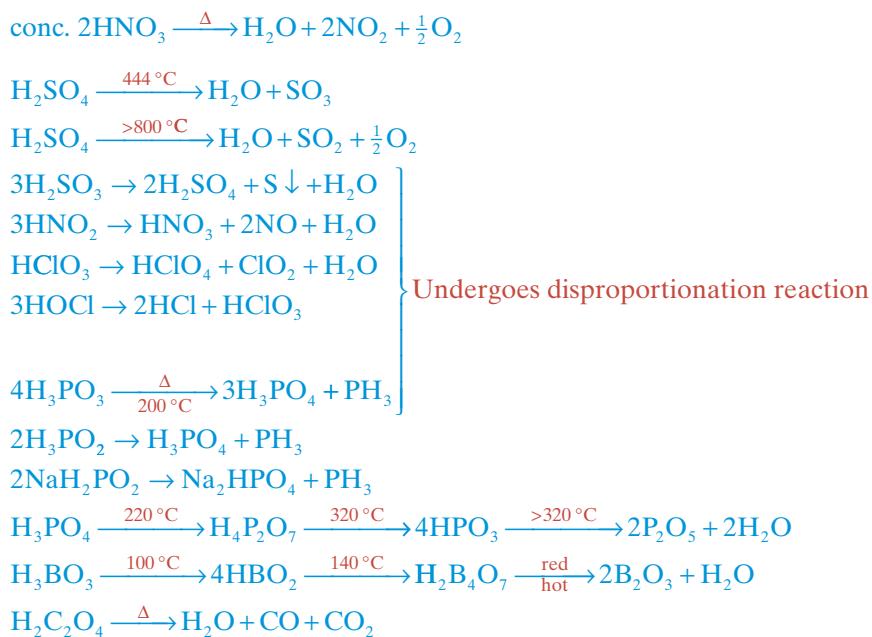
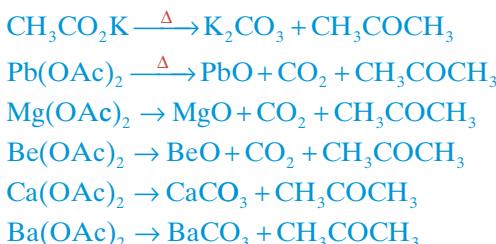
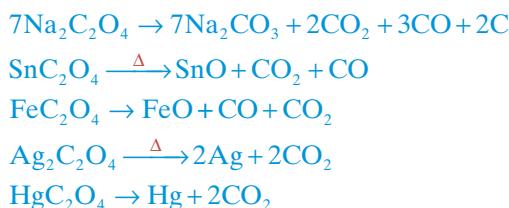
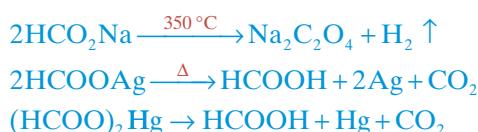
Colour does not even go on cooling to room temperature for HgI₂.

8. Heating effect on dichromate and chromate salts



9. Heating effect on phosphate salts



10. Heating effect on acids**11. Heating effect on acetate salts****12. Heating effect on oxalate salts****13. Heating effect on formate salts****SINGLE CORRECT CHOICE TYPE QUESTIONS**

1. Which of the following ions gives brown ring test with dil. H_2SO_4 ?

(A) NO_2^- (B) NO_3^-

(C) Both (A) and (B) (D) None of these
2. Which of the following cations gives red colour in flame?

(A) Cs^+ (B) Ba^{2+}

(C) Sr^{2+} (D) K^+
3. The sulphide ion gives purple colour with sodium nitroprusside. The purple colour is due to the formation of

(A) $\text{Na}_4[\text{Fe}(\text{CN})_3(\text{NOS})_3]$

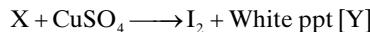
(B) $\text{Na}_4[\text{Fe}(\text{CN})_4(\text{NOS})_2]$

(C) $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$

(D) $\text{Na}_4[\text{Fe}(\text{NOS})_6]$

4. Which of the following statements is correct, about passing H_2S gas through acidified $K_2Cr_2O_7$ solution?
 (A) Milky colour of the solution is due to SO_3^{2-} .
 (B) Milky colour of the solution is due to SO_4^{2-} .
 (C) Milky colour of the solution is due to S.
 (D) Milky colour of the solution is due to Cr^{3+} .

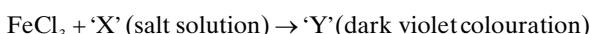
5. In the following sequence of reactions, identify compound Z.



$NaI + [Z]$ colourless compound

- (A) $Cu_2S_2O_3$ (B) Cu_2I_2
 (C) $Na_2S_4O_6$ (D) $Na_4[Cu_6(S_2O_3)_5]$

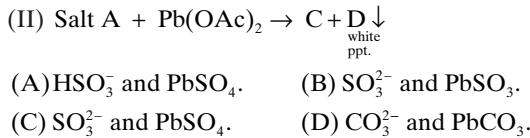
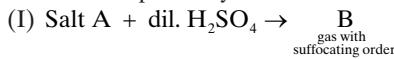
6. In the following reaction, the compounds X and Y are respectively



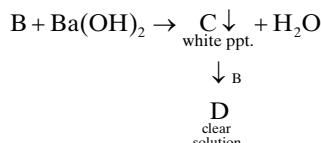
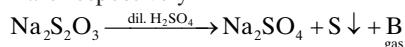
[colour disappears]

- (A) $Na_2S_2O_3$ and FeS_4O_6
 (B) $Na_2S_2O_3$ and $[Fe(S_2O_3)_2]$
 (C) Na_2SO_3 and $FeSO_4$
 (D) Na_2S and $(FeS + S)$

7. In the following reaction sequences, compounds A and D are respectively



8. In the following reaction sequences, compounds B and D are respectively



- (A) H_2S and $BaSO_3$.
 (B) SO_2 and $BaSO_3$.
 (C) H_2S and $Ba(HSO_3)_2$.
 (D) SO_2 and $Ba(HSO_3)_2$.

9. Which of the following pair of species gives a precipitate when mixed together?

- (A) Na^+ , HPO_4^{2-} (B) Ca^{2+} , NO_3^-
 (C) Fe^{3+} , NO_2^- (D) None of these.

10. $MCl_3 \xrightarrow[\text{of water}]{\text{huge amount}}$ white turbidity \xrightarrow{AcOH} clear solution.

Then M^{3+} is

- (A) Fe^{3+} (B) Sb^{3+}
 (C) Bi^{3+} (D) Au^{3+}

11. Choose the correct solubility order

- (A) $BaS < MnS < Sb_2S_3 < K_2S$
 (B) $K_2S < MnS < Sb_2S_3 < BaS$
 (C) $Sb_2S_3 < MnS < BaS < K_2S$
 (D) $Sb_2S_3 < BaS < MnS < K_2S$

12. Sodium nitroprusside solution is used to detect which of the following ions?

- (A) $S_2O_3^{2-}$ (B) Al^{3+}
 (C) Cu^{2+} (D) S^{2-}

13. On addition of excess $NaOH$ solution, which of the following will produce a coloured solution?

- (A) Solution of $NiCl_2$ (B) Solution of $CrCl_3$
 (C) Solution of $CuSO_4$ (D) Solution of $BaCl_2$

14. Which of the following conditions is not suitable for the brown ring test of NO_2^- ?

- (A) $FeSO_4$ added must be freshly prepared.
 (B) H_2SO_4 added should be concentrated.
 (C) Acetic acid may be used as an alternative acid.
 (D) Shaking or warming is not allowed.

15. The nitrite ion can be best destroyed by

- (A) NH_4Cl (B) NH_2CONH_2
 (C) NH_2CSNH_2 (D) $NH_2 - SO_2 - OH$

16. Choose the correct statement from the following:

- (A) Obtaining vinegar smell from acetate ion is not affected by conc. H_2SO_4 .
 (B) HCO_3^- ion gives the test with dil. H_2SO_4 as well as conc. H_2SO_4 .
 (C) No precipitate is obtained when $Pb(OAc)_2$ is added into HCO_3^- solution.
 (D) All of these

17. When a violet layer is obtained first in the layer test for an unknown sample, which of the following statements is incorrect?

- (A) I^- is confirmed.
 (B) Br^- may be present.
 (C) Br^- must be present.
 (D) No comment regarding the presence of Br^- ion.

18. Which of the following compounds produces white needle-like crystals on recrystallization?

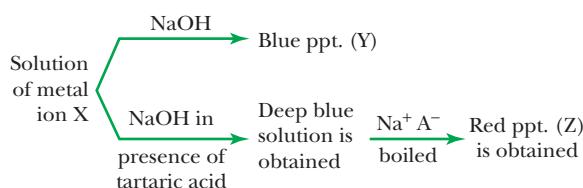
- (A) $PbCl_2$ (B) $BaSO_4$
 (C) $AgBr$ (D) $FePO_4$

19. When Ca^{2+} , Sr^{2+} and Ba^{2+} are taken together in a test tube and $Na_2C_2O_4$ solution is added, which of the following cations will form the precipitate first?

- (A) Ca^{2+}
 (B) Sr^{2+}
 (C) Ba^{2+}
 (D) All will form precipitate together.

20. On addition of dil. H_2SO_4 to the BaC_2O_4 solution, the gas(es) liberated is/(are)
 (A) CO only. (B) CO_2 only.
 (C) $CO + CO_2$. (D) None of these.
21. The NO_3^- ion can be confirmed by
 (A) addition of conc. H_2SO_4 in the presence of copper turnings.
 (B) addition of conc. $NaOH$ + Devarda's alloy.
 (C) the brown ring test only.
 (D) All of these.
22. Na_2SO_4 solution + $M^{2+} \rightarrow$ Yellow ppt. (A).
 The cation M^{2+} and yellow ppt. A are respectively
 (A) Sr^{2+} and $SrSO_4$
 (B) Hg^{2+} and $HgSO_4$
 (C) Hg^{2+} and $2HgO \cdot HgSO_4$
 (D) Hg^{2+} and $HgO \cdot 2HgSO_4$
23. Which of the following compounds on reaction with $NaOH$ and $NaBO_3$ (sodium perborate) give a yellow solution?
 (A) $Zn(OH)_2$ (B) $Al(OH)_3$
 (C) $Pb(OH)_2$ (D) $Cr(OH)_3$
24. The Canary yellow precipitate test gives positive observation only under boiling condition from which of the following acidic radicals?
 (A) AsO_3^{3-} (B) PO_4^{3-}
 (C) AsO_4^{3-} (D) $S_2O_3^{2-}$
25. Aqueous solution of a metal ion A on reaction with KI gives green ppt. (B) and the aqueous suspension of B when heated produces a red precipitate with finely distributed black particles. Then A is
 (A) Hg_2^{2+} (B) Hg^{2+}
 (C) Cu^{2+} (D) Pb^{2+}
26. The precipitate of Ag_2S is not obtained from which of the following solutions when H_2S is passed through them?
 (A) Aqueous suspension of $AgCl$.
 (B) $[Ag(S_2O_3)_2]^-$ solution.
 (C) $[Ag(CN)_2]^-$ solution.
 (D) $AgNO_3$ solution.
27. Which of the following cations gives yellow precipitate on addition of freshly prepared pyrogallol in slightly acidic medium?
 (A) Pb^{2+} (B) Bi^{3+}
 (C) Mn^{2+} (D) Sn^{2+}

28.



The cation X and the anion A are respectively

- (A) NH_4^+ , $CH_3CO_2^-$
 (B) HCO_3^- , Cu^{2+}
 (C) Pb^{2+} , $C_2O_4^{2-}$
 (D) Cu^{2+} , HCO_3^-

29. Metal ion solution + $Na_2S_2O_3 \xrightarrow{\text{on standing}}$ Violet colouration
 $\xrightarrow{\text{on standing}}$ Light green solution

The cation present in the given solution is

- (A) Fe^{2+} (B) Fe^{3+}
 (C) Cu^{2+} (D) Ag^+

30. $NiCl_2$ solution + NH_3 solution \rightarrow Green ppt.
 $\xrightarrow{\text{excess NH}_3 \text{ solution}}$ Deep blue solution

Finally Ni^{2+} ion is present in the
 (A) cationic part of the solution.

- (B) anionic part of the solution.
 (C) both in the cationic and anionic parts of solution.
 (D) None of these.

31. $KMnO_4 + NaOH(\text{hot conc.}) \xrightarrow{\Delta}$ Green solution (purple)

 $\xrightarrow{\text{on dilution}}$ Purple colour comes back

Which of the following statements is incorrect regarding the above reactions?

- (A) $NaOH$ provides alkaline medium only.
 (B) $NaOH$ acts as a reducing agent
 (C) The oxidation state of Mn in green solution is +6.
 (D) Both steps take place through redox reaction.

32. Aqueous solution of metal ion $M^{n+} + KI \rightarrow$ Black ppt. (N) $\xrightarrow{\text{aqueous suspension is heated}}$ Orange ppt. (P)

What is P?

- (A) $Bi(OH)_3$ (B) Hg_2I_2
 (C) BiI_3 (D) $BiO \cdot I$

33. The carmine red coloured flame in the flame test is given by

- (A) Cu^{2+} (B) Ca^{2+}
 (C) Li^+ (D) Sr^{2+}

34. In the flame test, a golden yellow coloured flame is observed. Then which of the following statements is incorrect?

- (A) Na^+ ion may only be present.
 (B) K^+ is absent.
 (C) The presence of Na^+ ion is confirmed.
 (D) Na^+ and K^+ ions both may be present together.

35. Which of the following sets of compounds is not soluble in the NH_4Cl solution?

- I. $Mn(OH)_2$ II. $Mg(OH)_2$ III. $Al(OH)_3$
 IV. $Zn(OH)_2$ V. $CaCO_3$
- (A) I, II and III (B) II, III and IV
 (C) II and IV (D) III and V

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. $\text{Na}_2\text{S}_2\text{O}_3$ solution + X \longrightarrow White ppt.
 $\xrightarrow{\text{excess Na}_2\text{S}_2\text{O}_3 \text{ solution}}$ Clear solution

Then X may be
(A) $\text{Pb}(\text{OAc})_2$ (B) CuSO_4
(C) NaNO_3 (D) AgNO_3

2. $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ cannot be separated using
(A) dil. HCl . (B) NaOH (excess).
(C) NH_3 solution. (D) Any of these.

3. Which cations among the following do not give ppt. of their sulphide with $(\text{NH}_4)_2\text{S}$?
(A) Al^{3+} (B) Fe^{2+}
(C) Sr^{2+} (D) Fe^{3+}

4. Which of the following processes result in a Prussian blue ppt.?
(A) $\text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{3-} \longrightarrow$
(B) $\text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{4-} \longrightarrow$
(C) $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{3-} \longrightarrow$
(D) $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{3-} \longrightarrow \text{P} \xrightarrow{\text{SnCl}_2}$

5. Which of the following acid radicals will produce H_2S gas on action of $[\text{Zn} + \text{dil. H}_2\text{SO}_4]$?
(A) S^{2-} (B) SO_4^{2-}
(C) SO_3^{2-} (D) HSO_4^-

6. Which of the following pairs of cations can be separated from each other by passing H_2S in dil. HCl medium?
(A) $\text{Sn}^{2+}, \text{Hg}^{2+}$ (B) $\text{Pb}^{2+}, \text{Mn}^{2+}$
(C) $\text{Sb}^{3+}, \text{Cu}^{2+}$ (D) $\text{Zn}^{2+}, \text{Cu}^{2+}$

7. Which of the following compounds will give yellow ppt. on addition of the $(\text{Na}_2\text{CrO}_4 + \text{AcOH})$ solution?
(A) BaCl_2 solution.
(B) Aqueous suspension of PbCO_3 .
(C) Aqueous suspension of BaSO_4 .
(D) Hot solution of PbCl_2 .

8. Salt A $\xrightarrow{\text{NaOH}}$ Gas B + Solution C
Solution C + $\text{Zn} + \text{NaOH} \longrightarrow$ Gas B
Then solid A may be
(A) NaNO_3 (B) NH_4NO_3

(C) AgNO_2 (D) NH_4NO_3

9. Which of the following pairs of cations can be separated from each other by adding hypo solution followed by filtration?
(A) $\text{Ca}^{2+}, \text{Ba}^{2+}$ (B) $\text{Ag}^+, \text{Cu}^{2+}$
(C) $\text{Hg}^{2+}, \text{Mg}^{2+}$ (D) $\text{Bi}^{3+}, \text{Pb}^{2+}$

10. Salt solution of M + $\text{NaN}_3 + \text{I}_2$ dissolved in KI soln \longrightarrow colourless gas is evolved.
Then salt M may be
(A) KCl (B) Na_2S
(C) $\text{N}_2\text{S}_2\text{O}_3$ (D) NH_4SCN

11. Which of the following acid radicals produce white precipitate on addition of AgNO_3 ?
(A) $\text{C}_2\text{O}_4^{2-}$ (B) NO_2^-
(C) Cl^- (D) HCO_3^-

12. To identify I_2 produced in a particular reaction, the suitable reagents are
(A) excess NaOH solution.
(B) presence of CCl_4 .
(C) excess KI solution.
(D) presence of starch.

13. The colour of acidic KMnO_4 can be discharged by
(A) Cl^- ion. (B) NO_2^- .
(C) NO_3^- . (D) FeCl_2 solution.

14. CO gas can be detected by which of the following methods?
(A) It turns lime water milky.
(B) It burns with a blue flame.
(C) It turns the PdCl_2 solution black.
(D) It reduces Fe_2O_3 to Fe.

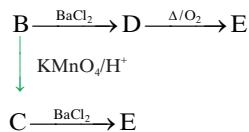
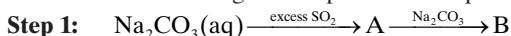
15. Which of the following aqueous suspensions give clear solution on heating?
(A) PbSO_4 (B) PbCl_2
(C) $\text{CH}_3\text{CO}_2\text{Ag}$ (D) None of these.

16. Sometimes turbidity appears in the Group II test of group analysis, even in the absence of Group II cations. This is due to
(A) the presence of Fe^{2+} cation.

COMPREHENSION TYPE QUESTIONS

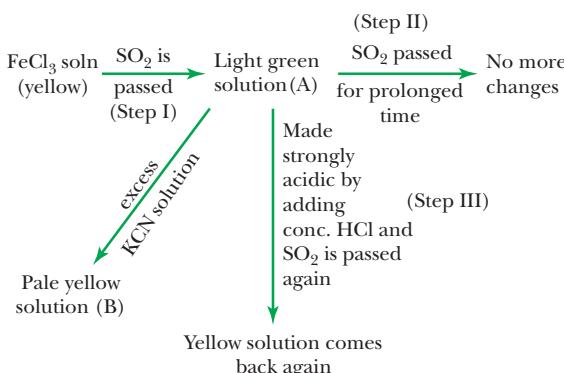
Passage 1: For Questions 1–3

Consider the following two-step reaction sequence.



1. Compounds A and B are
 - (A) NaHCO_3 and Na_2CO_3
 - (B) NaHCO_3 and Na_2SO_3
 - (C) NaHSO_3 and Na_2SO_3
 - (D) NaHSO_3 and Na_2CO_3
 2. Here compound E, insoluble in dilute HCl , will be
 - (A) BaCO_3
 - (B) BaSO_3
 - (C) BaSO_4
 - (D) BaS_2O_3
 3. Compound D treated with dilute H_2SO_4 gives a gas with pungent smell that turns lime water to milky turbidity. Compound D is
 - (A) BaCO_3
 - (B) BaSO_3
 - (C) BaSO_4
 - (D) Na_2SO_3

Passage 2: For Questions 4–6



19. Choose the correct statements from the following:

 - (A) Addition of Na_2CrO_4 can distinguish Group V cations.
 - (B) Addition of Na_2CrO_4 followed by acetic acid can distinguish Group V cations.
 - (C) Addition of $(\text{Na}_2\text{CrO}_4 + \text{acetic acid})$ cannot distinguish Group V cations.
 - (D) Addition of KCN followed by excess addition can distinguish Group I cations.

20. Which of following mixtures of cations can be separated by adding excess NH_3 solution?

 - (A) $\text{Zn}^{2+}, \text{Mn}^{2+}$
 - (B) $\text{Zn}^{2+}, \text{Cd}^{2+}$
 - (C) $\text{Zn}^{2+}, \text{Pb}^{2+}$
 - (D) $\text{Zn}^{2+}, \text{Cu}^{2+}$

Passage 3: For Questions 7–9

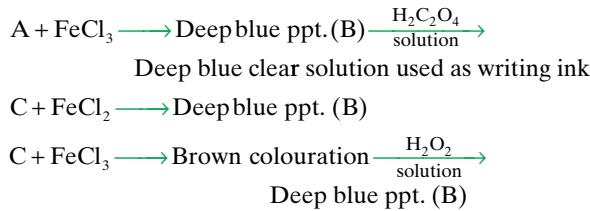
CO_3^{2-} ion and HCO_3^- ions can be distinguished from each other by several reagents like soluble salts of Ca^{2+} , Sr^{2+} , Ba^{2+} , Zn^{2+} , Mg^{2+} , Pb^{2+} , Cu^{2+} , Hg^{2+} , Ag^+ , etc. But all these reagents cannot be utilized for detection of both the radicals when they are present together.

7. Zn^{2+} cation forms a white ppt. with CO_3^{2-} but no precipitate is formed with HCO_3^- . The formula of the white precipitate is
(A) $\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ (B) ZnCO_3
(C) $\text{Zn}(\text{OH})_2 \cdot 3\text{ZnCO}_3$ (D) None of these.

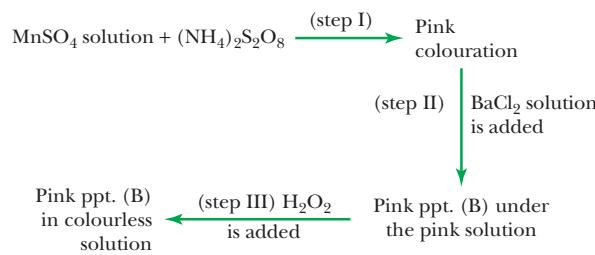
8. Which of following sets of cations can be used to detect both the radicals when they are present together in a mixture?
(A) $\text{Ca}^{2+}, \text{Hg}^{2+}$ (B) $\text{Zn}^{2+}, \text{Mg}^{2+}$
(C) $\text{Ag}^+, \text{Ba}^{2+}$ (D) $\text{Pb}^{2+}, \text{Sr}^{2+}$

9. Which of the following anions give precipitate with MgCl_2 solution only on boiling?
(A) CO_3^{2-} (B) HCO_3^-
(C) Both (A) and (B) (D) None of these.

Passage 4: For Questions 10–12



Passage 5: For Questions 13–15



Passage 6: For Questions 16–18

When acetic acid is added to a solution of sodium carbonate, the gas evolved does not change the purple colour of KMnO_4 but turns lime water milky forming a compound M. This compound becomes soluble by passing

the same gas in excess forming another compound (N). But same observation is not obtained with boric acid.

16. Purple colour of KMnO_4 does not change because
(A) the gas has no oxidizing property since the central atom has the minimum oxidation state.
(B) the gas has no reducing property since the central atom has the maximum oxidation state.
(C) the gas has no precipitation characteristics.
(D) the gas precipitates CaCO_3 from lime water.

17. The compounds M and N formed in the above sequence are respectively
(A) water soluble CaCO_3 and water soluble $\text{Ca}(\text{HCO}_3)_2$.
(B) water insoluble CaCO_3 and water insoluble $\text{Ca}(\text{HCO}_3)_2$.
(C) water insoluble CaCO_3 and water soluble $\text{Ca}(\text{HCO}_3)_2$.
(D) water soluble CaCO_3 and water insoluble $\text{Ca}(\text{HCO}_3)_2$.

18. The correct order of increasing acidity is
(A) boric acid < acetic acid < carbonic acid
(B) acetic acid < boric acid < carbonic acid
(C) carbonic acid < acetic acid < boric acid
(D) boric acid < carbonic acid < acetic acid

Passage 7: For Questions 19–21

There are two ores A_1 and A_2 of metal M. When ore A_1 is calcinated, a black solid S is obtained along with the liberation of CO_2 and water. The ore A_1 on treatment with HCl and KI gives a ppt. P and I_2 is liberated. The other ore A_2 on roasting gives a gas G and metal M is set free. When gas G is passed through K_2CrO_7 , it turns green.

19. The ore A_2 is
(A) malachite. (B) azurite.
(C) ruby copper. (D) copper glance.

20. The colour of precipitate P is
(A) brown. (B) white.
(C) yellow. (D) green.

21. Which of the following gases shows a similar behaviour towards $K_2Cr_2O_7$ as gas G?
(A) H_2S (B) SO_3
(C) CO_2 (D) SO_2

Passage 8: For Questions 22–25

A chemist opened a cupboard to find four bottles containing water solutions, each of which had lost its label. Bottles 1, 2 and 3 contained colourless solutions, whilst Bottle 4 contained a blue solution. The labels from the bottles were lying scattered on the floor of the cupboard. They were:

- copper (II)sulphate
- sodium carbonate
- lead nitrate
- hydrochloric acid

By mixing samples of the contents of the bottles, in pairs, the chemist made the following observations:

- (I) Bottle 1 + Bottle 2 white precipitate

- | | |
|---------------------------|------------------------|
| (II) Bottle 1 + Bottle 3 | white precipitate |
| (III) Bottle 1 + Bottle 4 | white precipitate |
| (IV) Bottle 2 + Bottle 3 | colourless gas evolved |
| (V) Bottle 2 + Bottle 4 | no visible reaction |
| (VI) Bottle 3 + Bottle 4 | blue precipitate |

Passage 9: For Questions 26–29

A great scientist 'Tom Cat' collected six sample solutions in six test tubes for a new discovery and tried for Nobel Prize (Chemistry). But his very close friend 'Jerry Mouse' all of a sudden appeared in the laboratory and kicked off AgNO_3 bottle on all these samples and spoiled the experiments, making all white precipitates. But 'Tom Cat' did not lose his enthusiasm and made the following observations from all the white precipitates formed.

Test tube	Observations
(I)	The ppt. is soluble on heating.
(II)	The anion present in test tube II does not give the brown ring test for nitrate if it is present with nitrate ion.
(III)	The ppt. becomes soluble on addition of excess of solution that was present in test tube III but on heating it produces a black ppt. which does not dissolve in NH_3 .
(IV)	The ppt. gives a clear solution with excess of solution that was present in test tube IV and that clear solution gives black metallic ppt. on heating together with evolution of acidic gas which turns acidic $\text{K}_2\text{Cr}_2\text{O}_7$ solution green.
(V)	The aqueous suspension of ppt. produces black metallic residue and an acidic gas on heating. This gas does not turn $\text{K}_2\text{Cr}_2\text{O}_7$ solution green.
(VI)	The ppt. is soluble in NH_3 but does not give brown ring test.

26. In which of the observations, black ppt. is Ag_2S .
(A) IV (B) III
(C) V (D) None of these.

27. White ppts. in I, IV and II are respectively
(A) Ag_2SO_3 , HCO_2Ag , AgBr
(B) AgNO_2 , HCO_2Ag , AgCl
(C) $\text{CH}_3\text{CO}_2\text{Ag}$, Ag_2SO_3 , AgNO_2
(D) HCO_2Ag , Ag_2CO_3 , AgNO_2

Passage 10: For Questions 30–33

- (I) A hot metal M burns in acidic gas A and produces B and C.
 - (II) B reacts with KMnO_4 giving rise to brown ppt.
 - (III) C reacts with dil. H_2SO_4 , giving the same gas A.
 - (IV) C on heating produces E and F.
 - (V) E reacts with dil. H_2SO_4 releasing rotten egg's smell.
 - (VI) F reacts with $\text{Pb}(\text{NO}_3)_2$ giving rise to white ppt. which does not dissolve in dil. mineral acid but is soluble in $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

31. E reacts with FeCl_2 solution and the precipitate obtained is

(A) FeS (B) S
(C) $\text{FeS} + \text{S}$ (D) Fe_3S_2

- 32.** Analogous sodium compound of B on heating produces a polysulphide having the unit of S_x^{2-} ion. The value of x is

- (A) 2 (B) 3 (C) 5 (D) 6

33. White precipitate obtained in observation

(A) $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ (B) $\text{Pb}(\text{OH})_2$
(C) PbSO_4 (D) $\text{PbSO}_4 \cdot \text{H}_2\text{O}$

Passage 11: For Questions 34–36

A white crystalline solid A on boiling with caustic soda solution gives a gas B which on passing through an alkaline solution of potassium tetraiodomercurate (II) solution gives a brown ppt. The substance A on heating evolves a neutral gas C which is called laughing gas.

34. The gas B is
(A) H_2S (B) NH_3
(C) HCl (D) CO_2

35. The gas C is
(A) N_2O (B) O_2
(C) NO (D) O_3

36. The substance A is
(A) NH_4Cl (B) NH_4NO_3
(C) NH_4NO_2 (D) NaNO_3

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
- (C) If Statement I is true but Statement II is false.
- (D) If Statement I is false but Statement II is true.

1. Statement I: Most of the wet test observations of K^+ and NH_4^+ are identical.

Statement II: Radius of K^+ ion is almost identical to that of NH_4^+ .

2. Statement I: $NaHCO_3$ and $NaOH$ cannot exist together.

Statement II: $NaOH$ is more soluble in water as compared to $NaHCO_3$.

3. Statement I: The colour of acidic $K_2Cr_2O_7$ solution is discharged by Na_2S or Na_2SO_4 solution.

Statement II: The maximum and minimum oxidation states possible for S atom are +VI and -II respectively.

4. Statement I: The aqueous suspension of Ag_2CO_3 on heating does not set free metallic Ag.

Statement II: The decomposition temperature of Ag_2O is $300^\circ C$, which cannot be achieved in aqueous medium.

5. Statement I: The aqueous suspensions of Ag_2CO_3 and Ag_2SO_3 , on heating produce Ag_2O and Ag respectively as precipitate.

Statement II: Ag_2O is a mild oxidizing agent which can oxidize SO_2 into SO_4^{2-} and itself is reduced to metallic Ag while similar reaction cannot take place with CO_2 .

6. Statement I: To prepare soda extract, any carbonate other than Na_2CO_3 cannot be used.

Statement II: All sodium salts are soluble in water.

7. Statement I: On addition of dil. H_2SO_4 , $S_2O_3^{2-}$ ion gives white turbidity.

Statement II: S–S linkage is weak enough due to $3d\pi - 3p\pi$ bonding in $S_2O_3^{2-}$ ion.

8. Statement I: Chlorides of Hg(I) and Hg(II) do not respond to chromyl chloride test.

Statement II: Chlorides of Hg(I) and Hg(II) are both diamagnetic in nature.

9. Statement I: The layer test of Br^- can be performed in the presence of Cl^- .

Statement II: The use of organic layer intensifies the observation.

10. Statement I: The same gas is liberated when Na_2S is treated with dil. HCl and Na_2SO_3 is treated with $Zn + dil. H_2SO_4$.

Statement II: The gaseous product is obtained through redox reaction in both the cases.

11. Statement I: The reddish brown ppt. formed by Group III reagents in the group separation of basic radicals confirms the presence of Fe^{3+} ion.

Statement II: The reddish brown precipitate in above reaction is of $Fe(OH)_3$.

12. Statement I: $SnCl_2$ and $HgCl_2$ cannot exist together.

Statement II: $Sn^{2+} + Hg^{2+} \longrightarrow Hg \downarrow + Sn^{4+}$; occurs spontaneously.

13. Statement I: The reddish brown vapour of chromyl chloride has the formula of CrO_2Cl_2 .

Statement II: CrO_2Cl_2 is paramagnetic in nature.

14. Statement I: ZnO (white) on heating becomes yellow in colour.

Statement II: The formation of f-centres is observed in hot ZnO which is also called metal excess defect.

15. Statement I: The chlorides of Be^{2+} and Mg^{2+} do not impart any colour to the flame test.

Statement II: The hydration energy of Be^{2+} is higher than that of Mg^{2+} .

16. Statement I: The NH_4OH in the Group IV reagents decreases the S^{2-} ion concentration.

Statement II: NH_4OH is an auxiliary reagent and not a precipitating reagent.

17. Statement I: The salt of NH_4^+ on reaction with any alkali produces NH_3 .

Statement II: OH^- is a very strong base as compared to NH_3 .

18. Statement I: In the solution of $[Zn(OH)_4]^{2-}$, the gradual addition of dil. HCl initially produces white precipitate of $Zn(OH)_2$ and on further addition of dil. HCl the white precipitate gets dissolved.

Statement II: $Zn(OH)_2$ is amphoteric in nature.

19. Statement I: $CuSO_4$ on reaction with $NaCN$ (excess) produces soluble complex of $[Cu(CN)_4]^{2-}$.

Statement II: $NaCN$ solution is slightly alkaline in nature.

20. Statement I: Hg^{2+} ion reacts with KI solution to produce yellow coloured HgI_2 precipitate.

Statement II: HgI_2 (red) and HgI_2 (yellow) both on reaction with excess KI produce soluble complex of $[HgI_4]^{2-}$ solution.

21. Statement I: In the brown ring test of NO_2^- or NO_3^- , the FeSO_4 solution must be freshly prepared.

Statement II: On exposure to sunlight, Fe^{2+} is converted into Fe^{3+} which does not give the brown ring test.

22. Statement I: In the Gries–Ilosvay test of NO_2^- ion, AcOH ($\text{pH} = 3$ to 4) is enough to cause diazotization of sulphanilic acid.

Statement II: Sulphanilic acid exists in zwitter ion form.

23. Statement I: An orange solution of dichromate turns yellow on addition of more acid.

Statement II: On addition of more acid, dichromate undergoes further polymerization.

24. Statement I: In the Group V reagents, the function of NH_4Cl is to decrease the concentration of CO_3^{2-} ions.

Statement II: This decrease in the concentration of CO_3^{2-} is due to the common ion effect of NH_4^+ .

25. Statement I: $\text{B}(\text{OMe})_3$ is more volatile than $\text{B}(\text{OH})_3$, though its molecular weight is higher than that of $\text{B}(\text{OH})_3$.

Statement II: Massive hydrogen bonding is possible in $\text{B}(\text{OH})_3$.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. How many of the following reagents can be used to distinguish between SO_2 and CO_2 ?

$\text{Ca}(\text{OH})_2$, (starch + KIO_3), $(\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4)$, $(\text{KMnO}_4 + \text{H}_2\text{SO}_4)$, $\text{Ba}(\text{OH})_2$, H_2O_2 , FeCl_3 , $\text{Zn}[\text{Fe}(\text{CN})_5(\text{NO})]$

2. Among the following, find out the total number of incorrect statement(s).

- (I) BO_3^{3-} , PO_4^{3-} , F^- and SiO_4^{4-} anions are called interfering radicals.
- (II) HgCl_2 reacts with carbonate ion and gives basic mercury (II) carbonate which does not give test with bicarbonate.
- (III) SO_3^{2-} and HSO_3^- can be distinguished by addition of neutral H_2O_2 solution against litmus paper.
- (IV) Zinc and sulphuric acid oxidize sulphite to sulphate.
- (V) AgNO_3 oxidizes suspension of sulphite solution to sulphate.
- (VI) Bromine water oxidizes BaSO_3 to BaSO_4

3. Find the number of reagent(s) which form white ppt with CO_3^{2-} ion.

BaCl_2 , CuSO_4 , HgCl_2 , $\text{Pb}(\text{CH}_3\text{COO})_2$, CaCl_2

4. When NaOH is added to $\text{K}_2\text{Cr}_2\text{O}_7$ solution, it becomes yellow. The change in oxidation state of Cr in this phenomenon is _____.

5. Among the following, the number of cations that give precipitate with Na_2HPO_4 solution is _____.

Mg^{2+} , K^+ , Mn^{2+} , Zn^{2+} , Ag^+ , Fe^{3+}

6. The number of water of crystallization in green vitriol is _____.

7. Epsom salt is isomorphous with green vitriol. The oxidation state of cation in the epsom salt is _____.

8. Among the following, the number of sulphides which are not soluble in yellow ammonium sulphide is _____.

CuS , Bi_2S_3 , As_2S_3 , SnS_2 , CdS .

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with one or more statements in Column II.

1. Match the reaction with the type of change.

Column I	Column II
(A) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta}$	(P) Disproportionation reaction
(B) $\text{MnO}_4^{2-} + \text{H}_2\text{O} \xrightarrow{\text{excess}}$	(Q) Green colour is associated with reactant or product
(C) $\text{H}_2\text{S} + \text{SO}_2 \longrightarrow$	(R) Comproportionation reaction
(D) $2\text{Br}^- + \text{Cl}_2 \longrightarrow$	(S) At least one product has zero oxidation state of the respective element

2. Match the radical with the associated change during analysis.

Column I	Column II
(A) HCO_3^-	(P) White precipitate on treatment with AgNO_3
(B) $\text{S}_2\text{O}_3^{2-}$	(Q) Reduces $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_6)_2]^{2-}$ to red precipitate on heating
(C) SO_3^{2-}	(R) Light green colouration with FeCl_3 solution is observed finally
	(S) Produces violet precipitate with $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$

3. Match the change observed during analysis of the radical.

Column I	Column II
(A) Colourless gas is evolved on addition of dil. H_2SO_4	(P) $\text{S}_2\text{O}_3^{2-}$
(B) Black precipitate is obtained when $\text{Hg}(\text{NO}_3)_2$ is added in little amount.	(Q) S^{2-}
(C) The precipitate obtained on addition of AgNO_3 produces the colourless soluble complex of $[(\text{AgNH}_3)_2]^+$ with NH_3 solution	(R) Cl^-
	(S) CH_3CO_2^-

4. Match the change observed during the analysis of the cation.

Column I	Column II
(A) Forms precipitate with NaOH and NH_4OH which is insoluble in excess of both the reagents	(P) Fe^{2+}
(B) Coloured precipitate is formed with KI which is soluble in excess of the reagent.	(Q) Hg^{2+}
(C) Forms precipitate with KCN , which is soluble in excess of the reagent	(R) Pb^{2+}
(D) Forms black precipitate with H_2S which is soluble in hot and dil. HNO_3	(S) Ag^+

5. Match the change observed with the reaction.

Column I	Column II
(A) No change is observed.	(P) $\text{CuSO}_4 + \text{excess KI}$
(B) Brown precipitate/ appearance	(Q) $\text{Pb}_3\text{O}_4 + \text{conc. HNO}_3$
(C) Pale green colouration	(R) $\text{FeCl}_3 + \text{H}_2\text{S}$
(D) White turbidity/ precipitate	(S) $\text{ZnCl}_2 + \text{H}_2\text{S}$
	(T) $\text{MgCl}_2 + \text{Na}_2\text{SO}_4$

6. Match the radical with the change observed on qualitative analysis.

Column I	Column II
(A) SO_4^{2-}	(P) Canary yellow precipitate with ammonium molybdate.
(B) NO_3^-	(Q) Brown ring test with acetic acid.
(C) NO_2^-	(R) Yellow precipitate with $\text{Hg}(\text{NO}_3)_2$ solution.
(D) PO_4^{3-}	(S) Evolves NH_3 gas with $(\text{Zn} + \text{conc. NaOH})$.

7. Match the compound with the change observed on qualitative analysis.

Column I	Column II
(A) $(\text{NH}_4)_2\text{CO}_3$	(P) Forms brown ring on reaction with FeSO_4 and conc. H_2SO_4
(B) $\text{Ag}_2\text{C}_2\text{O}_4$	(Q) Leaves no residue on heating.
(C) $\text{Pb}(\text{NO}_3)_2$	(R) Colourless acidic gas is evolved on heating.
(D) NH_4NO_3	(T) Residue is obtained on heating.
(E) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	

8. Match the cations with their properties.

Column I	Column II
(A) Cu^{2+}	(P) The chloride acts as very strong reducing agent in the laboratory
(B) Mn^{2+}	(Q) The corresponding sulphide is black in colour
(C) Zn^{2+}	(R) Gives precipitate with NaOH which is soluble in excess of NaOH
(D) Sn^{2+}	(S) Does not give precipitate with Group I reagent in the group analysis

ANSWERS

Single Correct Choice Type Questions

- | | | | | | |
|--------|---------|---------|---------|---------|---------|
| 1. (A) | 8. (D) | 15. (D) | 22. (C) | 29. (B) | 36. (D) |
| 2. (C) | 9. (D) | 16. (B) | 23. (D) | 30. (A) | 37. (B) |
| 3. (C) | 10. (B) | 17. (C) | 24. (C) | 31. (A) | 38. (A) |
| 4. (C) | 11. (C) | 18. (A) | 25. (A) | 32. (D) | |
| 5. (C) | 12. (D) | 19. (A) | 26. (A) | 33. (C) | |
| 6. (B) | 13. (B) | 20. (D) | 27. (B) | 34. (B) | |
| 7. (C) | 14. (B) | 21. (C) | 28. (D) | 35. (D) | |

Multiple Correct Choice Type Questions

- | | | | |
|-----------------------|-------------------|------------------------|-------------------|
| 1. (A), (B), (D) | 6. (B), (D) | 11. (A), (B), (C), (D) | 16. (B), (D) |
| 2. (A), (B), (C), (D) | 7. (A), (B), (D) | 12. (B), (C), (D) | 17. (B), (D) |
| 3. (A), (C), (D) | 8. (B), (D) | 13. (B), (D) | 18. (A), (C) |
| 4. (A), (D) | 9. (A), (C) | 14. (B), (C) | 19. (B), (C), (D) |
| 5. (A), (C) | 10. (B), (C), (D) | 15. (B), (C) | 20. (A), (C) |

Comprehension Type Questions

- | | | | | | |
|--------|---------|---------|---------|---------|---------|
| 1. (C) | 7. (A) | 13. (A) | 19. (D) | 25. (D) | 31. (A) |
| 2. (C) | 8. (C) | 14. (B) | 20. (B) | 26. (B) | 32. (C) |
| 3. (B) | 9. (B) | 15. (D) | 21. (A) | 27. (C) | 33. (D) |
| 4. (C) | 10. (B) | 16. (B) | 22. (B) | 28. (D) | 34. (B) |
| 5. (B) | 11. (A) | 17. (C) | 23. (C) | 29. (B) | 35. (A) |
| 6. (D) | 12. (C) | 18. (D) | 24. (A) | 30. (B) | 36. (B) |

Assertion–Reasoning Type Questions

- | | | | |
|--------|---------|---------|---------|
| 1. (A) | 8. (B) | 15. (B) | 22. (A) |
| 2. (B) | 9. (B) | 16. (D) | 23. (D) |
| 3. (D) | 10. (C) | 17. (A) | 24. (C) |
| 4. (A) | 11. (D) | 18. (A) | 25. (A) |
| 5. (A) | 12. (A) | 19. (D) | |
| 6. (A) | 13. (C) | 20. (D) | |
| 7. (A) | 14. (A) | 21. (A) | |

Integer Answer Type Questions

- | | | | |
|------|------|------|------|
| 1. 5 | 3. 3 | 5. 5 | 7. 2 |
| 2. 2 | 4. 0 | 6. 7 | 8. 3 |

Matrix–Match Type Questions

- | | |
|------------------------|---------------------|
| 1. (A) → (Q), (S) | (C) → (R) |
| (B) → (P), (Q) | (D) → (R), (S) |
| (C) → (R), (S) | |
| (D) → (S) | |
| 2. (A) → (P), (Q) | 6. (A) → (R) |
| (B) → (P), (R), (S) | (B) → (S) |
| (C) → (P), (R) | (C) → (Q), (S) |
| | (D) → (P) |
| 3. (A) → (P), (Q), (S) | 7. (A) → (Q), (R) |
| (B) → (Q) | (B) → (R), (T) |
| (C) → (P), (R), (S) | (C) → (T) |
| | (D) → (P), (Q) |
| 4. (A) → (P), (Q) | (E) → (T) |
| (B) → (Q), (R) | |
| (C) → (P), (S) | |
| (D) → (R), (S) | |
| 5. (A) → (T) | 8. (A) → (Q), (S) |
| (B) → (P), (Q) | (B) → (S) |
| | (C) → (R), (S) |
| | (D) → (P), (R), (S) |

8

Hydrogen and the Hydrides

8.1 | ELECTRONIC STRUCTURE

Hydrogen has the simplest atomic structure of all the elements, and consists of a nucleus containing one proton with a charge +1 and one orbital electron. The electronic structure may be written as $1s^1$. Atoms of hydrogen may attain stability in three different ways:

1. By forming an electron pair (covalent) bond with another atom

Non-metals typically form this type of bond with hydrogen, for example H_2 , H_2O , $HCl_{(gas)}$ or CH_4 , and many metals do so too.

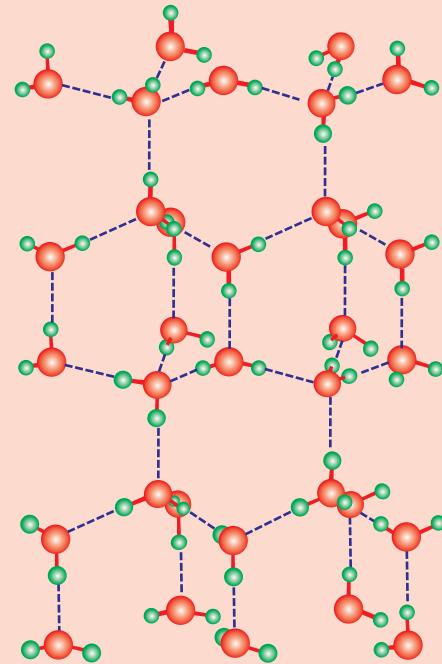
2. By losing an electron to form H^+

A proton is extremely small (radius approximately $1.5 \times 10^{-5} \text{ \AA}$, compared with 0.7414 \AA for hydrogen, and $1-2 \text{ \AA}$ for most atoms). Because H^+ is so small, it has a very high polarizing power, and therefore distorts the electron cloud on other atoms. Thus protons are always associated with other atoms or molecules. For example, in water or aqueous solutions of HCl and H_2SO_4 , protons exist as H_3O^+ , $H_9O_4^+$ or $H(H_2O)_n^+$ ions. Free protons do not exist under 'normal conditions', though they are found in low pressure gaseous beams, for example in a mass spectrometer.

3. By gaining an electron to form H^-

Crystalline solids such as LiH contain the H^- ion and are formed by highly electropositive metals (all of Group 1, and some of Group 2). However, H^- ions are uncommon.

Since hydrogen has an electronegativity of 2.1, it may use any of the three methods, but the most common way is forming covalent bonds.



Hydrogen bonding in water.

Contents

- 8.1** Electronic Structure
- 8.2** Position in the Periodic Table
- 8.3** Abundance of Hydrogen
- 8.4** Preparation of Hydrogen
- 8.5** Properties of Molecular Hydrogen
- 8.6** Isotopes of Hydrogen
- 8.7** Ortho and Para Hydrogen
- 8.8** Hydrides
- 8.9** The Hydrogen Ion
- 8.10** Hydrogen Bonding

8.2 | POSITION IN THE PERIODIC TABLE

Hydrogen is the first element in the periodic table, and is unique. There are only two elements in the first period, hydrogen and helium. Hydrogen is quite reactive, but helium is inert. There is no difficulty relating the structure and properties of helium to those of the other noble gases in Group 18, but the properties of hydrogen cannot be correlated with any of the main groups in the periodic table, and hydrogen is best considered on its own.

The structure of hydrogen atoms is in some ways like that of the alkali metals. The alkali metals (Group 1) also have just one electron in their outer shell, but they tend to lose this electron in reactions and form positive ions M^+ . Though H^+ are known, hydrogen has a much greater tendency to pair the electron and form a covalent bond.

The structure of hydrogen atoms is in some ways like that of the halogens (Group 17), since both are one electron short of a noble gas structure. In many reactions the halogens gain an electron and so form negative ions X^- . Hydrogen does not typically form a negative ion, although it does form ionic hydrides M^+H^- (e.g. LiH and CaH₂) with a few highly electropositive metals.

In some ways the structure of hydrogen resembles that of the Group 14 elements, since both have a half filled shell of electrons. There are a number of similarities between hydrides and organometallic compounds since the groups CH₃— and H— both have one remaining valency. Thus the hydride is often considered as part of a series of organometallic compounds, for example LiH, LiMe, LiEt; NH₃, NMe₃, NET₃; or SiH₄, CH₃SiH₃, (CH₃)₂SiCl₂, (CH₃)₃SiCl, (CH₃)₄Si. However, hydrogen is best treated as a group on its own.

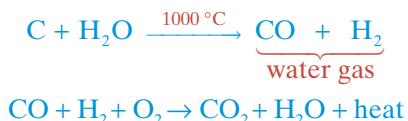
8.3 | ABUNDANCE OF HYDROGEN

Hydrogen is the most abundant element in the universe. Some estimates are that 92% of the universe is made up of hydrogen, and 7% helium, leaving only 1% for all of the other elements. However, the abundance of H₂ in the earth's atmosphere is very small. This is because the earth's gravitational field is too small to hold so light an element, though some H₂ is found in volcano gases. In contrast, hydrogen is the tenth most abundant element in the earth's crust (1520 ppm or 0.152% by weight). It also occurs in vast quantities as water in the oceans. Compounds containing hydrogen are very abundant, particularly water, living matter (carbohydrates and proteins), organic compounds, fossil fuels (coal, petroleum, and natural gas), ammonia and acids. In fact hydrogen is present in more compounds than any other element.

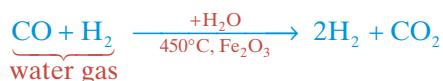
8.4 | PREPARATION OF HYDROGEN

Hydrogen is manufactured on a large scale by a variety of methods:

1. Hydrogen is made cheaply, and in large amounts, by passing steam over red hot coke. The product is water gas, which is a mixture of CO and H₂. This is an important industrial fuel since it is easy to make and it burns, evolving a lot of heat.



It is difficult to obtain pure H₂ from water gas, since CO is difficult to remove. The CO may be liquefied at a low temperature under pressure, thus separating it from H₂. Alternatively the gas mixture can be mixed with steam, cooled to 400°C and passed over iron oxide in a shift converter, giving H₂ and CO₂. The CO₂ so formed is easily removed either by dissolving in water under pressure, or reacting with K₂CO₃ solution, giving KHCO₃, and thus giving H₂ gas.

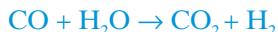


2. Hydrogen is also made in large amounts by the steam reformer process. The hydrogen produced in this way is used in the Haber process to make NH₃, and for hardening oils. Light hydrocarbons such as

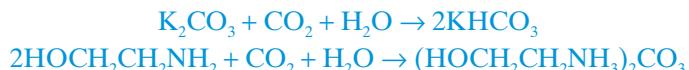
methane are mixed with steam and passed over a nickel catalyst at 800–900°C. These hydrocarbons are present in natural gas, and are also produced at oil refineries when ‘cracking’ hydrocarbons.



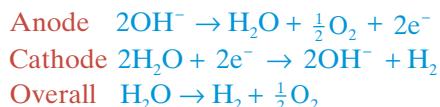
The gas emerging from the reformer contains CO, CO₂, H₂ and excess steam. The gas mixture is mixed with more steam, cooled to 400°C and passed into a shift converter. This contains an iron/copper catalyst and CO is converted into CO₂.



Finally the CO₂ is absorbed in a solution of K₂CO₃ or ethanolamine HOCH₂CH₂NH₂. The K₂CO₃ or ethanolamines are regenerated by heating.



3. In oil refineries, natural hydrocarbon mixtures of high molecular weight such as naphtha and fuel oil are ‘cracked’ to produce lower molecular weight hydrocarbons which can be used as petrol. Hydrogen is a valuable by-product.
4. Very pure hydrogen (99.9% pure) is made by electrolysis of water or solutions of NaOH or KOH. This is the most expensive method. Water does not conduct electricity very well, so it is usual to electrolyse aqueous solutions of NaOH or KOH in a cell with nickel anodes and iron cathodes. The gases produced in the anode and cathode compartments must be kept separate.



5. A large amount of pure hydrogen is also formed as a by-product from the chlor-alkali industry, in which aqueous NaCl is electrolysed to produce NaOH, Cl₂ and H₂.
6. The usual laboratory preparation is the reaction of dilute acids with metals, or of an alkali with aluminium.



7. Hydrogen can be prepared by the reaction of salt-like hydrides with water.



8.5 | PROPERTIES OF MOLECULAR HYDROGEN

Physical properties

Hydrogen is the lightest gas known, and because of its low density, it is used instead of helium to fill balloons for meteorology. It is colourless, odourless and almost insoluble in water. Hydrogen forms diatomic molecules H₂, and the two atoms are joined by a very strong covalent bond (bond energy 435.9 kJ mol⁻¹).

Chemical properties

Hydrogen is not very reactive under normal conditions. The lack of reactivity is due to kinetics rather than thermodynamics, and relates to the strength of the H–H bond. An essential step in H₂ reacting with another element is the breaking of the H–H bond to produce atoms of hydrogen. This requires 435.9 kJ mol⁻¹; hence there is high activation energy to such reactions. Consequently many reactions are slow, or require high temperatures, or catalysts (often transition metals). Many important reactions of hydrogen involve heterogeneous catalysis, where the catalyst first reacts with H₂ and either breaks or weakens the H–H bond, and thus lowers the activation energy. Examples include:

1. The Haber process for the manufacture of NH₃ from N₂ and H₂ using a catalyst of activated Fe at 380–450°C and 200 atmospheres pressure.

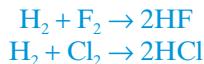
2. The hydrogenation of a variety of unsaturated organic compounds, (including the hardening of oils), using finely divided Ni, Pd or Pt as catalysts.
3. The production of methanol by reducing CO with H₂ over a Cu/Zn catalyst at 300 °C.

Thus hydrogen will react directly with most elements *under the appropriate conditions*.

Hydrogen burns in air or dioxygen, forming water, and liberates a large amount of energy. This is used in the oxy-hydrogen flame for welding and cutting metals. Temperatures of almost 3000 °C can be attained. Care should be taken with these gases since mixtures of H₂ and O₂ close to a 2:1 ratio are often explosive.



Hydrogen reacts with the halogens. The reaction with fluorine is violent, even at low temperatures. The reaction with chlorine is slow in the dark, but the reaction is catalysed by light (photocatalysis), and becomes faster in daylight, and explosive in sunlight. Direct combination of the elements is used to produce HCl.



A number of metals react with H₂, forming hydrides. The reactions are not violent, and usually require a high temperature. These are described in a later section.

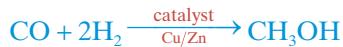
Large quantities of H₂ are used in the industrial production of ammonia by the Haber process. The reaction is reversible, and the formation of NH₃ is favoured by high pressure, the presence of a catalyst (Fe), and a low temperature. In practice a high temperature of 380–450 °C and a pressure of 200 atmospheres are used to get a reasonable conversion in a reasonable time.



Large amounts of H₂ are used for hydrogenation reactions, in which hydrogen is added to a double bond in an organic compound. An important example is the hardening of fats and oils. Unsaturated fatty acids are hydrogenated with H₂ and a palladium catalyst, forming saturated fatty acids which have higher melting points. By removing double bonds in the carbon chain in this way, edible oils which are liquid at room temperature may be converted into fats which are solid at room temperature. The reason for doing this is that solid fats are more useful than oils, for example in the manufacture of margarine.



Hydrogen is also used to reduce nitrobenzene to aniline (dyestuffs industry), and in the catalytic reduction of benzene (the first step in the production of nylon-66). It also reacts with CO to form methyl alcohol.



The hydrogen molecule is very stable, and has little tendency to dissociate at normal temperatures, since the dissociation reaction is highly endothermic.



However, at high temperatures, in an electric arc, or under ultraviolet light, H₂ does dissociate. The atomic hydrogen produced exists for less than half a second, after which it recombines to give molecular hydrogen and a large amount of heat. This reaction has been used in welding metals. Atomic hydrogen is a strong reducing agent, and is commonly prepared in solution by means of a zinc–copper couple or a mercury–aluminium couple.

Use of hydrogen as fuel

There has been much talk of *the hydrogen economy*. The idea is that hydrogen could replace coal and oil as the major source of energy. Burning hydrogen in air or dioxygen forms water and liberates a great deal of energy. In contrast to burning coal or oil in power stations, or petrol or diesel fuel in motor engines, burning hydrogen produces no pollutants like SO₂ and oxides of nitrogen that are responsible for acid rain, nor CO₂ that is responsible for the greenhouse effect, nor carcinogenic hydrocarbons, nor lead compounds. Hydrogen can be produced readily by electrolysis, and chemical methods. Hydrogen can be stored and transported as gas in cylinders, as liquid in very large cryogenic vacuum flasks, or ‘dissolved’ in various metals. (For example, the alloy LaNi₅ can absorb seven moles of hydrogen per mole of alloy at 2.5 atmospheres pressure and room temperature.) Liquid hydrogen is used as a fuel in space rockets for the Saturn

series and the space shuttle in the US space programme. Car engines have been modified to run on hydrogen. Note that the use of hydrogen involves the risk of an explosion, but so does the use of petrol.

8.6 | ISOTOPES OF HYDROGEN

If atoms of the same element have different mass numbers they are called isotopes. The difference in mass number arises because the nucleus contains a different number of neutrons. Naturally occurring hydrogen contains three isotopes: protium ${}^1\text{H}$ or H, deuterium ${}^2\text{H}$ or D, and tritium ${}^3\text{H}$ or T. Each of the three isotopes contains one proton and 0, 1 or 2 neutrons respectively in the nucleus. Protium is by far the most abundant.

Naturally occurring hydrogen contains 99.986% of the ${}^1\text{H}$ isotope, 0.014% of ${}^2\text{D}$ and $7 \times 10^{-16}\%$ of ${}^3\text{T}$, so the properties of hydrogen are essentially those of the lightest isotope.

These isotopes have the same electronic configuration and have essentially the same chemical properties. The only differences in chemical properties are the rates of reactions, and equilibrium constants. For example:

1. H_2 is more rapidly adsorbed on the surfaces than D_2 for chemisorption, while for physisorption D_2 is greater than H_2 .
2. H_2 reacts over 13 times faster with Cl_2 than D_2 , because H_2 has a lower energy of activation.

Differences in properties which arise from differences in mass are called *isotope effects*. Because hydrogen is so light, the percentage difference in mass between protium ${}^1\text{H}$, deuterium ${}^2\text{H}$ and tritium ${}^3\text{H}$ is greater than between the isotopes of any other element. Thus the isotopes of hydrogen show much greater differences in physical properties than are found between the isotopes of other elements. Some physical constants for H_2 , D_2 and T_2 are given in Table 8.1.

Table 8.1 Physical constants for hydrogen, deuterium and tritium

Physical constant	H_2	D_2	T_2
Mass of atom (amu)	1.0078	2.0141	3.0160
Freezing point (°C)	-259.0	-254.3	-252.4
Boiling point (°C)	-252.6	-249.3	-248.0
Bond length (Å)	0.7414	0.7414	(0.7414)
Heat of dissociation [†] (kJ mol ⁻¹)	435.9	443.4	446.9
Latent heat of fusion (kJ mol ⁻¹)	0.117	0.197	0.250
Latent heat of vaporization (kJ mol ⁻¹)	0.904	1.226	1.393
Vapour pressure [*] (mm Hg)	54	5.8	-

^{*}Measured at -259.1 °C.

[†]Measured at 25 °C.

Protium water H_2O dissociates to about three times the extent that heavy water D_2O does. The equilibrium constant for the dissociation of H_2O is 1.0×10^{-14} whilst for D_2O it is 3.0×10^{-15} .



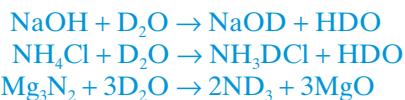
Protium bonds are broken more readily than deuterium bonds (up to 18 times more readily in some cases). Thus when water is electrolysed, H_2 is liberated much faster than D_2 , and the remaining water thus becomes enriched in heavy water D_2O . If the process is continued until only a small volume remains, then almost pure D_2O is obtained. About 29 000 litres of water must be electrolysed to give 1 litre of D_2O that is 99% pure. This is the normal way of separating deuterium. Heavy water D_2O undergoes all of the reactions of ordinary water, and is useful in the preparation of other deuterium compounds. Because D_2O has a lower dielectric constant, ionic compounds are less soluble in it than in water. Some physical properties of H_2O and D_2O are compared in Table 8.2.

Table 8.2 Physical constants for water and heavy water

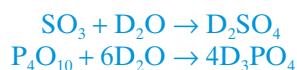
Physical constant	H ₂ O	D ₂ O
Freezing point (°C)	0	3.82
Boiling point (°C)	100	101.42
Density at 20 °C (g cm ⁻³)	0.917	1.017
Temperature of maximum density (°C)	4	11.6
Ionic product <i>K</i> _w at 25 °C	1.0 × 10 ⁻¹⁴	3.0 × 10 ⁻¹⁵
Dielectric constant at 20 °C	82	80.5
Solubility g NaCl/100 g water at 25 °C	35.9	30.5
Solubility g BaCl ₂ /100 g water at 25 °C	35.7	28.9

Deuterium compounds are commonly prepared by 'exchange' reactions where under suitable conditions deuterium is exchanged for hydrogen in compounds. Thus D₂ reacts with H₂ at high temperatures, forming HD, and it also exchanges with NH₃ and CH₄ to give NH₂D, NHD₂, ND₃ and CH₃D to CD₄. It is usually easier to prepare deuterated compounds using D₂O rather than D₂. The D₂O may be used directly in the preparation instead of H₂O, or exchange reactions may be carried out using D₂O.

Exchange reactions



Direct reactions



8.7 | ORTHO AND PARA HYDROGEN

The hydrogen molecule H₂ exists in two different forms known as *ortho* and *para* hydrogens. The nucleus of an atom has nuclear spin, in a similar way to electrons having a spin. In the H₂ molecule, the two nuclei may be spinning in either the same direction, or in opposite directions. This gives rise to spin isomerism that is two different forms of H₂ may exist. These are called *ortho* and *para* hydrogen. Spin isomerism is also found in other symmetrical molecules whose nuclei have spin momenta, e.g. D₂, N₂, F₂, Cl₂. There are considerable differences between the physical properties (e.g. boiling points, specific heats and thermal conductivities) of the *ortho* and *para* forms, because of differences in their internal energy. There are also differences in the band spectra of the *ortho* and *para* forms of H₂.

The *para* form has the lower energy, and at absolute zero the gas contains 100% of the *para* form. As the temperature is raised, some of the *para* form changes into the *ortho* form. At high temperatures the gas contains about 75% *ortho* hydrogen (Figure 8.1).

Para hydrogen is usually prepared by passing a mixture of the two forms of hydrogen through a tube packed with charcoal cooled to liquid air temperature. *Para* hydrogen prepared in this way can be kept for weeks at room temperature in a glass vessel, because the *ortho*-*para* conversion is slow in the absence of catalysts. Suitable catalysts include activated charcoal, atomic hydrogen, metals such as Fe, Ni, Pt and W and paramagnetic substances or ions (which contain unpaired electrons) such as O₂, NO, NO₂, Co²⁺ and Cr₂O₃.

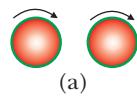


Figure 8.1 Ortho and para hydrogens:
(a) *ortho*, parallel spins;
(b) *para*, opposite spins.

8.8 | HYDRIDES

Binary compounds of the elements with hydrogen are called hydrides. The type of hydride which an element forms depends on its electronegativity, and hence on the type of bond formed. Whilst there is not a sharp division between ionic, covalent and metallic bonding, it is convenient to consider hydrides in three classes (Figure 8.2):

Figure 8.2 Types of hydrides and the periodic table.

1. ionic or salt-like hydrides.
 2. covalent or molecular hydrides.
 3. metallic or interstitial hydrides.

Ionic or salt-like hydrides

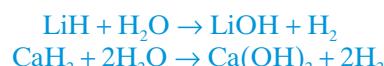
At high temperatures the metals of Group 1 (alkali metals) and the heavier Group 2 metals (alkaline earth metals) Ca, Sr and Ba form ionic hydrides such as NaH and CaH_2 . These compounds are solids with high melting points, and are classified as ionic (salt-like) hydrides. The evidence that they are ionic is:

1. Molten LiH (m.p. 691 °C) conducts electricity, and H₂ is liberated at the anode, thus confirming the presence of the hydride ion H⁻.
 2. The other ionic hydrides decompose before melting, but they may be dissolved in melts of alkali halides (e.g. CaH₂ dissolves in a eutectic mixture of LiCl/KCl), and when the melt is electrolysed then H₂ is evolved at the anode.
 3. The crystal structures of these hydrides are known, and they show no evidence of directional bonding.

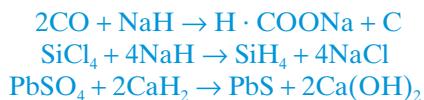
Lithium is more polarizing and hence more likely to form covalent compounds than the other metals. Thus if LiH is largely ionic, the others must be ionic, and thus contain the hydride ion H^- .

The density of these hydrides is greater than that of the metal from which they were formed. This is explained by H^- ions occupying holes in the lattice of the metal, without distorting the metal lattice. Ionic hydrides have high heats of formation, and are always stoichiometric.

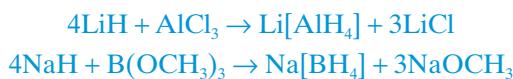
This type of hydride is only formed by elements with an electronegativity value appreciably lower than the value of 2.1 for hydrogen, thus allowing the hydrogen to attract an electron from the metal, forming M^+ and H^- . Group 1 hydrides are more reactive than the corresponding Group 2 hydrides, and reactivity increases down the group. Except for LiH, ionic hydrides decompose into their constituent elements on strong heating (400–500 °C). The hydride ion H^- is not very common, and it is unstable in water. Thus ionic hydrides all react with water and liberate hydrogen.



They are powerful reducing agents, especially at high temperatures, though their reactivity towards water limits their usefulness.



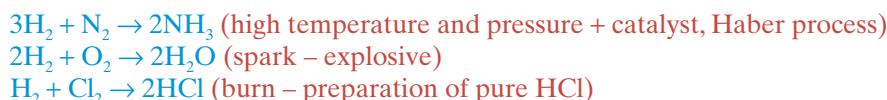
NaH has a number of uses as a reducing agent in synthetic chemistry. It is used to produce other important hydrides, particularly lithium aluminium hydride $\text{Li}[\text{AlH}_4]$ and sodium borohydride $\text{Na}[\text{BH}_4]$, which have important uses as reducing agents in both organic and inorganic syntheses.



Covalent hydrides

Hydrides of the *p*-block elements are covalent. This would be expected since there is only a small difference in electronegativity between these atoms and hydrogen. The compounds usually consist of discrete covalent molecules, with only weak van der Waals forces holding the molecules together, and so they are usually volatile, and have low melting and boiling points. They do not conduct electricity. The formula of these hydrides is XH_n or $\text{XH}_{(8-n)}$ where n is the group number (according to the A/B convention of the periodic table) to which X belongs. These hydrides are produced by a variety of synthetic methods:

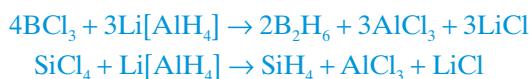
1. A few, as shown in Figure 8.3, may be made by direct action.



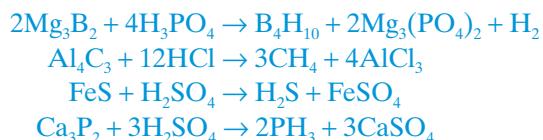
Group	III A	IV A	V A	VI A	VII A
B	C	N	O	F	
Al	Si	P	S	Cl	
Ga	Ge	As	Se	Br	
In	Sn	Sb	Te	I	
	Pb	Bi	Po		

Figure 8.3 Elements which form covalent hydrides by direct action.

2. Reaction of a halide with $\text{Li}[\text{AlH}_4]$ in a dry solvent such as ether.



3. Treating the appropriate binary compound with acid.



4. Reaction of an oxoacid with $\text{Na}[\text{BH}_4]$ in aqueous solution.



5. Converting one hydride into another by pyrolysis (heating).



6. A silent electric discharge or microwave discharge may produce long chains from simple hydrides.



The Group 13 hydrides are unusual in that they are electron deficient and polymeric, although they do not contain direct bonds between the Group 13 elements. The simplest boron hydride is called diborane B_2H_6 though more complicated structures such as B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} and $\text{B}_{10}\text{H}_{14}$ are known. Aluminium

hydride is polymeric (AlH_3)_n. In these structures, hydrogen appears to be bonded to two or more atoms, and this is explained in terms of multi-centre bonding.

In addition to the simple hydrides, the rest of the lighter elements except the halogens form polynuclear hydrides. The tendency to do this is strongest with the elements C, N and O, and two or more of the non-metal atoms are directly bonded to each other. The tendency is greatest with C which catenates (forms chains) of several hundreds of atoms. These are grouped into three homologous series of aliphatic hydrocarbons, and aromatic hydrocarbons based on benzene.

$\text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{C}_4\text{H}_{10}, \dots \text{C}_n\text{H}_{2n+2}$	(alkanes)
$\text{C}_2\text{H}_4, \text{C}_3\text{H}_6, \text{C}_4\text{H}_8, \dots \text{C}_n\text{H}_{2n}$	(alkenes)
$\text{C}_2\text{H}_2, \text{C}_3\text{H}_4, \text{C}_4\text{H}_6, \dots \text{C}_n\text{H}_{2n-2}$	(alkynes)
C_6H_6	(aromatic)

The alkanes are saturated, but alkenes have double bonds, and alkynes have triple bonds. Si and Ge only form saturated compounds, and the maximum chain length is $\text{Si}_{10}\text{H}_{22}$. The longest hydride chains formed by other elements are Sn_2H_6 , N_2H_4 and HN_3 , P_3H_5 , As_3H_5 , H_2O_2 and H_2O_3 , and H_2S_2 , H_2S_3 , H_2S_4 , H_2S_5 and H_2S_6 .

The melting point and boiling point of water stand out in Table 8.3 as being much higher than the others, but on closer examination the values for NH_3 and HF also seem higher than would be expected in their respective groups. This is due to hydrogen bonding, which is discussed later in this chapter.

Table 8.3 Melting and boiling points of some covalent hydrides

Compound	m.p. (°C)	b.p. (°C)
B_2H_6	-165	-90
CH_4	-183	-162
SiH_4	-185	-111
GeH_4	-166	-88
SnH_4	-150	-52
NH_3	-78	-33
PH_3	-134	-88
AsH_3	-117	-62
SbH_3	-88	-18
H_2O	0	+100
H_2S	-86	-60
HF	-83	+20
HCl	-115	-84
HBr	-89	-67
HI	-51	-35

Metallic (or interstitial) hydrides

Many of the elements in the *d*-block, and the lanthanide and actinide elements in the *f*-block, react with H_2 and form metallic hydrides. However, the elements in the middle of the *d*-block do not form hydrides. The absence of hydrides in this part of the periodic table is sometimes called: *the hydrogen gap*. (See Figure 8.2.)

Metallic hydrides are usually prepared by heating the metal with hydrogen under high pressure. *If heated to higher temperatures the hydrides decompose, and this may be used as a convenient method of making very pure hydrogen.* These hydrides generally have properties similar to those of the parent metals: they are hard, have a metallic lustre, conduct electricity, and have magnetic properties. *The hydrides are less dense than the parent metal, because the crystal lattice has expanded through the inclusion of hydrogen. This distortion of the crystal lattice may make the hydride brittle.* Thus when the hydride is formed, a solid piece of metal turns into finely powdered hydride. If the finely powdered hydrides are heated they decompose, giving hydrogen and very finely divided metal. These finely divided metals may be used as catalysts. They are also used in metallurgy in powder fabrication, and zirconium hydride has been used as a moderator in nuclear reactors.

In many cases the compounds are nonstoichiometric, for example LaH_n , TiH_n and PdH_n , where the chemical composition is variable. Typical formulae are $\text{LaH}_{2.87}$, $\text{YbH}_{2.55}$, $\text{TiH}_{1.8}$, $\text{ZrH}_{1.9}$, $\text{VH}_{1.6}$, $\text{NbH}_{0.7}$ and $\text{PdH}_{0.7}$. Such compounds were originally called *interstitial hydrides*, and it was thought that a varying number of interstitial positions in the metal lattice could be filled by hydrogen.

The nonstoichiometric compounds may be regarded as solid solutions. Metals which can 'dissolve' varying amounts of hydrogen in this way can act as catalysts for hydrogenation reactions. The catalysts are thought to be effective through providing H atoms rather than H_2 molecules. It is not certain whether the hydrogen is present in the interstitial sites as atoms of hydrogen, or alternatively as H^+ ions with delocalized electrons, but they have strongly reducing properties.

Even small amounts of hydrogen dissolved in a metal adversely affect its strength and make it brittle. Titanium is extracted by reducing TiCl_4 with Mg or Na in an inert atmosphere. If an atmosphere of H_2 is used, the Ti dissolves H_2 , and is brittle. Titanium is used to make supersonic aircraft, and since strength is important, it is produced in an atmosphere of argon.

Intermediate hydrides

A few hydrides do not fit easily into the above classification. Thus $(\text{BeH}_2)_n$ is polymeric, and is thought to be a chain polymer with hydrogen bridges. MgH_2 has properties in between those of ionic and covalent hydrides.

CuH , ZnH_2 , CdH_2 and HgH_2 have properties intermediate between metallic and covalent hydrides. They are probably electron deficient like $(\text{AlH}_3)_n$.

8.9 | THE HYDROGEN ION

The energy required to remove the electron from a hydrogen atom (i.e. the ionization energy of hydrogen) is 1311 kJ mol^{-1} . This is a very large amount of energy, and consequently the bonds formed by hydrogen in the gas phase are typically covalent. Hydrogen fluoride is the compound most likely to contain ionic hydrogen (i.e. H^+), since it has the greatest difference in electronegativity, but even here the bond is only 45% ionic.

Thus compounds containing H^+ will only be formed if the ionization energy can be provided by some other process. Thus if the compound is dissolved, for example in water, then the hydration energy may offset the very high ionization energy. In water H^+ are solvated, forming H_3O^+ , and the energy evolved is 1091 kJ mol^{-1} . The remainder of the 1311 kJ mol^{-1} ionization energy comes from the electron affinity (the energy evolved in forming the negative ion), and also the solvation energy of the negative ion.

Compounds which form solvated hydrogen ions in a suitable solvent are called acids. Even though the ions present are H_3O^+ (or even H_9O_4^+), it is customary to write the ion as H^+ , indicating a hydrated proton.

8.10 | HYDROGEN BONDING

In some compounds a hydrogen atom is attracted by rather strong forces to two atoms, for example in $[\text{F}—\text{H}—\text{F}]^-$. (Sometimes hydrogen is attracted to more than two atoms.) It was at first thought that hydrogen formed two covalent bonds, but it is now recognized that, since hydrogen has the electronic structure $1s^1$, it can only form one covalent bond. This type of bond is formed by hydrogen only with the most electronegative atoms (importantly, F, O, N and Cl) and called *hydrogen bond*. The hydrogen bond is most simply regarded as a weak electrostatic attraction between a lone pair of electrons on one atom and a covalently bonded hydrogen atom that carries a fractional charge $\delta+$ and is a special kind of dipole-dipole interaction.

Hydrogen bonds are very weak, and are typically about 10 kJ mol^{-1} , though hydrogen bonds may have bond energy from 4 to 45 kJ mol^{-1} . This is comparable with a C—C covalent bond of 347 kJ mol^{-1} . Despite their low bond energy, hydrogen bonds are of great significance both in biochemical systems and in normal chemistry. Hydrogen bonds are responsible for water being liquid at room temperature.

Hydrogen bonding was first used to explain the weakness of trimethylammonium hydroxide as a base compared with tetramethylammonium hydroxide. In the trimethyl compound, the OH group is hydrogen bonded to the Me_3NH group (shown by a dotted line in Figure 8.4), and this makes it more difficult for the OH group to ionize, and hence it is a weak base. In the tetramethyl compound, hydrogen bonding cannot occur, so the OH group ionizes and the tetramethyl compound is thus a much stronger base.

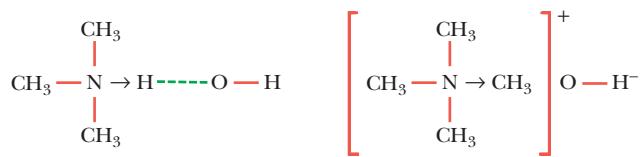


Figure 8.4 Structures of trimethyl and tetramethyl ammonium hydroxide.

Strong evidence for hydrogen bonding comes from structural studies. Examples include ice, (determined both by X-ray and neutron diffraction), the dimeric structure of formic acid (determined in the gas phase by electron diffraction), X-ray structures of the solids like sodium hydrogen carbonate and boric acid (Figure 8.5), and many others.

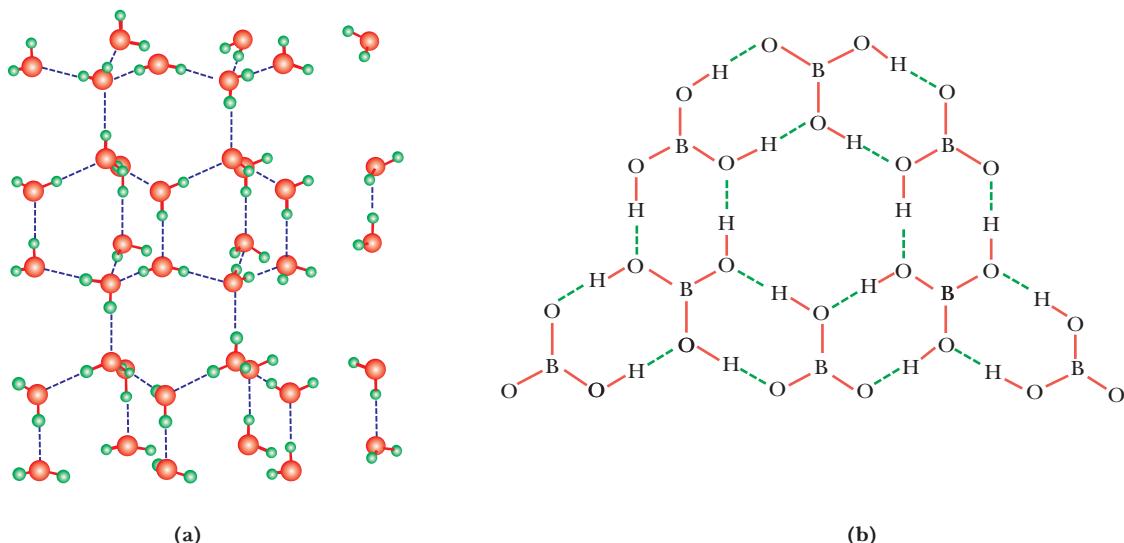


Figure 8.5 Hydrogen bonded structures. (a) Ice. (From Pauling, L., *The Nature of the Chemical Bond*, 3rd ed., pp. 449–504, Cornell University Press, Ithaca. 1960.) (b) A layer of crystalline H_3BO_3 .

There are two types of hydrogen bonding, *intermolecular* and *intramolecular* and these are discussed as follows along with their impact on properties of compounds.

Intermolecular hydrogen bonding

Intermolecular hydrogen bonding is an interaction between a hydrogen atom of one molecule and an electronegative atom of a second molecule which may be of the same compound (Figure 8.6) or different compounds. All these arise due to dipole-dipole interaction.

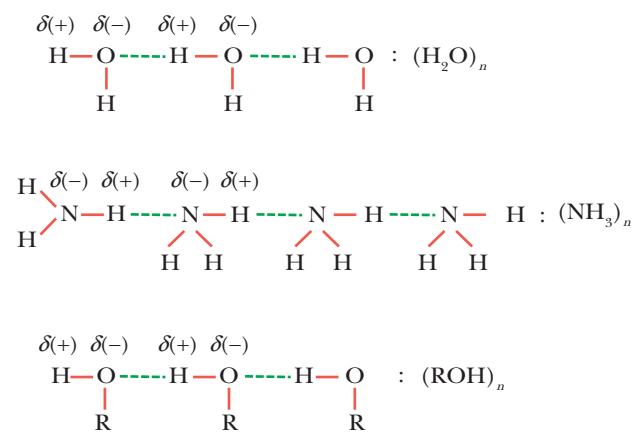


Figure 8.6 Examples of intermolecular hydrogen bonding between same molecules.

Dimerization of carboxylic acid is also an example of intermolecular hydrogen bonding (Figure 8.7).

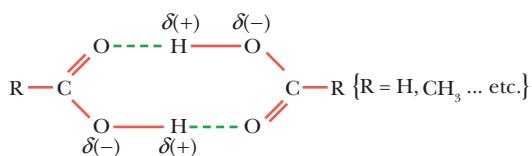


Figure 8.7 Carboxylic acid dimer.

Effect of intermolecular hydrogen bonding on physical properties

Intermolecular hydrogen bonding has a striking effect on the physical properties such as melting points, boiling points, and the enthalpies of vapourization and sublimation. In general, the melting and boiling points for a related series of compounds increase as the atoms get larger, owing to the increase in dispersive force or molecular weight. Some examples are:

1. Hydrides: Consider the boiling points, melting points and enthalpies of vapourization of hydrides given in Figures 8.8 (a), (b) and (c), respectively.

a. By extrapolating the boiling points of H_2Te , H_2Se and H_2S one would predict that the boiling point of H_2O should be about -100°C , while it is actually $+100^\circ\text{C}$. Thus, water boils at about 200°C higher than it would in the absence of hydrogen bonding.

The increasing order of boiling point is $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{O}$

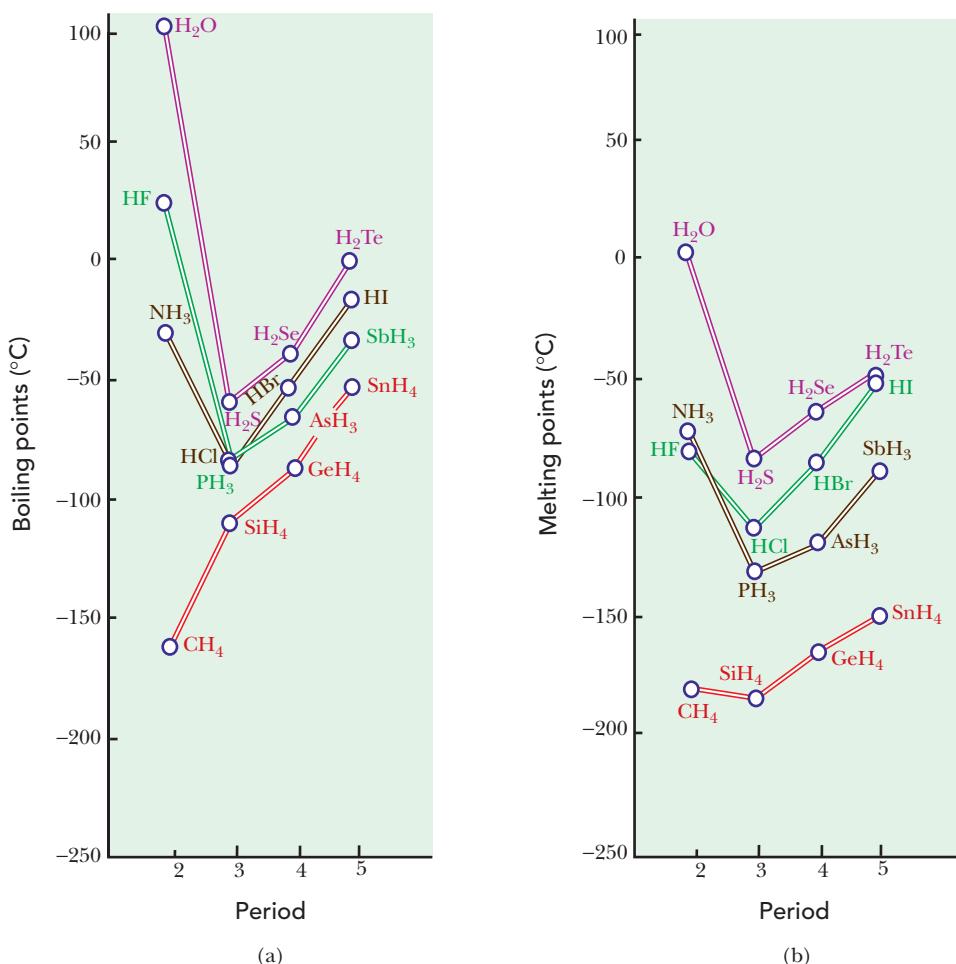


Figure 8.8 (a) Boiling points of hydrides. (b) Melting points of hydrides. (c) Enthalpies of vaporization of hydrides. (Adapted from Lagowski, J.J., *Modern Inorganic Chemistry*, Marcel Dekker, New York, p. 174.)

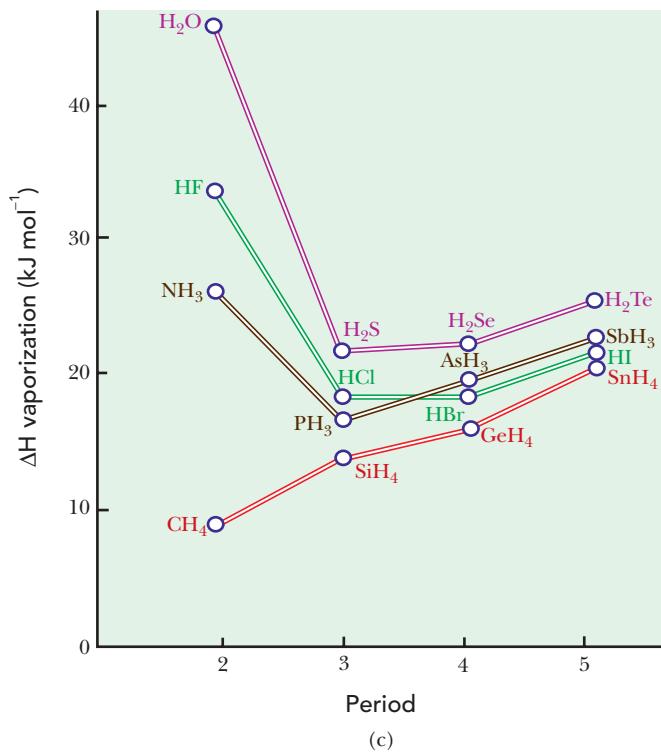


Figure 8.8 (Continued.)

- b.** In much the same way the boiling point of NH_3 is much higher than would be expected by comparison with PH_3 , AsH_3 and SbH_3 , and similarly HF boils much higher than HCl , HBr and HI . The reason for the higher than expected boiling points is hydrogen bonding. Note that the boiling points of the Group 14 hydrides CH_4 , SiH_4 , GeH_4 and SnH_4 change smoothly, as they do not involve hydrogen bonding. The hydrogen bonds in HF link the F atom of one molecule with the H atom of another molecule, thus forming a zig-zag chain $(\text{HF})_n$ in both the liquid and also in the solid (Figure 8.9).

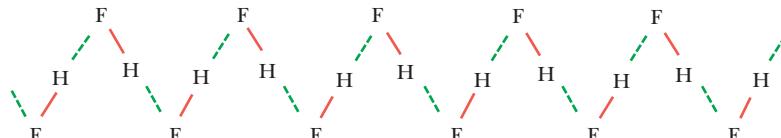
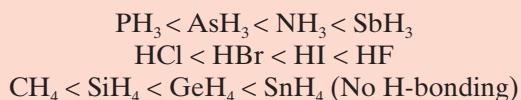


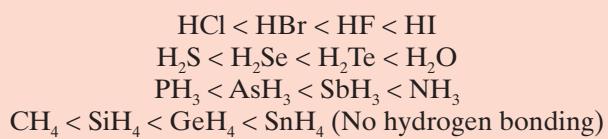
Figure 8.9 Hydrogen bonded chain in solid HF.

The increasing order of boiling point is

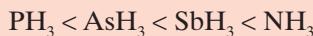
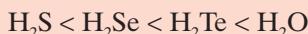
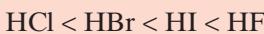


- c.** A similar pattern can be seen in the melting points and the enthalpies of vapourization of the hydrides, indicating hydrogen bonding in NH_3 , H_2O and HF, but not in CH_4 (Figure 8.8c).

The increasing order of melting point is



The increasing order of heat of vapourization is



2. Replacement of hydrogen with alkyl groups in the compounds that undergo hydrogen bonding reduces their boiling point. For example,
 - H_2O : 100°C ; CH_3OH : 63°C ; CH_3OCH_3 : -5°C
 - Me_2NH : 7°C ; Me_3N : 4°C
 - H_2SO_4 : 340°C (decomposition); Me_2SO_4 : 188°C
 - H_3PO_4 : 212°C (decomposition); Me_3PO_4 : 193°C
 - H_3BO_3 : 187°C (decomposition); Me_3BO_3 : 65°C
 - HF : 20°C ; CH_3F : -78°C
 - HN_3 : 37°C ; CH_3N_3 : 20°C
3. NH_2CONH_2 (urea) is a solid while CH_3COCH_3 (acetone) is liquid at room temperature due to more effective intermolecular hydrogen bonding in the former.
4. According to the molecular weight comparison with BF_3 (gas), B(OH)_3 is expected to be gas but it is solid due to massive intermolecular hydrogen bonding. In B(OH)_3 , on substitution with alkyl groups, though molecular weight increases yet hydrogen bonding interaction dominates over van der Waal's forces of attraction.
5. The change in molar entropy of vapourization is more for liquids containing hydrogen bonding as compared to the liquids that lacks hydrogen bonding. This is because hydrogen-bonded liquids undergo greater disorderliness on vapourization (Table 8.4).

Table 8.4 Entropy of Vapourization of some compounds

Compounds	H_2O	NH_3	CH_3OH	C_6H_6	$n\text{-C}_6\text{H}_{14}$	HBr	HF^*
ΔS_{vap} ($\text{JK}^{-1}\text{mol}^{-1}$)	109	97	105	87	85	88	26

Hydrogen bonded liquids Liquids having no hydrogen bonding

*HF has very strong intermolecular hydrogen bonding but on vapourization, all hydrogen bonds do not break and exist in the form of $(\text{HF})_2$ to $(\text{HF})_6$. Hence the number of molecules produced in vapour is sufficiently less as compared to H_2O or NH_3 and therefore it has exceptionally low value of ΔS_{vap} or randomness.

Intramolecular hydrogen bonding

In this case, the hydrogen bond is formed between hydrogen and an electronegative atom (F,O,N) within the same molecule. An intramolecular hydrogen bond results in cyclization of the molecules and prevents their association. The planar and strain-free rings are favoured (Figure 8.10).

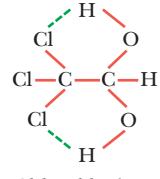
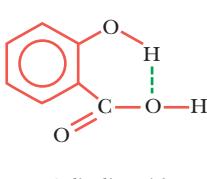
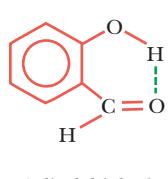
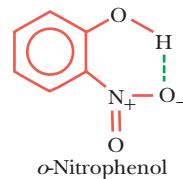
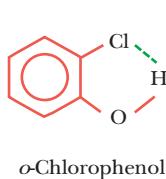
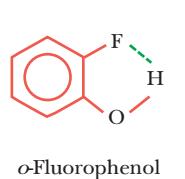


Figure 8.10 Some examples of planar and strain-free rings.

Note: *o*-Chlorophenol and chloral hydrate are the examples in which chlorine atoms form hydrogen bonding. It generally does not form H-bonding due to its low charge density.

Effect of intramolecular hydrogen bonding on physical and chemical properties

1. Acidity: The acidity of an acid depends upon the relative stabilities of the acid and its conjugate base. If the intramolecular H-bonding stabilizes the conjugate acid through chelation, then acidity of the acid decreases. For example

- a. The formation of an intramolecular hydrogen bond in *o*-nitrophenol reduces its acidity compared with *m*-nitrophenol and *p*-nitrophenol, where the formation of a hydrogen bond is not possible (Figure 8.11).

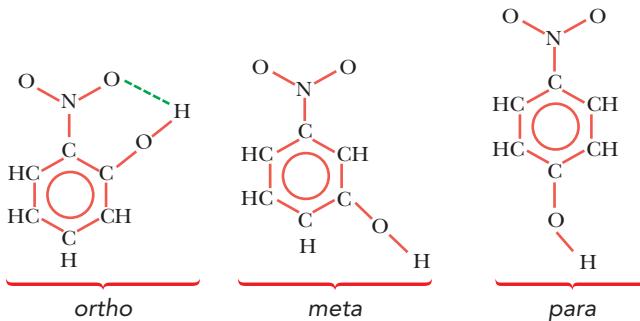


Figure 8.11 Structures of *ortho*, *meta* and *para* nitrophenol.

- b. If the intramolecular hydrogen bonding stabilizes the conjugate base through chelation, then, the acidity of acid increases. For example, K_{a1} of maleic acid is more compared to that of fumaric acid while K_{a2} of maleic acid is less than that of fumaric acid (Figure 8.12).

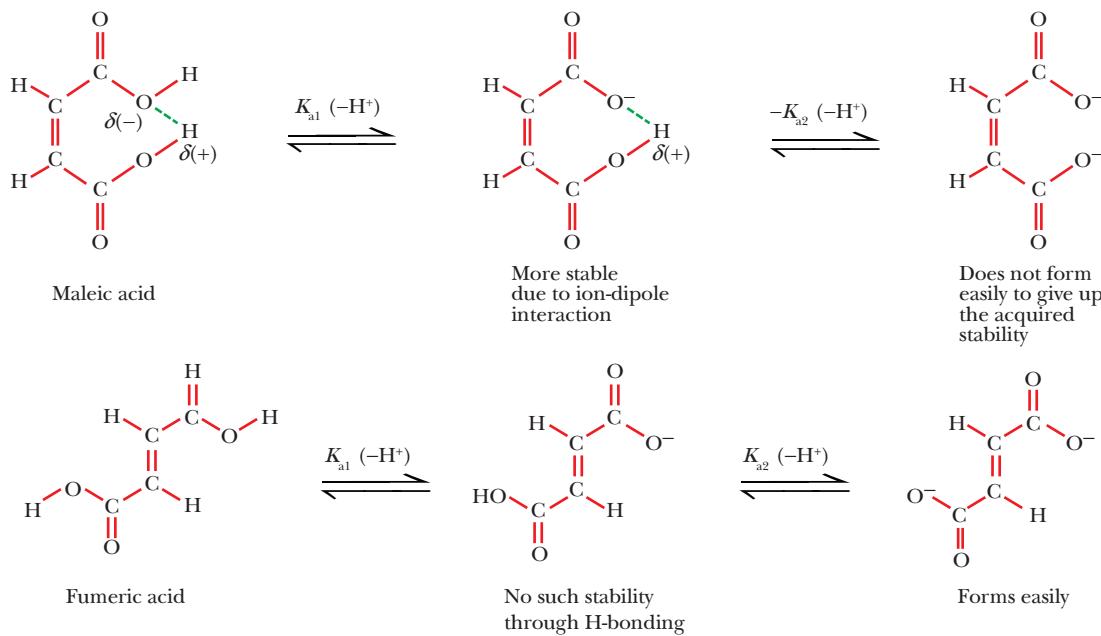


Figure 8.12 Comparison of acidity of maleic and fumaric acid.

- c. The K_{a1} of oxalic acid is much higher as compared with K_{a2} due to the formation of intramolecular hydrogen bonding in conjugate base after first dissociation (Figure 8.13).

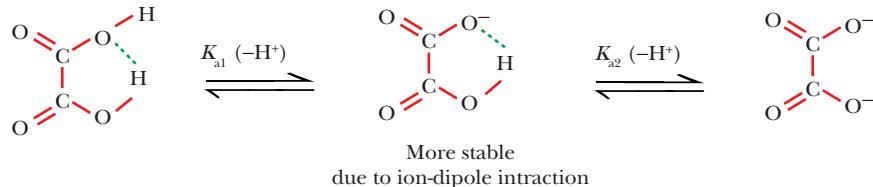


Figure 8.13 Acidic character of oxalic acid.

- d. *ortho*-Hydroxy benzaldehyde is less acidic as compared to *meta* and *para*-hydroxy benzaldehyde (Figure 8.14). Intramolecular bonding is possible in *ortho* isomer but both *meta* and *para* isomers easily lose hydrogen ion.

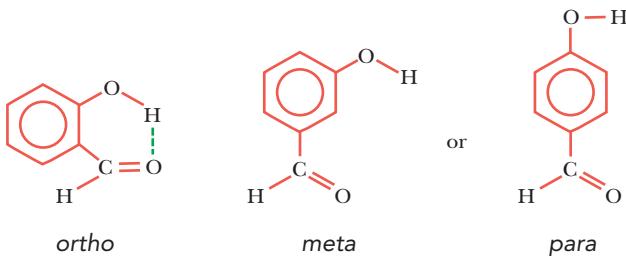


Figure 8.14 Acidic character of isomers of hydroxyl aldehydes.

2. **Melting and boiling points:** Intramolecular hydrogen bonding affects both the melting and boiling points of *ortho* and *para* isomers of compounds. In case of *ortho* isomer, the interacting group is close to each other and that leads to the formation of intramolecular hydrogen bonding preferably and no intermolecular association occurs. Thus, the *ortho* isomer remains as monomer in the liquid state and weak van der Waal's forces act among the monomeric molecules. While the *meta* and *para* isomers undergo intermolecular hydrogen bonding due to which the attraction between the molecules becomes high and they have much higher melting point and boiling points compared to that of *ortho* isomer (Figure 8.15). For example,

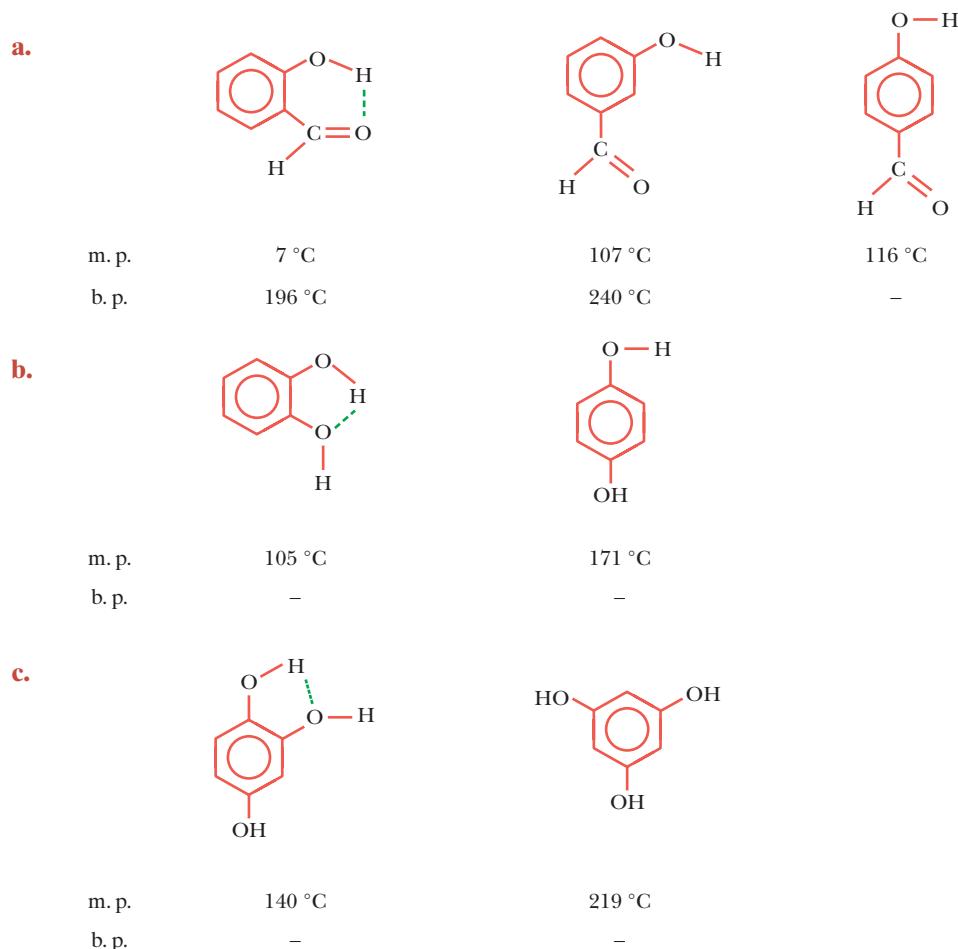


Figure 8.15 Melting and boiling point of *o*-, *m*- and *p*-isomers.

3. Isomeric distribution: Intramolecular hydrogen bonding also affects the isomeric distribution in equilibrium since it provides more stability through chelation (Figure 8.16).

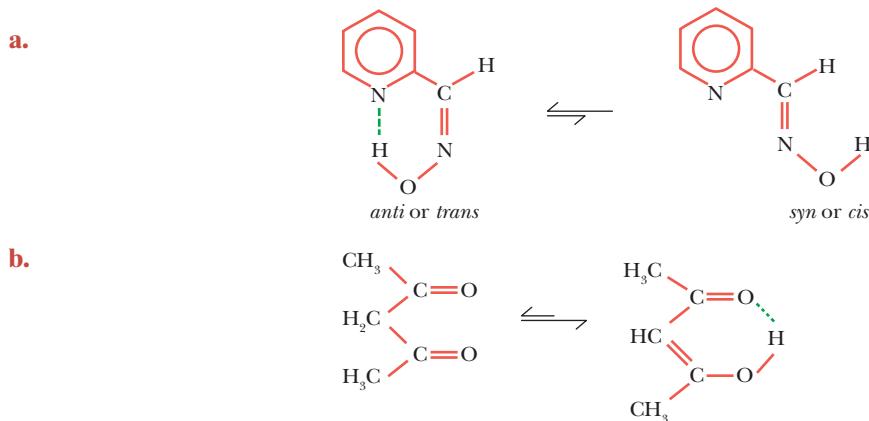


Figure 8.16 Chelating compounds.

4. Solubility: Intramolecular hydrogen bonding also affects the solubility which is less for *ortho*-isomer due to less solvent-solute interaction. For example, *ortho*-nitrophenol is less soluble in water compared to *meta*- and *para*-nitrophenol.

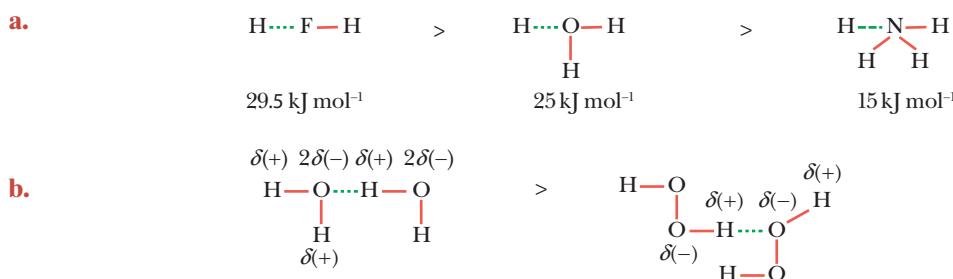
5. Viscosity: Isomeric compounds having intramolecular hydrogen bonding have lower value of surface tension and viscosity in comparison to compounds having intermolecular hydrogen bonding. This is because both of these two properties are directly proportional to the type of bonding. Viscosities of some compounds are given in Table 8.5 which clearly indicate that larger the scope of intermolecular association larger will be its viscosity.

Table 8.5 Viscosity of some compounds

Compounds	Viscosity (in millipoises at 20°C)
Water (H ₂ O)	10.05
Methanol (CH ₃ OH)	5.93
Dimethyl ether (CH ₃ OCH ₃)	2.30
Glycerine	8500

Strength of hydrogen bonding

The strength of hydrogen bonding depends on the polarity of H–A bond which further depends upon the difference in the electronegativity of H and A atoms.



The accumulated negative charge on oxygen atom in H_2O is more as compared to that in H_2O_2 .

Extent of hydrogen bonding

The extent of hydrogen bonding depends upon the moieties or sites available for hydrogen bonding, that is, greater the number sites available means more scope of hydrogen bonding. It is also true that hydrogen bonding occurs along the direction of the lone pair. For example,

- a. The extent of hydrogen bonding in H_2O_2 is more than in H_2O due to availability of greater number of sites per molecule (Figure 8.17)

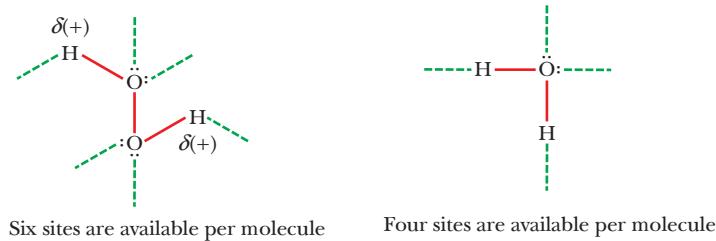


Figure 8.17 Hydrogen bonding in presence of lone pairs.

- b. Ethanol is less viscous as compared to glycerol (or glycerine). This is because ethanol can form maximum three hydrogen bonds per molecule while glycerol can form a maximum of nine hydrogen bonds per molecule (Figure 8.18).

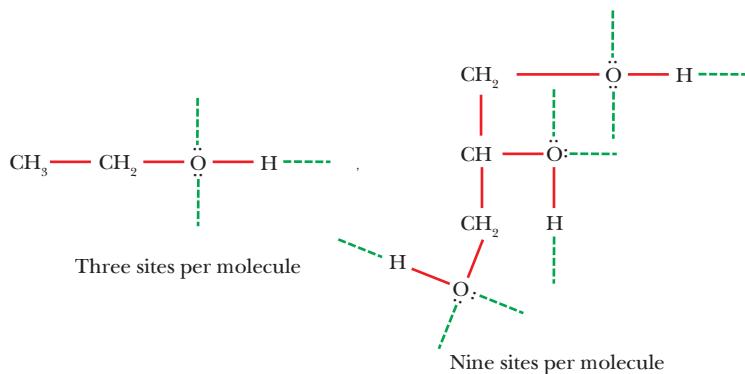
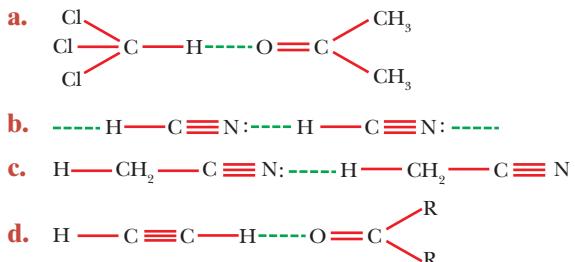


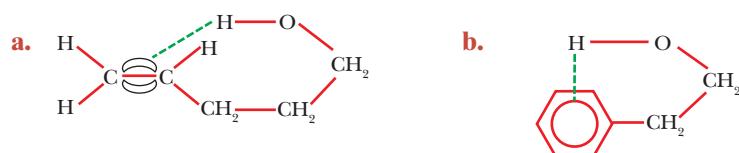
Figure 8.18 Hydrogen bonding based on number of bonding sites.

Special cases of hydrogen bonding

1. Hydrogen atom attached to carbon atom may also form significantly strong hydrogen bond.

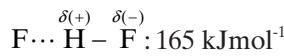


2. Hydrogen atom can also be attracted by π -electron cloud in some compounds and this is known as π -hydrogen bond. For example,

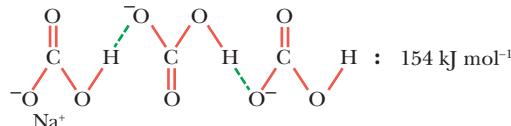


3. Hydrogen bonding may also be formed through ion-dipole interaction which is sufficiently stronger as compared to hydrogen bond formed by dipole-dipole interaction. For example,

a. In K^+HF_2^- , hydrogen and fluoride ions are held through ion-dipole interaction.



b. In NaHCO_3 , HCO_3^- ions are attracted to each other by hydrogen bond through ion-dipole interaction.

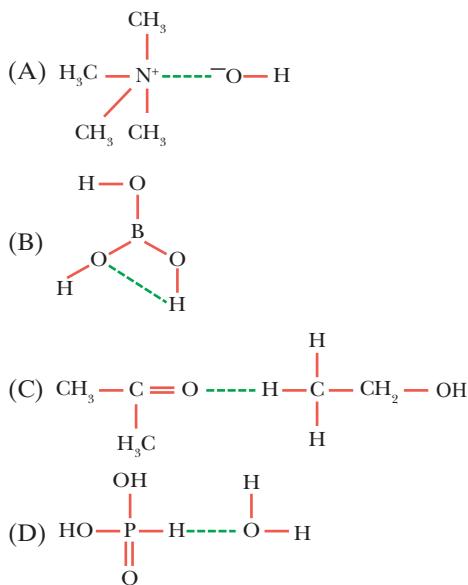


SINGLE CORRECT CHOICE TYPE QUESTIONS

- Hydrogen atom is almost _____ times larger than H^+ ion.
 - 50
 - 500
 - 5000
 - 50000
- The ionization energy order for H , H^+ , H^- is
 - $\text{H} < \text{H}^+ < \text{H}^-$
 - $\text{H}^- > \text{H} > \text{H}^+$
 - $\text{H}^- < \text{H}$
 - $\text{H}^+ > \text{H} > \text{H}^-$
- The most common way by which the hydrogen atom may attain stability is
 - forming covalent band.
 - forming H^+ .
 - forming H^- .
 - Both (B) and (C).
- The most abundant element in the Universe is
 - hydrogen.
 - oxygen.
 - nitrogen.
 - helium.
- Which of the following is/are the properties of H_2 ?
 - H_2 is the lightest gas known.
 - H_2 is not very reactive under normal conditions.
 - The bond energy of the $\text{H}-\text{H}$ bond is very high.
 - None is incorrect.
- Which of the following statements is incorrect regarding the use of H_2 as fuel?
 - It produces a lot of heat during burning.
 - Burning H_2 causes pollution.
 - Burning H_2 involves the risk of an explosion.
 - Burning of hydrogen produces water.
- Proton and deuteron are differentiated by their
 - number of protons.
 - number of neutrons.
- (C) number of electrons.
(D) charges.
- If the oxidation state of central atom in BH_3 is +3, then the oxidation states of the central atom in SiH_4 and CH_4 are, respectively,
 - +4, -4
 - +4, +4
 - 4, +4
 - 4, -4
- Choose the correct lattice energy order.
 - $\text{LiH} < \text{NaH} < \text{KH}$
 - $\text{MgH}_2 > \text{CaH}_2 < \text{SrH}_2$
 - $\text{LiH} < \text{NaH} > \text{KH}$
 - $\text{MgH}_2 > \text{CaH}_2 > \text{SrH}_2$
- At what temperature will water act as acid if K_w value of water at different temperature is as follows:
 - $K_w = 10^{-14}$ (at 25°C)
 - $K_w = 10^{-10}$ (at 80°C)
 - $K_w = 10^{-16}$ (at 4°C)
 - None of these.
- Choose the correct statement.
 - HCl is the most volatile among all halogen acids.
 - HCl is less easily liquefiable as compared to NH_3 .
 - Water has higher boiling point than that of HF .
 - All are correct.
- Choose the correct statement regarding maleic acid and fumaric acid.
 - $\text{p}K_{a_1}$ of maleic acid is greater than $\text{p}K_{a_1}$ of fumaric acid.
 - Both maleic acid and its first conjugate base have intramolecular hydrogen bonding.
 - Fumaric acid cannot form hydrogen bonding.
 - K_{a_2} of fumaric acid is less than that of maleic acid.

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. Which of the following representation of hydrogen bonding is(are) **incorrect**?



2. Hydrogen atom may attain stability by
- (A) forming an electron pair (covalent) bond with another atom.
 (B) losing an electron to form H^+ .
 (C) gaining an electron to form H^- .
 (D) None of these.

3. Which of the following properties of hydrogen atom are similar to those of halogens?

- (A) Formation of H^+ like X^+ .
 (B) Formation of H^- like X^- .
 (C) Formation of H_2 like X_2 .
 (D) None of these.

4. Which of the following processes can be used for preparation of H_2 gas?

- (A) Dissolving LiH in water.
 (B) Reaction of Al with NaOH solution.
 (C) Reaction of Zn with dilute H_2SO_4 .
 (D) Electrolysis of H_2O in the presence of KOH.

5. Which of the following properties of metallic hydrides are similar to those of their parent metal?

- (A) Hardness
 (B) Metallic lustre
 (C) Electrical conductivity
 (D) Magnetic property

6. Which of the following statements is correct regarding the conversion of metal into metallic hydride?

- (A) The density of metallic hydride is less than that of parent metal.
 (B) The crystal lattice expands through the inclusion of hydride.
 (C) A solid piece of a metal turns into powdered hydride.
 (D) None of these.

COMPREHENSION TYPE QUESTIONS

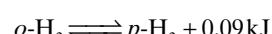
Passage 1: For Questions 1–3

H_2 , D_2 , T_2 are isotopes of each other.

1. The isotope effect arises due to
- (A) difference in number of electrons.
 (B) difference in number of protons.
 (C) difference in mass.
 (D) difference in properties.
2. Which of the following pairs shows maximum isotope effect?
- (A) ${}_1^1H$ and ${}_1^2D$
 (B) ${}_8^{16}O$ and ${}_8^{18}O$
 (C) ${}_{17}^{35}Cl$ and ${}_{17}^{37}Cl$
 (D) ${}_{6}^{12}C$ and ${}_{6}^{14}C$
3. Which of the following properties has incorrect order?
- (A) $H_2 < D_2 < T_2$: Boiling point order
 (B) $H_2 < D_2 < T_2$: Freezing point order
 (C) $H_2 < D_2 < T_2$: Latent heat of vapourization
 (D) $T_2O > H_2O > D_2O$: Equilibrium constant for dissociation

Passage 2: For Questions 4–6

Ortho hydrogen ($o\text{-H}_2$) and *para* hydrogen ($p\text{-H}_2$) have different energy contents and are related by the equilibrium relation.



4. Which of the following statements is correct?

- (A) The percentage of $o\text{-H}_2$ decreases with increase in temperature.
 (B) The percentage of $p\text{-H}_2$ increases with decrease in temperature.
 (C) At absolute zero Kelvin, the percentage of $o\text{-H}_2$ is maximum.
 (D) At room temperature, D_2 cannot show $o\text{-D}_2 \rightleftharpoons p\text{-D}_2$ equilibrium.

5. $o\text{-H}_2$ and $p\text{-H}_2$ differ in which of the following properties?

- (A) Spin of nucleus.
 (B) Nuclear magnetic moment.
 (C) Boiling point.
 (D) All of these.

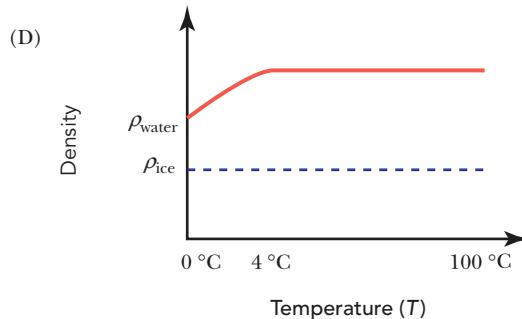
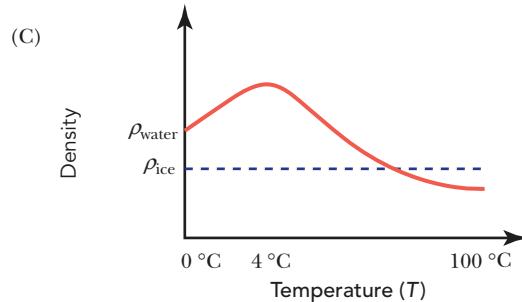
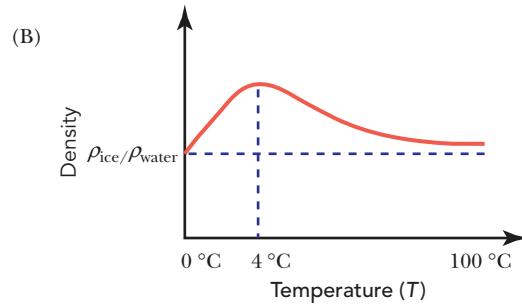
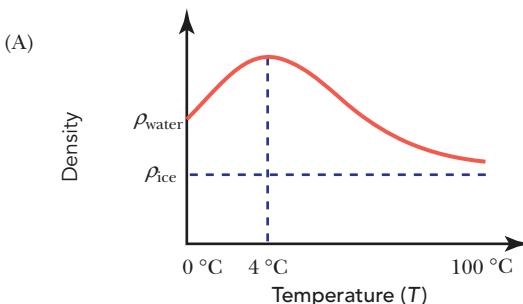
6. Choose the incorrect statement.

- (A) *Ortho* hydrogen has protons of parallel spin.
 (B) *Ortho* hydrogen is adsorbed more readily than *para* hydrogen by metal surface.
 (C) Both (A) and (B) are correct.
 (D) Neither (A) nor (B) is correct.

Passage 3: For Questions 7–9

Water on cooling to 0°C becomes ice. The main reason for this conversion is the hydrogen bonding.

7. Which of the following statements is correct?
 - (A) In ice, the hydrogen bonded H atoms are at equal distance from the other two covalently bonded H atoms around each O atom due to resonance.
 - (B) In ice, the hydrogen bonded H atoms are at longer distance as compared to the other two covalently bonded H atoms around each O atom.
 - (C) In ice, the hydrogen bonded H atoms are at shorter distance as compared to the other two covalently bonded H atoms around each O atom.
 - (D) None of these.
8. Two ice cubes when pressed against each other join together. This kind of joining phenomenon occurs
 - (A) just during pressing.
 - (B) after pressing when the pressure is released.
 - (C) during the whole process of pressing and releasing pressure.
 - (D) Cannot be predicted.
9. Which of the following curves is the correct representation of the density vs. temperature plot for water?



ASSERTION–REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
- (C) If Statement I is true but Statement II is false.
- (D) If Statement I is false but Statement II is true.

1. **Statement I:** H^- is a stronger reducing agent as compared to H atom.

Statement II: The electronic configuration of H and H^- is $1s^1$ and $1s^2$ respectively.

2. **Statement I:** Free protons (H^+) do not exist under normal conditions.

Statement II: H^+ ion is extremely small in size and has a very high polarizing power.

3. **Statement I:** The abundance of H_2 in the earth's atmosphere is very small.

Statement II: The Earth's gravitational field is too small to hold a light element such as hydrogen.

4. **Statement I:** H^- and He are stable to an equal extent.

Statement II: H^- and He both have $1s^2$ electronic configuration.

5. **Statement I:** Hydride shift and methyl shift occur in a similar manner during a carbocation rearrangement.

Statement II: The structure of hydrogen resembles that of the Group 14 elements.

6. **Statement I:** D_2 is more rapidly adsorbed chemically on the metal surface than H_2 .

Statement II: Van der Waal's forces of attraction are more in D_2 than in H_2 .

- 7. Statement I:** Ti is prepared in an atmosphere of Argon not H_2 .

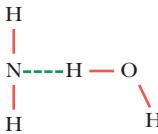
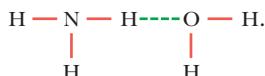
Statement II: Ti dissolves H_2 and becomes brittle.

- 8. Statement I:** Trimethyl ammonium hydroxide (compound A) is a weaker base compared to tetramethyl ammonium hydroxide (compound B).

Statement II: The release of OH from (compound B) is faster than that from (compound A) due to presence of hydrogen bonding in (compound A) and absence of such bonding in (compound B).

- 9. Statement I:** The correct presentation of exist-

ence of NH_3 in water is  not



Statement II: The polarity of O—H bond is more than that of the N—H bond.

- 10. Statement I:** The heat of vapourization of HF is higher than that of H_2O .

Statement II: The hydrogen bond strength in HF is higher than that in H_2O .

- 11. Statement I:** Boric acid is slippery in nature.

Statement II: Boric acid is monobasic in water.

- 12. Statement I:** CsCl (solid) can absorb HCl vapour while NaCl (solid) cannot do so.

Statement II: Absorbing HCl vapour, CsCl forms $Cs^+[HCl_2]^-$ through hydrogen bond.

- 13. Statement I:** Glycerol is more viscous than ethanol.

Statement II: Intermolecular hydrogen bonding is present in glycerol molecule.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. The total number of neutrons present in D_2O^{18} molecule is _____.

2. The mass number of the element obtained when tritium undergoes β -decay is _____.

3. The number of compounds among the following, which are monobasic in nature is _____.



4. The number of protons that can be accepted by hydrazine is _____.

5. The number of moieties available for H-bonding in one molecule of H_2SO_4 is _____.

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the metal hydrides with their properties.

Column I	Column II
(A) LiH	(P) Conducts electricity when melted.
(B) BeH ₂	(Q) The concept of hybridization is applicable.
(C) CH ₄	(R) Liberates hydrogen at the anode on electrolysis in molten condition.
(D) CaH ₂	(S) Produces hydrogen when dissolved in water.
	(T) Negative oxidation state of hydrogen atom.

2. Match the compounds with type of hydrogen bond.

Column I	Column II
(A) Maleic acid	(P) Intermolecular hydrogen bond is present
(B) NaHCO ₃ (s)	(Q) Intramolecular hydrogen bond is present.
(C) N ₂ H ₄ (liquid)	(R) Hydrogen bonding through ion-dipole interaction is present.
(D) <i>o</i> -fluorophenol	(S) Hydrogen bonding through dipole-dipole interaction is present.

3. Match the order of compounds with the property.

Column I	Column II	Column I	Column II
(A) $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$	(P) The boiling point order.	(C) $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$	(R) The bond polarity order.
(B) $\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$	(Q) The melting point order.	(S)	The acidic strength order.

ANSWERS

Single Correct Choice Type Questions

- | | | | |
|--------|--------|--------|---------|
| 1. (D) | 4. (A) | 7. (B) | 10. (D) |
| 2. (C) | 5. (D) | 8. (A) | 11. (D) |
| 3. (A) | 6. (B) | 9. (D) | 12. (B) |

Multiple Correct Choice Type Questions

- | | | |
|-----------------------|-----------------------|------------------|
| 1. (A), (B), (C), (D) | 2. (A), (B), (C) | 3. (B), (C) |
| 4. (A), (B), (C), (D) | 5. (A), (B), (C), (D) | 6. (A), (B), (C) |

Comprehension Type Questions

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (C) | 3. (D) | 5. (D) | 7. (B) | 9. (A) |
| 2. (A) | 4. (B) | 6. (D) | 8. (B) | |

Assertion–Reasoning Type Questions

- | | | | | |
|--------|--------|--------|---------|---------|
| 1. (B) | 4. (D) | 7. (A) | 10. (D) | 13. (B) |
| 2. (A) | 5. (A) | 8. (A) | 11. (B) | |
| 3. (A) | 6. (D) | 9. (A) | 12. (A) | |

Integer Answer Type Questions

- | | | | | |
|-------|------|------|------|-------|
| 1. 12 | 2. 3 | 3. 3 | 4. 2 | 5. 10 |
|-------|------|------|------|-------|

Matrix–Match Type Questions

- | | | |
|---|-------------------------------|---------------------------------|
| 1. (A) \rightarrow (P), (R), (S), (T) | 2. (A) \rightarrow (Q), (S) | 3. (A) \rightarrow (P) |
| (B) \rightarrow (Q), (T) | (B) \rightarrow (P), (R) | (B) \rightarrow (Q), (R) |
| (C) \rightarrow Q | (C) \rightarrow (P), (S) | (C) \rightarrow (P), (Q), (S) |
| (D) \rightarrow (P), (R), (S), (T) | (D) \rightarrow (Q), (S) | |

9

The *s*-Block Elements and their Compounds

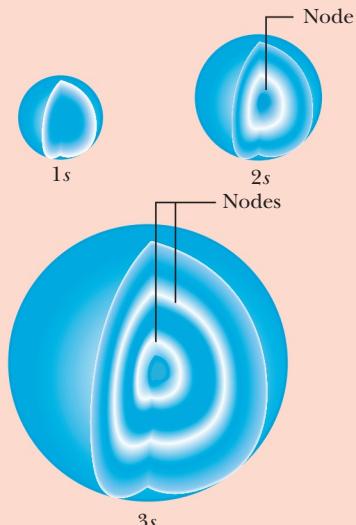
Contents

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- 9.2 Structures of the Metals, Hardness and Cohesive Energy
- 9.3 Flame Colours and Spectra
- 9.4 Colour of Compounds
- 9.5 Chemical Properties
- 9.6 Oxides, Hydroxides, Peroxides and Superoxides
- 9.7 Sulphides
- 9.8 Oxosalts – Carbonates, Bicarbonates, Nitrates, Nitrites and Sulphates
- 9.9 Halides and Polyhalides
- 9.10 Hydrides
- 9.11 Solubility and Hydration
- 9.12 Solutions of Metals in Liquid Ammonia
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- 9.19 Preparation of Sodium Carbonate
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Group 2 – The Alkaline Earth Elements

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- 9.34 Complexes
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- 9.36 Differences between Beryllium and the Other Group 2 Elements



The *s* orbitals become larger as the principal quantum number, *n*, becomes larger.

GROUP 1 – THE ALKALI METALS

The elements of Group 1 are all metals, excellent conductors of electricity, and typically soft and highly reactive. They have one loosely held valence electron in their outer shell, and typically form univalent, ionic and colourless compounds. The hydroxides and oxides are very strong bases, and the oxosalts are very stable.

Lithium, the first element in the group, shows considerable differences from the rest of the group. In all of the main groups the first element shows a number of differences from the later elements in the group.

Compounds of sodium and potassium are very common and in use for a long time. Some compounds of sodium are of industrial importance and many salts of potassium are used as fertilizers. In addition sodium and potassium are essential elements for animal life.

9.1 | GENERAL PROPERTIES

Electronic structure

Group 1 elements all have one valency electron in their outer orbital – an s electron which occupies a spherical orbital. Ignoring the filled inner shells the electronic structures may be written: $2s^1$, $3s^1$, $4s^1$, $5s^1$, $6s^1$ and $7s^1$ (Table 9.1). The single valence electron is a long distance from the nucleus, is only weakly held and is readily removed. Because of similarities in the electronic structures of these elements, many similarities in chemical behaviour would be expected.

Table 9.1 Electronic structures

Element	Symbol	Electronic structure	
Lithium	Li	$1s^2 2s^1$	or [He] $2s^1$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$	or [Ne] $3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	or [Ar] $4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$	or [Kr] $5s^1$
Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$	or [Xe] $6s^1$
Francium	Fr		[Rn] $7s^1$

Size of atoms and ions

Group 1 atoms are the largest in their horizontal periods in the periodic table. When the outer electron is removed to give a positive ion, the size decreases considerably. There are two reasons for this.

1. The outermost shell of electrons has been completely removed.
2. Having removed an electron, the positive charge on the nucleus is now greater than the charge on the remaining electrons, so that each of the remaining electrons is attracted more strongly towards the nucleus. This reduces the size further.

Positive ions are always smaller than the parent atom. Even so, the ions are very large, and they increase in size from Li^+ to Fr^+ as extra shells of electrons are added.

The Li^+ is much smaller than the other ions. For this reason, Li only mixes with Na above 380°C , and it is immiscible with the metals K, Rb and Cs, even when molten; nor will Li form substitutional alloys with them. In contrast the other metals Na, K, Rb and Cs are miscible with each other in all proportions.

Density

The atoms are large, so Group 1 elements have remarkably low densities. Lithium metal is only about half as dense as water, whilst sodium and potassium are slightly less dense than water (see Table 9.2).

Table 9.2 Size and density

	Metallic radius (Å)	Ionic radius M^+ six-coordinate (Å)	Density (g cm ⁻³)
Li	1.52	0.76	0.54
Na	1.86	1.02	0.97
K	2.27	1.38	0.86
Rb	2.48	1.52	1.53
Cs	2.65	1.67	1.90

Ionization energy

The first ionization energies for the atoms in this group are appreciably lower than those for any other group in the periodic table. The atoms are very large so the outer electrons are only held weakly by the nucleus: hence the amount of energy needed to remove the outer electron is not very large. On descending the group from Li to Na to K to Rb to Cs, the size of the atoms increases: the outermost electrons become less strongly held, so the ionization energy decreases.

The second ionization energy – that is the energy to remove a second electron from the atoms – is extremely high. The second ionization energy is always larger than the first, often by a factor of two, because it involves removing an electron from a smaller positive ion, rather than from a larger neutral atom. The difference between first and second ionization energies is much larger in this case since in addition it corresponds to removing an electron from a closed shell. A second electron is never removed under normal conditions, as the energy required is greater than that needed to ionize the noble gases. The elements commonly form M^+ ions. The first and second ionization energies for Group 1 elements is given in Table 9.3.

Table 9.3 Ionization energies

	First ionization energy (kJ mol ⁻¹)	Second ionization energy (kJ mol ⁻¹)
Li	520.1	7296
Na	495.7	4563
K	418.6	3069
Rb	402.9	2650
Cs	375.6	2420

Electronegativity and bond type

The electronegativity values for the elements in this group are very small – in fact the smallest values of any element (Table 9.4). Thus when these elements react with other elements to form compounds, a large electronegativity difference between the two atoms is probable, and ionic bonds are formed.

Na electronegativity	0.9
Cl electronegativity	3.0
Electronegativity difference	2.1

An electronegativity difference of approximately 1.7–1.8 corresponds to 50% ionic character. The value 2.1 exceeds this, so the bonding in NaCl is predominantly ionic. Similar arguments apply to other compounds: for example, the electronegativity difference in LiF is 3.0, and in KBr is 2.0, and both compounds are ionic. The chemistry of the alkali metals is largely that of their ions.

Table 9.4 Electronegativity values

Pauling's electronegativity	
Li	1.0
Na	0.9
K	0.8
Rb	0.8
Cs	0.7

9.2 | STRUCTURES OF THE METALS, HARDNESS AND COHESIVE ENERGY

At normal temperatures all the Group 1 metals adopt a body-centred cubic type of lattice with a coordination number of 8. However, at very low temperatures lithium forms a hexagonal close-packed structure with a coordination number of 12.

The metals are all very soft, and can be cut quite easily with a knife. Lithium is harder than the others, but is softer than lead.

The cohesive energy is the force holding the atoms or ions together in the solid. (This is the same in magnitude, but the opposite in sign, to the enthalpy of atomization, which is the energy required to break the solid up into gaseous atoms.) The cohesive energies of Group 1 metals are about half of those for Group 2, and one third of those for Group 13 elements. The magnitude of the cohesive energy determines the hardness, and it depends on the number of electrons that can participate in bonding and on the strength of the bonds formed. The softness, low cohesive energy and weak bonding in Group 1 elements are consequences of these metals having only one valency electron which can participate in bonding (compared with two or more electrons in most other metals), and of the large size and diffuse nature of the outer bonding electron. The atoms become larger on descending the group from lithium to caesium, so the bonds are weaker, the cohesive energy decreases (Table 9.5) and the softness of the metals increases.

Table 9.5 Cohesive energy

Cohesive energy (enthalpy of atomization) (kJ mol ⁻¹)	
Li	161
Na	108
K	90
Rb	82
Cs	78

Melting and boiling points

The generally low values for cohesive energy are reflected in the very low values of melting and boiling points in the group (Table 9.6). The cohesive energy decreases down the group, and the melting points decrease correspondingly.

The melting points range from lithium 181 °C to caesium 28.5 °C. These are extremely low values for metals, and contrast with the melting points of the transition metals, most of which are above 1000 °C.

Table 9.6 Melting and boiling points

	Melting point (°C)	Boiling point (°C)
Li	181	1347
Na	98	881

(continued)

Table 9.6 (continued)

	Melting point (°C)	Boiling point (°C)
K	63	766
Rb	39	688
Cs	28.5	705

9.3 | FLAME COLOURS AND SPECTRA

A result of the low ionization energies is that when these elements are irradiated with light, the light energy absorbed may be sufficient to make an atom lose an electron. Electrons emitted in this way are called photo-electrons, and this explains the use of caesium and potassium as cathodes in photoelectric cells.

Electrons may also be quite readily excited to a higher energy level, for example in the flame test. To perform this test, a sample of the metal chloride, or any salt of the metal moistened with concentrated HCl, is heated on a platinum or nichrome wire in a Bunsen burner flame. The heat from the burner excites one of the orbital electrons to a higher energy level. When the excited electron drops back to its original energy level it gives out the extra energy it obtained. The energy E is related to the wave number v by the Einstein relationship:

$$E = hv \quad (\text{where } h \text{ is Planck's constant})$$

For Group 1 metals, the energy emitted appears as visible light, thus giving the characteristic flame colourations (Table 9.7).

Table 9.7 Flame colours and wavelengths

	Colour	Wavelength (nm)	Wavenumber (cm ⁻¹)
Li	Crimson	670.8	14908
Na	Yellow	589.2	16972
K	Lilac	766.5	13046
Rb	Red-violet	780.0	12821
Cs	Blue	455.5	21954

The colour actually arises from electronic transitions in short-lived species which are formed momentarily in the flame. The flame is rich in electrons, and in the case of sodium the ions are temporarily reduced to atoms.



The sodium D-line (which is actually a doublet at 589.0 nm and 589.6 nm) arises from the electronic transition $3s^1 \rightarrow 3p^1$ in **sodium atoms** formed in the flame. The colours from different elements do not all arise from the same transition, or from the same species. Thus the red line for lithium arises from a short-lived LiOH species formed in the flame.

9.4 | COLOUR OF COMPOUNDS

Colour arises because the energy absorbed or emitted in electronic transitions corresponds to a wavelength in the visible region. The Group 1 metal ions all have noble gas configurations in which all the electrons are paired. Thus promoting an electron requires some energy to unpair an electron, some to break a full shell of electrons and some to promote the electron to a higher level. The total energy is large: hence there are no suitable transitions and the compounds are typically white. Any transitions which do occur will be of

high energy, will appear in the ultraviolet region rather than in the visible region, and will be invisible to the human eye. Compounds of Group 1 metals are typically white, except those where the anion is coloured, for example sodium chromate $\text{Na}_2[\text{CrO}_4]$ (yellow), potassium dichromate $\text{K}_2[\text{Cr}_2\text{O}_7]$ (orange), and potassium permanganate $\text{K}[\text{MnO}_4]$ (deep purple). In these cases the colour comes from the anions $[\text{CrO}_4]^{2-}$, $[\text{Cr}_2\text{O}_7]^{2-}$ or $[\text{MnO}_4]^-$ and not from the Group 1 metal ion.

When Group 1 elements form compounds (usually ionic, but there are a few covalent compounds), all the electrons are paired. Because of this Group 1 compounds are diamagnetic. There is one notable exception – the superoxides, which are discussed in Section 9.6.

9.5 | CHEMICAL PROPERTIES

Some important reactions of Group 1 elements are listed in Table 9.8.

Table 9.8 Some reactions of Group 1 metals

Reaction	Comment
$\text{M} + \text{H}_2\text{O} \rightarrow \text{MOH} + \text{H}_2$	The hydroxides are the strongest bases known
With excess dioxygen	
$\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}$	Monoxide is formed by Li and to a small extent by Na
$\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2$	Peroxide formed by Na and to a small extent by Li
$\text{K} + \text{O}_2 \rightarrow \text{KO}_2$	Superoxide formed by K, Rb, Cs
$\text{M} + \text{H}_2 \rightarrow \text{MH}$	Ionic ‘salt-like’ hydrides
$\text{Li} + \text{N}_2 \rightarrow \text{Li}_3\text{N}$	Nitride formed only by Li, Na_3N is reported but difficult to form.
$\text{M} + \text{P} \rightarrow \text{M}_3\text{P}$	All the metals form phosphides
$\text{M} + \text{As} \rightarrow \text{M}_3\text{As}$	All the metals form arsenides
$\text{M} + \text{Sb} \rightarrow \text{M}_3\text{Sb}$	All the metals form stibnides
$\text{M} + \text{S} \rightarrow \text{M}_2\text{S}$	All the metals form sulphides
$\text{M} + \text{Se} \rightarrow \text{M}_2\text{Se}$	All the metals form selenides
$\text{M} + \text{Te} \rightarrow \text{M}_2\text{Te}$	All the metals form tellurides
$\text{M} + \text{F}_2 \rightarrow \text{MF}$	All the metals form fluorides
$\text{M} + \text{Cl}_2 \rightarrow \text{MCl}$	All the metals form chlorides
$\text{M} + \text{Br}_2 \rightarrow \text{MBr}$	All the metals form bromides
$\text{M} + \text{I}_2 \rightarrow \text{MI}$	All the metals form iodides
$\text{M} + \text{NH}_3 \rightarrow \text{MNH}_2$	All the metals form amides

Reaction with water

Group 1 metals all react with water, liberating hydrogen and forming the hydroxides. The reaction becomes increasingly violent on descending the group. Thus lithium reacts gently, sodium melts on the surface of the water and the molten metal skates about vigorously and may catch fire (especially if localized), and potassium melts and always catches fire.



The standard electrode potentials E° (in volts) are $\text{Li}^+|\text{Li} = -3.05$, $\text{Na}^+|\text{Na} = -2.71$, $\text{K}^+|\text{K} = -2.93$, $\text{Rb}^+|\text{Rb} = -2.92$, $\text{Cs}^+|\text{Cs} = -2.92$. Lithium has the most negative standard electrode potential of any element in the periodic table, largely because of its high hydration energy. Standard electrode potentials E° and Gibbs free energy ΔG are related by the equation:

$$\Delta G = -nFE^\circ$$

where n is the number of electrons removed from the metal to produce the ion, and F is the Faraday constant.

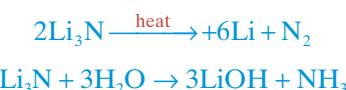
The reaction $\text{Li}^+ + \text{e} \rightarrow \text{Li}$ has the largest negative E° value, and hence the largest positive ΔG value. Thus the reaction does not occur. However, the reverse reaction $\text{Li} \rightarrow \text{Li}^+ + \text{e}$ has a large negative value of ΔG , so lithium liberates more energy than the other metals when it reacts with water. In view of this it is at first sight rather surprising that lithium reacts gently with water, whereas potassium, which liberates less energy, reacts violently and catches fire. The explanation lies in the kinetics (that is the rate at which the reaction proceeds), rather than in the thermodynamics (that is the total amount of energy liberated). Potassium has a low melting point, and the heat of reaction is sufficient to make it melt, or even vaporize. The molten metal spreads out, and exposes a larger surface to the water, so it reacts even faster, gets even hotter and catches fire.

Reaction with air

Chemically, Group 1 elements are very reactive, and tarnish rapidly in dry air. Sodium, potassium, rubidium and caesium form oxides of various types, but lithium forms a mixture of the oxide and the nitride, Li_3N .

Reaction with dinitrogen

Lithium is the only element in the group that reacts with dinitrogen to form a nitride. Lithium nitride, Li_3N , is ionic (3Li^+ and N^{3-}), and is ruby red. Two reactions of the nitride are of interest. First, on heating to a high temperature it decomposes to the elements, and second, it reacts with water, giving ammonia.



9.6 | OXIDES, HYDROXIDES, PEROXIDES AND SUPEROXIDES

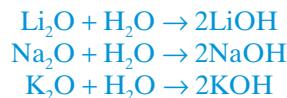
Reaction with air

The metals all burn in air to form oxides, though the product varies depending on the metal. Lithium forms the monoxide Li_2O (and some peroxide Li_2O_2), sodium forms the peroxide Na_2O_2 (and some monoxide Na_2O), and the others form superoxides of the type MO_2 .

All five metals can be induced to form the normal oxide, peroxide or superoxide by dissolving the metal in liquid ammonia and bubbling in the appropriate amount of dioxygen.

Normal oxides – monoxides

The monoxides are ionic, for example 2Li^+ and O^{2-} . Li_2O and Na_2O are pure white solids as expected, but surprisingly K_2O is pale yellow, Rb_2O is bright yellow and Cs_2O is orange. Metallic oxides are usually basic. The typical oxides M_2O are strongly basic oxides, and they react with water, forming strong bases.



Hydroxides

Sodium hydroxide NaOH is often called caustic soda, and potassium hydroxide is called caustic potash, because of their corrosive properties (for example on glass or on skin). These caustic alkalis are the strongest bases known in aqueous solution. The hydroxides of Na, K, Rb and Cs are very soluble in water, but LiOH is much less soluble (see Table 9.9). At 25°C a saturated solution of NaOH is about 27 molar, whilst saturated LiOH is only about 5 molar.

Table 9.9 Solubility of Group 1 hydroxides

Element	Solubility (g/100 g H ₂ O)
Li	13.0 (25 °C)
Na	108.3 (25 °C)
K	112.8 (25 °C)
Rb	197.6 (30 °C)
CS	385.6 (15 °C)

The bases react with acids to form salts and water, and are used for many neutralizations.

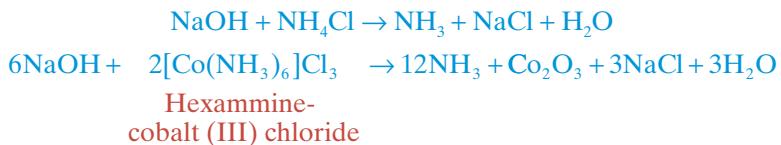


The bases also react with CO₂, even traces in the air, forming the carbonate. LiOH is used to absorb carbon dioxide in closed environments such as space capsules (where its light weight is an advantage in reducing the launching weight).



They also react with the amphoteric oxides, Al₂O₃ forming aluminates, SiO₂ (or glass) forming silicates, SnO₂ forming stannates, PbO₂ forming plumbates and ZnO forming zincates.

The bases liberate ammonia from both ammonium salts and coordination complexes where ammonia is attached to a transition metal ion (ammine complexes).



NaOH reacts with H₂S to form sulphides S²⁻, and hydrogen sulphides SH⁻, and it is used to remove mercaptans from petroleum products.



The hydroxides react with alcohols, forming alkoxides.



KOH resembles NaOH in all its reactions, but as KOH is much more expensive it is seldom used. However, KOH is much more soluble in alcohol, thus producing OC₂H₅⁻ ions by the equilibrium



This accounts for the use of alcoholic KOH in organic chemistry. Group 1 hydroxides are thermally stable, illustrating the strong electropositive nature of the metals. On heating, many hydroxides decompose, losing water and forming the oxide.

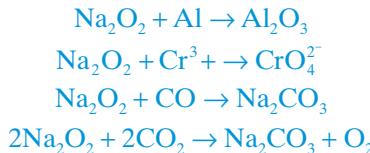
Peroxides and superoxides

The peroxides all contain the $[\text{O}-\text{O}-]^{2-}$ ion. They are diamagnetic (all the electrons are paired), and are oxidizing agents. They may be regarded as salts of the dibasic acid H₂O₂, and they react with water and acid, giving hydrogen peroxide H₂O₂.



Na₂O₂ is pale yellow in colour. It is used industrially for bleaching wood pulp, paper and fabrics such as cotton and linen. It is a powerful oxidant, and many of its reactions are dangerously violent, particularly with materials that are reducing agents such as aluminium powder, charcoal, sulphur and many organic

liquids. Because it reacts with CO_2 in the air it has been used to purify the air in submarines and confined spaces, as it both removes CO_2 and produces O_2 . Potassium superoxide KO_2 is even better for this purpose. Some typical reactions are:



The industrial process for forming sodium peroxide is a two-stage reaction in the presence of excess air:



The superoxides contain the ion $[\text{O}_2]^-$, which has an unpaired electron, and hence they are paramagnetic and are all coloured (LiO_2 and NaO_2 yellow, KO_2 orange, RbO_2 brown and CsO_2 orange).

Superoxides are even stronger oxidizing agents than peroxides, and give both H_2O_2 and O_2 with either water or acids.



KO_2 is used in space capsules, submarines, and breathing masks, because it both produces dioxygen and removes carbon dioxide. Both functions are important in life support systems.

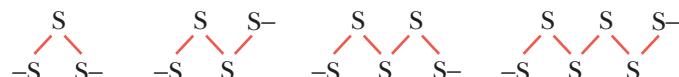


Sodium superoxide cannot be prepared by burning the metal in dioxygen at atmospheric pressure, but it is made commercially and in good yields by reacting sodium peroxide with dioxygen at a high temperature and pressure (450 °C and 300 atmospheres) in a stainless steel bomb.

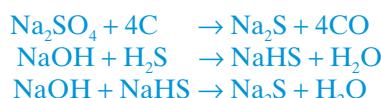


9.7 | SULPHIDES

The metals all react with sulphur, forming sulphides such as Na_2S , and polysulphides Na_2S_n where $n = 2, 3, 4, 5$ or 6. The polysulphide ions are made from zig-zag chains of sulphur atoms.



Sodium sulphide can also be made by heating sodium sulphate with carbon, or by passing H_2S into NaOH solution.



Group 1 sulphides hydrolyse appreciably in water, giving strongly alkaline solutions:



Na_2S is used to make organic sulphur dyestuffs, and in the leather industry to remove hair from hides. Na_2S is readily oxidized by air to form sodium thiosulphate, which is used in photography to dissolve silver halides, and as a laboratory reagent for iodine titrations.

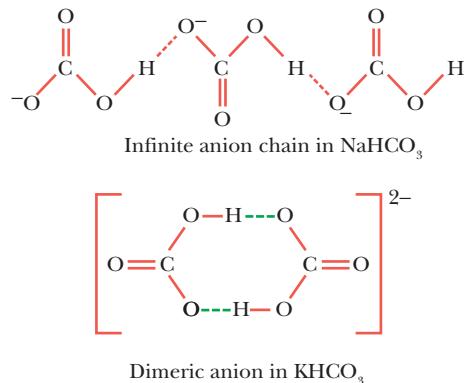


9.8 | OXOSALTS – CARBONATES, BICARBONATES, NITRATES, NITRITES AND SULPHATES

Group 1 metals are highly electropositive and thus form very strong bases, and have quite stable oxosalts.

The carbonates are remarkably stable, and will melt before they eventually decompose into oxides at temperatures above 1000 °C. Li_2CO_3 is considerably less stable and decomposes more readily.

Because Group 1 metals are so strongly basic, they also form solid bicarbonates (also called hydrogen-carbonates). No other metals form solid bicarbonates, though NH_4HCO_3 also exists as a solid. Bicarbonates evolve carbon dioxide and turn into carbonates on gentle warming. This is one test for bicarbonates in qualitative analysis. The crystal structures of NaHCO_3 and KHCO_3 both show hydrogen bonding, but are different. In NaHCO_3 the HCO_3^- ions are linked into an infinite chain, whilst in KHCO_3 a dimeric anion is formed.



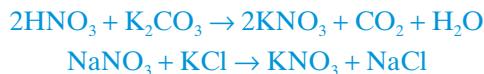
Lithium is exceptional in that it does not form solid bicarbonate, though LiHCO_3 can exist in solution. All the carbonates and bicarbonates are soluble in water except NaHCO_3 and Li_2CO_3 .

Commercially Li_2CO_3 is added as an impurity to Al_2O_3 to lower its melting point in the extraction of aluminium by electrolysis. Na_2CO_3 is used as washing soda to soften water in hard water areas. NaHCO_3 is used in baking powder and in fire extinguishers. NaHCO_3 can be used on its own to make cakes or bread ‘rise’ since it decomposes between 50 °C and 100 °C, giving bubbles of CO_2 .

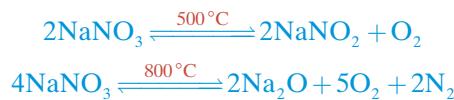


Baking powder is more commonly used, and contains NaHCO_3 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and starch. The $\text{Ca}(\text{H}_2\text{PO}_4)_2$ is acidic and when moistened it reacts with NaHCO_3 , giving CO_2 . The starch is a filler. An improved ‘combination baking powder’ contains about 40% starch, 30% NaHCO_3 , 20% $\text{NaAl}(\text{SO}_4)_2$ and 10% $\text{Ca}(\text{H}_2\text{PO}_4)_2$. The $\text{NaAl}(\text{SO}_4)_2$ slows the reaction down so the CO_2 is given off more slowly.

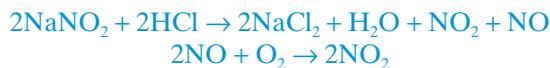
The nitrates can all be prepared by the action of HNO_3 on the corresponding carbonate or hydroxide, and they are all very soluble in water. LiNO_3 is used for fireworks and red-coloured distress flares. Large deposits of NaNO_3 are found in Chile, and are used as a nitrogenous fertilizer. Solid LiNO_3 and NaNO_3 are deliquescent, and because of this KNO_3 is used in preference to NaNO_3 in gunpowder (gunpowder is a mixture of KNO_3 , sulphur and charcoal). KNO_3 is usually obtained from synthetic nitric acid and K_2CO_3 , but at one time it was made from NaNO_3 :



Group 1 nitrates are fairly low melting solids, and are amongst the most stable nitrates known. However, on strong heating they decompose into nitrites, and at higher temperatures to the oxide. LiNO_3 decomposes more readily than the others, forming the oxide.



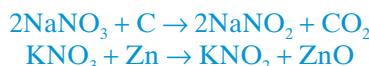
Nitrites are important in the manufacture of organonitrogen compounds, the most important being the azo dyes. Small amounts of NaNO_2 are used in molten salt baths with NaNO_3 , and some is used as a food preservative. Nitrites are easily recognized in the laboratory, because on treatment with dilute acids they produce brown fumes of NO_2 .



NaNO_2 is manufactured by absorbing oxides of nitrogen in Na_2CO_3 solution.



They can also be made by thermal decomposition of nitrates and the chemical reduction of nitrates:



or by reacting NO with a hydroxide.



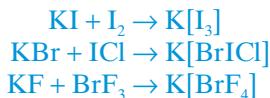
About 55% of sodium sulphate is made synthetically, as a by-product from the manufacture of HCl, and also from many neutralization processes that use H_2SO_4 . About 45%, mainly Glauber's salt $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is mined.

The major use of Na_2SO_4 – some 70% – is in the paper industry, and about 10% is used in detergents, and 10% in glass manufacture. In the Kraft paper making process, a strong alkaline solution of Na_2SO_4 is used to dissolve the lignin that holds the cellulose fibres together in wood chips. The cellulose fibres are then turned into corrugated cardboard and brown paper.

9.9 | HALIDES AND POLYHALIDES

Since Li^+ is the smallest ion in the group, it would be expected to form hydrated salts more readily than the other metals. LiCl , LiBr and LiI form trihydrates $\text{LiX} \cdot 3\text{H}_2\text{O}$, but the other alkali metal halides form anhydrous crystals.

The alkali metal halides react with the halogens and interhalogen compounds forming ionic polyhalide compounds:



9.10 | HYDRIDES

Group 1 metals all react with hydrogen, forming ionic or salt-like hydrides M^+H^- . However, the ease with which they do so decreases from lithium to caesium. These hydrides contain the H^- ion (which is not commonly found, since hydrogen usually forms H^+ ions). It can be proved that H^- ions exist because on electrolysis hydrogen is liberated at the anode.

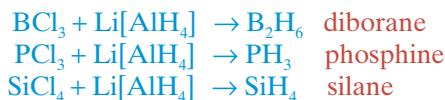
The hydrides react with water, liberating hydrogen, and lithium hydride is used as a source of hydrogen for military purposes and for filling meteorological balloons.



Lithium also forms a complex hydride $\text{Li}[\text{AlH}_4]$, called lithium aluminium hydride, which is a useful reducing agent. It is made from lithium hydride in dry ether solution.



Lithium aluminium hydride is ionic, and the $[\text{AlH}_4]^-$ ion is tetrahedral. $\text{Li}[\text{AlH}_4]$ is a powerful reducing agent and is widely used in organic chemistry, as it reduces carbonyl compounds to alcohols. It reacts violently with water, so it is necessary to use absolutely dry organic solvents, for example ether which has been dried over sodium. $\text{Li}[\text{AlH}_4]$ will also reduce a number of inorganic compounds.



Sodium tetrahydridoborate (sodium borohydride) $\text{Na}[\text{BH}_4]$ is another hydride complex. It is ionic, comprising tetrahedral $[\text{BH}_4]^-$ ions. It is best obtained by heating sodium hydride with trimethyl borate:



Other tetrahydridoborates of Group 1 and 2 metals can be made from sodium salts. These tetrahydridoborates are used as reducing agents, and the alkali metal compounds (particularly those of Na and K) are becoming increasingly used as they are much less sensitive to water than $\text{Li}[\text{AlH}_4]$. Thus $\text{Na}[\text{BH}_4]$ can be crystallized from cold water, and $\text{K}[\text{BH}_4]$ from hot water, so they have the advantage that they can be used in aqueous solutions. The others react with water.



9.11 | SOLUBILITY AND HYDRATION

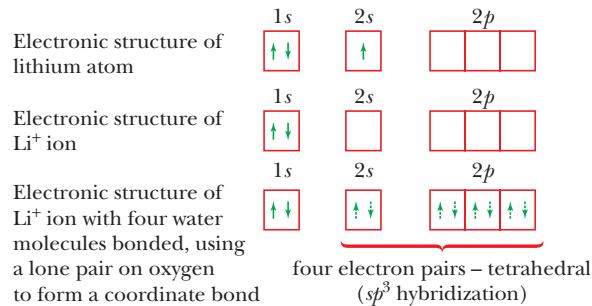
All the simple salts dissolve in water, producing ions, and consequently the solutions conduct electricity. Since Li^+ ions are small, it might be expected that solutions of lithium salts would conduct electricity better than solutions of the same concentration of sodium, potassium, rubidium or caesium salts. The small ions should migrate more easily towards the cathode, and thus conduct more than the larger ions. However, ionic mobility or conductivity measurements in aqueous solution (Table 9.10) give results in the opposite order $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. The reason for this apparent anomaly is that the ions are hydrated in solution. Since Li^+ is very small, it is heavily hydrated. This makes the radius of the hydrated ion large, and hence it moves only slowly. In contrast, Cs^+ is the least hydrated, and the radius of the hydrated Cs^+ ion is smaller than the radius of hydrated Li^+ , and hence hydrated Cs^+ moves faster, and conducts electricity more readily.

Table 9.10 Ionic mobilities and hydration

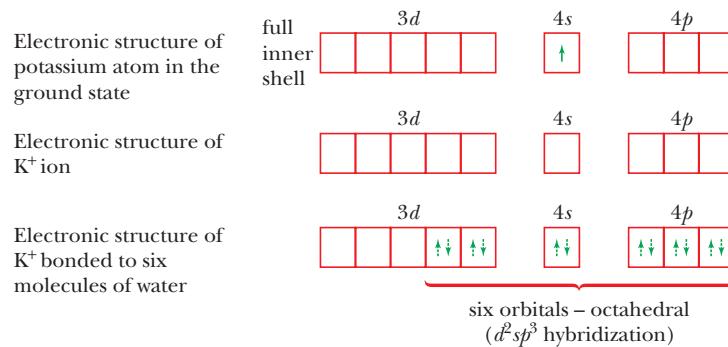
	Ionic radius (Å)	Ionic mobility at infinite dilution	Approx. radius hydrated ion (Å)	Approx. hydration number	Hydration terms		
					ΔH°	ΔS°	ΔG° (kJ mol ⁻¹)
Li^+	0.76	33.5	3.40	25.3	-544	-134	-506
Na^+	1.02	43.5	2.76	16.6	-435	-100	-406
K^+	1.38	64.5	2.32	10.5	-352	-67	-330
Rb^+	1.52	67.5	2.28	10.0	-326	-54	-310
Cs^+	1.67	68.0	2.28	9.9	-293	-50	-276

The hydration number is the average number of water molecules associated with the metal ion. The values need not be whole numbers, and are obtained by measuring the transference of water in a conductivity cell.

Some water molecules touch the metal ion and bond to it, forming a complex. These water molecules constitute the *primary shell* of water. Thus Li^+ is tetrahedrally surrounded by four water molecules. This may be explained by the oxygen atoms of the four water molecules using a lone pair to form a coordinate bond to the metal ion. With four electron pairs in the valence shell the VSEPR theory predicts a tetrahedral structure. Alternatively, using valence bond theory, the $2s$ orbital and the three $2p$ orbitals form four sp^3 hybrid orbitals which are filled by the lone pairs from the oxygen atoms.



With the heavier ions, particularly Rb⁺ and Cs⁺, the number of water molecules increases to six. VSEPR theory predicts an octahedral structure. Valence bond theory also indicates an octahedral arrangement using one *s* orbital, three *p* orbitals and two *d* orbitals for bonding.



Note that the *d* orbitals comprise a group of three (called *t_{2g}* orbitals), and a group of two (called *e_g* orbitals). Only the group of two is used for bonding.

A *secondary layer* of water molecules further hydrates the ions, though these are only held by weak ion – dipole attractive forces. The strength of such forces is inversely proportional to the distance, that is to the size of the metal ion. Thus the secondary hydration decreases from lithium to caesium, and accounts for Li⁺ being the most heavily hydrated.

The decrease in hydration from Li⁺ to Cs⁺ is also shown in the crystalline salts, for nearly all lithium salts are hydrated, commonly as trihydrates. Many sodium salts are hydrated (e.g. Na₂CO₃ · 10H₂O, Na₂CO₃ · 7H₂O and Na₂CO₃ · H₂O). Few potassium salts and no rubidium or caesium salts are hydrated.

The solubility of most of the salts of Group 1 elements in water decreases on descending the group. For a substance to dissolve the energy evolved when the ions are hydrated (hydration energy) must be larger than the energy required to break the crystal lattice (lattice energy). Conversely, if the solid is insoluble, the hydration energy is less than the lattice energy.

The reason why the solubility of most Group 1 metals decreases on descending the group is that the lattice energy only changes slightly, but the free energy of hydration changes rather more. For example, the difference in lattice energy between NaCl and KCl is 67 kJ mol⁻¹, and yet the difference in $\Delta G_{\text{hydration}}$ for Na⁺ and K⁺ is 76 kJ mol⁻¹ (Table 9.11). Thus KCl is less soluble than NaCl.

Table 9.11 Hydration and lattice energy values for Group 1 halides at 25 °C

	Free energy of hydration ΔG° (kJ mol ⁻¹)	Lattice energy (kJ mol ⁻¹)			
		MF	MCl	MBr	MI
Li ⁺	-506	-1035	-845	-800	-740
Na ⁺	-406	-908	-770	-736	-690
K ⁺	-330	-803	-703	-674	-636
Rb ⁺	-310	-770	-674	-653	-515
Cs ⁺	-276	-720	-644	-623	-590

The Group 1 fluorides and carbonates are exceptional in that their solubilities increase rapidly on descending the group (Table 9.12). The reason for this is that their lattice energies change more than the hydration energies on descending the group.

Table 9.12 Solubilities of Group 1 halides

	Solubility (Molar value first, g/100g H ₂ O given in brackets)			
	MF	MCl	MBr	MI
Li	0.1 (0.27)	19.6 (830)	20.4 (177)	8.8 (165)
Na	1.0 (4.22)	6.2 (36)	8.8 (91)	11.9 (179)
K	15.9 (92.3)	4.8 (34.7)	7.6 (67)	8.7 (144)
Rb	12.5 (130.6)	7.5 (91)	6.7 (110)	7.2 (152)
Cs	24.2 (367.0)	11.0 (186)	5.1 (108)	3.0 (79)

9.12 | SOLUTIONS OF METALS IN LIQUID AMMONIA

In the presence of impurities or catalysts such as Fe, the alkali metals react with liquid ammonia to form a metal amide and hydrogen.



If all catalysts and impurities are absent, then Group 1 metals, and to a lesser extent the elements Ca, Sr and Ba in Group 2 and the lanthanide elements Eu and Yb, dissolve directly in very high concentration in liquid ammonia. The metal can be recovered simply by allowing the ammonia to boil off. The solubilities of some Group 1 elements in ammonia are given in Table 9.13.

Table 9.13 Solubilities in liquid ammonia

Element	Solubility (g metal/100 g NH ₃)	
	-33.4 °C	0 °C
Li	10.9	11.3
Na	25.1	23.0
K	47.1	48.5

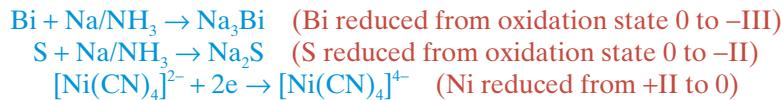
Note that -33.4 °C is the boiling point of liquid ammonia at one atmosphere pressure. The 0 °C data were measured under pressure.

Dilute solutions of alkali metals in liquid ammonia are dark blue in colour, and the main species present are solvated metal ions and solvated electrons. If the blue solution is allowed to stand, the colour slowly fades until it disappears owing to the formation of a metal amide. At concentrations above 3 M, solutions are copper-bronze coloured and have a metallic lustre because metal ion clusters are formed.

These solutions of metals in liquid ammonia conduct electricity better than any salt in any liquid, and the conductivity is similar to that of pure metals (specific conductivity of Hg = 10⁴ ohm⁻¹; Na/NH₃ = 0.5 × 10⁴ ohm⁻¹; K/NH₃ = 0.45 × 10⁴ ohm⁻¹). Conduction is mainly due to the presence of solvated electrons.

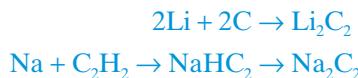
These solutions of metals in liquid ammonia act as powerful reducing agents for the elements of Groups 14, 15 and 16, for many compounds and coordination complexes, and they will even reduce an aromatic ring.

These reductions can be carried out in liquid ammonia, but not in water, because the alkali metals are stronger reducing agents than is hydrogen, and so will react with water and liberate hydrogen. The metals can exist for some time in liquid ammonia.



9.13 | COMPOUNDS WITH CARBON

If lithium is heated with carbon, an ionic carbide Li_2C_2 is formed. The other metals do not react with carbon directly, but do form similar carbides when heated with ethyne (formerly called acetylene), or when ethyne is passed through a solution of the metal in liquid ammonia.



These compounds contain the carbide ion $[\text{C}\equiv\text{C}]^{2-}$ or hydridocarbide ion $[\text{C}\equiv\text{C}-\text{H}]^-$. The most important reaction of carbides is with water, when they give ethyne (acetylene). Thus they are termed acetylides.



LiC_2H is used in the industrial manufacture of vitamin A.

The metals potassium, rubidium and caesium react with graphite by invading the space between the layers of carbon in the graphite lattice. They form highly coloured interstitial carbides that are nonstoichiometric, (that is of variable composition), ranging from C_{60}K (grey), to C_{36}K (blue), to a maximum invasion corresponding to C_8K (bronze).

9.14 | COMPLEXES, CROWNS AND CRYPTS

Group 1 metals stand out from the other groups in their weak tendency to form complexes. This is predictable because the factors favouring complex formation are small size, high charge, and empty orbitals of low energy for forming the bonds, and Group 1 metal ions are very large and have a low charge (+1).

A number of aqua complexes are known such as $[\text{Li}(\text{H}_2\text{O})_4]^+$ and a primary hydration shell of four H_2O molecules arranged tetrahedrally is found in various crystalline salts. Na^+ and K^+ also have the same primary hydration shell, but Rb^+ and Cs^+ coordinate six H_2O molecules.

However, some organic chelating agents (particularly salicaldehyde and β -diketones) are extremely strong complexing agents, and Group 1 ions form complexes with these. These ligands are very strong complexing agents because they are multidentate, that is they have more than one donor group so they form more than one bond to the metal, and also because they form a ring or chelate compound by bonding to the metal. Examples include salicaldehyde, acetylacetone, benzoylacetone, methyl salicylate, o-nitrophenol, and o-nitrocresol. The metal usually attains a coordination number of 4 or 6 (see Figure 9.1).

An important development in the chemistry of the alkali metals is the discovery of complexes with polyethers, and 'cryptate complexes' with macrocyclic molecules with nitrogen and oxygen.

An example is dibenzo-18-crown-6 (see Figure 9.2), and the name indicates that there are two benzene rings in the compound, 18 atoms make up a crown-shaped ring, and six of the ring atoms are oxygen. These six oxygen atoms may complex with a metal ion, even with large ions like Group 1 ions that are not very good at forming complexes. The organic part of the molecule is puckered to give the crown arrangement, and the oxygen atoms with their lone pairs are nearly planar about the metal ion at the centre of the ring. The bonding of the metal ion to the polyether is largely electrostatic, and a close fit between the size of the metal ion and the size of the hole in the centre of the polyether is essential. Thus a crown-4 (a cyclic polyether with four oxygens) is selective for Li^+ , Na^+ prefers crown-5, and K^+ prefers crown-6. It is possible to get complexes with the unusual coordination number of 10, for example K^+ (dibenzo-30-crown-10). Polyethers of this type act as ion carriers inside living cells to transport ions across cell membranes, and thus maintain the balance between Na^+ and K^+ inside and outside cells.

The cryptates are three-dimensional equivalents of the crown ethers, but contain nitrogen atoms which provide branching and act as extra donor sites in addition to the oxygen atoms to bond to the metal ion. They are called cryptates because they wrap round and hide the cation. A typical crypt is the molecule $\text{N}[\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2]_3\text{N}$ (Figure 9.3). This is called (cryptand-222) and forms a complex $[\text{Rb}(\text{crypt})]\text{CNS} \cdot \text{H}_2\text{O}$ in which six oxygen atoms and two nitrogen atoms in the crypt molecule bond to the metal ion, giving the metal ion a coordination number of 8. The complex presents a hydrocarbon exterior, and so is soluble in organic solvents.

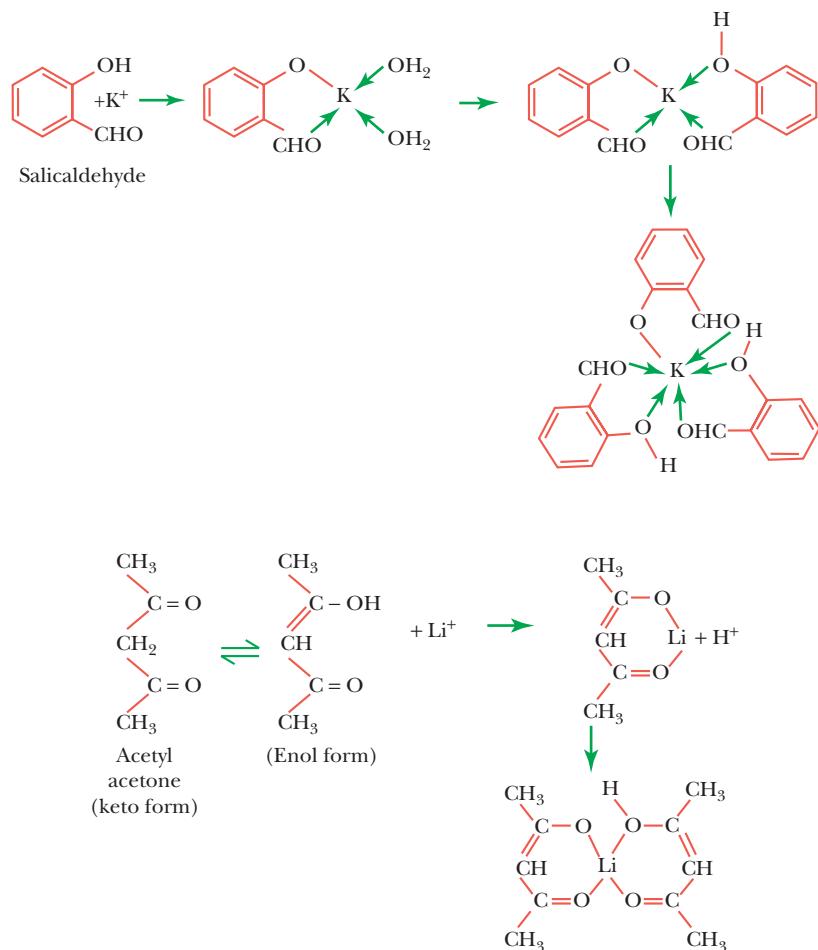


Figure 9.1 Salicaldehyde and acetylacetone complexes.

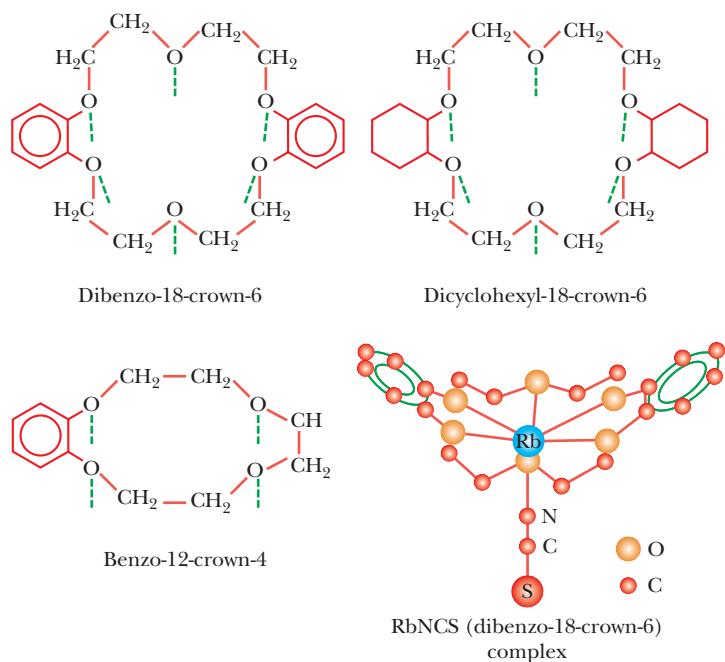


Figure 9.2 Structures of some crown ethers.

An unusual compound $[\text{Na}(\text{cryptand-222})]^+\text{Na}^-$ can be formed by cooling a solution of Na in ethylamine with cryptand-222. This is a golden-yellow, diamagnetic solid which is only stable below -10°C . The interesting feature is that it contains Na^- , the sodide ion. Crystallographic studies show that the radius of Na^- is about 2.3 \AA . Electron transfer has occurred between two sodium atoms, forming Na^+ and Na^- . The large crypt ligand completely shields the Na^+ ion and prevents it recombining with Na^- . Other alkalide compounds containing K^- potasside, Rb^- rubidide and Cs^- caesium ions have been made in a similar way. They are all yellow-brown in colour, and are less stable.

If the reaction is carried out with an excess of cryptand, some unusual complexes called electrides are formed. These are black solids and are paramagnetic, so they contain unpaired electrons. They have formulae such as $[\text{Cs}^+(\text{cryptand-222})]^-[(\text{cryptand-222}) \cdot e^-]$ in which an electron is trapped in a hole of radius approximately 2.4 \AA .

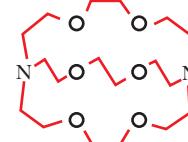


Figure 9.3 Cryptand-222 ligand.

9.15 | BIOLOGICAL IMPORTANCE

Living organisms require at least 27 elements, of which 15 are metals. Metals required in major quantities are K, Mg, Na and Ca. Minor quantities of Mn, Fe, Co, Cu, Zn and Mo, and trace amounts of V, Cr, Sn, Ni and Al, are required by at least some organisms.

Bulk quantities of Group 1 and 2 metals are required, mainly to balance the electrical charges associated with negatively charged organic macro-molecules in the cell, and also to maintain the osmotic pressure inside the cell, to keep it turgid and prevent its collapse.

In view of the close similarity of chemical properties between Na and K, it is surprising that their biological functions are very different. Na^+ ions are actively expelled from cells, whereas K^+ ions are not. This ion transport is sometimes called a sodium pump, and it involves both the active expulsion of Na^+ and the active take-up of K^+ . Analysis of the fluids inside and outside animal cells shows that ion transport really does occur. In animal cells the concentration of K^+ is about 0.15 M and the concentration of Na^+ is about 0.01 M . In body fluids (lymph and blood) the concentrations of K^+ and Na^+ are about 0.003 M and 0.15 M respectively. The transport of ions requires energy, and this is obtained by the hydrolysis of ATP. It is estimated that hydrolysis of one ATP molecule to ADP provides enough energy to move three Na^+ ions out of the cell, and two K^+ and one H^+ ions back in to the cell. The mechanism for ion transport involves polyethers natural to the organism.

The different ratio of Na^+ to K^+ inside and outside cells produces an electrical potential across the cell membrane, which is essential for the functioning of nerve and muscle cells. The movement of glucose into cells is associated with Na^+ ions; they enter the cell together. This is favoured by a high concentration gradient. The Na^+ ions entering the cell in this way must then be expelled. The movement of amino acids is similar. K^+ ions inside the cell are essential for the metabolism of glucose, the synthesis of proteins, and the activation of some enzymes.

The 1987 Nobel Prize for Chemistry was awarded to C. J. Pedersen, J.M. Lehn and D. Cram for their work on the discovery and applications of crown ethers and cryptates.

9.16 | DIFFERENCES BETWEEN LITHIUM AND THE OTHER GROUP 1 ELEMENTS

The properties of lithium and its compounds differ far more from those of the other Group 1 elements than the other Group 1 elements and compounds differ among themselves. Apart from having the same oxidation number as the rest of Group 1, lithium compounds may show closer similarities with Group 2 elements (particularly magnesium) than they show towards their own group. Some of the differences are set out below:

1. The melting and boiling points of lithium metal are much higher than those for the other Group 1 elements.

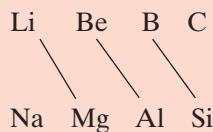
2. Lithium is much harder than the other Group 1 metals.
3. Lithium reacts the least readily with oxygen, forming the normal oxide. It forms a peroxide only with great difficulty, and the higher oxides are unstable.
4. Lithium hydroxide is less basic than the other hydroxides in the group, and therefore many of its salts are less stable. Li_2CO_3 , LiNO_3 and LiOH all form the oxide on gentle heating, though the analogous compounds of the rest of the group are stable. Another example of the less basic nature is that though lithium forms a bicarbonate in solution, it does not form a solid bicarbonate, whereas the others all form stable solid bicarbonates.
5. Lithium forms a nitride Li_3N . None of the other Group 1 elements forms a nitride, but Group 2 elements form nitrides.
6. Lithium reacts directly with carbon to form an ionic carbide. None of the other Group 1 elements do this, but Group 2 elements all react similarly with carbon.
7. Lithium has a greater tendency to form complexes than have the heavier elements, and ammoniated salts such as $[\text{Li}(\text{NH}_3)_4]\text{I}$ exist as solids.
8. Li_2CO_3 , Li_3PO_4 and LiF are all insoluble in water, and LiOH is only sparingly soluble. The rest of Group 1 form soluble compounds, but the corresponding magnesium salts are insoluble or sparingly soluble.
9. The halides and alkyls of lithium are far more covalent than the corresponding sodium compounds, and because of this covalency they are soluble in organic solvents.
10. The lithium ion itself, and also its compounds, are more heavily hydrated than those of the rest of the group.

Several generalizations may be drawn from this apparently anomalous behaviour of lithium.

The first element in each of the main groups (Li, Be, B, C, N, O and F) differs from the rest of the group. This is partly because the first element is much smaller than the subsequent elements, and consequently it is more likely to form covalent compounds (Fajans' rules) and complexes.

The first element in a group can form a maximum of four conventional electron pair bonds. This is because the outer shell of electrons contains only one s orbital and three p orbitals. The subsequent elements can use d orbitals for bonding: they can attain a coordination number of 6, by using one s , three p and two d orbitals. For this reason the coordination number attained by a complex or a covalent compound of the first element in a group is commonly 4 and for the subsequent elements the coordination number is commonly 6.

The similarity between lithium (the first member of Group 1) and magnesium (the second element in Group 2) is called a diagonal relationship. Diagonal relationships also exist between other pairs of elements Be and Al, B and Si as shown:



The diagonal relationship arises because of the effects of both size and charge. On descending a group, the atoms and ions increase in size. On moving from left to right in the periodic table, the size decreases. Thus on moving diagonally, the size remains nearly the same. For example, lithium is smaller than sodium, and magnesium is also smaller than sodium, and hence lithium and magnesium are similar in size. The sizes of $\text{Li}^+ = 0.76 \text{ \AA}$ and $\text{Mg}^{2+} = 0.72 \text{ \AA}$ are close, and so in situations where size is important their behaviour should be similar.

Beryllium and aluminium also show a diagonal relationship. In this case the sizes are not so close ($\text{Be}^{2+} = 0.45 \text{ \AA}$ and $\text{Al}^{3+} = 0.535 \text{ \AA}$), but the charge per unit area is similar ($\text{Be}^{2+} 2.36$ and $\text{Al}^{3+} 2.50$) because the charges are 2+ and 3+ respectively.

$$\text{Charge per unit area} = \frac{(\text{ionic charge})}{4 \pi \cdot (\text{ionic radius})^2}$$

It is sometimes suggested that the diagonal relationship arises because of a diagonal similarity in electronegativity values.

Li	Be	B	C
1.0	1.5	2.0	2.5
Na	Mg	Al	Si
0.9	1.2	1.5	1.8

Since ionic size and electronegativity are closely related, this is part of the same picture.

9.17 | PREPARATION OF SODIUM HYDROXIDE

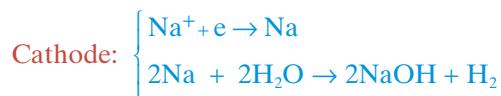
NaOH and Cl₂ are produced simultaneously by the electrolysis of an aqueous solution of NaCl. NaOH is the most important alkali used in industry, and Cl₂ is also an extremely important industrial chemical. Sodium carbonate is included with the other two chemicals for two reasons – first because in many applications such as making paper, soap and detergents it can be used interchangeably with sodium hydroxide, and second because Na₂CO₃ can quite easily be converted into NaOH (or vice versa) using the lime–caustic soda process. In this process, the reaction is reversible, and depending on the relative demands and cost of sodium carbonate and sodium hydroxide it may be used in either direction. Nowadays the reverse reaction is carried out on a limited scale, converting Na₂CO₃ to NaOH.



All three chemicals are classed as 'heavy inorganic chemicals' because of the very large tonnages involved.

9.18 | ELECTROLYTIC PROCESSES

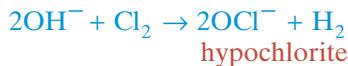
In the electrolysis of brine, reactions occur at both the anode and the cathode.



Side reactions may also occur if the products mix:



or



and also another reaction may occur to a small extent at the anode:

The electrolysis of brine is carried out on industrial scale using two types of cells—diaphragm and mercury cathode that were first developed in 1890's.



Diaphragm cell

In a diaphragm cell (Figure 9.4), brine is constantly added, and NaOH and Cl₂ are produced continuously. A porous diaphragm of asbestos is used to keep the H₂ and Cl₂ gases (produced at the electrodes) separated from one another. If H₂ and Cl₂ gases mix they react, and the reaction may be explosive. In daylight (and more so in sunlight) a photolytic reaction takes place which produces chlorine atoms. These lead to an explosive chain reaction with hydrogen.

The diaphragm also separates the anode and cathode compartments. This reduces the chance that NaOH produced in the cathode compartment can mix and react with Cl₂ produced in the anode compartment. This reduces the chance of the side reaction producing sodium hypochlorite, NaOCl. However, some sodium

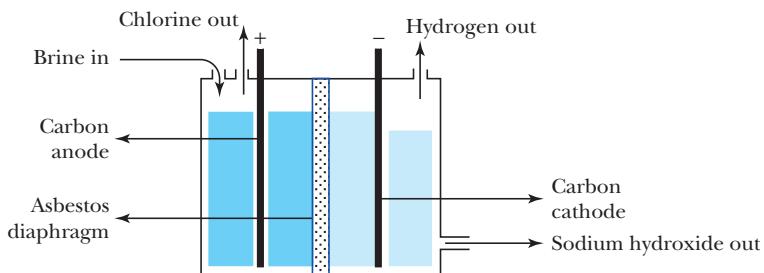


Figure 9.4 A diaphragm cell.

hydroxide or OH^- may diffuse into the other compartment, and this is inhibited by maintaining the level of electrolyte higher in the anode compartment than in the cathode compartment, so there is a small positive flow from the anode to the cathode compartment. Traces of dioxygen are produced in a side reaction. This reacts with the carbon electrodes, gradually destroying them and forming CO_2 .

Less than half the NaCl is converted to NaOH , and a mixture of about 11% NaOH and 16% NaCl is usually obtained. This solution is concentrated in a steam evaporator, when a considerable amount of NaCl crystallizes out, giving a final solution containing 50% NaOH and 1% NaCl . *It is important to note that NaOH made in this way always contains some NaCl .*

Mercury cathode cell

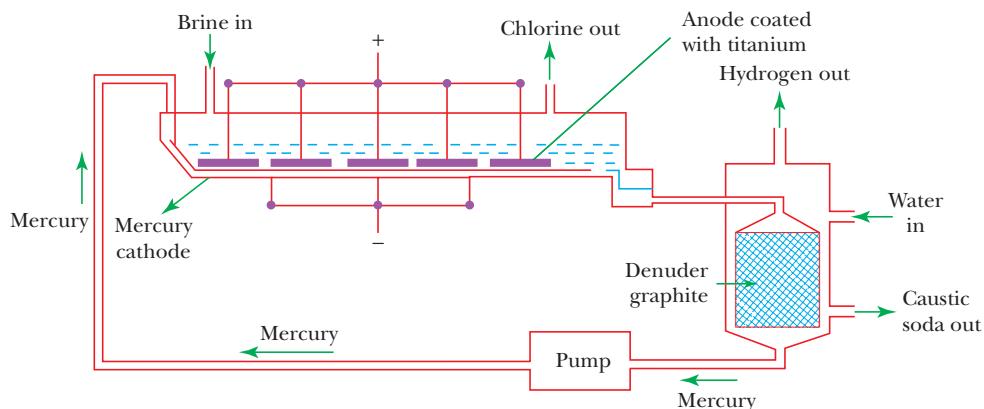
During the electrolysis of brine, Na^+ ions migrate towards the cathode, and when they get there the ions are discharged.



If the cathode is made of mercury, the Na atoms produced dissolve in the mercury and form an amalgam, or loose alloy. The amalgam is pumped to a different compartment called the denuder, where water trickles over lumps of graphite (here acting as an inert solid). The water and the Na in the amalgam react, and in this way *pure* NaOH at 50% strength is obtained.



The clean mercury is recycled back to the electrolysis tank. Originally the anodes were made of graphite, but because traces of dioxygen are produced in a side reaction they become pitted, owing to the formation of CO_2 . The anodes are now made of steel coated with titanium. (See Figure 9.5.) Titanium is very resistant to corrosion, and this not only overcomes the problem of pitting and forming CO_2 , but also lowers the electrical resistance.

Figure 9.5 Mercury cathode cell for Cl_2 and NaOH .

9.19 | PREPARATION OF SODIUM CARBONATE

Most of the Na_2CO_3 is produced synthetically by the Solvay (ammonia–soda) process. However, since prehistoric times a natural deposit called Trona, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, has been obtained from dried-up lake beds in Egypt. Large amounts are now mined, particularly in the USA and Kenya. Trona is sometimes called sodium sesquicarbonate (*sesqui* means one and a half), and this is converted to sodium carbonate by heating.



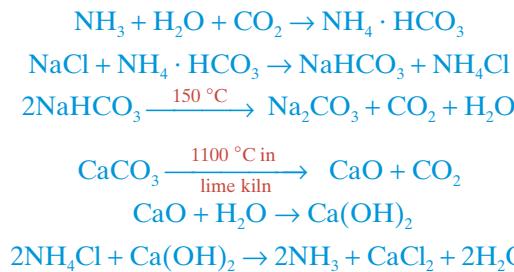
It is mentioned earlier that sodium carbonate (soda ash) can be used instead of NaOH in applications such as making paper, soap and detergents, and that sodium carbonate can be used to make NaOH by the lime–caustic soda process. However, as NaOH is at present cheap and plentiful, not much sodium carbonate is used for these purposes. With the increased use of detergents, there has been a decline in the use of ‘washing soda’ $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ for water softening.

9.20 | THE SOLVAY (OR AMMONIA – SODA) PROCESS

There have been many attempts to make Na_2CO_3 , by using the overall reaction:



The process is much more complicated than the overall equation implies, and to make things worse the reaction is reversible and only 75% of the NaCl is converted. The first stage in the process is to purify saturated brine, and then react it with gaseous ammonia. The ammoniated brine is then carbonated with CO_2 , forming NaHCO_3 . This is insoluble in the brine solution because of the common ion effect and so can be filtered off, and on heating to 150°C it decomposes to anhydrous Na_2CO_3 (called light soda ash in industry because it is a fluffy solid with a low packing density of about 0.5 g cm^{-3}). Next CO_2 is stripped (removed) by heating the solution, and the CO_2 is reused. Then the NH_3 is driven off by adding alkali (a slurry of lime in water), and the ammonia is reused. Lime (CaO) is obtained by heating limestone (CaCO_3), and this also provides the CO_2 required. When lime is mixed with water it gives $\text{Ca}(\text{OH})_2$.



Thus the materials consumed are NaCl and CaCO_3 , and there is one useful product, Na_2CO_3 , and one byproduct, CaCl_2 . There is little requirement for CaCl_2 , so only a little is recovered from solution, and the rest is wasted. The largest use of Na_2CO_3 is for glass making, and this requires ‘heavy ash’, which is $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. To obtain this, the ‘light ash’ produced in the Solvay process (which is anhydrous Na_2CO_3) is recrystallized from hot water.

GROUP 2 – THE ALKALINE EARTH ELEMENTS

The Group 2 elements show the same trends in properties as were observed with Group 1. However, beryllium stands apart from the rest of the group, and differs much more from them than lithium does from the rest of Group 1. The main reason for this is that the beryllium atom and Be^{2+} are both extremely small, and the relative increase in size from Be^{2+} to Mg^{2+} is four times greater than the increase between Li^+ and Na^+ . Beryllium also shows some diagonal similarities with aluminium in Group 13. Beryllium and barium compounds are all very toxic.

The elements form a well graded series of highly reactive metals, but are less reactive than Group 1. They are typically divalent, and generally form colourless ionic compounds. The oxides and hydroxides are

less basic than those of Group 1: hence their oxosalts (carbonates, sulphates, nitrates) are less stable to heat. Magnesium is an important structural metal, and is used in large amounts. Several compounds are used in vast quantities: limestone (CaCO_3) is used to make quicklime CaO and cement, and large amounts of chalk are also used. Other compounds used on a large scale include gypsum CaSO_4 fluorite CaF_2 (magnesite MgCO_3 and barytes BaSO_4).

Mg^{2+} and Ca^{2+} are essential elements in the human body, and Mg^{2+} is an important constituent of chlorophyll.

9.21 | GENERAL PROPERTIES

Electronic structure

All Group 2 elements have two s electrons in their outer shell. Ignoring the filled inner orbitals, their electronic structures may be written $2s^2$, $3s^2$, $4s^2$, $5s^2$, $6s^2$ and $7s^2$ (Table 9.14).

Table 9.14 Electronic structures

Element	Symbol	Electronic structure	
Beryllium	Be	$1s^2 2s^2$	or $[\text{He}] 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$	or $[\text{Ne}] 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	or $[\text{Ar}] 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$	or $[\text{Kr}] 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$	or $[\text{Xe}] 6s^2$
Radium	Ra		$[\text{Rn}] 7s^2$

Size of atoms and ions

Group 2 atoms are large, but are smaller than the corresponding Group 1 elements as the extra charge on the nucleus draws the orbital electrons in. Similarly the ions are large, but are smaller than those of Group 1, especially because the removal of two orbital electrons increases the effective nuclear charge even further. Thus, these elements have higher densities than Group 1 metals (Table 9.15).

Table 9.15 Size and density

	Metallic radius (\AA)	Ionic radius M^{2+} six-coordinate (\AA)	Density (g cm^{-3})
Be	1.12	0.31*	1.85
Mg	1.60	0.72	1.74
Ca	1.97	1.00	1.55
Sr	2.15	1.18	2.63
Ba	2.22	1.35	3.62
Ra		1.48	5.5

*Four-coordinate radius, six-coordinate value = 0.45 \AA .

Group 2 metals are silvery white in colour. They have two valency electrons which may participate in metallic bonding, compared with one electron for Group 1 metals. Consequently Group 2 metals are harder, have higher cohesive energy, and have much higher melting points and boiling points than Group 1 elements (see Table 9.16), but the metals are relatively soft. The melting points do not vary regularly, mainly because the metals adopt different crystal structures.

Table 9.16 Melting and boiling points of Group 1 and 2 elements

	Melting point (°C)	Boiling point (°C)		Melting point (°C)	Boiling point (°C)
Be	1287	(2500)	Li	181	1347
Mg	649	1105	Na	98	881
Ca	839	1494	K	63	766
Sr	768	1381	Rb	39	688
Ba	727	(1850)	Cs	28.5	705
Ra	(700)	(1700)			

Figures in brackets are approximate.

Ionization energy

The third ionization energy is so high that M^{3+} ions are never formed. The ionization energy for Be^{2+} is high, and its compounds are typically covalent. Mg also forms some covalent compounds. However, the compounds formed by Mg, Ca, Sr and Ba are predominantly divalent and ionic. Since the atoms are smaller than those in Group 1, the electrons are more tightly held so that the energy needed to remove the first electron (first ionization energy) is greater than for Group 1. Once one electron has been removed, the ratio of charges on the nucleus to orbital electrons is increased, so that the remaining electrons are more tightly held. Hence the energy needed to remove a second electron is nearly double that required for the first (Table 9.17). The total energy required to produce gaseous divalent ions for Group 2 elements (first ionization energy + second ionization energy) is over four times greater than the energy required to produce M^+ from Group 1 metals. The fact that ionic compounds are formed shows that the energy given out when a crystal lattice is formed more than offsets that used in producing ions.

Table 9.17 Ionization energies and electronegativity

	Ionization energy (kJ mol ⁻¹)			Pauling's electronegativity
	1st	2nd	3rd	
Be	899	1757	14 847	1.5
Mg	737	1450	7731	1.2
Ca	590	1145	4910	1.0
Sr	549	1064		1.0
Ba	503	965		0.9
Ra	509	979	(3281)	

Estimated value in brackets.

Electronegativity

The electronegativity values of Group 2 elements are low, but are higher than the values for Group 1. When Mg, Ca, Sr and Ba react with elements such as the halogens and dioxygen at the right hand side of the periodic table, the electronegativity difference is large and the compounds are ionic.

The value for Be is higher than for the others. BeF_2 has the biggest electronegativity difference for a compound of Be and so is the most likely compound of Be to be ionic. BeF_2 has a very low conductivity when fused, and is regarded as covalent.

Hydration energies

The hydration energies of the Group 2 ions are four or five times greater than for Group 1 ions. This is largely due to their smaller size and increased charge, and $\Delta H_{\text{hydration}}$ decreases down the group as the size of the ions increases (Table 9.18). In the case of Be a further factor is the very strong complex $[Be(H_2O)_4]^{2+}$

that is formed. The crystalline compounds of Group 2 contain more water of crystallization than the corresponding Group 1 compounds. Thus NaCl and KCl are anhydrous but $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ all have water of crystallization. Note that the number of molecules of water of crystallization decreases as the ions become larger.

Table 9.18 Hydration energies

	Ionic radius (Å)	ΔH hydration (kJ mol ⁻¹)
Be^{2+}	0.31*	-2494
Mg^{2+}	0.72	-1921
Ca^{2+}	1.00	-1577
Sr^{2+}	1.18	-1443
Ba^{2+}	1.35	-1305

* Four-coordinate radius.

Since the divalent ions have a noble gas structure with no unpaired electrons, their compounds are diamagnetic and colourless, unless the acid radical is coloured.

Solubility and lattice energy

The solubility of most salts decreases with increased atomic weight, though the usual trend is reversed with the fluorides and hydroxides in this group. Solubility depends on the lattice energy of the solid, and the hydration energy of the ions as explained below.

Some lattice energy values for Group 2 compounds are listed in Table 9.19. The lattice energies are much higher than the values for Group 1 compounds, because of the effect of the increased charge on the ions. Taking any one particular negative ion, the lattice energy decreases as the size of the metal increases. The hydration energy also decreases as the metal ions become larger (Table 9.20).

Table 9.19 Lattice energies of some compounds (kJ mol⁻¹)

	MO	MCO_3	MF_2	MI_2
Mg	-3923	-3178	-2906	-2292
Ca	-3517	-2986	-2610	-2058
Sr	-3312	-2718	-2459	
Ba	-3120	-2614	-2367	

Table 9.20 Enthalpies of hydration

	ΔH (kJ mol ⁻¹)
Be^{2+}	-2494
Mg^{2+}	-1921
Ca^{2+}	-1577
Sr^{2+}	-1443
Ba^{2+}	-1305

Solutions of the metals in liquid ammonia

The metals Ca, Sr and Ba dissolve in liquid ammonia as do the Group 1 metals. Dilute solutions are bright blue in colour due to the spectrum from the solvated electron. These solutions decompose very slowly, forming amides and evolving hydrogen, but the reaction is accelerated by many transition metals and their compounds.



Evaporation of the ammonia from solutions of Group 1 metals yields the metal, but with Group 2 metals evaporation of ammonia gives hexammoniates of the metals. These slowly decompose to give amides



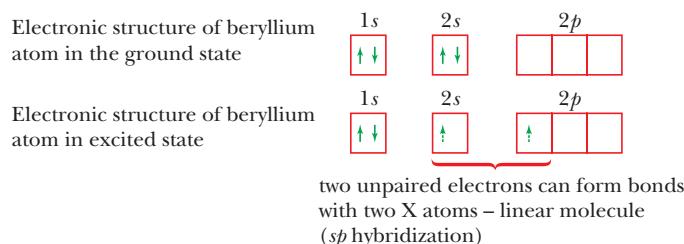
Concentrated solutions of the metals in ammonia are bronze coloured, due to the formation of metal clusters.

9.22 | ANOMALOUS BEHAVIOUR OF BERYLLIUM

Be differs from the rest of the group for three reasons.

1. It is extremely small, and Fajans' rules state that small highly charged ions tend to form covalent compounds.
2. Be has a comparatively high electronegativity. Thus when beryllium reacts with another atom, the difference in electronegativity is seldom large, which again favours the formation of covalent compounds. Even BeF_2 (electronegativity difference 2.5) and BeO (electronegativity difference 2.0) show evidence of covalent character.
3. Be is in the second row of the periodic table, and the outer shell can hold a maximum of eight electrons. (The orbitals available for bonding are one $2s$ and three $2p$ orbitals.) Thus Be can form a maximum of four conventional electron pair bonds, and in many compounds the maximum coordination number of Be is 4. The later elements can have more than eight outer electrons, and may attain a coordination number of 6 using one s , three p and two d orbitals for bonding.

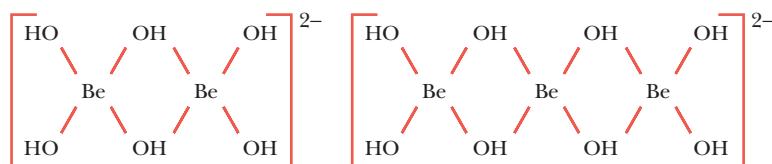
Thus we should expect Be to form mainly covalent compounds, and commonly have a coordination number of 4. Anhydrous compounds of Be are predominantly two-covalent, and BeX_2 molecules should be linear.



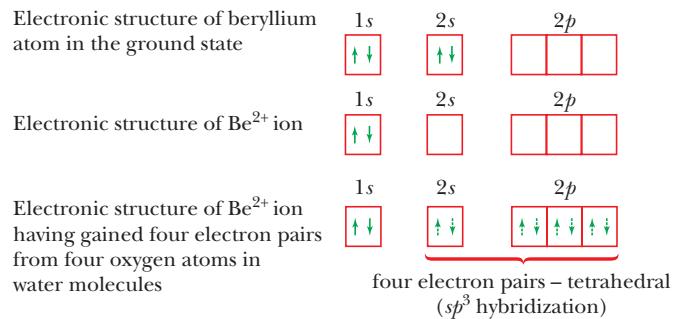
In fact linear molecules exist only in the gas phase, as this electronic arrangement has not filled the outer shell of electrons. In the solid state fourfold coordination is always achieved. There are several ways by which this can be achieved:

1. Two ligands that have a lone pair of electrons may form coordinate bonds using the two unfilled orbitals in the valence shell of Be. Thus two F^- ions might coordinate to BeF_2 , forming $[\text{BeF}_4]^{2-}$. Similarly diethyl ether can coordinate to $\text{Be}^{(\text{II})}$ in BeCl_2 , forming $[\text{BeCl}_2(\text{OEt}_2)]_2$.
2. The BeX_2 molecules may polymerize to form chains, containing bridging halogen groups, for example $(\text{BeF}_2)_n$, $(\text{BeCl}_2)_n$. Each halogen forms one normal covalent bond, and uses a lone pair to form a coordinate bond.
3. $(\text{BeMe}_2)_n$ has essentially the same structure as $(\text{BeCl}_2)_n$ but the bonding in the methyl compound is best regarded as three-centre two-electron bonds covering one Me and two Be atoms.
4. A covalent lattice may be formed with a zinc blende or wurtzite structure (coordination number 4), for example by BeO and BeS .

In water beryllium salts are extensively hydrolyzed to give a series of hydroxo complexes of unknown structure. They may be polymeric and of the type:



If alkali is added to these solutions the polymers break down to give the simple mononuclear beryllate ion $[\text{Be}(\text{OH})_4]^{2-}$, which is tetrahedral. Many beryllium salts contain the hydrated ion $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ rather than Be^{2+} , and the hydrated ion too is a tetrahedral complex ion. Note that the coordination number is 4. Forming a hydrated complex increases the effective size of the beryllium ion, thus spreading the charge over a larger area. Stable ionic salts such as $[\text{Be}(\text{H}_2\text{O})_4]\text{SO}_4$, $[\text{Be}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ and $[\text{Be}(\text{H}_2\text{O})_4]\text{Cl}_2$ are known.



Beryllium salts are acidic when dissolved in pure water because the hydrated ion hydrolyses, producing H_3O^+ . This happens because the Be–O bond is very strong, and so in the hydrated ion this weakens the O–H bonds, and hence there is a tendency to lose protons. The initial reaction is



but this may be followed by further polymerization, involving hydroxobridged structures $[\text{Be}_2\text{OH}]^{3+}$, $[\text{Be}_3(\text{OH})_4]^{3+}$. In alkaline solutions $[\text{Be}(\text{OH})_4]^{2-}$ is formed. The other Group 2 salts do not interact so strongly with water, and do not hydrolyze appreciably.

Beryllium salts rarely have more than four molecules of water of crystallization associated with the metal ion, because there are only four orbitals available in the second shell of electrons, whereas magnesium can have a coordination number of 6 by using some $3d$ orbitals as well as $3s$ and $3p$ orbitals.

9.23 | CHEMICAL PROPERTIES

Some important reactions of Group 2 elements are listed in Table 9.21

Table 9.21 Some reactions of Group 2 elements

Reaction	Comment
$\text{M} + 2\text{H}_2\text{O} \rightarrow \text{M}(\text{OH})_2 + \text{H}_2$	Be probably reacts with steam, Mg with hot water, and Ca, Sr and Ba react rapidly with cold water
$\text{M} + 2\text{HCl} \rightarrow \text{MCl}_2 + \text{H}_2$	All the metals react with acids, liberating hydrogen
$\text{Be} + \text{NaOH} \rightarrow \text{Na}_2[\text{Be}(\text{OH})_4] + \text{H}_2$	Be is amphoteric
$2\text{M} + \text{O}_2 \rightarrow 2\text{MO}$	Normal oxide formed by all group members with excess dioxygen
$\text{Ba} + \text{O}_2 \rightarrow \text{BaO}_2$	Ba also forms the peroxide
$\text{M} + \text{H}_2 \rightarrow \text{MH}_2$	Ionic ‘salt-like’ hydrides formed at high temperatures by Ca, Sr and Ba
$3\text{M} + \text{N}_2 \rightarrow \text{M}_3\text{N}_2$	All form nitrides at high temperatures
$3\text{M} + 2\text{P} \rightarrow \text{M}_3\text{P}_2$	All the metals form phosphides at high temperatures
$\text{M} + \text{S} \rightarrow \text{MS}$	All the metals form sulphides
$\text{M} + \text{Se} \rightarrow \text{MSe}$	All the metals form selenides
$\text{M} + \text{Te} \rightarrow \text{MTe}$	All the metals form tellurides
$\text{M} + \text{F}_2 \rightarrow \text{MF}_2$	All the metals form fluorides
$\text{M} + \text{Cl}_2 \rightarrow \text{MCl}_2$	All the metals form chlorides
$\text{M} + \text{Br}_2 \rightarrow \text{MBr}_2$	All the metals form bromides
$\text{M} + \text{I}_2 \rightarrow \text{MI}_2$	All the metals form iodides
$3\text{M} + 2\text{NH}_3 \rightarrow 2\text{M}(\text{NH}_2)_2$	All the metals form amides at high temperatures

Reaction with water

The reduction potential of beryllium is much less than those for the rest of the group. (Standard electrode potentials E° of $\text{Be}^{2+}|\text{Be}$ -1.85 , $\text{Mg}^{2+}|\text{Mg}$ -2.37 , $\text{Ca}^{2+}|\text{Ca}$ -2.87 , $\text{Sr}^{2+}|\text{Sr}$ -2.89 , $\text{Ba}^{2+}|\text{Ba}$ -2.91 , $\text{Ra}^{2+}|\text{Ra}$ -2.92 volts.)

This indicates that beryllium is much less electropositive (less metallic) than the others, and beryllium does not react with water. There is some doubt whether it reacts with steam to form the oxide BeO , or fails to react at all.

Ca, Sr and Ba have reduction potentials similar to those of the corresponding Group 1 metals, and are quite high in the electrochemical series. They react with cold water quite readily, liberating hydrogen and forming metal hydroxides.



Magnesium has an intermediate value, and it does not react with cold water but it decomposes hot water.



or



Mg forms a protective layer of oxide, so despite its favourable reduction potential it does not react readily unless the oxide layer is removed by amalgamating with mercury. In the formation of the oxide film it resembles aluminium.

9.24 | HYDROXIDES

$\text{Be}(\text{OH})_2$ is amphoteric, but the hydroxides of Mg, Ca, Sr and Ba are basic. The basic strength increases from Mg to Ba, and Group 2 shows the usual trend that basic properties increase on descending a group.

Solutions of $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ are called lime water and baryta water respectively, and are used to detect carbon dioxide. When CO_2 is bubbled through these solutions, they become 'turbid' or 'milky' due to the formation of a suspension of solid particles of CaCO_3 or BaCO_3 . If excess CO_2 is passed through these 'milky' solutions then the turbidity disappears as soluble bicarbonates form with the excess CO_2 . Baryta water is rather too sensitive as it gives a positive test for CO_2 by exhaling breath on it, whereas with lime water, breath (or other gas) must be blown through the solution as bubbles.



The bicarbonates of Group 2 metals are only stable in solution. Caves in limestone regions often have stalactites growing down from the roof, and stalagmites growing up from the floor. Water percolating through the limestone contains some $\text{Ca}^{2+}(\text{HCO}_3^-)_2$ in solution. The soluble bicarbonate decomposes slowly into the insoluble carbonate, and this results in the slow growth of the stalactites and stalagmites.



9.25 | HARDNESS OF WATER

Hard water contains dissolved salts such as magnesium and calcium carbonates, bicarbonates or sulphates. It is difficult to produce lather from soap with hard water, and an insoluble scum is formed. The metal ions Ca^{2+} and Mg^{2+} react with the stearate ions from the soap, forming an insoluble scum of calcium stearate before any lather is produced. Hard water also produces scale (insoluble deposits) in water pipes, boilers, and kettles.

'Temporary hardness' is due to the presence of $\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$. It is called 'temporary' because it can be removed by boiling, which drives off CO_2 and upsets the equilibrium.



Thus the bicarbonates decompose into carbonates, and calcium carbonate is precipitated. If this is filtered off, or allowed to settle, the water is free from hardness. Temporary hardness can also be removed by adding slaked lime to precipitate calcium carbonate. This is called 'lime softening', and by operating at pH 10.5, temporary hardness due to HCO_3^- can be almost completely removed.

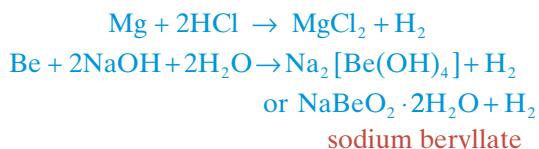


‘Permanent hardness’ is not removed by boiling, and is due mainly to $MgSO_4$ or $CaSO_4$ in solution. Small quantities of pure water are prepared in the laboratory either by distilling the water, or by passing it through an ion-exchange resin, when the Ca^{2+} and Mg^{2+} ions are replaced by Na^+ . The sodium salts do not affect the lathering power. Ion-exchange methods are widely used in industry. Water may also be softened by adding various phosphates, such as trisodium phosphate Na_3PO_4 , sodium pyrophosphate $Na_4P_2O_7$, sodium tripolyphosphate $Na_5P_3O_{10}$, or Grahams salt (Calgon) $(NaPO_3)_n$. These form a complex with the calcium and magnesium ions and ‘sequester’ them, that is keep them in solution. At one time large quantities of sodium carbonate were used in the lime–soda process to soften water. The effect of adding Na_2CO_3 is to precipitate $CaCO_3$.



9.26 | REACTION WITH ACIDS AND BASES

The metals all react with acids and liberate H_2 , although Be reacts slowly. Be is rendered passive by concentrated HNO_3 , i.e. it does not react. This is because concentrated HNO_3 is a strong oxidizing agent and it forms a very thin layer of oxide on the surface of the metal, which protects it from further attack by the acid. Be is amphoteric, as it also reacts with $NaOH$, giving H_2 and sodium beryllate. Mg, Ca, Sr and Ba do not react with $NaOH$, and are purely basic. This illustrates that basic properties increase on descending the group.



9.27 | OXIDES AND PEROXIDES

All the elements in this group burn in O_2 to form oxides MO . Be metal is relatively unreactive in the massive form, and does not react below $600^\circ C$, but the powder is much more reactive and burns brilliantly. The elements also burn in air, forming a mixture of oxide and nitride. Mg burns with dazzling brilliance in air, and evolves a lot of heat. This is used to start a thermite reaction with aluminium, and also to provide light in flash photography using light bulbs, not electronics.



BeO is usually made by ignition of the metal, but the other metal oxides are usually obtained by thermal decomposition of the carbonates MCO_3 . Other oxosalts such as $M(NO_3)_2$ and MSO_4 , and also $M(OH)_2$, all decompose to the oxide on heating. The oxosalts are less stable to heat than the corresponding Group 1 salts because the metals and their hydroxides are less basic than those of Group 1.

CaO (quicklime) is made in enormous quantities by heating $CaCO_3$ in a lime kiln.



MgO is not very reactive, especially if it has been ignited at high temperatures, and for this reason it is used as a refractory. BeO is also used as a refractory. They combine a number of properties that make them useful for lining furnaces. These factors are:

1. High melting points (BeO approx. $2500^\circ C$, MgO approx. $2800^\circ C$).
2. Very low vapour pressures.
3. Very good conductors of heat.
4. Chemical inertness.
5. Electrical insulators.

All Be compounds should be used with care as they are toxic and dust or smoke cause berylliosis.

CaO , SrO and BaO react exothermically with water, forming hydroxides.



$\text{Mg}(\text{OH})_2$ is extremely insoluble in water (approx. $1 \times 10^{-4} \text{ g l}^{-1}$ at 20°C) but the other hydroxides are soluble and the solubility increases down the group ($\text{Ca}(\text{OH})_2$ approx. 2 g l^{-1} ; $\text{Sr}(\text{OH})_2$ approx. 8 g l^{-1} ; $\text{Ba}(\text{OH})_2$ approx. 39 g l^{-1}). $\text{Be}(\text{OH})_2$ is soluble in solutions containing an excess of OH^- , and is therefore amphoteric. $\text{Mg}(\text{OH})_2$ is weakly basic, and is used to treat acid indigestion. The other hydroxides are strong bases. $\text{Ca}(\text{OH})_2$ is called slaked lime.

BeO is covalent and has a 4:4 zinc sulphide (wurtzite) structure, but all the others are ionic and have a 6:6 sodium chloride structure.

As the atoms get larger, the ionization energy decreases and the elements also become more basic. BeO is insoluble in water but dissolves in acids to give salts, and in alkalis to give beryllates, which on standing precipitate as the hydroxide. BeO is therefore amphoteric. MgO reacts with water, forming $\text{Mg}(\text{OH})_2$ which is weakly basic. CaO reacts very readily with water, evolving a lot of heat and forming $\text{Ca}(\text{OH})_2$ which is a moderately strong base. $\text{Sr}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ are even stronger bases. The oxides are usually prepared by thermal decomposition of the carbonates, nitrates or hydroxides. The increase in basic strength is illustrated by the temperatures at which the carbonates decompose:

BeCO_3	MgCO_3	CaCO_3	SrCO_3	BaCO_3
$<100^\circ\text{C}$	540°C	900°C	1290°C	1360°C

The carbonates are all ionic, but BeCO_3 is unusual because it contains the hydrated ion $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ rather than Be^{2+} .

CaCO_3 occurs as two different crystalline forms, calcite and aragonite. Both forms occur naturally as minerals. Calcite is the more stable: each Ca^{2+} is surrounded by six oxygen atoms from CO_3^{2-} ions. Aragonite is a metastable form, and its standard enthalpy of formation is about 5 kJ mol^{-1} higher than that of calcite. In principle aragonite should decompose to calcite, but a high energy of activation prevents this happening. Aragonite can be made in the laboratory by precipitating from a hot solution. Its crystal structure has Ca^{2+} surrounded by nine oxygen atoms. This is a rather unusual coordination number.

Calcium oxide (lime) is prepared on a large scale by heating CaCO_3 in lime kilns.



Lime is used:

1. In steel making to remove phosphates and silicates as slag.
2. By mixing with SiO_2 and alumina or clay to make cement.
3. For making glass.
4. For softening water.
5. To make CaC_2 .
6. To make slaked lime $\text{Ca}(\text{OH})_2$ by treatment with water.

Bleaching powder is made by passing Cl_2 into slaked lime. Though bleaching powder is often written as $\text{Ca}(\text{OCl})_2$, it is really a mixture.



Soda lime is a mixture of NaOH and $\text{Ca}(\text{OH})_2$ and is made from quicklime (CaO) and aqueous sodium hydroxide. It is much easier to handle than NaOH .

Peroxides are formed with increasing ease and increasing stability as the metal ions become larger. Barium peroxide BaO_2 is formed by passing air over BaO at 500°C . SrO_2 can be formed in a similar way but this requires a high pressure and temperature. CaO_2 is not formed in this way, but can be made as the hydrate by treating $\text{Ca}(\text{OH})_2$ with H_2O_2 and then dehydrating the product. Crude MgO_2 has been made using H_2O_2 , but no peroxide of beryllium is known. The peroxides are white ionic solids containing the $[\text{O} - \text{O}]^{2-}$ ion and can be regarded as salts of the very weak acid hydrogen peroxide. Treating peroxides with acid liberates hydrogen peroxide.



9.28 | SULPHATES

The solubility of the sulphates in water decreases down the group. $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$. Thus BeSO_4 and MgSO_4 are soluble, but CaSO_4 is sparingly soluble, and the sulphates of Sr, Ba and Ra are virtually insoluble. The significantly higher solubilities of BeSO_4 and MgSO_4 are due to the high enthalpy of solvation of the smaller Be^{2+} and Mg^{2+} ions. Epsom salt $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is used as a mild laxative. Calcium sulphate can exist as a hemihydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ which is important in the building trade as plaster of Paris. This is made by partially dehydrating gypsum.



When powdered plaster of Paris $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is mixed with correct amount of water it sets into a solid mass of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (another crystallographic modification of gypsum). Plaster of Paris is used for plastering walls, and also to make plaster casts (moulds) for a variety of purposes, industrial, sculptural, and in hospitals to encase limbs so that broken bones are set straight. Alabaster is a fine grained form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ which is shiny like marble, and is used to make ornaments. CaSO_4 is slightly soluble in water (2g per litre), so objects made from alabaster or gypsum cannot be kept outdoors. BaSO_4 is both insoluble in water and opaque to X-rays and is used as a 'barium meal' to provide a shadow of the stomach or duodenum on an X-ray picture, which is useful in diagnosing stomach or duodenal ulcers. The sulphates all decompose on heating, giving the oxides:



In the same way as with the stability and thermal decomposition of the carbonates, the more basic the metal is, the more stable the sulphate is. This is shown by the temperatures at which decomposition occurs:

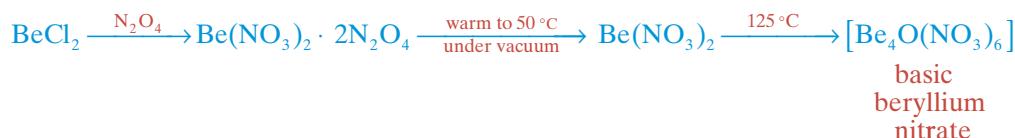
BeSO ₄	MgSO ₄	CaSO ₄	SrSO ₄
500 °C	895 °C	1149 °C	1374 °C

Heating the sulphates with carbon reduces them to sulphides. Most barium compounds are made from barium sulphide.



9.29 | NITRATES

Nitrates of the metals can all be prepared in solution and can be crystallized as hydrated salts by the reaction of HNO_3 with carbonates, oxides or hydroxides. Heating the hydrated solids does not give the anhydrous nitrate because the solid decomposes to the oxide. Anhydrous nitrates can be prepared using liquid dinitrogen tetroxide and ethyl acetate. Beryllium is unusual in that it forms a basic nitrate in addition to the normal salt.



Basic beryllium nitrate is covalent and has an unusual structure (Figure 9.6b). Four Be atoms are located at the corners of a tetrahedron, with six NO_3^- groups along the six edges of the tetrahedron, and the (basic) oxygen at the centre. The structure is of interest partly because beryllium is unique in forming a series

of stable covalent molecules of formula $[\text{Be}_4\text{O}(\text{R}_6)]$ where R may be NO_3^- , HCOO^- , CH_3COO^- , $\text{C}_2\text{H}_5\text{COO}^-$, $\text{C}_6\text{H}_5\text{COO}^-$, etc. Thus, basic beryllium nitrate is one of a series of similar molecules (cf. basic beryllium acetate (Figure 9.7a)). The structure is also of interest because the NO_3^- groups act as bidentate ligands in forming a bridge between two Be atoms (Figure 9.6a). (See 'Chelates' in Chapter 5 for a discussion of multidentate groups.)

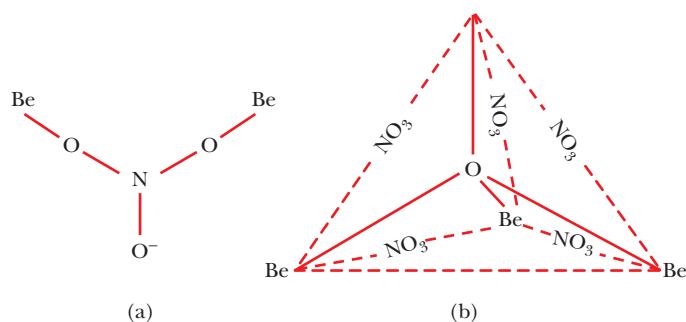
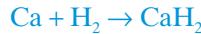
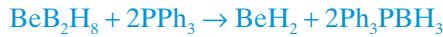


Figure 9.6 (a) A bridging NO_3^- group. (b) Basic beryllium nitrate.

9.30 | HYDRIDES

The elements Mg, Ca, Sr and Ba all react with hydrogen to form hydrides MH_2 . Beryllium hydride is difficult to prepare, and less stable than the others. Impure BeH_2 (contaminated with various amounts of ether) was first made by reducing BeCl_2 with lithium aluminium hydride $\text{Li}[\text{AlH}_4]$. Pure samples can be obtained by reducing BeCl_2 with lithium borohydride $\text{Li}[\text{BH}_4]$ to give BeB_2H_8 , then heating BeB_2H_8 in a sealed tube with triphenylphosphine PPh_3 .



The hydrides are all reducing agents and are hydrolysed by water and dilute acids with the evolution of hydrogen.



CaH_2 , SrH_2 and BaH_2 are ionic, and contain the hydride ion H^- . Beryllium and magnesium hydrides are covalent and polymeric. $(\text{BeH}_2)_n$ presents an interesting structural problem. In the gas phase it seems probable that several species may be present comprising polymeric chains and rings. The solid exists in both amorphous and crystalline forms. Both are thought to be polymeric and to contain hydrogen bridges between beryllium atoms.

9.31 | HALIDES

Halides MX_2 can be made by heating the metals with the halogen, or by the action of halogen acid on either the metal or the carbonate. The beryllium halides are covalent, hygroscopic and fume in air due to hydrolysis. They sublime, and they do not conduct electricity. Anhydrous beryllium halides cannot be obtained from materials made in aqueous solutions because the hydrated ion $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ is formed, e.g. $[\text{Be}(\text{H}_2\text{O})_4]\text{Cl}_2$ or $[\text{Be}(\text{H}_2\text{O})_4]\text{F}_2$. Attempts to dehydrate result in hydrolysis.



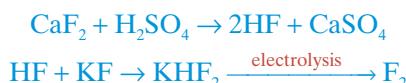
The anhydrous halides are best prepared by the following reactions. Reaction with CCl_4 is a standard method for making anhydrous chlorides which cannot be obtained by dehydrating hydrates.



The anhydrous halides are polymeric. Beryllium chloride vapour contains BeCl_2 and $(\text{BeCl}_2)_2$, but the solid is polymerized.

Beryllium fluoride is very soluble in water, owing to the high solvation energy of Be in forming $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$. The other fluorides MF_2 are all almost insoluble.

Fluorides of the other metals are ionic, have high melting points, and are insoluble in water. CaF_2 is a white, insoluble, high melting solid. It is very important industrially, and is the main source of both F_2 and HF.



CaF_2 is also used to make prisms and cell windows for spectrophotometers.

The chlorides, bromides and iodides of Mg, Ca, Sr and Ba are ionic, have much lower melting points than the fluorides, and are readily soluble in water. The solubility decreases somewhat with increasing atomic number. The halides all form hydrates, and they are hygroscopic (absorb water vapour from the air). CaCl_2 is widely used for treating ice on roads, particularly in very cold countries, because a 30% eutectic mixture of $\text{CaCl}_2/\text{H}_2\text{O}$ freezes at -55°C , compared with $\text{NaCl}/\text{H}_2\text{O}$ at -18°C . CaCl_2 is also used to make concrete set more quickly and to improve its strength, and as 'brine' in refrigeration plants. A minor use is in laboratories as a desiccant (drying agent). Anhydrous MgCl_2 is important in the electrolytic method for extracting magnesium.

9.32 | NITRIDES

The alkaline earth elements all burn in dinitrogen and form ionic nitrides M_3N_2 . This is in contrast to Group 1 where Li_3N is the only nitride formed.



Because the N_2 molecule is very stable, it requires a lot of energy to convert N_2 into N^{3-} nitride ions. The large amount of energy required comes from the very large amount of lattice energy evolved when the crystalline solid is formed. The lattice energy is particularly high because of the high charges on the ions M^{2+} and N^{3-} . Li is alone in Group I in forming a nitride, and here the very small size of Li^+ results in a high lattice energy.

Be_3N_2 is rather volatile in accord with the greater tendency of Be to covalency, but the other nitrides are not volatile. All the nitrides are all crystalline solids which decompose on heating and react with water, liberating ammonia and forming either the metal oxide or hydroxide, e.g.



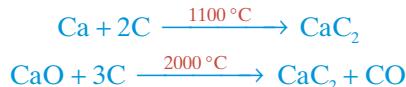
9.33 | CARBIDES

When BeO is heated with C at $1900\text{--}2000^\circ\text{C}$ a brick red coloured ionic carbide of formula Be_2C is formed. It is unusual because it reacts with water, forming methane, and is thus called a methanide.



Group 2 metals typically form ionic carbides of formula MC_2 . The metals Mg, Ca, Sr and Ba form carbides of formula MC_2 , either when the metal is heated with carbon in an electric furnace, or when their oxides are heated with carbon. CaC_2 made in this way is a grey coloured solid, but is colourless when pure. BeC_2 is made by heating Be with ethyne.

On heating, MgC_2 changes into Mg_2C_3 . This contains C_3^{4-} , and it reacts with water to form propyne $\text{CH}_3\text{C} \equiv \text{CH}$ (methyl acetylene).



Calcium carbide is the best known. It reacts with water, liberating ethyne (formerly called acetylene), and is thus called an acetylidyde.



At one time this reaction was the main source of ethyne for oxy-acetylene welding. Production of CaC_2 has declined because ethyne is now obtained from processing oil.

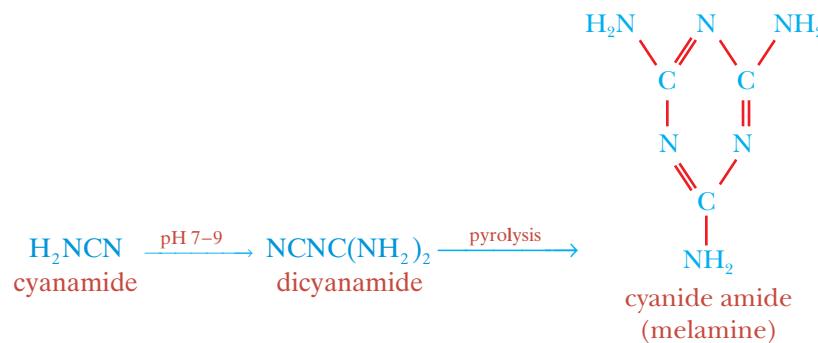
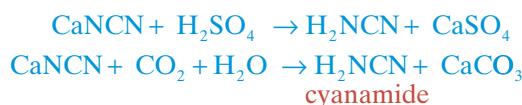
CaC_2 is an important chemical intermediate. When CaC_2 is heated in an electric furnace with atmospheric dinitrogen at 1100°C , calcium cyanamide CaNCN is formed. This is an important reaction because it is one method of fixing atmospheric dinitrogen. (The Haber process for NH_3 is another method of fixing dinitrogen.)



The cyanamide ion $[\text{N}=\text{C}=\text{N}]^{2-}$ is isoelectronic with CO_2 , and has the same linear structure. CaNCN is produced on a large scale, particularly in locations where there is cheap electricity. Cyanamide is widely used (particularly in SE Asia and the Far East) as a slow acting nitrogenous fertilizer, as it hydrolyses slowly over a period of months. CaNCN has the advantage over more soluble nitrogenous fertilizers such as NH_4NO_3 or urea, in that it is not washed away with the first rainstorm.



Other important industrial uses of CaNCN are the manufacture of cyanamide H_2NCN which is used to make urea and thiourea, and of melamine which forms hard plastics with formaldehyde.



It is interesting that BaC_2 also reacts with N_2 , but it forms a cyanide $\text{Ba}(\text{CN})_2$, not a cyanamide $(\text{NCN})^{2-}$.

9.34 | COMPLEXES

Group 2 metals are not noted for their ability to form complexes. The factors favouring complex formation are small highly charged ions with suitable empty orbitals of low energy which can be used for bonding. All the elements in the group form divalent ions, and these are smaller than the corresponding Group 1 ions: hence Group 2 elements are better at forming complexes than Group 1 elements. Be is appreciably smaller than the others, and so Be forms many complexes. Of the others, only Mg and Ca show much tendency to form complexes in solution, and these are usually with oxygen-donor ligands.

Beryllium fluoride BeF_2 readily coordinates two extra F^- ions, forming the $[\text{BeF}_4]^{2-}$ complex. The tetrafluoroberyllates $\text{M}_2[\text{BeF}_4]$ are well known complex ions, and resemble the sulphates in properties.

In a similar way complexes of the type $\text{BeCl}_2 \cdot \text{D}_2$ are formed (where D is an ether, aldehyde or ketone with an oxygen atom which has a lone pair of electrons that can be donated). These complexes, like $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ are tetrahedral.

Many stable chelate complexes of Be are known, including beryllium oxalate $[\text{Be}(\text{ox})_2]^{2-}$, with β -diketones such as acetylacetone, and with catechol. In all of these the Be^{2+} ion is tetrahedrally coordinated (see Figure 9.7b).

A complex with an unusual structure called basic beryllium acetate $[\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6]$ is formed if $\text{Be}(\text{OH})_2$ is evaporated with acetic acid (see Figure 9.7a). Basic beryllium acetate is soluble in organic solvents. It is covalent, and thus has a fairly low melting point (285°C) and boiling point (330°C). These are low enough for it to be distilled, which is useful in the purification of beryllium.

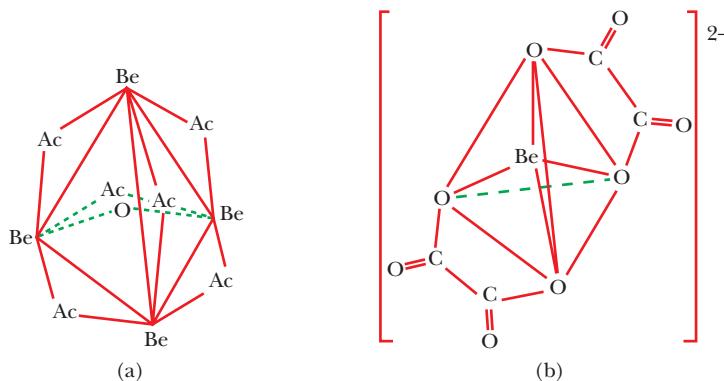
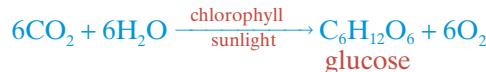


Figure 9.7 (a) Basic beryllium acetate $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$. (b) Beryllium oxalate complex $[\text{Be}(\text{ox})_2]^{2-}$.

Be compounds are said to taste sweet, but do **not** test this for yourself as they are extremely toxic. This is due to their very high solubility and their ability to form complexes with enzymes in the body. Be displaces Mg from some enzymes because it has a stronger complexing ability. Contact with the skin causes dermatitis, and inhaling dust or smoke causes a disease called berylliosis which is rather like silicosis.

Magnesium forms a few halide complexes such as $[\text{NEt}_4]_2[\text{MgCl}_4]$, but Ca, Sr and Ba do not.

From the viewpoint of life on this planet the most important complex formed by magnesium is chlorophyll. The magnesium is at the centre of a flat heterocyclic organic ring system called a porphyrin, in which four nitrogen atoms are bonded to the magnesium (see Figure 9.8a). Chlorophyll is the green pigment in plants which absorbs light in the red region from sunlight, and makes the energy available for photosynthesis. In this process CO_2 is converted into sugars.



Almost all life ultimately depends on chlorophyll and photosynthesis. The dioxygen in the atmosphere is a by-product of photosynthesis, and foodstuffs are either parts of plants, or animals which feed on plants.

Calcium and the rest of the group only form complexes with strong complexing agents. Examples include acetylacetone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, (which has two donor oxygen atoms), and ethylenediaminetetraacetic acid, EDTA, which has four donor oxygen atoms and two donor nitrogen atoms in each molecule (Figure 9.8b). The free acid H_4EDTA is insoluble, and the disodium salt $\text{Na}_2\text{H}_2\text{EDTA}$ is the most used reagent.



EDTA will form six-coordinate complexes with most metal ions in solution provided that the pH is suitably adjusted. Since Be is invariably four-coordinate it does not complex appreciably with EDTA. In contrast, calcium and magnesium complex with EDTA, and titrations are performed using EDTA in

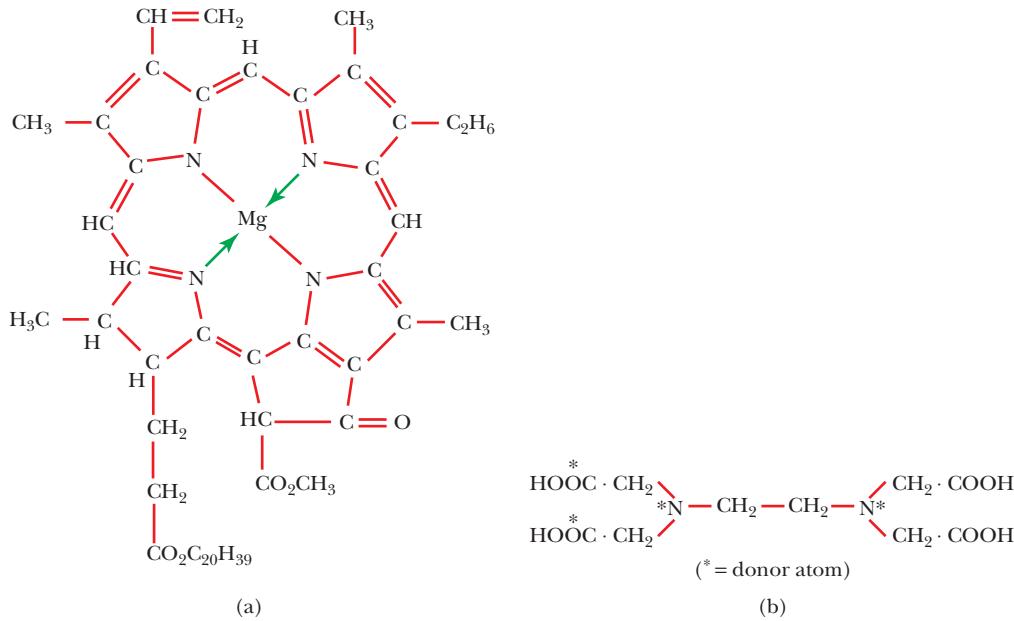


Figure 9.8 (a) Chlorophyll a. (b) Ethylenediaminetetraacetic acid EDTA.

buffered solutions to estimate the amounts of Ca^{2+} and Mg^{2+} present to determine the ‘hardness’ of the water. EDTA titrations of Ca^{2+} and Mg^{2+} are carried out at higher pH than those of many other metals (e.g. Zn^{2+} , Cd^{2+} and Pb^{2+}) as their complexes are less stable, and at lower pH values the EDTA is protonated instead of the Ca or Mg complex forming.

9.35 | BIOLOGICAL ROLE OF Mg^{2+} AND Ca^{2+}

Mg^{2+} ions are concentrated in animal cells and Ca^{2+} are concentrated in the body fluids outside the cell, in much the same way that K^+ concentrates inside the cell and Na^+ outside. Mg^{2+} ions form a complex with ATP, and are constituents of phosphohydrolases and phosphotransferases, which are enzymes for reactions involving ATP and energy release. They are also essential for the transmission of impulses along nerve fibres. Mg^{2+} is important in chlorophyll, in the green parts of plants. Ca^{2+} is important in bones and teeth as apatite $Ca_3(PO_4)_2$, and the enamel on teeth as fluoroapatite $[3(Ca_3(PO_4)_2) \cdot CaF_2]$. Ca^{2+} ions are important in blood clotting, and are required to trigger the contraction of muscles and to maintain the regular beating of the heart.

9.36 | DIFFERENCES BETWEEN BERYLLIUM AND THE OTHER GROUP 2 ELEMENTS

Beryllium is anomalous in many of its properties and shows a diagonal relationship to aluminium in Group 13:

1. Beryllium is very small and has a high charge density so by Fajans' rules it has a strong tendency to covalency. Thus the melting points of its compounds are lower (BeF_2 m.p. 800°C whilst the fluorides of the rest of group melt about 1300°C). The Be halides are all soluble in organic solvents and hydrolyse in water rather like the aluminium halides. The other Group 2 halides are ionic.
 2. Beryllium hydride is electron deficient and polymeric, with multicentre bonding, like aluminium hydride.
 3. The halides of beryllium are electron deficient, and are polymeric, with halogen bridges. BeCl_2 usually forms chains but also exists as the dimer. AlCl_3 is dimeric.
 4. Beryllium forms many complexes – not typical of Groups 1 and 2.

5. Be is amphoteric, liberating H_2 with $NaOH$ and forming beryllates. Al forms aluminates.
6. $Be(OH)_2$, like $Al(OH)_3$, is amphoteric.
7. Be, like Al, is rendered passive by nitric acid.
8. The standard electrode potentials for Be and Al, -1.85 volts and -1.66 volts respectively, are much closer than the value for Be is to the values for Ca, Sr and Ba (-2.87 , -2.89 and -2.90 volts) respectively.
9. Be salts are extensively hydrolyzed.
10. Be salts are among the most soluble known.
11. Beryllium forms an unusual carbide Be_2C , which, like Al_4C_3 , yields methane on hydrolysis.

There is plainly a diagonal similarity between beryllium in Group 2 and aluminium in Group 3. Just as was the case with lithium and magnesium, the similarity in atomic and ionic sizes is the main factor underlying this relationship.

SINGLE CORRECT CHOICE TYPE QUESTIONS

1. In the following reaction, which of the following compounds crystallize out first?

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2SO_4 + Na_2Cr_2O_7 + H_2O$$

(A) $Na_2Cr_2O_7$
 (B) H_2O
 (C) Na_2SO_4
 (D) $Na_2Cr_2O_7$ and Na_2SO_4 equally
2. Choose the correct order of lattice enthalpy in the following.

(A) $LiF > NaCl > NaF > LiCl$
 (B) $LiF > LiCl > NaF > NaCl$
 (C) $LiF > NaF > NaCl > LiCl$
 (D) $LiCl > LiF > NaF > NaCl$
3. Match the ions in Column I with their ionic radius (in \AA) given in Column II and select the correct code.

Column I	Column II
(P) Mg^{2+}	(1) 1.37
(Q) K^+	(2) 1
(R) Li^+	(3) 0.76
(S) Ca^{2+}	(4) 0.72

Code:

P	Q	R	S
(A) 2	1	3	4
(B) 1	2	3	4
(C) 4	3	1	2
(D) 4	1	3	2
4. Identify the correct order.

(A) $CsCl < RbCl < KCl < NaCl < LiCl$: Solubility in water
 (B) $CsCl < RbCl < KCl < NaCl < LiCl$: Melting point
 (C) $CsCl > RbCl > KCl > NaCl > LiCl$: % Ionic character
 (D) $CsCl > RbCl > KCl > NaCl > LiCl$: Lattice energy
5. Aqueous solution of Na_2SO_4 is crystallized out above and below $32^\circ C$. The respective products are

(A) Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$
 (B) $Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4
 (C) Na_2SO_4 and Na_2SO_4
 (D) $Na_2SO_4 \cdot 10H_2O$ and $Na_2SO_4 \cdot 10H_2O$
6. Which of the following compounds does not have similarity in structure with the other three compounds?

(A) $FeSO_4 \cdot 7H_2O$
 (B) $Na_2CO_3 \cdot 7H_2O$
 (C) $MgSO_4 \cdot 7H_2O$
 (D) $ZnSO_4 \cdot 7H_2O$
7. The melting point of an eutectic mixture of $Na_2CO_3 + K_2CO_3$ is

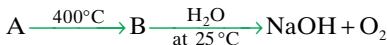
(A) higher than that of Na_2CO_3 ,
 (B) higher than that of K_2CO_3 ,
 (C) lower than that of both Na_2CO_3 and K_2CO_3 ,
 (D) lower than that K_2CO_3 only.
8. Which of the following statements is not correct?

(A) Common salt absorbs water because it is hygroscopic.
 (B) Common salt is used to clear snow on the road.
 (C) Anhydrous $MgCl_2$ can be prepared by heating a double salt of it, i.e. $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$.
 (D) $CaSO_4$ and $BaSO_4$ are reacted with coke to produce CaS and BaS respectively.
9. KOH is preferably used to absorb CO_2 because

(A) KOH is more soluble than $NaOH$ in water.
 (B) KOH is a stronger base than $NaOH$.
 (C) $KHCO_3$ is soluble in water and $NaHCO_3$ is insoluble in water.
 (D) KOH is cheaper than $NaOH$.
10. Ozonized oxygen is passed through dry powdered KOH. Which option is not correct regarding the product obtained in the above process?

- (A) It is an orange coloured solid.
 (B) It is paramagnetic in nature.
 (C) It is used in submarines for oxygenating the air.
 (D) It is also prepared by passing O₂ in blue solution of K in liquid NH₃

11. A + H₂O → NaOH



B is used for oxygenating in submarines. A and B are respectively:

- (A) Na₂O₂ and Na₂O
 (B) Na₂O and Na₂O₂
 (C) Na₂O₂ and O₂
 (D) Na₂O and O₂

12. Electrolysis of KH produces H₂

- (A) at the cathode.
 (B) at the anode.
 (C) either at the cathode or at the anode.
 (D) Cannot be predicted.

13. Which of the following is the most soluble in water?

- (A) CsClO₄
 (B) NaClO₄
 (C) KClO₄
 (D) LiClO₄

14. Which of the following statements is correct?

- (A) NaHCO₃ and KHCO₃ have similar crystal structure.
 (B) Li₂CO₃ decomposes to give Li₂O and CO₂.
 (C) Li₂CO₃ is soluble in water.
 (D) All are correct.

15. If Na⁺ ion is larger than Mg²⁺ and S²⁻ ion is larger than Cl⁻ ion, which of the following will be least soluble in water?

- (A) NaCl
 (B) Na₂S
 (C) MgCl₂
 (D) MgS

16. In which of following cases is the value of x maximum?

- (A) CaSO₄ · xH₂O
 (B) BaSO₄ · xH₂O
 (C) MgSO₄ · xH₂O
 (D) All have the same value of x.

17. Among LiCl, RbCl, BeCl₂, MgCl₂, the compounds with greatest and least ionic character respectively are

- (A) LiCl and RbCl
 (B) RbCl and BeCl₂
 (C) RbCl and MgCl₂
 (D) MgCl₂ and BeCl₂

18. Which of the following properties show a reverse trend of radius on moving from Mg to Ba within the group?

- (A) Density
 (B) Solubility of sulphate
 (C) Solubility of oxalate
 (D) Basicity of M(OH)₂

19. Compound M on heating leaves no residue and N₂ is also not obtained. Aqueous solution of M reacts with alkali and all the gases are evolved. The resulting solution is treated with Al in alkaline medium to liberate a gas that produces a deep blue solution with Ni(NO₃)₂ solution. M is

- (A) NH₄NO₃
 (B) NH₄NO₂
 (C) NH₄Cl
 (D) NH₄Br

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. MgO can be used as refractory material because

- (A) it has a very high melting point.
 (B) it has a very low vapour pressure.
 (C) it is a very good conductor of heat.
 (D) it is chemically inert.

2. The temporary hardness of water is caused by which of the following compound(s).

- (A) CaCl₂
 (B) Mg(HCO₃)₂
 (C) Ca(HCO₃)₂
 (D) MgSO₄

3. When KO₂ reacts with water, the products are

- (A) KOH
 (B) H₂O₂
 (C) K₂O₂
 (D) O₂

4. KO₃ or Na₂O₂ is used in submarines or space capsules because

- (A) it absorbs CO₂.
 (B) it releases O₂.
 (C) it produces corresponding carbonate on reaction with CO₂.
 (D) None of these.

5. Na₂O can be prepared by

- (A) Na₂O₂ + CO →
 (B) Na + NaNO₃ →
 (C) Na + NaNO₂ →
 (D) Na₂O₂ + Na →

6. Which of the following properties are in the increasing order from top to bottom for metal ions in Group 1?

- (A) Ionic radius
 (B) Hydrated radius
 (C) Ionic mobility
 (D) Hydration number

7. Which of the following hydrides are electron deficient?
 (A) BeH_2
 (B) CaH_2
 (C) AlH_3
 (D) KH
8. In which of the following cases, does N_2 evolve as a gaseous product?
 (A) KNO_3 reacts with K on heating.
 (B) Na_2O_2 reacts with NH_3 .
 (C) NH_3 reacts with bleaching powder.
 (D) None of these.
9. Which of the following elements liberate H_2 on reaction with NaOH ?
 (A) Be
 (B) Al
 (C) B
 (D) None of these.
10. Which of the following statements are correct regarding the diagonal relationship between Al and Be?
 (A) BeO and Al_2O_3 are amphoteric in nature.
 (B) Carbides of both produce the same gas on hydrolysis.
 (C) Both can form complexes.
 (D) Hydrides of both the elements are covalent in nature.

*COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1–3

Hard water contains dissolved salts such as magnesium and calcium chlorides, bicarbonates, or sulphates. There are two kinds of hardness of water, i.e. temporary hardness and permanent hardness.

1. Temporary hardness can be removed by
 (A) boiling hard water.
 (B) adding slaked lime.
 (C) adding dil. H_2SO_4 .
 (D) adding milk of magnesia.
2. When Graham's salt (calgon) is used for removal of permanent hardness of water, Ca^{2+} and Mg^{2+} are sequestered in the form of
 (A) precipitate.
 (B) solution.
 (C) colloidal solution.
 (D) sedimentation.
3. Permanent hardness of water can be removed by
 (A) distillation.
 (B) passing it through ion-exchange resins.
 (C) adding various phosphates.
 (D) adding Na_2CO_3 solution.

Passage 2: For Questions 4–6

Several alkali metals and alkaline earth metals when dissolved in NH_3 produce a bright blue solution.

4. This bright blue solution is due to
 (A) solvated metal ion.
 (B) solvated electron.
 (C) high extent of hydration.
 (D) All of these.
5. The characteristic(s) of the resulting solution is/are:
 (A) It acts as a very good fuel.

- (B) It acts as a very good reducing agent.
 (C) It acts as a very good oxidizing agent.
 (D) It shows attraction towards magnetic field.

6. On addition of more metal to this solution which of the following characteristics get changed?
 (A) Electrical conductivity.
 (B) Colour.
 (C) Magnetic behaviour.
 (D) None of these.

Passage 3: For Questions 7–9



7. Which of the following characteristics are mainly different for gases C and D?
 (A) Colour
 (B) Smell
 (C) Burning characteristics in air
 (D) Hybridization
8. When gas C is passed through bleaching powder suspension, another gas F comes out, which can also be obtained by
 (A) heating NH_4NO_3 .
 (B) heating NH_4NO_2 .
 (C) heating $(\text{NH}_4)_2\text{CrO}_7$.
 (D) heating $\text{Ba}(\text{N}_3)_2$.
9. Gas D catches fire automatically when it comes in contact with the air and this is due to
 (A) presence of PH_3 ,
 (B) presence of O_2 ,
 (C) presence of P_2H_4 .
 (D) presence of H_2 .

*One or more than one correct answers.

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
- If Statement I is true but Statement II is false.
- If Statement I is false but Statement II is true.

1. Statement I: Be is amphoteric in nature.

Statement II: The ionization energy of Be is the highest among the alkaline earth metals.

2. Statement I: For purification of CO_2 by Girbotol process ethanol amine is chosen for absorption of CO_2 , not NaOH or KOH .

Statement II: Ethanol amine absorbs CO_2 at $30 - 60^\circ\text{C}$ while it releases CO_2 at $100 - 150^\circ\text{C}$.

3. Statement I: $\text{BeH}_2(s)$ and $\text{CaH}_2(s)$ have the same structure.

Statement II: Be and Ca are both alkaline earth metal elements.

4. Statement I: CaCl_2 is formed as a by-product in the Solvay process for Na_2CO_3 preparation.

Statement II: During the recovery of NH_3 , CaCl_2 is obtained when $\text{Ca}(\text{OH})_2$ is used to react with NH_4Cl .

5. Statement I: Na_2CO_3 solution is strongly alkaline in nature.

Statement II: Hydrolysis of CO_3^{2-} ions produces undissociated H_2CO_3 and OH^- ions in solution.

6. Statement I: The hydration energy of Be^{2+} is much higher as compared to that of Li^+ .

Statement II: First ionization energy of Be is greater than that of Li.

7. Statement I: BaSO_4 is used in diagnosing stomach or duodenal ulcers.

Statement II: BaSO_4 is insoluble in water and in several acids and is opaque to X-rays.

8. Statement I: When an electron is added to Na^+ ion, the size of the ion decreases.

Statement II: In the process of $\text{Na}^+ \rightarrow \text{Na}$, the inter-electric repulsion increases.

9. Statement I: Na and K on reaction with H_2O , catch fire.

Statement II: The reaction is highly exothermic, as a result of which the remaining solid metal melts and local heating is so high that the released H_2 catches fire.

10. Statement I: $\text{NaOH} + \text{NH}_4^+ - \text{salt} \rightarrow \text{NH}_3 \uparrow + \text{Na}^+ + \text{H}_2\text{O}$

Statement II: $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$; it is the strong acid-strong base reaction which releases more energy and shifts towards greater stability.

11. Statement I: Superoxides are stronger oxidizing agents than peroxides.

Statement II: Superoxides accept electrons in the same energy level, i.e. π^* orbital while peroxides accept electrons in the higher energy σ_{2p}^* orbital.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

- The number of rings formed in $[\text{Ca}(\text{EDTA})]^{2-}$ is _____.
- The total number of electrons in one molecule of Mg_2C_3 is _____.
- Among the following the number of pairs of compounds, for which the thermal stability order is correct is _____.
 - $\text{BeCO}_3 > \text{SrCO}_3$
 - $\text{MgO} > \text{BaO}$
 - $\text{Li}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$
 - $\text{CaSO}_4 < \text{BaSO}_4$
 - $\text{Li}_3\text{N} > \text{Na}_3\text{N}$
 - $\text{LiClO}_4 < \text{KClO}_4$

4. Among the following compounds, the number of compounds which do not produce acidic or basic solutions when dissolved in water is _____.

NaCl , BeCl_2 , BaCl_2 , Li_2O , MgO , CaH_2 , CaSO_4

5. Cl_2 gas is passed through a compound A and produces bleaching powder. The number of protons in A is _____.

6. The ratio of the number of water of crystallization in gypsum and that in plaster of Paris is _____.

7. Among the following elements, the number of elements that release H_2 on reaction with NaOH is _____.

Be, Al, B, Mg, Ca, Zn, Sn

8. The number of bicarbonates that do not exist in solid form among the following is _____.
 LiHCO₃, NaHCO₃, Ca(HCO₃)₂, KHCO₃,
 NH₄HCO₃, Ba(HCO₃)₂ Mg(HCO₃)₂
9. The number of planes of symmetry in [BeH₄]²⁻ is _____.
 10. What is the number of ions among the following for which hydrated ion has higher ionic mobility than Be²⁺(aq)?
 Li⁺(aq), Na⁺(aq), Mg²⁺(aq), Ca²⁺(aq)
 11. The percentage water loss when gypsum is heated to get plaster of Paris is _____.
 _____.

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the chemical properties with the compounds.

Column I	Column II
(A) Ca	(P) Produces H ₂ on reaction with H ₂ O.
(B) CaH ₂	(Q) Produces Ca(OH) ₂ on reaction with H ₂ O.
(C) CaO	(R) The compound is ionic.
(D) CaC ₂	(S) Can absorb N ₂ under hot conditions.

2. Match the compounds with their characteristics.

Column I	Column II
(A) BeCO ₃	(P) Least soluble in water.
(B) MgCO ₃	(Q) Least thermally stable.
(C) CaCO ₃	(R) Produces MO + CO ₂ on heating with the help of bunsen burner.
(S)	Produces basic oxides on thermal decomposition.

3. Match the compounds with the properties.

Column I	Column II
(A) CaSO ₄ · 2H ₂ O	(P) Stored under kerosene.
(B) LiI	(Q) Most covalent alkali metal halide.
(C) Na	(R) Insoluble in water.
(D) KF	(S) Soluble in water without any reaction with water.

4. Match the compounds with their uses/properties.

Column I	Column II
(A) NaCO ₃ · 10H ₂ O	(P) Dessicating agent.
(B) CaCl ₂ (anhydride)	(Q) Used for preparing freezing mixture.
(C) CaSO ₄ (anhydride)	(R) Washing soda.
(D) NaCl	(S) Dead burnt.
	(T) Soluble in water.

ANSWERS

Single Correct Choice Type Questions

- | | | | | |
|--------|--------|---------|---------|---------|
| 1. (C) | 5. (A) | 9. (C) | 13. (D) | 17. (B) |
| 2. (B) | 6. (B) | 10. (D) | 14. (B) | 18. (B) |
| 3. (D) | 7. (C) | 11. (B) | 15. (D) | 19. (A) |
| 4. (C) | 8. (A) | 12. (B) | 16. (C) | |

Multiple Correct Choice Type Questions

- | | | | | |
|-----------------------|------------------|------------------|------------------|------------------------|
| 1. (A), (B), (C), (D) | 3. (A), (B), (D) | 5. (B), (C), (D) | 7. (A), (C) | 9. (A), (B), (C) |
| 2. (B), (C) | 4. (A), (B) | 6. (A), (C) | 8. (A), (B), (C) | 10. (A), (B), (C), (D) |

Comprehension Type Questions

- | | | | | |
|--------------------|------------------------------|-------------------------|-------------------------|---------------|
| 1. (A), (B) | 3. (A), (B), (C), (D) | 5. (B), (D) | 7. (B), (C), (D) | 9. (C) |
| 2. (B) | 4. (B) | 6. (A), (B), (C) | 8. (B), (C), (D) | |

Assertion–Reasoning Type Questions

- | | | | |
|---------------|---------------|---------------|----------------|
| 1. (B) | 4. (A) | 7. (A) | 10. (A) |
| 2. (A) | 5. (A) | 8. (D) | 11. (A) |
| 3. (D) | 6. (B) | 9. (A) | |

Integer Answer Type Questions

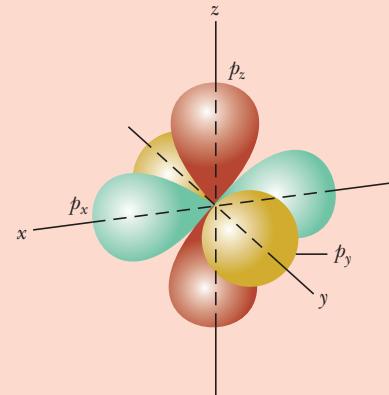
- | | | | |
|--------------|--------------|-------------|---------------|
| 1. 5 | 4. 3 | 7. 5 | 10. 4 |
| 2. 42 | 5. 38 | 8. 4 | 11. 75 |
| 3. 5 | 6. 4 | 9. 6 | |

Matrix–Match Type Questions

- | | |
|---|---|
| 1. (A) → (P), (Q), (S)
(B) → (P), (Q), (R)
(C) → (Q), (R)
(D) → (Q), (R), (S) | 3. (A) → (R)
(B) → (Q), (S)
(C) → (P)
(D) → (S) |
| 2. (A) → (Q), (R)
(B) → (R), (S)
(C) → (P), (S) | 4. (A) → (R), (T)
(B) → (P), (T)
(C) → (S)
(D) → (Q), (T) |

10

The *p*-Block Elements and their Compounds



The orientations of the three *p* orbitals in a *p* subshell.

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- 10.2 General Properties
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PART 1: THE GROUP 13 ELEMENTS

Boron is a non-metal, and always forms covalent bonds. Normally it forms three covalent bonds at 120° using sp^2 hybrid orbitals. There is no tendency to form univalent compounds. All BX_3 compounds are electron deficient, and may accept an electron pair from another atom, thus forming a coordinate bond. BF_3 is commercially important as a catalyst.

The four elements Al, Ga, In and Tl all form trivalent compounds. The heavier members show the ‘inert pair effect’, and univalent compounds become increasingly important in the order $Ga \rightarrow In \rightarrow Tl$. These four elements (Table 10.1) are more metallic, and more ionic, than B. They are moderately reactive metals. Their compounds are on the borderline between ionic and covalent. Many of their compounds are covalent when anhydrous, but they form ions in solution.

Table 10.1 Electronic structures and oxidation states

Element	Symbol	Electronic	Configuration	Oxidation states*
Boron	B	[He]	$2s^2 2p^1$	III
Aluminium	Al	[Ne]	$3s^2 3p^1$	(I) III
Gallium	Ga	[Ar]	$3d^{10} 4s^2 4p^1$	I III
Indium	In	[Kr]	$4d^{10} 5s^2 5p^1$	I III
Thallium	Tl	[Xe]	$4f^{14} 5d^{10} 6s^2 6p^1$	I III

*The most important oxidation states (generally the most abundant and stable) are shown in bold. Other well-characterized but less important states are shown in normal type. Oxidation states that are unstable, or in doubt, are given in parentheses.

10.1 | OXIDATION STATES AND TYPES OF BONDS

The (+III) oxidation state

The elements all have three outer electrons. Apart from Tl they normally use these to form three bonds, giving an oxidation state of (+III). Are the bonds ionic or covalent? Covalency is suggested by the following:

1. Fajans’ rules – small size of the ions and their high charge of 3+ favours the formation of covalent bonds.
2. The sum of the first three ionization energies is very large, and this also suggests that bonds will be largely covalent.
3. The electronegativity values are higher than for Groups 1 and 2, and when reacting with other elements the difference is not likely to be large.

Boron is considerably smaller than the other elements and thus has a higher ionization energy than the others. The ionization energy is so high that B always forms covalent bonds.

Many simple compounds of the remaining elements, such as $AlCl_3$ and $GaCl_3$ are covalent when anhydrous. However, Al, Ga, In and Tl all form metal ions in solution. The type of bonds formed depends on which is most favourable in terms of energy. This change from covalent to ionic happens because the ions are hydrated, and the amount of hydration energy evolved exceeds the ionization energy. Consider $AlCl_3$: 5137 kJ mol⁻¹ are required to convert Al to Al^{3+} , $\Delta H_{hydration}$ for Al^{3+} is -4665 kJ mol⁻¹ and $\Delta H_{hydration}$ for Cl^- is -381 kJ mol⁻¹. Thus the total hydration energy is:

$$-4665 + (3 \times -381) = -5808 \text{ kJ mol}^{-1}$$

This exceeds the ionization energy, so $AlCl_3$ ionizes in solution.

The (+I) oxidation state – the ‘inert pair effect’

In the s-block, Group 1 elements are univalent, and Group 2 elements are divalent. In Group 13 we would expect the elements to be trivalent. In most of their compounds this is the case, but some of

the elements show lower valency states as well. There is an increasing tendency to form univalent compounds on descending the group. Compounds with Ga(I), In(I) and Tl(I) are known. With Ga and In the (+I) oxidation state is less stable than the (+III) state. However, the stability of the lower oxidation state increases on descending the group. Tl(I) thallous compounds are more stable than Tl(III) thallic compounds.

How and why does monovalency occur? The atoms in this group have an outer electronic configuration of s^2p^1 . Monovalency is explained by the s electrons in the outer shell remaining paired, and not participating in bonding. This is called the 'inert pair effect'. If the energy required to unpair them exceeds the energy evolved when they form bonds, then the s electrons will remain paired. The strength of the bonds in MX_3 compounds decreases down the group. The mean bond energy for chlorides are $\text{GaCl}_3 = 242$, $\text{InCl}_3 = 206$ and $\text{TlCl}_3 = 153 \text{ kJ mol}^{-1}$. Thus the s electrons are most likely to be inert in thallium.

The inert pair effect is not the explanation of why monovalency occurs in Group 13. It merely describes what happens, i.e. two electrons do not participate in bonding. The reason that they do not take part in bonding is energy. The univalent ions are much larger than the trivalent ions, and (+I) compounds are ionic, and are similar in many ways to Group 1 elements.

The inert pair effect is not restricted to Group 13, but also occurs among the heavier elements in other groups in the p -block. Examples from Group 14 are Sn^{2+} and Pb^{2+} , and examples from Group 15 are Sb^{3+} and Bi^{3+} . The lower oxidation state becomes more stable on descending the group. Thus Sn^{2+} is a reducing agent but Pb^{2+} is stable and Sb^{3+} is a reducing agent but Bi^{3+} is stable. When the s electrons remain paired, the oxidation state is, always two lower than the usual oxidation state for the group.

Thus in the s -block, Groups 1 and 2 show only the group valency. Groups in the p -block show variable valency, differing in steps of two. Variable valency also occurs with elements in the d -block. This arises from using different numbers of d electrons for bonding, so in this case the valency can change in steps of one (e.g. Cu^+ and Cu^{2+} , Fe^{2+} and Fe^{3+}).

10.2 | GENERAL PROPERTIES

Melting points, boiling points and structures

The melting points of the Group 13 elements do not show a regular trend as did the metals of Groups 1 and 2. The Group 13 values are not strictly comparable because B and Ga have unusual crystal structures.

Boron has an unusual crystal structure which results in the melting point being very high. There are at least four different allotropic forms. All allotropes consist of polymeric icosahedron. Figures 10.1(a) and (b) are an example of regular and polymeric icosahedrons, respectively.

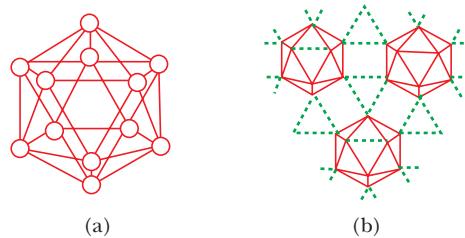


Figure 10.1 (a) B_{12} icosahedron. (b) Structure of α -rhombohedral boron.

The elements Al, In and Tl all have close-packed metal structures. Gallium has an unusual structure having discrete diatomic molecules rather than a metallic structure. This accounts for the incredibly low melting point of gallium of 30°C . Ga is also unusual because the liquid expands when it forms the solid, i.e. the solid is less dense than the liquid. This property is unique to Ga, Ge and Bi.

The boiling point of B is unusually high, but the values for Ga, In and Tl decrease on descending the group as expected (Table 10.2). Note that the boiling point for Ga is in line with the others, whereas its melting point is not. The very low melting point is due to the unusual crystal structure, but the structure no longer exists in the liquid.

Table 10.2 Melting and boiling points

	Melting point (°C)	Boiling point (°C)
B	2180	3650
Al	660	2467
Ga	30	2403
In	157	2080
Tl	303	1457

Size of atoms and ions

The metallic radii of the atoms do not increase regularly on descending the group (Table 10.3). However, the values are not strictly comparable. Boron is not a metal, and the radius given is half the closest approach in the structure. Ga has an unusual structure, and the value given is half the closest approach. The others have close-packed metal structures.

The ionic radii for M^{3+} increase down the group, though not in the regular way observed in Groups 1 and 2. There are two reasons for this:

1. There is no evidence for the existence of B^{3+} under normal conditions, and the value is an estimate.
2. The electronic structures of the elements are different. Ga, In and Tl follow immediately after a row of ten transition elements. They therefore have ten *d* electrons, which are less efficient at shielding the nuclear charge than the *s* and *p* electrons. (Shielding is in the order *s* > *p* > *d* > *f*.) Poor shielding of the nuclear charge results in the outer electrons being more firmly held by the nucleus. Thus atoms with a d^{10} inner shell are smaller and so have higher ionization energies than would otherwise be expected. This contraction in size is sometimes called the *d*-block contraction. In a similar way Tl follows immediately after 14 *f*-block elements. The size and ionization energy of Tl are affected even more by the presence of 14 *f* electrons, which shield the nuclear charge even less effectively. The contraction in size from these *f*-block elements is called the *lanthanide contraction*.

Table 10.3 Ionic and covalent radii and electronegativity values

Metallic radius (Å)	Ionic radius		Pauling's electronegativity
	M^{3+} (Å)	M^+ (Å)	
B	(0.885)	(0.27)	—
Al	1.43	0.535	—
Ga	(1.225)	0.620	1.20
In	1.67	0.800	1.40
Tl	1.70	0.885	1.50

For values in brackets see text.

The large difference in size between B and Al results in many differences in properties. Thus B is a non-metal, has a very high melting point, always forms covalent bonds, and forms an acidic oxide. In contrast, Al is a metal, has a much lower melting point, and its oxide is amphoteric. (It is safe to generalize in this way, but unsafe to argue quantitatively that Al^{3+} is twice the size of B^{3+} or that the metallic radii differ by a factor of 1.6, as B^{3+} does not exist, and B is not a metal.)

Electropositive character

The electropositive or metallic nature of the elements increases from B to Al, but then decreases from Al to Tl.

The increase in metallic character from B to Al is the usual trend on descending a group associated with increasing size. However, Ga, In and Tl do not continue the trend. The elements are less likely to lose electrons (and are thus less electropositive), because of the poor shielding by *d* electrons described previously.

The standard electrode potential E° for M^{3+}/M become less negative from Al to Ga to In and the potential becomes positive for Tl (Table 10.4).

Table 10.4 Standard electrode potentials E°

	$M^{3+} M$ (volts)	$M^{3+} M$ (volts)
B	(-0.87*)	
Al	-1.66	+0.55
Ga	-0.56	-0.79 [†]
In	-0.34	-0.18
Tl	+1.26	-0.34

* For $H_3BO_3 + 3H^+ + 3e \rightarrow B + 3H_2O$

[†]Value in acidic solution.

Ionization energy

The ionization energies increase as expected (first ionization energy < second ionization energy < third ionization energy). The sum of the first three ionization energies for each of the elements is very high. Thus boron has no tendency to form ions, and always forms covalent bonds. The other elements normally form covalent compounds except in solution.

The ionization energy values do not decrease smoothly down the group (Table 10.5). The decrease from B to Al is the usual trend on descending a group associated with increased size. The poor shielding by *d* electrons and the resulting *d-block contraction* affect the values for the later elements.

Table 10.5 Ionization energies

	Ionization energy (kJ mol ⁻¹)			
	1st	2nd	3rd	Sum of three
B	801	2427	3659	6887
Al	577	1816	2744	5137
Ga	579	1979	2962	5520
In	558	1820	2704	5082
Tl	589	1971	2877	5437

10.3 | PREPARATION OF BORON

The preparation of boron from borax or colemanite is a two-step process.

Step 1: Preparation of B_2O_3



Step 2: Reduction of B_2O_3



10.4 | REACTIONS OF BORON

Pure crystalline boron is very unreactive. However, it is attacked at high temperatures by strong oxidizing agents such as a mixture of hot concentrated H_2SO_4 and HNO_3 , or by sodium peroxide. In contrast, finely divided amorphous boron (which contains between 2% and 5% of impurities) is more reactive. It burns in air or dioxygen, forming the oxide. It also burns at white heat in dinitrogen, forming the nitride BN (Figure 10.2). This is a slippery white solid with a layer structure similar to graphite. Boron also burns in the halogens, forming trihalides. It reacts directly with many elements, forming borides, which are hard and refractory. It reduces strong HNO_3 and H_2SO_4 slowly, and also liberates H_2 from fused NaOH .

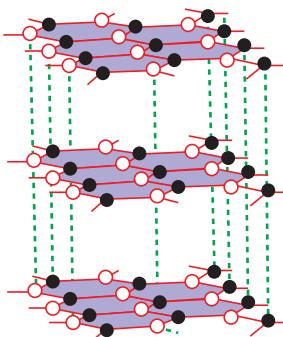


Figure 10.2 Structure of boron nitride.

Some important reactions of amorphous boron are listed in Table 10.6.

Table 10.6 Some reactions of amorphous boron

Reaction	Comment
$4\text{B} + 3\text{O}_2 \rightarrow 2\text{B}_2\text{O}_3$	At high temperature
$2\text{B} + 3\text{S} \rightarrow \text{B}_2\text{S}_3$	At 1200°C
$2\text{B} + \text{N}_2 \rightarrow 2\text{BN}$	At very high temperature
$2\text{B} + 3\text{F}_2 \rightarrow 2\text{BF}_3$	At high temperature
$2\text{B} + 3\text{Cl}_2 \rightarrow 2\text{BCl}_3$	
$2\text{B} + 3\text{Br}_2 \rightarrow 2\text{BBr}_3$	
$2\text{B} + 3\text{I}_2 \rightarrow 2\text{BI}_3$	
$2\text{B} + 6\text{NaOH} \rightarrow 2\text{Na}_3\text{BO}_3 + 3\text{H}_2$	When fused with alkali
$2\text{B} + 2\text{NH}_3 \rightarrow 2\text{BN} + 3\text{H}_2$	At very high temperature
$\text{B} + \text{M} \rightarrow \text{M}_x\text{B}_y$	Many metals form borides (not Group 1) often nonstoichiometric

10.5 | REACTIONS OF THE OTHER ELEMENTS

Some important reactions of elements of Group 13 are listed in Table 10.7.

Table 10.7 Some reactions of the other Group 13 metals

Reaction	Comment
$4\text{M} + 3\text{O}_2 \rightarrow \text{M}_2\text{O}_3$	All react at high temperature Al very strongly exothermic
$2\text{Al} + \text{N}_2 \rightarrow 2\text{AlN}$	Only Al at high temperature
$2\text{M} + 3\text{F}_2 \rightarrow 2\text{MF}_3$ $2\text{M} + 3\text{Cl}_2 \rightarrow 2\text{MCl}_3$ $2\text{M} + 3\text{Br}_2 \rightarrow 2\text{MBr}_3$	All the metals form trihalides } } TI^+ also formed
$2\text{M} + 3\text{I}_2 \rightarrow 2\text{MI}_3$ $\text{TI} + \text{I}_2 \rightarrow \text{TI}^+[\text{I}_3]^-$	Al, Ga, In only Thallium(I) triiodide formed

(Continued)

Table 10.7 (Continued)

Reaction	Comment
$2M + 6HCl \rightarrow 2MCl_3 + 3H_2$	All react with dilute mineral acids, Al passivated by HNO_3 particularly when concentrated
$Al + NaOH + H_2O \rightarrow NaAlO_2 + H_2$ $Na_3AlO_3 + H_2$	Al and Ga only
$M + NH_3 \rightarrow MNH_2$	All the metals form amides

Reaction with water and air

The metal Al is silvery white. Thermodynamically Al should react with water and with air, but in fact it is stable in both. The reason is that a very thin oxide film forms on the surface and protects the metal from further attack. This layer is only 10^{-4} to 10^{-6} mm thick. If the protective oxide covering is removed, for example by amalgamating with mercury, then the metal readily decomposes cold water, forming Al_2O_3 and liberating hydrogen.

Aluminium articles are often ‘anodized’ to give a decorative finish. This is done by electrolysing dilute H_2SO_4 with the aluminium as the anode. This produces a much thicker layer of oxide on the surface (10^{-2} mm). This layer can take up pigments, thus colouring the aluminium.

Aluminium burns in dinitrogen at high temperatures, forming AlN. The other elements do not react.

Reaction with acids and alkalis

Aluminium dissolves in dilute mineral acids liberating hydrogen.



However, concentrated HNO_3 renders the metal passive because it is an oxidizing agent, and produces a protective layer of oxide on the surface. Aluminium also dissolves in aqueous $NaOH$ (and is therefore amphoteric), liberating hydrogen and forming aluminates. (The nature of aluminates is discussed in Section 10.7.)

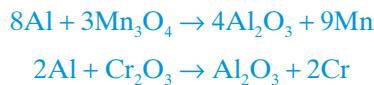


Reaction with dioxygen

Aluminium burns readily in air or dioxygen, and the reaction is strongly exothermic. This is known as the *Thermite reaction*.



The *Thermite reaction* evolves so much energy that it can be dangerous. The aluminium becomes white hot, and often causes fires. For this precise reason mixtures of Al and an oxide such as Fe_2O_3 or SiO_2 (to provide the oxygen) were used to make incendiary bombs during World War II. Warships are sometimes made of aluminium alloys to reduce their weight. A thermite reaction can be started if the ship is hit by a missile. Such fires on ships caused considerable casualties in the Falklands Islands conflict. The very strong affinity of Al for oxygen is used in the metallurgical extraction of other metals from their oxides.



Reaction with the halogens and sulphate

Aluminium reacts with the halogens quite readily, even when cold, forming trihalides.

Aluminium sulphate is used in large amounts. It is made by treating bauxite with H_2SO_4 . It is used as a coagulant and precipitant in treating both drinking water and sewage. It is also used in the paper industry, and as a mordant in dyeing.

Alums

Aluminium ions may crystallize from aqueous solutions, forming double salts. These are called *aluminium alums* and have the general formula $[M^I(H_2O)_6][Al(H_2O)_6](SO_4)_2$. M^I is a singly charged cation such as Na^+ , K^+ or NH_4^+ . The crystals are usually large octahedra, and are extremely pure. Purity is especially important in some applications. Potash alum $[K(H_2O)_6][Al(H_2O)_6](SO_4)_2$ is used as a mordant in dyeing. In this application Al^{3+} is precipitated as $Al(OH)_3$ on cloth to help the dyes bind to the cloth as aluminium complexes. It is essential that Fe^{3+} is absent in order to obtain the 'true' bright colours. Double salts break up in solution, into their constituent ions. Crystals are made up of $[M(H_2O)_6]^+$, $[Al(H_2O)_6]^{3+}$ and two SO_4^- ions. The ions are simply the right size and charge to crystallize together. Apart from this, it is also used for (i) purification of water; (ii) as coagulant and to stop bleeding; (iii) tanning of leather, etc.

Some M^{3+} ions other than Al^{3+} also form *alums* of formula $[M^I(H_2O)_6][M^{III}(H_2O)_6](SO_4)_2$. The most common trivalent ions are Fe^{3+} and Cr^{3+} , but others include Ti^{3+} , V^{3+} , Mn^{3+} , Co^{3+} , In^{3+} , Rh^{3+} , Ir^{3+} and Ga^{3+} .

Note: Li^+ cannot form alum due to its small size.

Cement

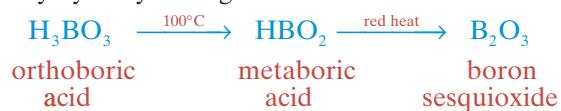
Aluminium compounds, particularly tricalcium aluminate $Ca_3Al_2O_6$, are very important as constituents of Portland and high alumina cements. The formula of tricalcium aluminate is better written $Ca_9[Al_6O_{18}]$, because it contains 12-membered rings of $Al-O-Al-O$ made by joining six AlO_4 tetrahedra. Portland cement is made by heating the correct mixture of limestone ($CaCO_3$) with sand (SiO_2) and clay (aluminosilicate) at a temperature of 1450–1600 °C in a rotary kiln. When mixed with sand and water Portland cement sets to give concrete, a hard whitish insoluble solid, similar in appearance to Portland stone. (Portland stone is limestone quarried on Portland Bill in Dorset, England.) Between 2% and 5% of gypsum $CaSO_4 \cdot 2H_2O$ is added to slow down the setting process, as slow setting greatly increases the strength. The composition of cement is usually given in terms of the oxides. A typical composition for Portland cement is CaO 70%, SiO_2 20%, Al_2O_3 5%, Fe_2O_3 3%, $CaSO_4 \cdot 2H_2O$ 2%.

High alumina cement is made by fusing limestone and bauxite with small amounts of SiO_2 and TiO_2 at 1400–1500 °C in either an open hearth furnace or a rotary kiln. High alumina cement is more expensive than is Portland cement, but has one major advantage over Portland cement – it sets much quicker and develops high strength within one day. It is used to make beams for bridges and buildings. High alumina cement has good resistance to sea water and dilute mineral acids. It withstands temperatures up to 1500 °C and so may be used with refractory bricks in furnaces. A typical analysis of high alumina cement is CaO 40%, Al_2O_3 40%, SiO_2 10%, Fe_2O_3 10%. There has been much publicity over structural failures of beams made of high alumina cement. Failure is due to prolonged exposure to hot wet conditions, or using too much water when mixing the sand and cement. This latter results in it setting too quickly and thus not having time to crystallize properly.

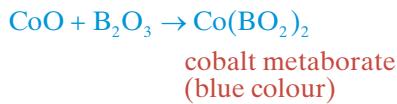
10.6 | COMPOUNDS OF BORON AND OXYGEN

Boron sesquioxide and the borates

These are the most important compounds of boron. Sesqui means one and a half, so the oxide should have a formula $MO_{1\frac{1}{2}}$, or M_2O_3 . All the elements in the group form sesquioxides when heated in dioxygen. B_2O_3 is made more conveniently by dehydrating boric acid:



B_2O_3 is a typical non-metallic oxide and is acidic in its properties. It is the anhydride of orthoboric acid, and it reacts with basic (metallic) oxides, forming salts called borates or metaborates. In the borax bead test, B_2O_3 or borax $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ is heated in a Bunsen burner flame with metal oxides on a loop of platinum wire. The mixture fuses to give a glass-like metaborate bead. Metaborate beads of many transition metals have characteristic colours, and so this reaction provides a means of identifying the metal. This simple test provided the first proof that vitamin B_{12} contained cobalt.



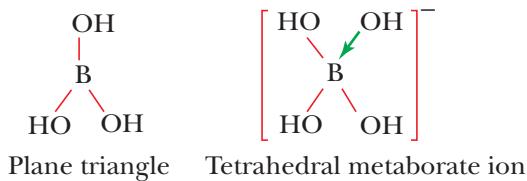
However, it is possible to force B_2O_3 to behave as a basic oxide by reacting with very strongly acidic compounds. Thus with P_2O_5 or As_2O_5 , boron phosphate or boron arsenate are formed.



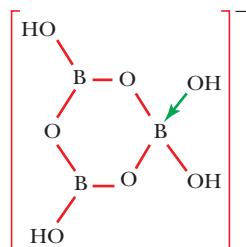
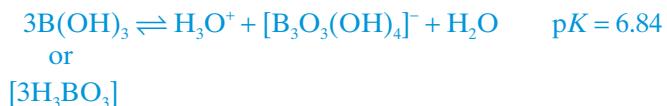
Orthoboric acid H_3BO_3 is soluble in water, and behaves as a weak monobasic acid. It does not donate protons like most acids, but rather it accepts OH^- . It is therefore a Lewis acid, and is better written as $\text{B}(\text{OH})_3$.



or



Polymeric metaborate species are formed at higher concentrations, for example:



Orthoboric acid can be prepared by:

1. Acidification of borax

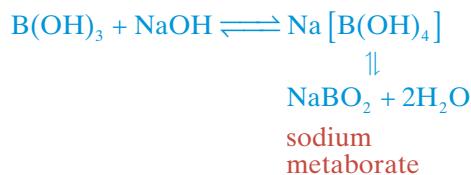


2. Hydrolysis of BX_3 or BH_3

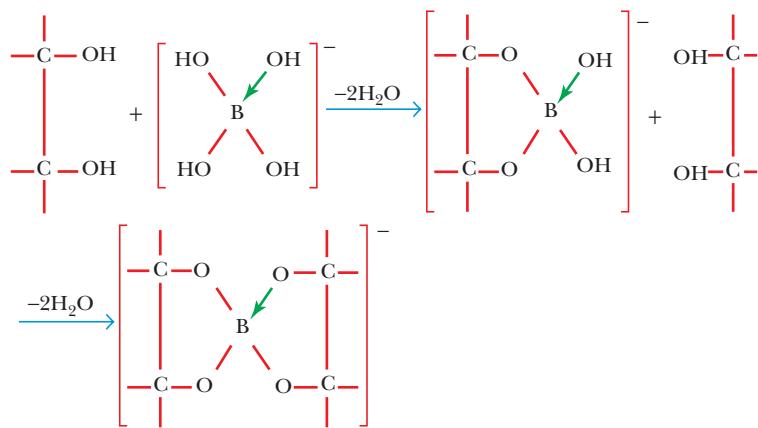


Acidic properties of H_3BO_3 or $\text{B}(\text{OH})_3$

Since $\text{B}(\text{OH})_3$ only partially reacts with water to form H_3O^+ and $[\text{B}(\text{OH})_4]^-$, it behaves as a weak acid. Thus H_3BO_3 or $(\text{B}(\text{OH})_3)$ cannot be titrated satisfactorily with NaOH , as a sharp end point is not obtained. If certain organic polyhydroxy compounds such as glycerol, mannitol or sugars are added to the titration mixture, then $\text{B}(\text{OH})_3$ behaves as a strong monobasic acid. It can now be titrated with NaOH , and the end point is detected using phenolphthalein as indicator (indicator changes at pH 8.3–10.0).

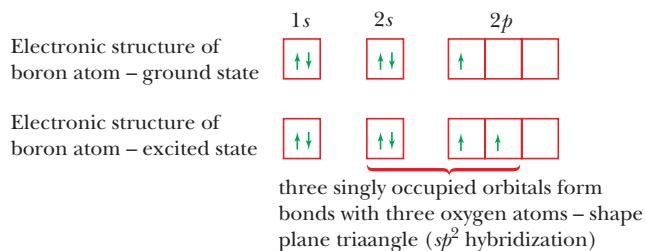


The added compound must be a *cis*-diol, to enhance the acidic properties in this way. (This means that it has OH groups on adjacent carbon atoms in the *cis* configuration.) The *cis*-diol forms very stable complexes with the $[\text{B}(\text{OH})_4]^-$ formed by the forward reaction above, thus effectively removing it from solution. The reaction is reversible. Thus removal of one of the products at the right hand side of the equation upsets the balance, and the reaction proceeds completely to the right. Thus all the $\text{B}(\text{OH})_3$ reacts with NaOH: in effect it acts as a strong acid in the presence of the *cis*-diol *except ethylene glycol*.



Structures of borates

In the simple borates, each B atom is bonded to three oxygen atoms, arranged at the corners of an equilateral triangle. This would be predicted from the orbitals used for bonding.



Thus orthoboric acid contains triangular BO_3^{3-} units. In the solid the $\text{B}(\text{OH})_3$ units are hydrogen bonded together into two-dimensional sheets with almost hexagonal symmetry. (See Figure 10.3.) The layers are quite a large distance apart (3.18 Å), and thus the crystal breaks quite easily into very fine particles. At one time orthoboric acid was used as a mildly antiseptic talcum powder for babies, because it forms a fine powder. It is no longer used since it sometimes caused a rash.

The orthoborates contain discrete BO_3^{3-} ions, and examples include $\text{Mg}_3(\text{BO}_3)_2$ and the lanthanide orthoborates $\text{Ln}^{\text{III}}\text{BO}_3$. In the metaborates simple units (BO_3 planar triangular units or BO_4 tetrahedra) join together to form a variety of polymeric chain and ring structures (see Figure 10.4).

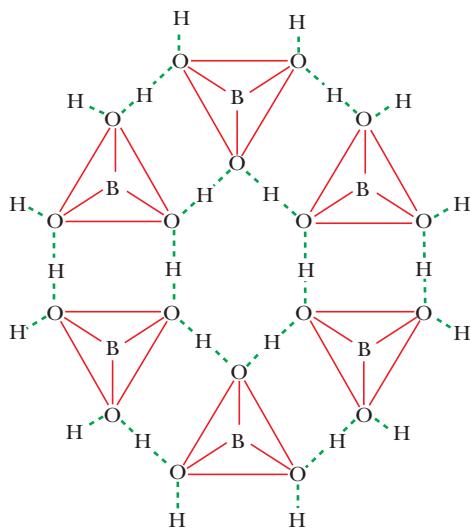


Figure 10.3 Hydrogen bonded structure of orthoboric acid.

Three triangular units share corners and form a ring in sodium and potassium metaborates NaBO_2 and KBO_2 (Figure 10.4a) which are better written as $\text{Na}_3[\text{B}_3\text{O}_6]$ and $\text{K}_3[\text{B}_3\text{O}_6]$.

Borax is usually written as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ but is actually made from two tetrahedra and two triangular units joined as shown (Figure 10.4b) and should be written as $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$.

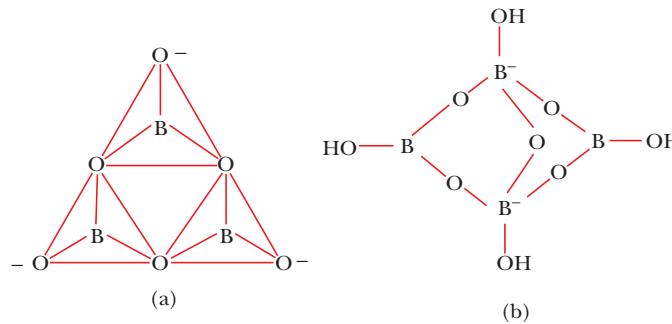
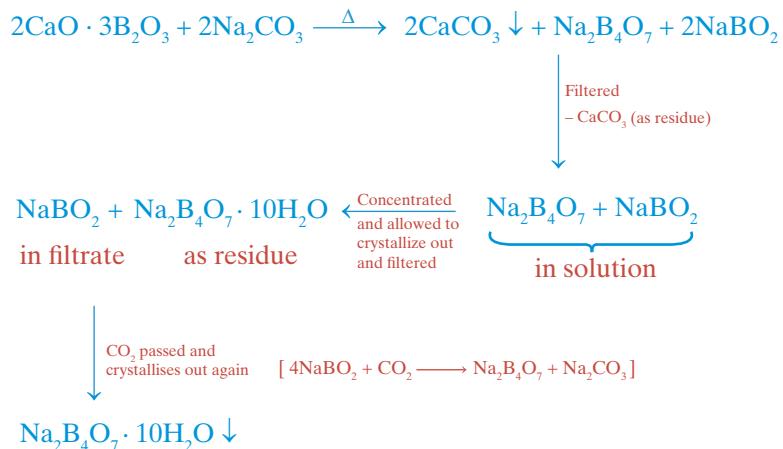


Figure 10.4 Structures of some borates, (a) Metaborate ring $\text{K}_3[\text{B}_3\text{O}_6]$ made up of triangular BO_3 units, (b) Borax ($\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$) is made up of two triangular and two tetrahedral units. This ion is $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$, and the other water molecules are associated with the metal ions.

Borax

The most common pyroborate is borax $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$. It can be prepared by the following sequence of reactions.



It is a useful primary standard for titrating against acids.



One of the products H_3BO_3 is itself a weak acid. Thus the indicator used to detect the end point of this reaction must be one that is unaffected by H_3BO_3 . Methyl orange is normally used, which changes in the pH range 3.1–4.4.

One mole of borax reacts with two moles of acid. This is because when borax is dissolved in water both $B(OH)_3$ and $[B(OH)_4]^-$ are formed, but only the $[B(OH)_4]^-$ reacts with HCl.

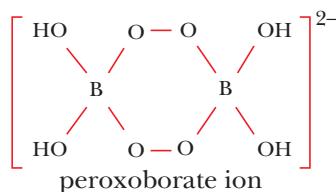
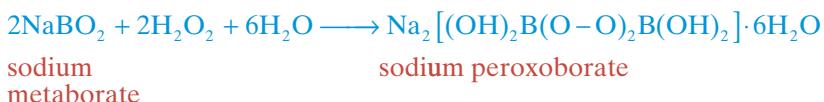


Borax is also used as a buffer since its aqueous solution contains equal amounts of weak acid and its salt.

Sodium peroxoborate

Large amounts of sodium peroxoborate are produced, and there are two main preparative methods:

1. Electrolysis of a solution of sodium borate (containing some Na_2CO_3).
2. By oxidizing boric acid or sodium metaborate with hydrogen peroxide.



Sodium peroxoborate is used as a brightener in washing powders. It is compatible with enzymes which are added to some ‘biological’ powders. In very hot water (over 80°C) the peroxide linkages O—O break down to give H_2O_2 .

Qualitative analysis of boron compounds

When borates are treated with HF (or with concentrated H_2SO_4 and CaF_2) the volatile compound BF_3 is formed. If the BF_3 gas produced is introduced into a flame (for example a Bunsen flame) the flame gives a characteristic green coloration.



An alternative test is to make the ester methyl borate $B(OCH_3)_3$. The suspected borate sample is mixed with concentrated H_2SO_4 to form H_3BO_3 , and warmed with methyl alcohol in a small evaporating basin.



The concentrated H_2SO_4 removes the water formed. The mixture is then set on fire. Methyl borate is volatile, and colours the flame green.

Fluoroboric acid

H_3BO_3 dissolves in aqueous HF, forming fluoroboric acid HBF_4^- .



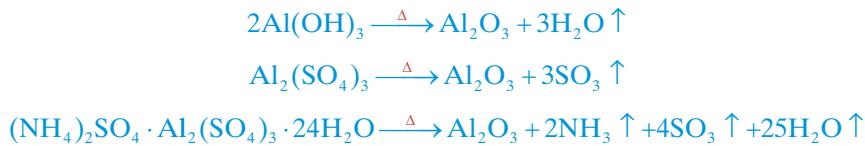
Fluoroboric acid is a strong acid, and commercial solutions contain 40% acid. The $[\text{BF}_4]^-$ ion is tetrahedral.

10.7 | THE OTHER GROUP 13 OXIDES

Alumina Al_2O_3 exists principally in two crystalline forms called $\alpha\text{-Al}_2\text{O}_3$ or corundum, and $\gamma\text{-Al}_2\text{O}_3$, and in addition there is a fibrous form which is made commercially.

Preparation of Al_2O_3

It can be prepared by heating $\text{Al}(\text{OH})_3$, $\text{Al}_2(\text{SO}_4)_3$ and ammonium alum.



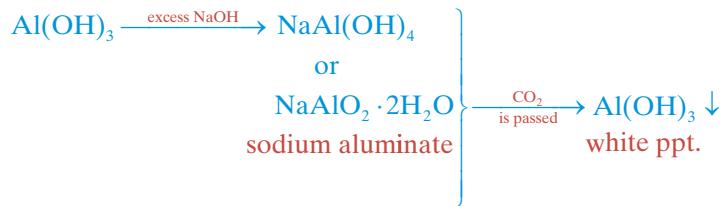
Alumina is white, but it can be coloured by the addition of Cr_2O_3 or Fe_2O_3 . White sapphires are gem quality corundum. Synthetic rubies can be made by strongly heating a mixture of Al_2O_3 and Cr_2O_3 , for example in an oxy-hydrogen flame. Rubies are very hard, and are used for jewellery and to make bearings in watches and instruments. Thus ruby is a mixed oxide. Blue sapphires are another mixed oxide containing traces of Fe^{2+} , Fe^{3+} and Ti^{4+} .

Aluminium has a very strong affinity for oxygen. The enthalpy of formation of Al_2O_3 is $-1670 \text{ kJ mol}^{-1}$, higher (more negative) than for practically all other metal oxides. Thus Al may be used in the thermite reduction of less stable metal oxides.



Amphoteric behaviour – aluminates

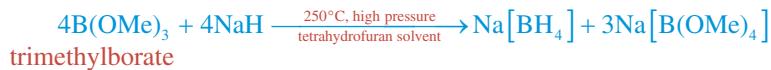
$\text{Al}(\text{OH})_3$ is amphoteric. It reacts principally as a base, i.e. it reacts with acids to form salts that contain the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ion. However, $\text{Al}(\text{OH})_3$ shows some acidic properties when it dissolves in NaOH , forming sodium aluminate. (However, $\text{Al}(\text{OH})_3$ is reprecipitated by the addition of carbon dioxide, showing that the acidic properties are very weak.)



The formula of aluminates is often written as $\text{NaAlO}_2 \cdot 2\text{H}_2\text{O}$ (which is equivalent to $[\text{Al}(\text{OH})_4]^-$).

10.8 | TETRAHYDRIDOBORATES (BOROHYDRIDES)

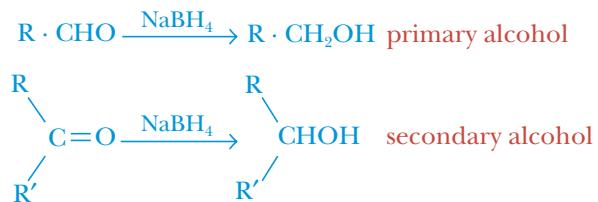
Stable complexes containing the group $[\text{BH}_4]^-$ are well known. These should be called tetrahydridoborates, though the old name borohydride is still widely used. The tetrahydridoborate ion $[\text{BH}_4]^-$ is tetrahedral, and the sodium salt $\text{Na}[\text{BH}_4]$ is the most important compound. It is usually prepared from trimethylborate. It is ionic, and has a sodium chloride structure.



Other tetrahydridoborates are made by treating $\text{Na}[\text{BH}_4]$ with the appropriate metal chloride. The alkali metal tetrahydridoborates are white ionic solids and react with water with varying ease. Thus $\text{Li}[\text{BH}_4]$ reacts violently with water, but $\text{Na}[\text{BH}_4]$ may be recrystallized from cold water with only slight decomposition, and $\text{K}[\text{BH}_4]$ is quite stable.



The alkali metal tetrahydridoborates are valuable reducing agents in both inorganic and organic chemistry. $\text{Na}[\text{BH}_4]$ is stable in alcoholic and aqueous solutions. This makes it a useful reagent for reducing aldehydes to primary alcohols, and ketones to secondary alcohols. It is a nucleophilic reagent, and attacks sites of low electron density. Thus other functional groups such as $\text{C}=\text{C}$, COOH and NO_2 are not normally attacked.



Not all tetrahydridoborates are ionic. The beryllium, aluminium borohydrides become increasingly covalent and volatile. In these the $[\text{BH}_4]^-$ group acts as a ligand and forms covalent compounds with metal ions (Figure 10.5).

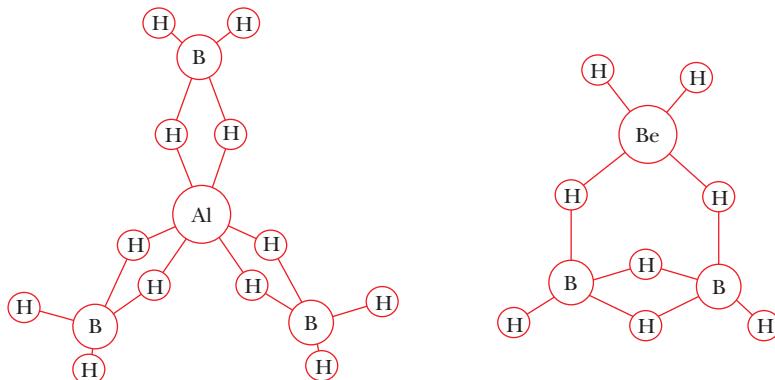
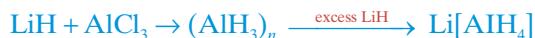


Figure 10.5 Structures of $\text{Al}(\text{BH}_4)_3$ and $\text{Be}(\text{BH}_4)_2$. (After H.J. Eméleus and A.G. Sharpe, *Modern Aspects of Inorganic Chemistry*, 4th ed., 1973, Routledge and Kegan Paul.)

The other elements in the group also form electron-deficient hydrides. $(\text{AlH}_3)_n$ is a white involatile solid. It is a reducing agent and reacts violently with water. It is extensively polymerised by 3-centre hydrogen bridges similar to those in diborane. Aluminium hydride is best made from $\text{Li}[\text{AlH}_4]$ and AlCl_3 . It can be made from LiH and AlCl_3 in either solution, but with excess LiH lithium aluminium hydride $\text{Li}[\text{AlH}_4]$ is formed instead.

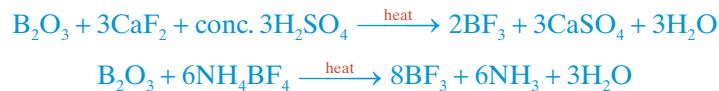


$\text{Li}[\text{AlH}_4]$ is a most useful organic reducing agent because it will reduce functional groups, but in general it does not attack double bonds. It is analogous to the borohydrides but cannot be used in aqueous solutions.

10.9 | HALIDES

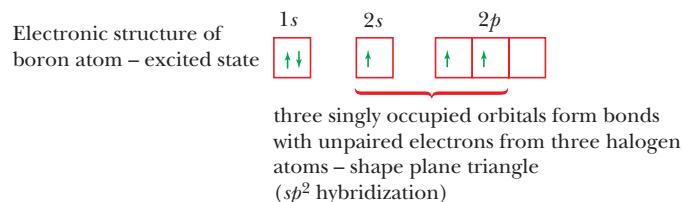
Trihalides

All the elements form trihalides. The boron halides are covalent. BF_3 is gaseous, BCl_3 and BBr_3 are liquid and BI_3 is solid. BF_3 is by far the most important. It is a colourless gas, boiling point -101°C , and is made in large quantities:



Both BF_3 gas and its complex with diethyl ether $(\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{BF}_3$ (a viscous liquid) are commercially available.

The shape of the BF_3 molecule is a planar triangle with bond angles of 120° . This is predicted by VSEPR theory as the most stable shape for three outer electron pairs round B. The valence bond theory also predicts a planar triangle with hybridization of one s and two p orbitals used for bonding. However, the B atom only has six electrons in its outer shell and this is termed *electron deficient*.



The bond lengths in BF_3 are 1.30 \AA , and are significantly shorter than the sum of the covalent radii ($\text{B} = 0.80\text{ \AA}$, $\text{F} = 0.72\text{ \AA}$). The bond energy is very high: 646 kJ mol^{-1} , which is higher than for any single bond. The shortness and strength of the bonds is interpreted in terms of a $p\pi$ - $p\pi$ interaction, that is the bonds possess some double bond character. The empty $2p_z$ atomic orbital on B which is not involved in hybridization is perpendicular to the triangle containing the sp^2 hybrid orbitals. This p_z orbital may accept an electron pair from a full p_z orbital on any one of the three fluorine atoms. Thus a dative π bond is formed, and the B atom attains an octet of electrons. If one localized double bond existed, then there would be one short bond and two longer ones. However, all measurements show that the three bond lengths are identical. The old valence bond explanation of this was resonance between three structures with the double bond in different positions (Figure 10.6). The modern explanation is that the double bond is delocalized. The four p_z atomic orbitals from B and the three F atoms form a four-centre π molecular orbital covering all four atoms which contains two bonding electrons. Delocalized π bonding is described more fully in Chapter 3.

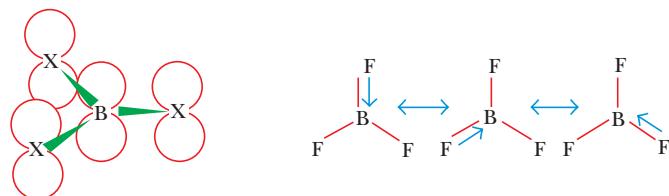
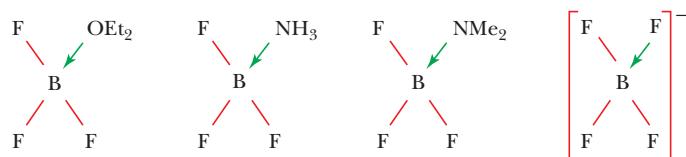


Figure 10.6 Structure of BF_3 .

The empty $2p_z$ orbital on the boron atom in BF_3 can also be filled by a lone pair of electrons from donor molecules such as Et_2O , NH_3 , $(\text{CH}_3)_3\text{N}$ or by ions such as F^- . When this occurs, a tetrahedral molecule or ion is formed.

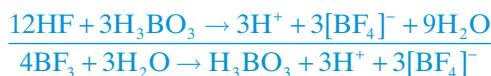


Once a tetrahedral complex has been formed, the possibility for π bonding no longer exists. In $\text{H}_3\text{N} \rightarrow \text{BF}_3$ the $\text{B}-\text{F}$ distance is 1.38 Å, and in $\text{Me}_3\text{N} \rightarrow \text{BF}_3$ the distance is 1.39 Å, much longer than the 1.30 Å in BF_3 . Since the boron halides will accept electron pairs from numerous atoms and ions such as F^- , O , N , P and S , they are acting as strong Lewis acids.

BF_3 is produced from B_2O_3 or borax:



The boron halides are all hydrolysed by water. BF_3 hydrolyses incompletely and forms fluoborates. This is because the HF first formed reacts with the H_3BO_3 ,



The other halides hydrolyse completely, giving boric acid.



The fluoride of Al is ionic and has high melting point. The other halides are largely covalent when anhydrous. AlCl_3 and AlBr_3 exist as dimers, thus attaining an octet of electrons. The dimeric formula is retained when the halides dissolve in non-polar solvents such as benzene. However, when the halides dissolve in water, the high enthalpy of hydration is sufficient to break the covalent dimer into $[\text{M} \cdot 6\text{H}_2\text{O}]^{3+}$ and 3X^- ions. At low temperatures AlCl_3 exists as a close packed lattice of Cl^- with Al^{3+} occupying octahedral holes. On heating Al_2Cl_6 species are formed and the volume of the solid greatly increases (Figure 10.7). This illustrates how close the bonding in this compound is to the ionic/covalent border.

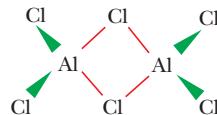


Figure 10.7 Structure of AlCl_3 dimer.

Group 13 elements have only three valency electrons. When these are used to form three covalent bonds, the atom has a share in only six electrons. The compounds are therefore electron deficient. The BX_3 halides attain an octet by π bonding. The other elements in the group have larger atoms and cannot get effective π overlap, so they polymerize to remedy the electron deficiency.

AlCl_3 can be prepared by the following methods:



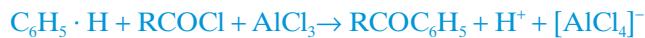
\downarrow cooled



AlCl_3 is an important industrial chemical. Anhydrous AlCl_3 (and to a lesser extent AlBr_3) is used as the 'catalyst' in a variety of Friedel-Crafts type of reactions for alkylations and acylations.



This is not true 'catalytic' action, as the AlCl_3 is used up, and the formation of $[\text{AlCl}_4]^-$ or $[\text{AlBr}_4]^-$ is an essential part of the reaction. Acylations are similar:



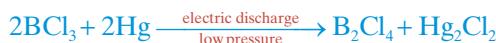
AlCl_3 is also used to catalyse the reaction to make ethyl bromide (which is used to make the petrol additive PbEt_4).



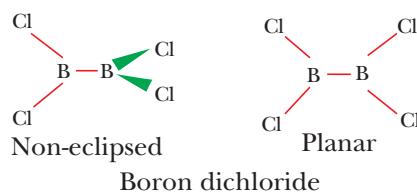
AlCl_3 is also used in the manufacture of anthraquinone (used in the dyestuffs industry), and dodecylbenzene (used to make detergents), and in the isomerization of hydrocarbons (petroleum industry).

Dihalides

Boron forms halides of formula B_2X_4 . These decompose slowly at room temperature. B_2Cl_4 can be made as follows:



There is free rotation about the $\text{B}-\text{B}$ bond, and in the gaseous and liquid states the molecule adopts a non-eclipsed conformation. In the solid state the molecule is planar, because of crystal forces and ease of packing.



Note: Important information

Gallium and indium also form 'dihalides':



These are more properly written $\text{Ga}^+[\text{GaCl}_4]^-$ and $\text{In}^+[\text{InCl}_4]^-$ and contain M(I) and M(III) rather than Ga(II) and In(II).

10.10 | COMPLEXES

Group 13 elements form complexes much more readily than the *s*-block elements, because of their smaller size and increased charge. Tetrahedral hydride and halide complexes such as $\text{Li}[\text{AlH}_4]$ and $\text{H}[\text{BF}_4]$ have already been mentioned. In addition many octahedral complexes are also known. The most important octahedral complexes are those with chelate groups, for example β -diketones such as acetylacetone, oxalate ions and also 8-hydroxyquinoline. (See Figure 10.8.) The latter complex has been used in the gravimetric determination of aluminium.

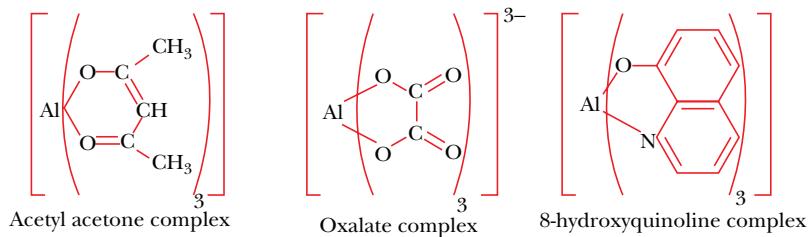


Figure 10.8 Some complexes.

10.11 | DIFFERENCES BETWEEN BORON AND THE OTHER ELEMENTS (ANOMALOUS BEHAVIOUR OF BORON)

Boron differs significantly from the other elements in Group 13, mainly because the atoms are very small. It is always covalent, and it is non-metallic. In addition, boron shows a diagonal relationship with silicon in Group 14.

1. B_2O_3 is an acidic oxide; like SiO_2 . This is in contrast to Al_2O_3 , which is amphoteric.
 2. H_3BO_3 , which may be written $\text{B}(\text{OH})_3$, is acidic, whilst $\text{Al}(\text{OH})_3$ is amphoteric.
 3. Simple borates and silicate ions can polymerize, forming isopolyacids. Both are built on similar structural principles, namely by sharing oxygen atoms. Complicated chains, rings, sheets and other structures are formed in this way. Aluminium forms no analogous compounds.
 4. The hydrides of B are gaseous, readily hydrolysed and spontaneously inflammable. In contrast aluminium hydride is a polymeric solid $(\text{AlH}_3)_n$. SiH_4 is gaseous, readily hydrolysed and inflammable.
 5. Apart from BF_3 , the halides of B and Si hydrolyze readily and vigorously. The aluminium halides are only partly hydrolysed in water.

10.12 | BORON HYBRIDES

Compounds known

None of the Group 13 elements react directly with hydrogen, but several interesting hydrides are known. The boron hydrides are sometimes called boranes by analogy with the alkanes (hydrocarbons). Almost 20 boranes have been reported, and 11 are well characterized. They fall into two series (Table 10.8):

1. $B_nH_{(n+4)}$ (called *nido*-boranes).
 2. A less stable series $B_nH_{(n+6)}$ (called *arachno*-boranes).

In cases where the nomenclature is ambiguous, as for example for pentaborane, it is usual to include the number of hydrogen atoms in the name.

Table 10.8 The two series of boranes

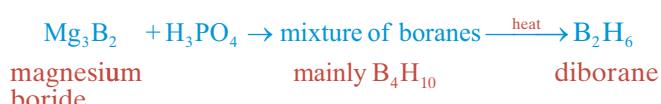
Nido-boranes $B_nH_{(n+4)}$	m.p. (°C)	b.p. (°C)	Arachno-boranes $B_nH_{(n+6)}$	m.p. (°C)	b.p. (°C)
B_2H_6 diborane	-165	-93	B_4H_{10} tetraborane	-120	18
B_5H_9 pentaborane-9	-47	60	B_5H_{11} pentaborane-11	-122	65
B_6H_{10} hexaborane-10	-62	108	B_6H_{12} hexaborane-12	-82	
B_8H_{12} octaborane-12	dec		B_8H_{14} octaborane-14	dec	
			B_9H_{15} (nonaborane or (enneaborane)	3	
$B_{10}H_{14}$ decaborane	-100	213			

dec = decomposes

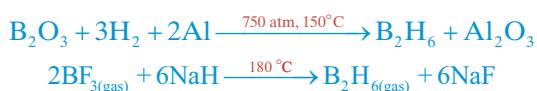
Preparation

Diborane is the simplest and most studied of the hydrides. It is used to prepare the higher boranes, and is an important reagent in synthetic organic chemistry. For the latter purpose it is normally generated *in situ*.

Diborane may be prepared by a variety of methods. Boranes were first prepared by Alfred Stock, who pioneered this branch of chemistry between 1912 and 1936. He heated Mg and B to give magnesium boride Mg_2B_2 , and then treated this with orthophosphoric acid. The reaction gives a mixture of products.



Many other methods have been used:



There are several convenient laboratory preparations:

- Reducing the etherate complexes of the boron halides with $\text{Li}[\text{AlH}_4]$.



- Reacting $\text{Na}[\text{BH}_4]$ and iodine in the solvent diglyme. Diglyme is a polyether $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$.



- Reducing BF_3 with $\text{Na}[\text{BH}_4]$ in diglyme.



Method (3) is particularly useful when diborane is required as a reaction intermediary. It is produced in situ, and used without the need to isolate or purify it.

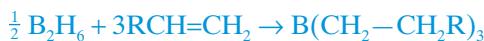
Diborane is a colourless gas, and must be handled with care as it is highly reactive. It catches fire spontaneously in air and explodes with dioxygen. The heat of combustion is very high. In the laboratory it is handled in a vacuum frame. Since it reacts with the grease used to lubricate taps, special taps must be used. It is instantly hydrolysed by water, or aqueous alkali. At red heat the boranes decompose to boron and hydrogen.



10.13 | REACTIONS OF THE BORANES

Hydroboration

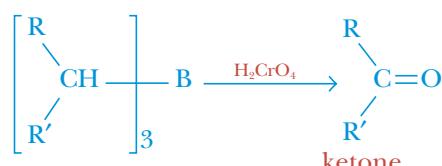
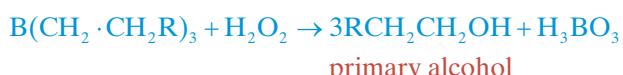
A very important reaction occurs between B_2H_6 (or $\text{BF}_3 + \text{NaBH}_4$) and alkenes and alkynes.

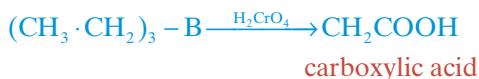


The reactions are carried out in dry ether under an atmosphere of dinitrogen because B_2H_6 and the products are very reactive. The alkylborane products BR_3 are not usually isolated. They may be converted as follows:

- to hydrocarbons by treatment with carboxylic acids,
- to alcohols by reaction with alkaline H_2O_2 , or
- to either ketones or carboxylic acids by oxidation with chromic acid.

The complete process is called hydroboration, and results in *cis*-hydrogenation, or *cis*-hydration. Where the organic molecule is not symmetrical, the reaction follows the anti-Markovnikov rule, that is B attaches to the least substituted C atom.





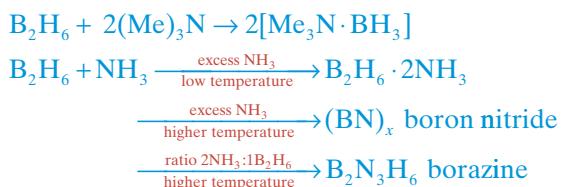
Hydroboration is a simple and useful process for two main reasons:

1. The mild conditions required for the initial hydride addition.
2. The variety of products which can be produced using different reagents to break the B—C bond.

H.C. Brown won the Nobel Prize for Chemistry in 1979 for work on these organoboron compounds.

Reaction with ammonia

All the boranes act as Lewis acids and can accept electron pairs. Thus they react with amines, forming simple adducts. They also react with ammonia, but the products depend on the conditions:



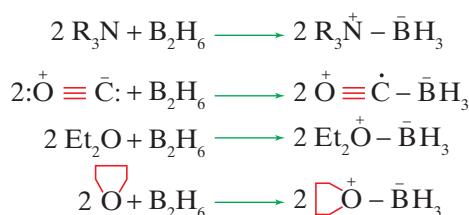
The products formed, i.e. boron nitride or borazine can be determined by fixing the temperature.

NH_3 , RNH_2 and R_2NH cleave amines asymmetrically also forming $[\text{L}_2\text{BH}_2]^+[\text{BH}_4]^-$ type of salts which can be converted into cyclic compounds on heating. For example, the compound $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ is ionic, and comprises $[\text{H}_3\text{N} \rightarrow \text{BH}_2 \leftarrow \text{NH}_3]^+$ and $[\text{BH}_4]^-$ ions. On heating, it forms borazine.



where $\text{L} = \text{NH}_3$, RNH_2 , and R_2NH .

While compounds like R_3N , CO , Et_2O , tetrahydrofuran, react with B_2H_6 forming the adduct associated with symmetrical cleavage.



Boron nitride is a white slippery solid. One B atom and one N atom together have the same number of valency electrons as two C atoms. Thus boron nitride has almost the same structure as graphite, with sheets made up of hexagonal rings of alternate B and N atoms joined together. The sheets are stacked one on top of the other, giving a layer structure (Figure 10.9).

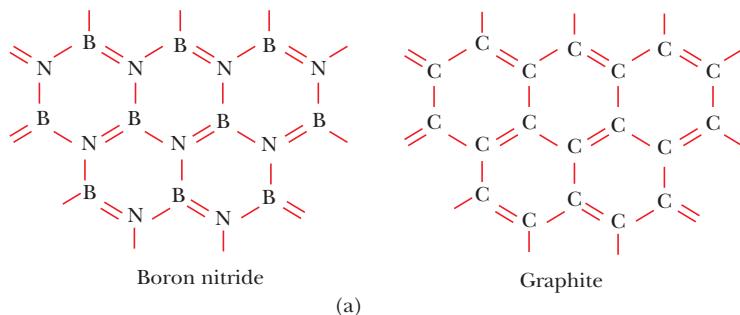


Figure 10.9 Similarity in structure between (a) boron nitride and graphite, (b) borazine and benzene.

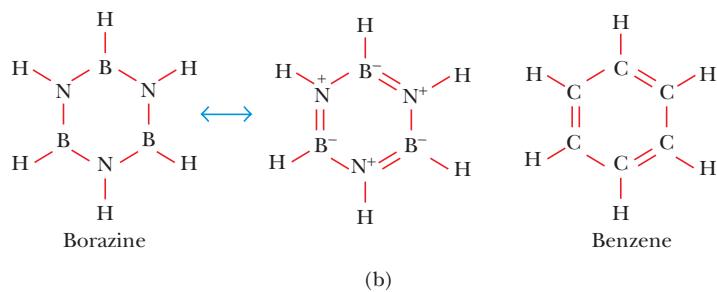
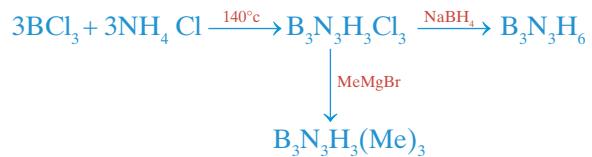


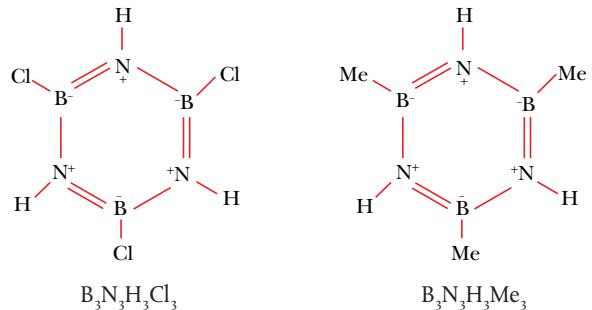
Figure 10.9 (Continued)

Borazine $B_3N_3H_6$ is sometimes called ‘inorganic benzene’ because its structure shows some formal similarity with benzene, with delocalized electrons and aromatic character. Their physical properties are also similar.

Borazine and substituted borazines are now made:



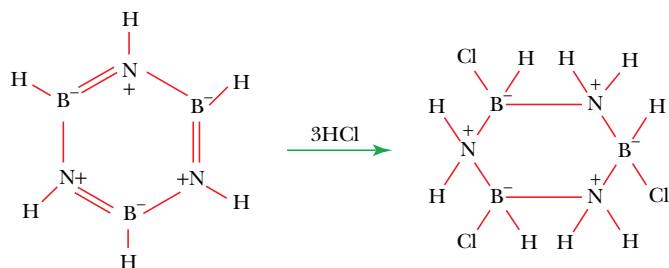
The structures of $B_3N_3H_3Cl_3$ and $B_3N_3H_3(Me)_3$ are as follows.



Borazine forms π complexes such as $B_3N_3H_6 - Cr(CO)_3$ with transition metal compounds. Borazine is considerably more reactive than benzene, and addition reactions occur quite readily:



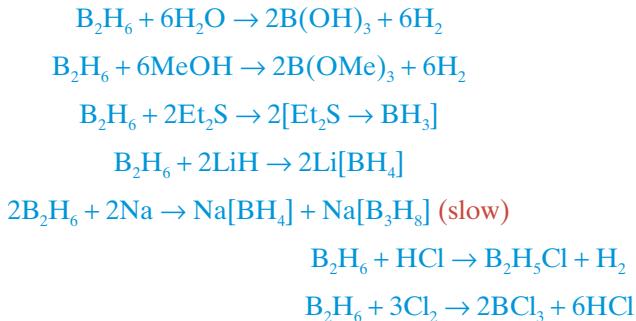
Here the protonation takes place at the N atom because the electron density on each atom in the ring is not identical and is more on the N atom due to its higher electronegativity.



If heated with water, borazine hydrolyses slowly.



Some other reactions of boranes



10.14 | STRUCTURES OF THE BORANES

The bonding and structures of the boranes are of great interest. They are different from all other hydrides. There are not enough valency electrons to form conventional two-electron bonds between all of the adjacent pairs of atoms, and so these compounds are termed electron deficient.

In diborane there are 12 valency electrons, three from each B atom and six from the H atoms. Electron diffraction results indicate the structure shown in Figures 10.10 and 10.11.

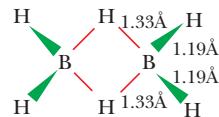


Figure 10.10 The structure of diborane.

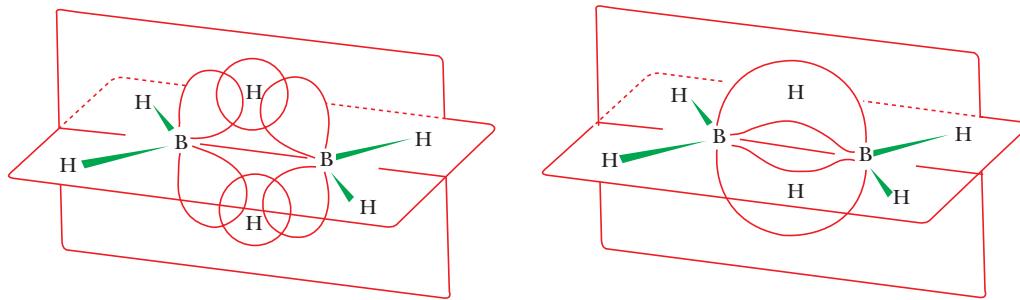


Figure 10.11 Overlap of approximately sp^3 hybrid orbitals from B with an s orbital from H to give a 'banana-shaped' three-centre two-electron bond.

10.15 | ORGANOMETALLIC COMPOUNDS

Besides the carboranes and the alkylboranes discussed earlier, all the Group 13 trihalides will react with Grignard reagents and organolithium reagents, forming trialkyl or triaryl compounds:



The aluminium compounds are unusual because they have dimeric structures, and appear to have three-centre bonds involving sp^3 hybrid orbitals on Al and C in Al—C—Al bridges (Figure 10.12).

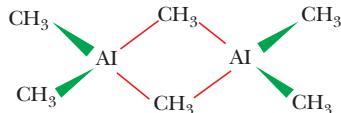


Figure 10.12 Structure of aluminium trimethyl dimer.

SINGLE CORRECT CHOICE TYPE QUESTIONS

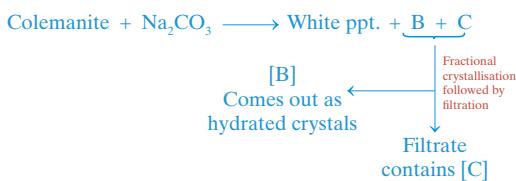
- The highest and the lowest melting point of elements in Group 13, are of respectively
(A) B, Al (B) Tl, B (C) B, Ga (D) B, Tl
- The electropositive character is the maximum for which of the following elements in Group 13?
(A) Al (B) Tl (C) B (D) In
- Boric acid cannot be titrated with NaOH satisfactorily because it is a weak acid. But on addition of diols it behaves as a strong acid. However, on addition of which of the following diols, the titration with NaOH is still not satisfactory on using phenolphthalein as indicator?
(A) Glycerol (B) Mannitol
(C) Sorbitol (D) Ethylene glycol
- The sum of first three ionization energies is the highest for which of the following elements?
(A) Tl (B) Al (C) Ga (D) B
- The first ionization energy for which of the following elements is the highest?
(A) Tl (B) Ga (C) Al (D) In

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

- Which of the following substances expand when they form a solid from liquid state?
(A) H₂O (B) Ga (C) Ge (D) Bi
- Diborane can be prepared by which of the following methods?
(A) Mg₃B₂ + H₃PO₄ $\xrightarrow{\text{heating}}$
(B) BX₃ + LiAlH₄ $\xrightarrow[\text{X = F, Cl, Br}]{\text{ether}}$
(C) BF₃(g) + NaH $\xrightarrow{180^\circ}$
(D) NaBH₄ + I₂ $\xrightarrow[\text{solution}]{\text{in diglyme}}$
- Limited LiH + AlCl₃ \longrightarrow P Which of the following statements is/are correct regarding P?
(A) It is an electron deficient molecule.
(B) It is a non-volatile solid
(C) It acts as a strong reducing agent.
(D) There are 3c-2e bonds in P.
- The most common trivalent cations forming alum is/are
(A) Fe³⁺ (B) Cr³⁺ (C) Al³⁺ (D) Ce³⁺

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1 – 2



- The white precipitate is of
(A) Ca(HCO₃)₂
(B) CaCO₃
(C) Borax
(D) NaBO₂
- On passing _____ gas, compound C converts into B again. The gas is
(A) H₂ (B) CO₂ (C) CO (D) N₂

Passage 2: For Questions 3 – 4

Borazine is more reactive than benzene and addition reactions occur quite readily but hydrolyses occurs slowly.



3. Which of the following statements is incorrect?
 - (A) Maximum number of atoms present in one plane for borazine is 12.
 - (B) The protonation occurs on B-atom in the above reaction with HCl.
 - (C) The product may exist either in the chair or boat form.
 - (D) None of these.
4. Which of the product(s) is/are formed during the hydrolysis of $\text{B}_3\text{N}_3\text{H}_6$?
 - (A) $\text{B}(\text{OH})_3$
 - (B) NH_3
 - (C) H_2
 - (D) All of these

Passage 3: For Questions 5 – 7

Cement is made by heating the mixture of limestone, sand and clay at a temperature of 1450–1600 °C in a rotary kiln. The gypsum is also added between 2–5%.

5. The purpose of addition of gypsum into the cement is
 - (A) to slow down the setting process.
 - (B) to fasten the setting process.
 - (C) to increase its strength.
 - (D) Both (A) and (C).
6. The highest percentage of which compound is present in Portland cement?
 - (A) CaO
 - (B) Al_2O_3
 - (C) SiO_2
 - (D) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
7. Which of the following is/are the properties of high alumina cement?
 - (A) It has good sea-water resistance
 - (B) It can withstand very high temperature
 - (C) It has good resistance towards dilute mineral acid
 - (D) All of these.

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I
- (C) If Statement I is true but Statement II is false.
- (D) If Statement I is false and Statement II is true.

- 1. Statement I:** In alum, M^+ cannot be Li^+ .

Statement II: Li^+ has the smallest size among alkali metal ions.

- 2. Statement I:** Borax solution is acidic in nature.

Statement II: Borax solution acts as a buffer solution also.

- 3. Statement I:** Borazon (cubic boron nitride) is hard while inorganic graphite is slippery in nature.

Statement II: Both have two dimensional-layer structure.

- 4. Statement I:** Aluminium is amphoteric in nature.

Statement II: Aluminium dissolves in dil. HCl as well as in aqueous solution of NaOH evolving H_2 .

- 5. Statement I:** Alum may be used as an antiseptic.

Statement II: Coagulation of colloidal particles in blood is caused by ions present in alum.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. How many compounds given below are correctly matched with their uses?

(i) Borax solution	:	Buffer
(ii) AlCl_3	:	Friedel-Crafts reaction
(iii) Al_2O_3	:	Abrasive powder
(iv) $\text{Al}(\text{OH})_3$:	High alumina cement
(v) $\text{B}(\text{OH})_3$:	Manufacture of optical glasses
(vi) NaBH_4	:	Reducing agent
2. Find the number of H_2 molecules formed from the hydrolysis of one molecule of diborane.

3. Find the number of compounds from the following with which diborane cleaves unsymmetrically forming $[\text{L}_2\text{H}_2\text{B}]^+ [\text{BH}_4^-]$ type of complex.

NH_3 , Et_3N , Et_2NH , EtNH_2 , CO, tetrahydrofuran

4. The maximum number of boron atoms that lie in one plane for the anionic part of borax is _____.

5. The number of sp^3 hybridized atoms in sodium peroxaborate is _____.

6. The number of H_2O molecules required for complete hydrolysis of one molecule of borazine is _____.

7. The number of sp^3 hybridized orbitals in one molecule of borax is _____.

8. When one mole of ammonium alum is heated, the number of moles of gaseous product is _____.
 9. The number of bridge ($3c-2e$) bonds present in $\text{Al}(\text{BH}_4)_3$ is _____.
 10. The tricalcium aluminate is better written as $\text{Ca}_9[\text{Al}_6\text{O}_{18}]$. The anionic part has very similar structure of beryl's anion. The number of Al-O-Al linkage in this structure is _____.

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with one or more statements in Column II.

1. Match the compounds with similar skeleton structure.

Column I	Column II
(A) Borazole	(P) Al_2Br_6
(B) Boron nitride	(Q) Cyclohexane
(C) $\text{B}_3\text{N}_3\text{H}_6\text{Cl}_3$	(R) Benzene
(D) Diborane	(S) Graphite

2. Match the boron halides with their properties.

Column I	Column II
(A) BF_3	(P) Molecule has highest boiling point.
(B) BCl_3	(Q) Compound is liquid.

Column I Column II

(C) BBr_3	(R) Molecule has most effective back bonding.
(D) BI_3	(S) Molecule is solid.
	(T) Compound is gaseous.

3. Match the reactions with the type of products formed.

Column I	Column II
(A) $\text{B}_2\text{H}_6 + \text{MeOH}$	(P) Addition reaction.
(B) $\text{B}_2\text{H}_6 + \text{Et}_2\text{S}$	(Q) Produces ionic compound.
(C) $\text{B}_2\text{H}_6 + \text{MeNH}_2$	(R) Adduct formation.
(D) $\text{B}_2\text{H}_6 + \text{CH}_2 = \text{CHR}$	(S) Evolves hydrogen.

ANSWERS

Single Correct Choice Type Questions

- | | | | |
|--------|--------|--------|--------|
| 1. (C) | 3. (D) | 5. (A) | 7. (B) |
| 2. (A) | 4. (D) | 6. (A) | 8. (C) |

Multiple Correct Choice Type Questions

- | | | | |
|-----------------------|-----------------------|-------------|------------------|
| 1. (A), (B), (C), (D) | 3. (A), (B), (C), (D) | 5. (B), (C) | 7. (B), (C), (D) |
| 2. (A), (B), (C), (D) | 4. (A), (B), (C), (D) | 6. (A), (C) | |

Comprehension Type Questions

- | | | | |
|--------|--------|--------|--------|
| 1. (B) | 3. (B) | 5. (D) | 7. (D) |
| 2. (B) | 4. (D) | 6. (A) | |

Assertion–Reasoning Type Questions

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (A) | 2. (D) | 3. (C) | 4. (A) | 5. (A) |
|--------|--------|--------|--------|--------|

Integer Answer Type Questions

- | | | | | |
|------|------|-------|-------|-------|
| 1. 5 | 3. 3 | 5. 16 | 7. 19 | 9. 6 |
| 2. 6 | 4. 3 | 6. 9 | 8. 31 | 10. 6 |

Matrix-Match Type Questions

1. (A) → (R)
(B) → (S)
(C) → (Q)
(D) → (P)

2. (A) → (R), (T)
(B) → (Q)
(C) → (Q)
(D) → (P), (S)

3. (A) → (S)
(B) → (R)
(C) → (Q)
(D) → (P)

PART 2: THE GROUP 14 ELEMENTS

Carbon is extremely widespread in nature. It is an essential constituent of all living matter, as proteins, carbohydrates and fats. Carbon dioxide is essential in photosynthesis, and is evolved in respiration. Organic chemistry is devoted to the chemistry of carbon-containing compounds. Inorganic compounds produced on a large scale include carbon black, coke, graphite, carbonates, carbon dioxide, carbon monoxide (as a fuel gas), urea, calcium carbide, calcium cyanamide and carbon disulphide. There is great interest in organometallic compounds, carbonyls and π bonding complexes.

The discovery that flint (hydrated SiO_2) had a sharp cutting edge was very important in the development of human technology. Nowadays silicon is important in a number of materials produced in high tonnages. These include cement, ceramics, clays; bricks, glass and the silicone polymers. The very pure element is important in the microelectronics industries (transistors and computer chips).

Germanium is little known, but tin and lead are very well known and have been used as metals since before Biblical times. Lead sheet was used on the floor in the Hanging Gardens of Babylon (one of the wonders of the ancient world) to prevent the water escaping.

The electronic configuration and common oxidation states of Group 14 elements are given in Table 10.9.

Table 10.9 Electronic structures and oxidation states

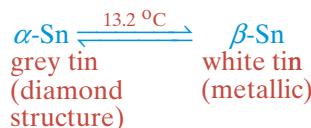
Element		Electronic structure	Oxidation states*
Carbon	C	[He]	$2s^2 2p^2$ IV
Silicon	Si	[Ne]	$3s^2 3p^2$ (II) IV
Germanium	Ge	[Ar]	$3d^{10} 4s^2 4p^2$ II IV
Tin	Sn	[Kr]	$4d^{10} 5s^2 5p^2$ II IV
Lead	Pb	[Xe]	$4f^{14} 5d^{10} 6s^2 6p^2$ II IV

*The most important oxidation states (generally the most abundant and stable) are shown in bold. Other well-characterized but less important states are shown in normal type. Oxidation states that are unstable, or in doubt, are given in parentheses.

10.16 | STRUCTURE AND ALLOTROPY OF THE ELEMENTS

Carbon exists in a large number of allotropic forms. These include diamond, α - and β -graphite, a rare hexagonal form of diamond, and a variety of discrete molecules such as C_{60} , which are really clusters of carbon atoms, and are called collectively fullerenes.

Si, Ge and Sn also have a diamond type of structure, though Sn exists as a metallic form. Pb exists only in the metallic form. *Ge is unusual because the liquid expands when it forms the solid. This property is unique to Ga, Ge and Bi.*



Diamond is extremely unreactive, and in contrast graphite is quite reactive.

Diamonds are typically colourless, though industrial diamonds are often black. Most naturally occurring diamonds contain a trace of nitrogen, but 'blue diamonds' contain a trace of Al instead. In diamond each C atom is tetrahedrally surrounded by four other C atoms, each at a distance of 1.54 Å. The tetrahedra are linked together into a three-dimensional giant molecule. The unit cell is cubic. Strong covalent bonds extend in all directions. Thus the melting point is abnormally high (about 3930 °C) and the structure is very hard (see Figure 10.13). (In a rare modification of diamond, the tetrahedra are arranged differently to give a wurtzite-like structure and a hexagonal unit cell.)

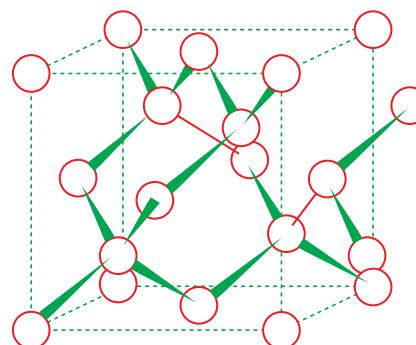


Figure 10.13 The crystal structure of diamond. (Wells, A.F., *Structural Inorganic Chemistry*, Clarendon Press, Oxford.)

Graphite is composed of flat two-dimensional sheets of carbon atoms. Each sheet is a hexagonal net of C atoms, and may be regarded as a fused system of benzene rings (Figure 10.14). The layers are held together by relatively weak van der Waals forces. In α -graphite the layers are arranged in the sequence ABAB... with the third layer exactly above the first layer. In β -graphite the order of layers is ABCABC... The two forms are interconvertible. Heating turns β into α , and grinding turns α into β . In both forms the C–C bond lengths within a sheet are 1.41 Å (similar to the C–C distance of 1.40 Å in benzene). The distance between layers is 3.35 Å. This interlayer distance is large – appreciably more than twice the covalent radius of carbon ($2 \times 1.54 \text{ \AA} = 3.08 \text{ \AA}$). Thus bonding between layers is weak. Graphite cleaves easily between the layers, which accounts for the remarkable softness of the crystals (>1 on Mohs' scale). (See Appendix N for Mohs' scale.) Graphite is used as a lubricant, either on its own or in graphited oil. In contrast, diamond is hard (10 on Mohs' scale) and has abrasive properties. The wide spacing of sheets in graphite also means that the atoms do not pack together to fill space very effectively. Thus the density of graphite (2.22 g cm⁻³) is lower than that of diamond (3.51 g cm⁻³).

In graphite only three of the valency electrons of each carbon atom are involved in forming, σ bonds (using sp^2 hybrid orbitals). The fourth electron forms a π bond. The π electrons are delocalized over the whole sheet, and as they are mobile, graphite conducts electricity. *Conduction can occur in a sheet, but not from one sheet to another. Electrical conductivity of graphite is more than that of diamond while the thermal conductivity of diamond is greater than that of graphite.*

Graphite is thermodynamically more stable than diamond, and its free energy of formation is 1.9 kJ mol⁻¹ lower at room temperature and ordinary pressure. Thermodynamically it is favourable for diamonds to turn into graphite. They do not normally do so because there is a high energy of activation for the process. If this activation energy is available, the change does occur, and diamond tipped drills do burn out and form graphite if they get too hot. The reverse process is not thermodynamically possible, and it requires very forcing high energy conditions to convert graphite to diamond. Graphite can be converted to synthetic diamonds at 1600 °C by a pressure of 50 000–60 000 atmospheres.

When an electric spark is struck between graphite electrodes, soot is produced. (An atmosphere of argon is required to prevent the formation of CO₂ and CO.) This soot is mainly carbon black, but contains significant amounts of a C₆₀ carbon cluster compound sometimes called buckminster fullerene. Smaller amounts of other similar fullerenes C₃₂, C₅₀, C₇₀, C₇₆ and C₈₄ may also be produced. The fullerenes are easily extracted from the soot by dissolving them in benzene or hydrocarbon solvents, giving a wine red solution and finally mustard-coloured crystals. The different compounds are separated chromatographically.

Note: (i) The number of five-membered rings in all fullerenes is 12.

(ii) The number of six-membered rings in a fullerene is $\left(a = \frac{n}{2} - 10 \right)$ where n is the number of carbon atoms. For example in C₆₀, it is 20, C₇₀ it is 25.

This allotrope of carbon differs from diamond and graphite (which form lattices), in that the fullerenes form discrete molecules. The C₆₀ molecule looks rather like a soccer ball, and is sometimes called 'a bucky ball'. It consists of a fused system of five- and six-membered rings (Figure 10.26). Fullerenes are covalent; hence their solubility in organic solvents. However, they can easily be reduced electrochemically, and react with Group 1 metals, forming solids such as K₃C₆₀. This compound behaves as a superconductor below 18 K, which means that it carries an electric current with zero resistance. C₆₀ reacts with OsO₄, which adds across one of the double bonds in the cage. It also forms platinum complexes.

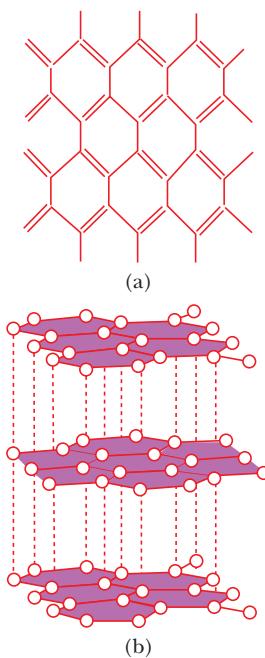


Figure 10.14 (a) The structure of a graphite sheet, (b) Structure of α -graphite.

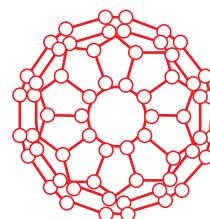


Figure 10.15 Structure of buckminster fullerene.

10.17 | DIFFERENCES BETWEEN CARBON, SILICON AND THE REMAINING ELEMENTS

In general, the first element in a group differs from the rest of the group because of its smaller size and higher electronegativity. These result in the first element having a higher ionization energy, being more covalent, and being less metallic.

Using the classical theory of bonding, the first atom is limited to forming a maximum of four covalent bonds, because only *s* and *p* orbitals are available for bonding. This would limit the coordination number to 4 in these compounds. The majority of carbon compounds are either three- or four-coordinate. However, multi-centre bonds are now well established, and a number of compounds are known where carbon has higher coordination numbers, as shown in Table 10.10.

In addition, carbon differs from the other elements in its unique ability to form *p*π–*p*π multiple bonds, such as C=C, C≡C, C=O, C=S and C≡N. The later elements do not form *p*π–*p*π bonds, principally because the atomic orbitals are too large and diffuse to obtain effective overlap, but they can use *d* orbitals in multiple bonding, particularly between Si and N or O. Thus N(SiH₃)₃ is planar and has *p*π–*d*π bonding but N(CH₃)₃ is pyramidal and has no π bonding (see Figure 10.26).

Carbon also differs from the others in its marked ability to form chains (catenation). This is because the C–C bonds are very strong, and the bonds Si–Si, Ge–Ge and Sn–Sn decrease progressively in strength (Table 10.11).

Carbon and silicon have only *s* and *p* electrons, but the other elements follow a completed transition series with ten *d* electrons. Thus some differences are expected, and carbon and silicon differ both from one another and from the rest of the group, while germanium, tin and lead form a graded series.

Table 10.10 Some carbon compounds with higher coordination numbers

Compound	Coordination number
Al ₂ (CH ₃) ₆	5
B ₁₀ C ₂ H ₁₀ R ₂	6
Li ₄ (CH ₃) ₄	7
[Co ₈ C(CO) ₁₈] ²⁻	8

Table 10.11 Bond energies

Bond	Bond energy (kJ mol ⁻¹)	Remarks
C–C	348	Forms many chains of great length
Si–Si	297	Forms a few chains up to Si ₈ H ₁₈ in hydrides and Si ₁₆ F ₃₄ , Si ₆ Cl ₁₄ , Si ₄ Br ₁₀ with halogens
Ge–Ge	260	Forms a few chains up to Ge ₆ H ₁₄ in hydrides and Ge ₂ Cl ₆ with Cl
Sn–Sn	240	Forms dimmer Sn ₂ H ₆ in hydrides

10.18 | PHYSICAL PROPERTIES

Covalent radii

The covalent radii increase down the group (Table 10.12). *The difference in size between Si and Ge is less than might be otherwise expected because Ge has a full 3d shell which shields the nuclear charge rather ineffectively. In a similar way the small difference in size between Sn and Pb is because of the filling of the 4f shell.*

Table 10.12 Radii, melting points and electronegativity values

Covalent radius (Å)	Ionization energies (kJ mol ⁻¹)				Melting point (°C)	Boiling point (°C)	Pauling's electro-negativity values
	1st	2nd	3rd	4th			
C	0.77	1086	2354	4622	6223	4100	2.5
Si	1.17	786	1573	3232	4351	1420	1.8
Ge	1.22	760	1534	3300	4409	945	1.8
Sn	1.40	707	1409	2943	3821	232	1.8
Pb	1.46	715	1447	3087	4081	327	1.8

Ionization energy

The ionization energies decreases from C to Si sharply, but then the decrease is less and finally increases for lead. This is because of the effects of filling of *d* and *f* shells and the electrons are low shielding in nature.

Melting points

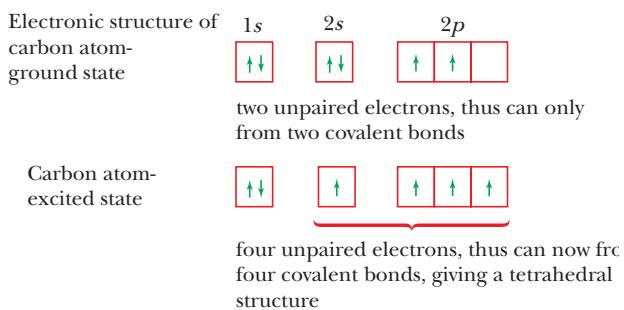
C has an extremely high melting point. Si melts appreciably lower than C, but the values for Si and Ge are still high. They all have the very stable diamond type of lattice. Melting involves breaking the strong covalent bonds in this lattice, and so requires a lot of energy. The melting points decrease on descending the group because the M—M bonds become weaker as the atoms increase in size (Table 10.12). Sn and Pb are metallic, and have much lower melting points. They do not use all four outer electrons for metallic bonding.

Metallic and non-metallic character

The change from non-metal to metal with increasing atomic number is well illustrated in Group 14, where C and Si are non-metals, Ge has some metallic properties, and Sn and Pb are metals. The increase in metallic character shows itself in the structures and appearance of the elements, in physical properties such as malleability and electrical conductivity, and in chemical properties such as the increased tendency to form M^{2+} ions and the acidic or basic properties of the oxides and hydroxides.

Four-covalent compounds

The majority of the compounds are four-covalent. In this case all four outer electrons take part in bonding. In the valence bond theory this is explained by promoting electrons from the ground state to an excited state. The energy needed to unpair and promote the electron is more than repaid by the energy released on forming two extra covalent bonds. The distribution of the four orbitals results in a tetrahedral structure, consistent with sp^3 hybridization.



10.19 | CHEMICAL REACTIVITY

The elements in this group are relatively unreactive. But reactivity increases down the group. The M^{II} oxidation state becomes increasingly stable on descending the group. Pb often appears more noble (unreactive) than expected.

C, Si and Ge are unaffected by water. Sn reacts with steam to give SnO_2 and H_2 . Pb is unaffected by water, probably because of a protective oxide film.

C, Si and Ge are unaffected by dilute acids. Sn dissolves in dilute HNO_3 forming $Sn(NO_3)_2$. Pb dissolves slowly in dilute HCl , forming the sparingly soluble $PbCl_2$ and quite readily in dilute HNO_3 , forming $Pb(NO_3)_2$ and oxides of nitrogen. Pb also dissolves in organic acids (e.g. acetic, citric and oxalic acids). Pb does not dissolve in dilute H_2SO_4 because a surface coating of $PbSO_4$ is formed.

Diamond is unaffected by concentrated acids, but graphite reacts with hot concentrated HNO_3 , forming mellitic acid, and with a mixture of hot concentrated HF/HNO_3 , forming graphite oxide. Si is oxidized and fluorinated by concentrated HF/HNO_3 . Ge dissolves slowly in hot concentrated H_2SO_4 and in HNO_3 . Sn dissolves in several concentrated acids. Pb does not dissolve in concentrated HCl because a surface coating of $PbCl_2$ is formed.

C is unaffected by alkalis. Si reacts slowly with cold aqueous solutions of NaOH, and readily with hot solutions, giving solutions of silicates $[\text{SiO}_4]^{4-}$. Sn and Pb are slowly attacked by cold alkali, and rapidly by hot alkali, giving stannates $\text{Na}_2[\text{Sn}(\text{OH})_6]$ and plumbates $\text{Na}_2[\text{Pb}(\text{OH})_6]$. Thus Sn and Pb are amphoteric.

Diamond does not react with the halogens, but graphite reacts with F_2 at 500°C , forming intercalation compounds or graphite fluoride $(\text{CF})_n$. Si and Ge react readily with all the halogens, forming volatile halides SiX_4 and GeX_4 . Sn and Pb are less reactive. Sn reacts with Cl_2 and Br_2 in the cold, and with F_2 and I_2 on warming, giving SnX_4 . Pb reacts with F_2 in the cold, forming PbF_2 , and with Cl_2 on heating, giving PbCl_2 .

Inert pair effect

The inert pair effect shows itself increasingly in the heavier members of the group. There is a decrease in stability of the (+IV) oxidation state and an increase in the stability of the (+II) state on descending the group. Ge(+II) is a strong reducing agent whereas Ge(+IV) is stable. Sn(+II) exists as simple ions which are strongly reducing but Sn(+IV) is covalent and stable. Pb(+II) is ionic, stable and more common than Pb(+IV) , which is oxidizing. The lower valencies are more ionic because the radius of M^{2+} is greater than that of M^{4+} and according to Fajans' rules, the smaller the ion the greater the tendency to covalency.

10.20 | CARBIDES

Compounds of carbon and a less electronegative element are called carbides. This excludes compounds with N, P, O, S and the halogens from this section. Carbides are of three main types:

1. ionic or salt-like
2. interstitial or metallic
3. covalent

The formulae of some of the compounds cannot be rationalized by the application of simple valency rules. All three types are prepared by heating the metal or its oxide with carbon or a hydrocarbon at temperatures of 2000°C .

Salt-like carbides

It is convenient to group these depending on whether the structure contains C , C_2 or C_3 anions.

Beryllium carbide Be_2C is a red solid and may be made by heating C and BeO at 2000°C . Aluminium carbide Al_4C_3 is a pale yellow solid formed by heating the elements in an electric furnace. Be_2C contains individual C atoms/ions, but the structure of Al_4C_3 is complex. It is misleading to formulate the structure as 4Al^{3+} and 3C^{4-} as such a high charge separation is unlikely. Both Be_2C and Al_4C_3 are called *methanides* because they react with H_2O , yielding methane.

Carbides with a C_2 unit are well known. They are formed mainly by the elements in Group 1 ($\text{M}^{\text{I}}\text{C}_2$); Group 2 ($\text{M}^{\text{II}}\text{C}_2$); the coinage metals (Cu, Ag, Au); Zn and Cd; and some of the lanthanides (LnC_2 and $\text{Ln}_4(\text{C}_2)_3$). These are all colourless ionic compounds and contain the carbide ion $(-\text{C}\equiv\text{C}-)^{2-}$. By far the most important compound is CaC_2 . This is made commercially by strongly heating lime and coke:



The reaction is endothermic, and a temperature of 2200°C is required. These carbides react exothermically with water, liberating ethyne (formerly called acetylene), so they are called *acetylides*.



At one time calcium carbide was the major source of acetylene for oxy-acetylene welding, but ethyne is now obtained mainly from oil. CaC_2 is an important chemical intermediate and is used on an industrial scale to produce calcium cyanamide. Cyanamide is used as a nitrogenous fertilizer, and to make urea and melamine.



One of the two carbides of magnesium Mg_2C_3 contains a C_3 unit, and on hydrolysis with water it yields propyne $\text{CH}_3-\text{C}\equiv\text{CH}$.

Interstitial carbides

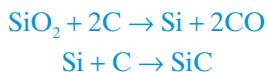
These are formed mostly by transition elements, and some of the lanthanides and actinides. The Cr, Mn, Fe, Co and Ni groups form a large number of carbides with a wide range of stoichiometries. They are typically infusible or are very high melting, and are very hard. For example, TaC has a melting point of 3900 °C, and is very hard (9–10 on Mohs' scale of hardness), and WC is also very hard. Both are used to make cutting tools for lathes. Interstitial carbides retain many of the properties of metals. *They conduct electricity by metallic conduction, and have a lustre like a metal.*

In these compounds, C atoms occupy octahedral holes in the close-packed metal lattice, and so do not affect the electrical conductivity of the metal. Provided that the size of the metal is greater than 1.35 Å, the octahedral holes are large enough to accommodate C atoms without distorting the metal lattice. (Since we are considering a metal lattice, 12-coordinate radii must be used.) If all the octahedral holes are occupied the formula is MC. Interstitial carbides are generally unreactive. They do not react with H₂O like ionic carbides. Most react slowly with concentrated HF or HNO₃.

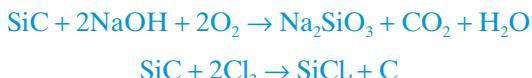
The hardness and density are increased for these carbides while malleability and ductility are decreased.

Covalent carbides

SiC and B₄C are the most important. Silicon carbide is hard (9.5 on Mohs' scale), infusible and chemically inert. It is widely used as an abrasive called **carborundum**, and it is prepared by heating quartz or sand with an excess of coke in an electric furnace at 2000–2500 °C.



SiC is very unreactive. It is unaffected by acids (except H₃PO₄), but it does react with NaOH and air, and with Cl₂ at 100 °C.



SiC is often dark purple, black or dark green due to traces of Fe and other impurities, but pure samples are pale yellow to colourless. SiC has a three-dimensional structure of Si and C atoms, each atom tetrahedrally surrounded by four of the other kind. There are a large number of different crystal forms based on either the diamond or wurtzite structures. Boron carbide is even harder than silicon carbide and is used both as an abrasive and as a shield from radiation. Its formula is more correctly represented by B₁₃C₂.

10.21 | OXYGEN COMPOUNDS OF CARBON

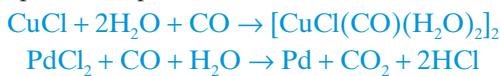
Carbon forms more oxides than the other elements, and these oxides differ from those of the other elements because they contain $p\pi-p\pi$ multiple bonds between C and O. Two of these oxides, CO and CO₂, are extremely stable and important. Three are less stable: C₃O₂, C₅O₂ and C₁₂O₉. Others which are even less stable include graphite oxide, C₂O and C₂O₃.

Carbon monoxide CO

CO is a colourless, odourless, poisonous gas. It is formed when C is burned in a limited amount of air. In the laboratory it is prepared by dehydrating formic acid with concentrated H₂SO₄ or by reaction between K₄[Fe(CN)₆] and concentrated H₂SO₄ (while dilute H₂SO₄ evolves highly poisonous HCN gas).



CO can be detected because it burns with a blue flame. It also reduces an aqueous PdCl₂ solution to metallic Pd. CO can be absorbed by aqueous suspension of CuCl



When passed through a solution of I_2O_5 it liberates I_2 , i.e. it reduces I_2O_5 to I_2 . This reaction is used to estimate CO quantitatively. The I_2 is titrated with $Na_2S_2O_3$.



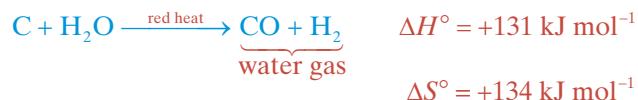
CO is toxic because it forms a complex with haemoglobin in the blood, and this complex is 300 times more stable than oxy-haemoglobin. This prevents the haemoglobin in the red blood corpuscles from carrying oxygen round the body. This causes an oxygen deficiency, leading to unconsciousness and then death. CO is sparingly soluble in water and is a neutral oxide. CO is an important fuel, because it evolves a considerable amount of heat when it burns in air.



The following are all important industrial fuels:

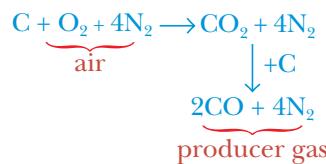
1. *Water gas*: an equimolecular mixture of CO and H_2 .
2. *Producer gas*: a mixture of CO and N_2 .
3. *Coal gas*: a mixture of CO, H_2 , CH_4 and CO_2 , produced at a gasworks by distilling coal, and stored in large gas holders. This was the 'town gas' supplied to peoples' homes for cooking and heating. In the UK it has now been replaced by natural gas (CH_4), but town gas is still used in some countries.

Water gas is made by blowing steam through red or white hot coke.



The water gas reaction is strongly endothermic ($\Delta G = \Delta H - T\Delta S$). Thus the coke cools down, and at intervals the steam must be turned off and air blown through to reheat the coke. It is a particularly good fuel, i.e. it has a high calorific value, because both CO and H_2 burn and evolve heat.

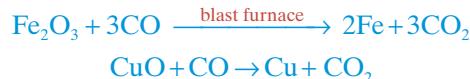
Producer gas is made by blowing air through red hot coke.



The overall reaction is exothermic, so the coke does not cool down as with water gas.



Producer gas is a less efficient fuel than water gas, i.e. it has a lower calorific value, as only part of the gas will burn. The approximate composition of producer gas is 70% N_2 , 25% CO, 4% CO_2 with traces of CH_4 , H_2 and O_2 . CO is a good reducing agent and can reduce many metal oxides to the metal.

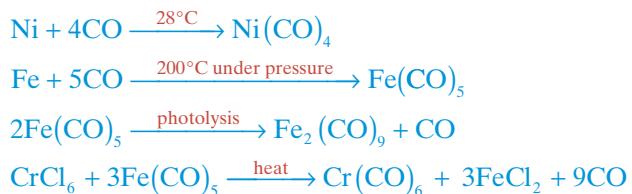


CO is an important ligand. It can donate an electron pair to many transition metals, forming carbonyl compounds. The number of CO molecules bonded to the metal in this way is generally in accordance with the effective atomic number rule (see Chapter 5). However, the bonding is more complicated than this implies. A number of different stoichiometries are formed (Table 10.13).

Table 10.13 Binary metal carbonyls formed by the first row transition elements

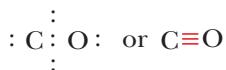
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$	
						$Fe_2(CO)_9$	$Co_4(CO)_{12}$		
						$Fe_3(CO)_{12}$	$Co_6(CO)_{16}$		

Carbonyl compounds may be made by a variety of reactions:



In the Mond process (now obsolete) for purifying nickel, nickel carbonyl $\text{Ni}(\text{CO})_4$ was made from Ni and CO at 50°C . (Water gas was used as the source of CO.) $\text{Ni}(\text{CO})_4$ is a gas and can be separated from other metals and impurities. The $\text{Ni}(\text{CO})_4$ gas was then decomposed at 230°C .

The bonding in CO may be represented as three electron pairs shared between the two atoms:



It is better represented using the molecular orbital theory (see Chapter 3).

CO is the most studied organometallic ligand. Because of the back bonding it is sometimes called a π acceptor ligand. The drift of π electron density from M to C makes the ligand more negative, which in turn enhances its σ donating power. Thus CO forms weak bonds to Lewis acids (electron pair acceptors) such as BF_3 as only σ bonding is involved. In contrast CO forms strong bonds to transition metals where both σ and π bonding can occur. Other π acceptor ligands include CN^- , RNC , and NO^+ . Comparing these ligands, the strengths of the σ bonds are in the order $\text{CN}^- > \text{RNC} > \text{CO} > \text{NO}^+$, whilst their π acceptor properties are in the reverse order.

CO is a very versatile ligand. It may act as a bridging group between the two metal atoms, for example in di-iron ennea carbonyl $\text{Fe}_2(\text{CO})_9$ (Figure 10.16). CO may stabilize metal clusters by the C forming a multi-centre bond with three metal atoms, and the π^* orbitals in CO may be involved in bonding to other metal atoms.

Carbon monoxide is quite reactive, and combines readily with O, S and the halogens F, Cl and Br.



The carbonyl halides are readily hydrolyzed by water, and react with ammonia to form urea:



Carbonyl chloride is extremely toxic, and was used as a poisonous gas in World War I. Nowadays it is produced in quite large quantities to make tolylene diisocyanate which is an intermediate in the manufacture of polyurethane plastics.

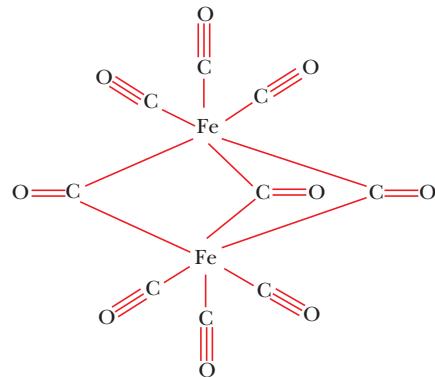
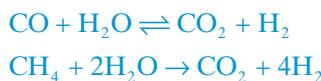


Figure 10.16 Structure of $\text{Fe}_2(\text{CO})_9$.

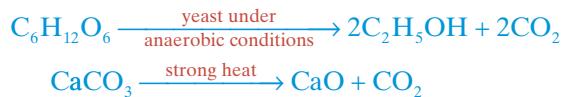
Carbon dioxide CO_2

CO_2 is a colourless, odourless gas. It is a major industrial chemical and its main industrial source is as a by-product from the manufacture of hydrogen for making ammonia.

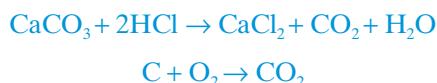


Preparation of CO_2

CO_2 is recovered from fermentation processes in breweries, from the gases evolved from calcining limestone in lime kilns and from the flue gases from coal-burning electric power stations.



It is obtained in small amounts by the action of dilute acids on carbonates. It can also be made by burning carbon in excess of air.

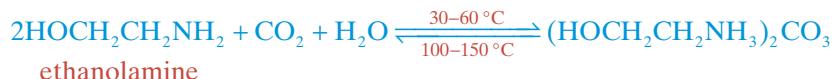


Recovery of CO_2

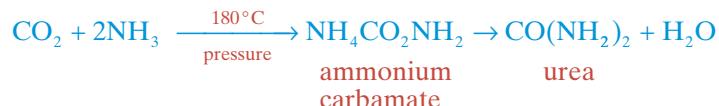
CO_2 is recovered by absorbing it in either aqueous Na_2CO_3 or ethanolamine.



Girbotol process

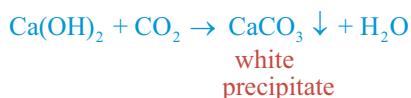


CO_2 gas can be liquified under pressure between -57 $^{\circ}\text{C}$ and $+31$ $^{\circ}\text{C}$. About 80% is sold in liquid form, and 20% as solid. The solid is produced as white snow by expanding the gas from cylinders. (Expansion causes cooling.) This is compacted into blocks and sold. Solid CO_2 sublimes directly to the vapour state (without going through the liquid state) at -78 $^{\circ}\text{C}$ under atmospheric pressure. Over half the CO_2 produced is used as a refrigerant. Solid CO_2 is called 'dry ice' or 'cardice', and is used to freeze meat, frozen foods and ice cream, and in the laboratory as a coolant. Over a quarter is used to carbonate drinks (Coca-Cola, lemonade, beer etc.). Other uses include the manufacture of urea, as an inert atmosphere, and for neutralizing alkalis.



Small scale uses of CO_2 include use in fire extinguishers, blasting in coal mines, as an aerosol propellant, and for inflating life-rafts.

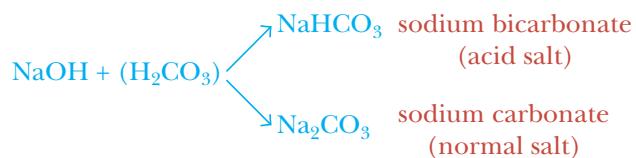
CO_2 gas is detected by its action on lime water $\text{Ca}(\text{OH})_2$ or baryta water $\text{Ba}(\text{OH})_2$, as a white insoluble precipitate of CaCO_3 or BaCO_3 is formed. If more CO_2 is passed through the mixture, the cloudiness disappears as the soluble bicarbonate is formed.



CO_2 is an acidic oxide, and reacts with bases, forming salts. It dissolves in water but it is only slightly hydrated to carbonic acid H_2CO_3 , and the solution contains few carbonate or bicarbonate ions. A hydrate $\text{CO}_2 \cdot 8\text{H}_2\text{O}$ can be crystallized at 0°C under a pressure of 50 atmospheres CO_2 .



Carbonic acid gives rise to two series of salts, hydrogencarbonates (otherwise called bicarbonates), and carbonates.



The structure of CO_2 is linear O—C—O. Both C—O bonds are the same length. In addition to σ bonds between C and O. There is a three-centre four-electron π bond covering all three atoms. This adds two π bonds to the structure in addition to the two π bonds. Thus the C—O bond order is two.

Biologically, carbon dioxide is important in the processes of photosynthesis, where the green parts of plants manufacture glucose sugar. Ultimately all animal and plant life depends on this process.

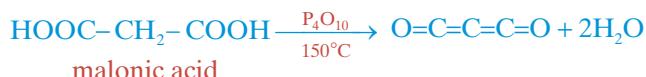


The reverse reaction occurs during the process of respiration, where animals and plants release energy.



Carbon suboxides

Carbon suboxide C_3O_2 is a foul-smelling gas, boiling point 6°C . It is made by dehydrating malonic acid with P_4O_{10} .



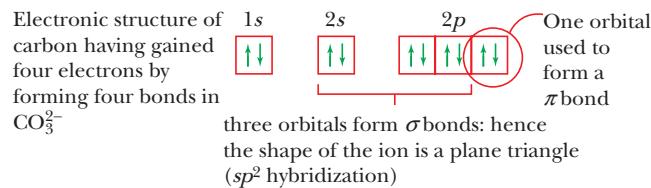
It is stable at -78°C and the molecule is linear. At room temperature the gas polymerizes to a yellow solid, and at higher temperatures to red and purple solids. The oxide reacts with H_2O , giving malonic acid, and with HCl and NH_3 as follows:



There are disputed reports that C_5O_2 is formed by thermolysis of C_3O_2 . The only other stable suboxide is C_{12}O_9 . This is a white solid, and is the anhydride of mellitic acid $\text{C}_6(\text{COOH})_6$.

10.22 | CARBONATES

There are two series of salts from carbonic acid H_2CO_3 , namely carbonates CO_3^{2-} and hydrogencarbonates HCO_3^- . The CO_3^{2-} ion is flat. The CO_4^{4-} ion does not exist, even though SiO_4^{4-} does. This is probably because C is too small, and the situation is analogous to the formation of NO_3^- and PO_4^{3-} in Group 15. The structure of the CO_3^{2-} ion may be represented as follows:



The π bonding in the CO_3^{2-} ion is best described using a delocalized π molecular orbital covering all four atoms. (See Chapter 3.)

Carbonate ions are colourless and hence the carbonates of Group 1 and 2 metals are white. Though Ag^+ salts are typically white, Ag_2CO_3 is yellow due to the strong polarizing effect of Ag^+ . $(\text{NH}_4)_2\text{CO}_3$ and Group 1 carbonates are readily soluble in water, except Li_2CO_3 which is only slightly soluble.



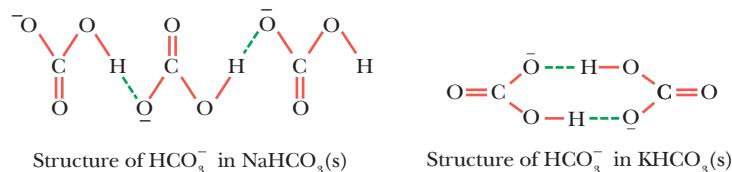
Group 1 carbonates are stable to heat, and melt without decomposing. Group 2 carbonates all decompose if heated sufficiently strongly. Their stability increases as the size of the metal ion increases. Most other carbonates decompose easily.



	BeCO_3	MgCO_3	CaCO_3	SrCO_3	BaCO_3
Decomposition temperature	<100 °C	540 °C	900 °C	1290 °C	1360 °C

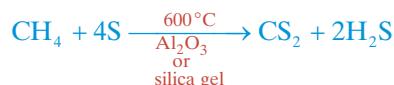
The only solid bicarbonates known are those of the Group 1 metals and of NH_4^+ . These are colourless solids, and are somewhat less soluble than the corresponding carbonates. They decompose easily on heating. The solid structures of these contain polymeric chains of HCO_3^- groups hydrogen bonded together.

The structures of sodium and potassium bicarbonates are as follows:



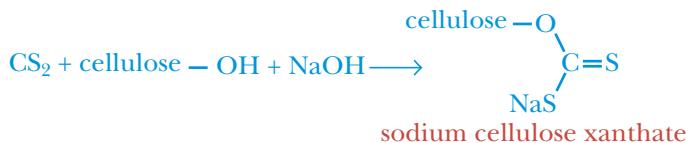
10.23 | SULPHIDES OF CARBON

Carbon disulphide CS_2 is the most important sulphide of carbon. It is a colourless volatile liquid, b.p. 46 °C. It is dangerous to handle because it is very flammable, it has a very low flash point (30 °C) and it ignites spontaneously at 100 °C. It is very poisonous, affecting the brain and central nervous system. Pure samples smell like ether, but organic impurities frequently give it an extremely foul smell. At one time it was produced by heating charcoal and S vapour at about 850 °C. Nowadays it is produced mainly from a gas phase reaction between natural gas and sulphur, catalysed by Al_2O_3 or silica gel.



The main uses of CS, are as follows:

1. The manufacture of viscose rayon (artificial silk) and cellophane. CS_2 reacts with cellulose and NaOH to form sodium cellulose dithiocarbonate (cellulose xanthate).



This is dissolved in lye (aqueous alkali) to give a viscous solution called 'viscose'. On acidification, 'viscose' is converted back to cellulose in the form of fibres (either rayon or cellulose wool), or as a thin film (cellophane).

2. The manufacture of CCl_4 (see later under 'Halides').
 3. Smaller amounts are used as a solvent for S in the cold vulcanization of rubber.

CS₂ reacts with aqueous NaOH, giving a mixture of sodium carbonate and sodium trithiocarbonate:



CS₂ reacts with NH₃, giving ammonium dithiocarbamate:



CS₂ is a linear molecule with a similar structure to CO₂. CS₂ forms complexes more readily than CO₂.

Sunlight changes CS_2 to CS, which is why CS_2 is stored in dark coloured bottles. A high frequency electric charge also converts CS_2 vapour to CS. CS is unlike CO , and is a highly reactive radical even at the temperature of liquid air. Passing an arc through CS_2 gives C_3S_2 . This is thought to have the structure $\text{S}=\text{C}=\text{C}=\text{S}$. It is a red liquid that polymerizes slowly (as does C_3O_2).

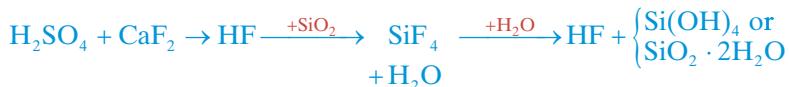
10.24 | OXIDES OF SILICON

Two oxides of silicon, SiO and SiO_2 , have been reported. Silicon monoxide is thought to be formed by high temperature reduction of SiO_2 with Si, but its existence at room temperature is in doubt.



Silicon dioxide SiO_2 is commonly called silica, and it is widely found as sand and quartz. Group 14 elements typically form four bonds. Carbon can form $p\pi-p\pi$ double bonds and hence CO_2 is a discrete molecule and is a gas. Silicon cannot form double bonds in this way using $p\pi-p\pi$ orbitals. (A substantial number of silicon compounds are now known to contain $p\pi-d\pi$ bonds in which the silicon atom appears to use d orbitals for bonding.) Thus SiO_2 forms an infinite three-dimensional structure, and SiO_2 is a high melting solid.

Silica is unreactive. It is an acidic oxide and so does not react with acids. However, it does react with HF, forming silicon tetrafluoride SiF_4 . This reaction is used in qualitative analysis to detect silicates: when the SiF_4 comes into contact with a drop of water it is hydrolysed to silicic acid. This can be seen as a white solid forming on the surface of the drop of water.



SiO_2 is an acidic oxide. It dissolves slowly in aqueous alkali, and more rapidly in fused alkalis MOH or fused carbonates M_2CO_3 , forming silicates.



This reaction accounts for ground glass stoppers sticking in reagent bottles containing NaOH. Of the halogens, only fluorine attacks SiO_2 .

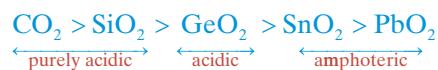


Silica gel is amorphous and very porous. It is obtained by dehydrating silicic acid, and contains about 4% water. It is widely used as a drying agent, a catalyst, and in chromatography.

Kieselguhr is another form of SiO_2 . It is a fine white powder, and is used in filtration plants, as an abrasive, and as an inert filler. (Gelignite is a mixture of the explosive nitrobenzene (liquid) and inert kieselguhr (solid)).

10.25 | OXIDES OF TIN AND LEAD

Dioxides like MO_2 are available for all the group elements and their acidity order decreases down the group as follows:



All monoxides are also available except SiO under ordinary conditions. Here also, the order of acidic character is as follows:



Oxides of Tin

There are two oxides of tin, SnO (grey) and SnO_2 (white).

Preparation

When SnC_2O_4 is heated in the absence and in presence of air, SnO and SnO_2 are formed, respectively.



Other methods are:

For SnO :



For SnO_2 :



Properties

SnO and SnO_2 are both amphoteric in nature which is supported by the following reactions with:

Acids:



SnO_2 only reacts with (or dissolves) in hot conc. H_2SO_4 ; though it does not dissolve in aqua regia.



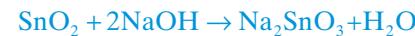
Alkali:



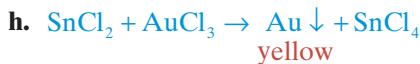
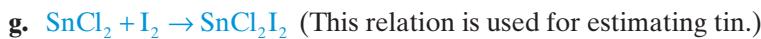
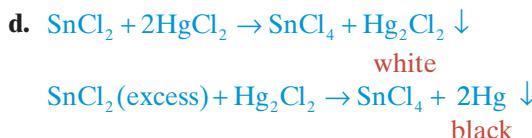
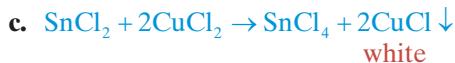
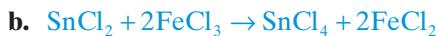
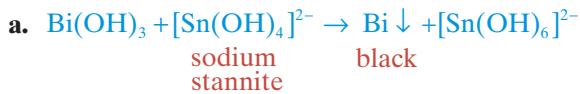
But under hot conditions $\text{Sn}(\text{II})$ is oxidized into $\text{Sn}(\text{IV})$.



The reactions of SnO_2 with alkali are as follows:



The increased stability of lower valence state on descending a group is illustrated by the fact that Sn^{2+} is a strong reducing agent while Pb^{2+} is stable. For example, consider the following reactions



Oxides of Lead

There are four oxides of lead:

- PbO:** It exists in two forms, yellow variety is massicot and red or reddish-yellow variety is litharge.
- PbO₂:** It is dark brown in colour.
- Pb₂O₃:** It is a mixed oxide of $\text{PbO} \cdot \text{PbO}_2$ reddish-yellow in colour.
- Pb₃O₄:** It is red in colour and known as red lead. It is also a mixed oxide of $2\text{PbO} \cdot \text{PbO}_2$.

Preparation of PbO

This oxide can be prepared by heating $\text{Pb}(\text{NO}_3)_2$ or any of the higher oxides as follows:

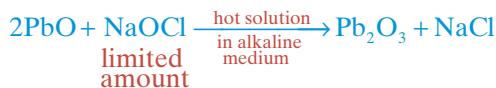


The reaction is generally not used to prepare PbO as $\text{Pb}(\text{NO}_3)_2$ is explosive in nature. Other reactions that give PbO are as follows.



Preparation of Pb_2O_3

Pb_2O_3 can be prepared by the following reaction:



Properties of Pb_2O_3

On reaction of Pb_2O_3 with HNO_3 , brown precipitate of PbO_2 is obtained which validates that Pb_2O_3 is a mixed oxide of $\text{PbO} \cdot \text{PbO}_2$.



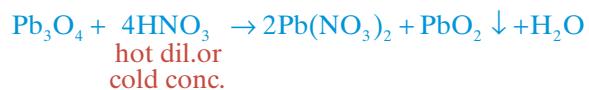
Preparation of Pb_3O_4

When PbO is heated in the presence of air, it gains weight due to addition of oxygen.



Properties of Pb_3O_4

Pb_3O_4 decomposes at 500°C producing O_2 and PbO as shown above. It reacts with different acids as follows:



The last two reactions produce the same products as the reactions of PbO_2 with acids because Pb_3O_4 contains PbO_2 and PbO where PbO simply produces $\text{PbSO}_4/\text{PbCl}_2$ and H_2O . Similarly, if we carry out the same reactions of H_2SO_4 and HCl with Pb_2O_3 , same products are obtained.

10.26 | SILICATES

Occurrence in the Earth's crust

About 95% of the Earth's crust is composed of silicate minerals, aluminosilicate clays, or silica. These make up the bulk of all rocks, sands, and their breakdown products clays and soil. Many building materials are silicates: granite, slates, bricks, and cement. Ceramics and glass are also silicates.

The three most abundant elements are O, Si and Al. Together they make up 81% of the earth's crust, that is four out of five atoms are one of these. This is a much higher abundance than in the earth as a whole or in the universe.

Soluble silicates

Silicates can be prepared by fusing an alkali metal carbonate with sand in an electric furnace at about 1400°C .



The product is a soluble glass of sodium or potassium silicate. It is dissolved in hot water under pressure, and is filtered from any insoluble material. The composition of the product varies, but is approximately $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$. They are used in liquid detergent preparations to keep the pH high, so that grease and fat can be dissolved by forming a soap. Soluble silicates must not be used if the water is hard, or they will

react with Ca^{2+} to form insoluble calcium silicate. Sodium silicate is also used as an adhesive (for example for pasting paper, bonding paper pulp and corrugated cardboard), in asbestos roof tiles, in fireproof paint and putty, and in making silica gel. The majority of silicate minerals are very insoluble, because they have an infinite ionic structure and because of the great strength of the Si—O bond.

10.27 | CLASSIFICATION OF SILICATES

The way in which the $(\text{SiO}_4)^{4-}$ tetrahedral units are linked together provides a convenient classification of the many silicate minerals.

Orthosilicates (neso-silicates)

A wide variety of minerals contain discrete $(\text{SiO}_4)^{4-}$ tetrahedra, that is they share no corners (see Figure 10.17). They have the formula $\text{M}^{\text{II}}_2[\text{SiO}_4]$, where M may be Be, Mg, Fe, Mn or Zn, or $\text{M}^{\text{IV}}[\text{SiO}_4]$, for example ZrSiO_4 . Different structures are formed depending on the coordination number adopted by the metal.

In willemite $\text{Zn}_2[\text{SiO}_4]$, and phenacite $\text{Be}_2[\text{SiO}_4]$, the Zn and Be atoms have a coordination number of 4, and occupy tetrahedral holes. In forsterite $\text{Mg}_2[\text{SiO}_4]$, the Mg has a coordination number of 6 and occupies octahedral holes.

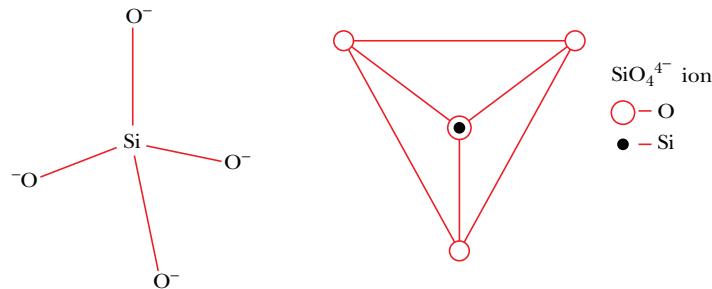


Figure 10.17 Structure of orthosilicates. (After T. Moeller.)

Pyrosilicates (soro-silicates, disilicates)

Two tetrahedral units are joined by sharing the O at one corner, thus giving the unit $(\text{Si}_2\text{O}_7)^{6-}$. This is the simplest of the condensed silicate ions. The name *pyro* comes from the similarity in structure with pyro-phosphates such as $\text{Na}_4\text{P}_2\text{O}_7$, and these were named because they can be made by heating orthophosphates (see Figure 10.18). Examples are thortveitite, $\text{Sc}_2[\text{Si}_2\text{O}_7]$, hemimorphite, $\text{Zn}_4(\text{OH})[\text{Si}_2\text{O}_7]$ and number of lanthanide disilicates having similar formula $\text{Ln}_2[\text{Si}_2\text{O}_7]$.

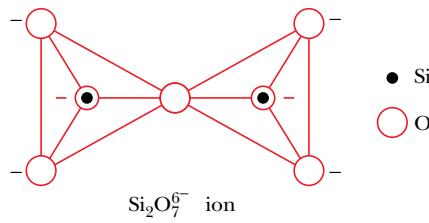


Figure 10.18 Structure of pyrosilicates $\text{Si}_2\text{O}_7^{6-}$. (After T. Moeller.)

Cyclic silicates

If two oxygen atoms per tetrahedron are shared, ring structures may be formed of general formula $(\text{SiO}_3)^{2n-}$ (Figure 10.19). Rings containing three, four, six and eight tetrahedral units are known, but those with three and six are the most common. The cyclic ion $\text{Si}_3\text{O}_9^{6-}$ occurs in wollastonite $\text{Ca}_3[\text{Si}_3\text{O}_9]$ and in

benitoite $\text{BaTi}[\text{Si}_3\text{O}_9]$. The $\text{Si}_6\text{O}_{18}^{12-}$ unit occurs in beryl $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$. In beryl the Si_6O_{18} units are aligned one above the other, leaving channels. Na^+ , Li^+ and Cs^+ are commonly found in these channels, and because of the channels the mineral is permeable to gases consisting of small atoms or molecules, e.g. helium. Beryl and emerald are both gemstones. Emerald has the same formula as beryl except that it contains 1–2% Cr which gives it a strong green colour.

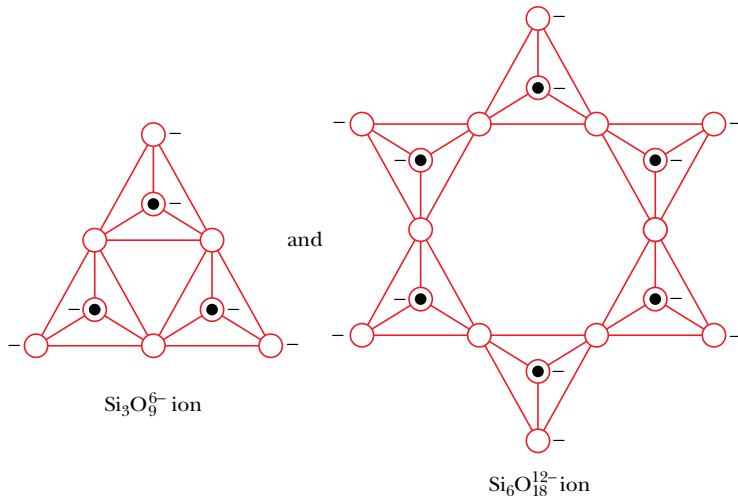


Figure 10.19 Structure of cyclic silicates $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$. (After T. Moeller.)

Chain silicates

Simple chain silicates or pyroxenes are formed by the sharing of the O atoms on two corners of each tetrahedron with other tetrahedra. This gives the formula $(\text{SiO}_3)_n^{2n-}$ (see Figures 10.20 and 10.21). A large number of important minerals form chains, but there are a variety of different structures formed because the arrangement of the tetrahedra in space may vary and thus affect the repeat distance along the chain. The most common arrangement repeats after every second tetrahedron, for example in spodumene $\text{LiAl}[(\text{SiO}_3)_2]$ (which is the main source of Li), enstatite $\text{Mg}_2[(\text{SiO}_3)_2]$, and diopside $\text{CaMg}[(\text{SiO}_3)_2]$. Wollastonite $\text{Ca}_3[(\text{SiO}_3)_3]$ has a repeat unit of three tetrahedra, and others are known with repeat units of 4, 5, 6, 7, 9 and 12.

Double chains can be formed when two simple chains are joined together by shared oxygens. These minerals are called amphiboles, and they are well known. There are several ways of forming double chains, giving formulae $(\text{Si}_2\text{O}_5)_n^{2n-}$, $(\text{Si}_4\text{O}_{11})_n^{6n-}$, $(\text{Si}_6\text{O}_{17})_n^{10-}$ and others. (See Figure 10.22.)

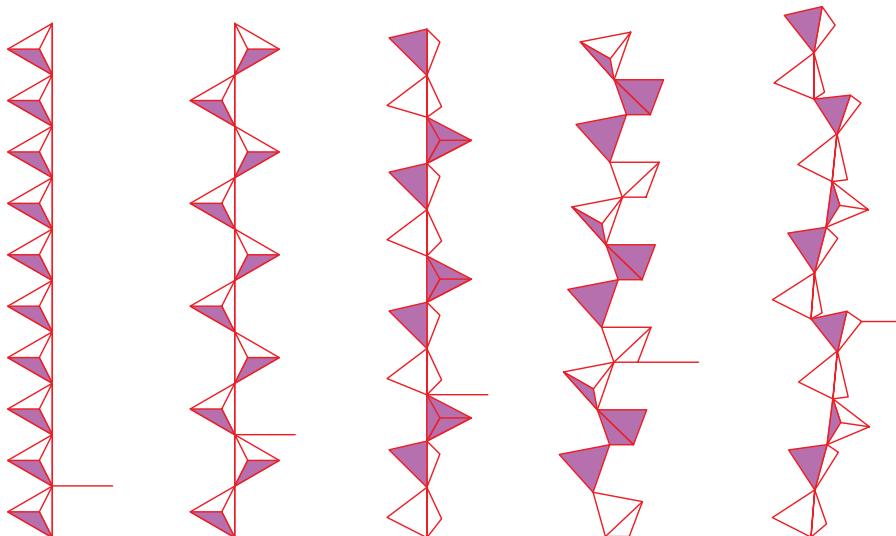


Figure 10.20 Structure of various single chains.

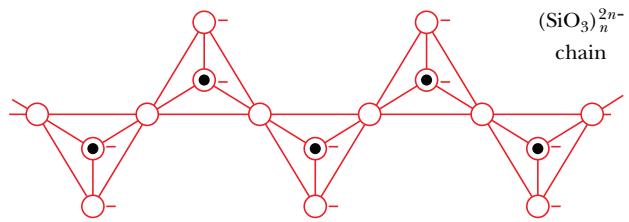


Figure 10.21 Structure of pyroxenes $(\text{SiO}_3)_n^{2n-}$. (After T. Moeller.)

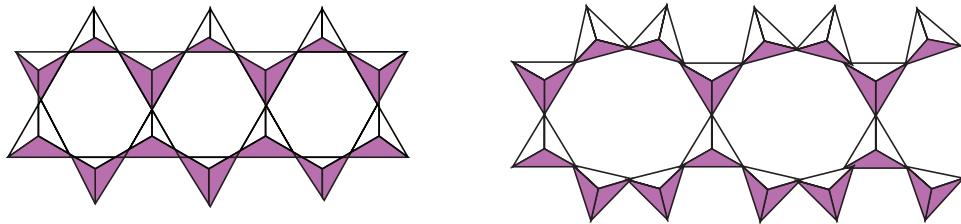


Figure 10.22 Structure of various double chains.

The most numerous and best known amphiboles are the asbestos minerals. These are based on the structural unit $(\text{Si}_4\text{O}_{11})_n^{6n-}$. In this structure (Figure 10.23) some tetrahedra share two corners, whilst others share three corners. Examples include tremolite, $\text{Ca}_2\text{Mg}_5[(\text{Si}_4\text{O}_{11})_2](\text{OH})_2$, and crocidolite $\text{Na}_2\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}[(\text{Si}_4\text{O}_{11})_2](\text{OH})_2$. Amphiboles always contain hydroxyl groups, which are attached to the metal ions.

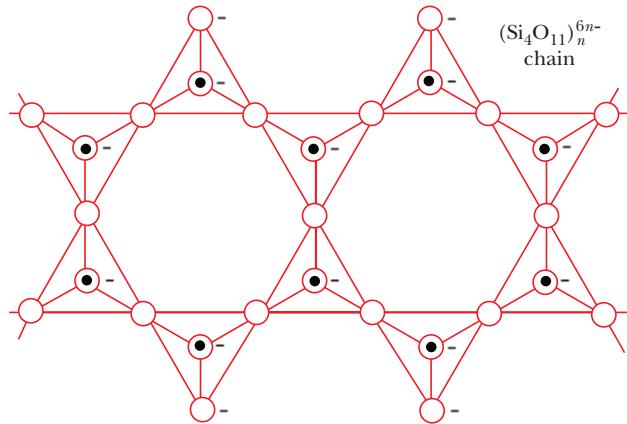


Figure 10.23 Structure of amphiboles $(\text{Si}_4\text{O}_{11})_n^{6n-}$ (After T. Moeller.)

Sheet silicates (phyllo-silicates)

When SiO_4 units share three corners the structure formed is an infinite two-dimensional sheet of empirical formula $(\text{Si}_2\text{O}_5)_n^{2n-}$ (see Figure 10.24). There are strong bonds within the $\text{Si}-\text{O}$ sheet, but much weaker forces hold each sheet to the next one. Thus these minerals tend to cleave into thin sheets.

Structures with simple planar sheets are rare. A large number of sheet silicates are important and well known. These have slightly more complicated structures, and are made up of either two or three layers joined together. These include:

1. Clay minerals (kaolinite, pyrophyllite, talc)
2. White asbestos (chrysotile, biotite)
3. Micas (muscovite and margarite)
4. Montmorillonites (Fullers earth, bentonite and vermiculite)

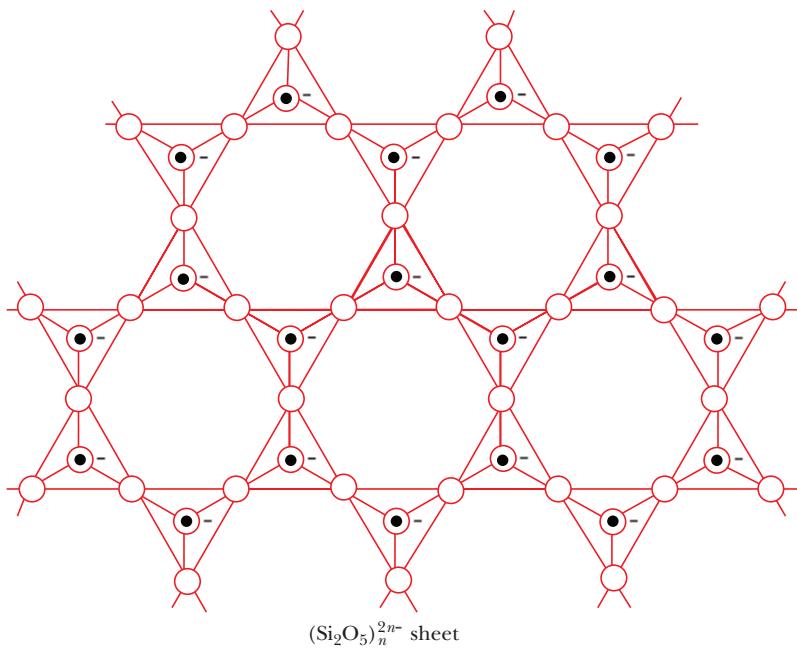


Figure 10.24 Structure of sheet silicates $(\text{Si}_2\text{O}_5)_n^{2n-}$ (After T. Moeller.)

If in talc $\text{Mg}_3(\text{OH})_2[(\text{Si}_2\text{O}_5)_2]$ substitution of Mg^{2+} in the brucite sheet occurs, and if also replacement of Si^{4+} with Al^{3+} occurs in the silicate sheet, then vermiculites are formed. A typical formula is $\text{Na}_x(\text{Mg}, \text{Al}, \text{Fe})_3(\text{OH})_2[(\text{Si}, \text{Al})_2\text{O}_5)_2] \cdot \text{H}_2\text{O}$.

Three-dimensional silicates

Sharing all four corners of a SiO_4 tetrahedron results in a three-dimensional lattice of formula SiO_2 (quartz, tridymite, cristobalite etc.). These contain no metal ions, but three-dimensional structures can form the basis of silicate structures if there is isomorphous replacement of some of the Si^{4+} by Al^{3+} plus an additional metal ion. This gives an infinite three-dimensional lattice, and the additional cations occupy holes in the lattice. Replacing one quarter of the Si^{4+} in SiO_2 with Al^{3+} gives a framework ion $\text{AlSi}_3\text{O}_8^-$. The cations are usually the larger metal ions such as K^+ , Na^+ , Ca^{2+} or Ba^{2+} . The smaller ions Fe^{3+} , Cr^{3+} and Mn^{2+} which were common in the chain and sheet silicates do not occur in the three-dimensional silicates because the cavities in the lattice are too large. Replacements of one quarter or one half of the Si atoms are quite common, giving structures $\text{M}^{\text{I}}[\text{AlSi}_3\text{O}_8]$ and $\text{M}^{\text{II}}[\text{Al}_2\text{Si}_2\text{O}_8]$. Such replacements result in three groups of minerals:

1. Feldspars
2. Zeolites
3. Ultramarines.

The feldspars are the most important rock forming minerals and constitute two thirds of the igneous rocks. For example, granite is made up of feldspars, with some micas and quartz. Feldspars are divided into two classes:

Orthoclase feldspars	Plagioclase feldspars
orthoclase	$\text{K}[\text{AlSi}_3\text{O}_8]$
celsian	$\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$
	albite
	$\text{Na}[\text{AlSi}_3\text{O}_8]$
	anorthite
	$\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$

The orthoclases are more symmetrical than are plagioclases as K^+ and Ba^{2+} are just the right size to fit into the lattice whilst Na^+ and Ca^{2+} , being smaller, allow distortion.

Zeolites

Zeolites have a much more open structure than the feldspars. The anion skeleton is penetrated by channels, giving a honeycomb-like structure. These channels are large enough to allow them to exchange certain ions. They can also absorb or lose water and other small molecules without the structure breaking down. Zeolites are often used as ion-exchange materials, and as molecular sieves. Natrolite $\text{Na}_2[\text{Al}_2\text{Si}_3\text{O}_{10}] \cdot 2\text{H}_2\text{O}$ is a natural ion exchanger. Permutit water softeners use sodium zeolites. Zeolites take Ca^{2+} ions from hard water and replace them by Na^+ , thereby softening the water. The sodium zeolite natrolite gradually becomes a calcium zeolite, and eventually has to be regenerated by treatment with a strong solution of NaCl , when the reverse process takes place. In addition to naturally occurring minerals, many synthetic zeolites have been made. Zeolites also act as molecular sieves by absorbing molecules which are small enough to enter the cavities, but not those which are too big to enter. They can absorb water, CO_2 , NH_3 and EtOH , and they are useful for separating straight chain hydrocarbons from branched chain compounds.

The mineral lapis lazuli is a splendid blue colour and was highly prized as a pigment for oil paintings in the middle ages. It contains ultramarine $\text{Na}_8[(\text{AlSiO}_4)_6]\text{S}_2$, in which the colour is produced by the poly-sulphide ion. The ultramarines are a group of related compounds, which contain no water, but do contain anions such as Cl^- , SO_4^{2-} and S_2^{2-} . Some examples of ultramarines are:

ultramarine	$\text{Na}_8[(\text{AlSiO}_4)_6]\text{S}_2$
sodalite	$\text{Na}_8[(\text{AlSiO}_4)_6]\text{Cl}_2$
nosean	$\text{Na}_8[(\text{AlSiO}_4)_6]\text{SO}_4$

10.28 | GLASS

A small amount of glass is made of silica. This has excellent properties, but very high temperatures are needed to produce it. *Silica glass* is too expensive for general use, but is used in scientific instruments.

The temperature required for melting can be reduced by adding various oxides to the melt, thus obtaining *silicate glass*. A number of oxides may be used including Na_2O , K_2O , MgO , CaO , BaO , B_2O_3 , Al_2O_3 , PbO and ZnO . Glass is a solid solution, and so its composition may vary. The amount of oxide added is not very large, and so the SiO_4 tetrahedra have a significant role in the structure. If only Na_2O or K_2O were used, the glass would be water soluble. Normal domestic glass for windows is a *calcium-alkali silicate glass* made by fusing the alkali metal carbonate, CaCO_3 and SiO_2 . (The carbonates decompose to oxides on heating.) If Na_2CO_3 is used we obtain *soda glass*, which is also used for cheap laboratory glassware. Using K_2CO_3 gives *potash glass*. Most of the CaO may be replaced by PbO , giving *lead glass*, which has a higher refractive index, and is used for making optical parts and glass ornaments. If Al_2O_3 is used, Al^{3+} may be present in the structure as a free metal ion, or it may replace Si^{4+} in SiO_4 tetrahedra. If B_2O_3 is used, B^{3+} replaces some Si^{4+} in the tetrahedral skeleton. *Borosilicate glasses* containing B, and sometimes Al as well, are important. They have a low coefficient of expansion, and can withstand heat changes without cracking. They contain less alkali and so are less prone to chemical attack. Such glasses are widely used for laboratory equipment as in Pyrex glassware.

Additives for fining, for decolorizing and for colouring may be used when making glass. Fining agents such as NaNO_3 or As_2O_3 are added to remove bubbles. The fining agent decomposes and gives off large bubbles of gases in the melt, which sweep out the small bubbles that are always formed. Decolorizing agents may be added to eliminate impurities and to obtain colourless glass. Fe^{3+} gives a yellow-brown colour, a mixture of Fe^{3+} and Fe^{2+} gives a green colour and Fe^{2+} gives a light blue colour. Other colouring agents may be added – Co^{2+} gives a deep blue, and colloidal particles of Cu give ruby-red colours. CaF_2 is sometimes added as a clouding agent to make *opal glass*.

10.29 | ORGANOSILICON COMPOUNDS AND THE SILICONES

Organosilicon compounds

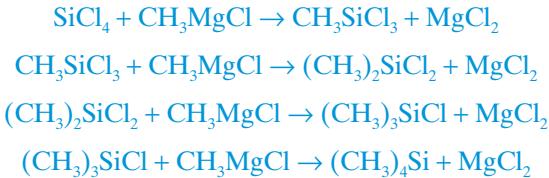
Si—C bonds are almost as strong as C—C bonds. Thus silicon carbide SiC is extremely hard and stable. Many thousands of organosilicon compounds containing Si—C bonds have been made, most since 1950. Many of these are inert, and stable to heat (e.g. SiPh_4 can be distilled in air at 428°C) However, the vast range of organic compounds is not replicated by silicon for three main reasons:

1. Silicon has little tendency to bond to itself (catenate) whilst carbon has a strong tendency to do so. The largest chains formed by Si are contained in $\text{Si}_{16}\text{F}_{34}$ and Si_8H_{18} , but these compounds are exceptional. This is related to the weakness of Si—Si bonds in contrast to the strength of C—C bonds (see Table 13.4).
2. Silicon does not form $p\pi-p\pi$ double bonds, whilst carbon does so readily. (Note that a disilene $\text{Me}_2\text{Si}=\text{SiMeH}$ has been isolated, but only by using matrix isolation methods with solid argon. Various transient reaction species with $\text{Si}=\text{C}$ and $\text{Si}=\text{N}$ bonds are known, and $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)(\text{C}_{10}\text{H}_{15})$ exists as crystals at room temperature, and is stable in the absence of air. These are rare exceptions.)
3. Silicon forms a number of compounds containing $p\pi-d\pi$ double bonds in which the silicon atom uses d orbitals (see later).

Preparation of organosilicon compounds

There are several ways of forming Si—C bonds:

1. By a Grignard reaction



This is useful in the laboratory, or on a small scale.

2. Using an organolithium compound



This also is useful in the laboratory, and R may be alkyl or aryl.

3. By the Rochow 'Direct Process':

Alkyl or aryl halides react directly with a fluidized bed of silicon in the presence of large amounts (10%) of a copper catalyst.



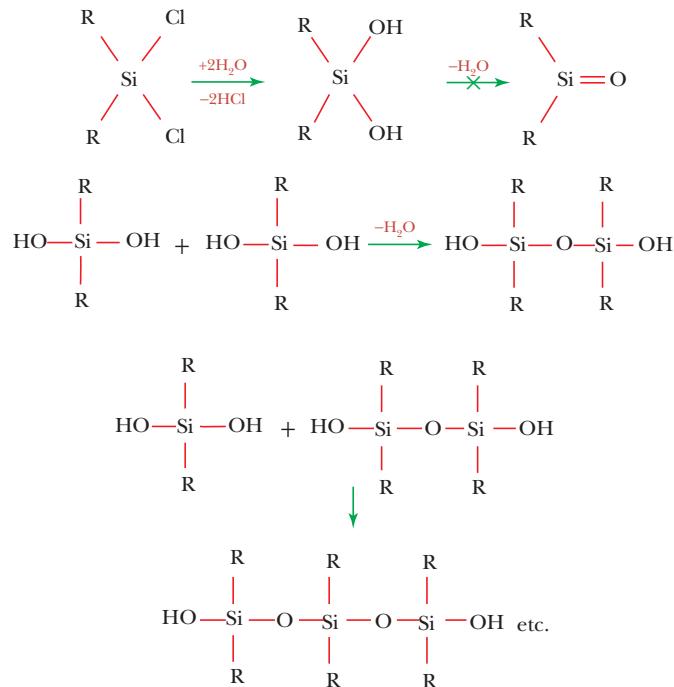
This is the main industrial method for making methyl and phenyl chlorosilanes which are of considerable commercial importance in the production of silicones. The yield is about 70%, with varying amounts of other products: MeSiCl_3 (10%) and Me_3SiCl (5%), and smaller amounts of Me_4Si and SiCl_4 and others such as MeSiHCl_2 . Both Grignard and direct methods yield a mixture of products, and very careful fractionation is important as the boiling points are close: Me_3SiCl (57.7°C), MeSiCl_3 (66.4°C) and Me_2SiCl_2 (69.6°C).

Except for Ph_3SiCl , which is solid, the products are volatile liquids. They are highly reactive and flammable and the reaction with water is strongly exothermic.

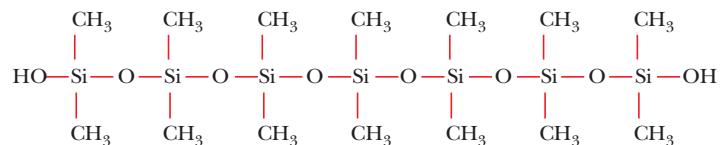
Silicones

The silicones are a group of organosilicon polymers. They have a wide variety of commercial uses as fluids, oils, elastomers (rubbers) and resins.

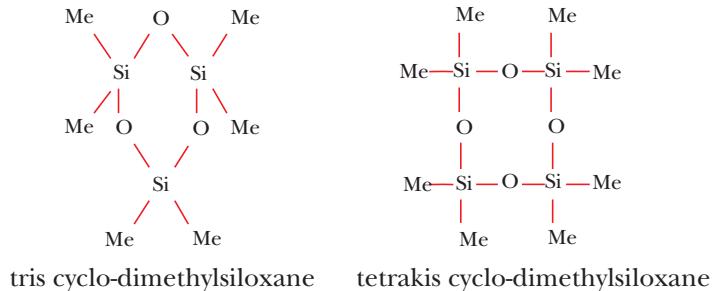
The complete hydrolysis of SiCl_4 yields SiO_2 , which has a very stable three-dimensional structure. The fundamental research of F. S. Kipping on the hydrolysis of alkyl substituted chlorosilanes led, not to the expected silicon compound analogous to a ketone but to long-chain polymers called silicones.



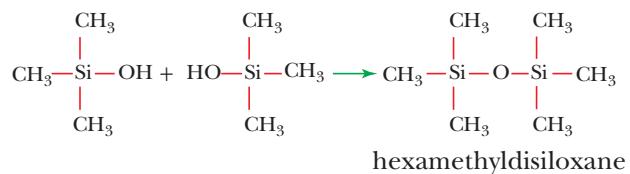
The starting materials for the manufacture of silicones are alkyl or aryl substituted chlorosilanes. Methyl compounds are mainly used, though some phenyl derivatives are used as well. Hydrolysis of dimethyldichlorosilane ($\text{CH}_3)_2\text{SiCl}_2$ gives rise to straight chain polymers and, as an active OH group is left at each end of the chain, polymerization continues and the chain increases in length. $(\text{CH}_3)_2\text{SiCl}_2$ is therefore a chain building unit. Normally, high polymers are obtained.



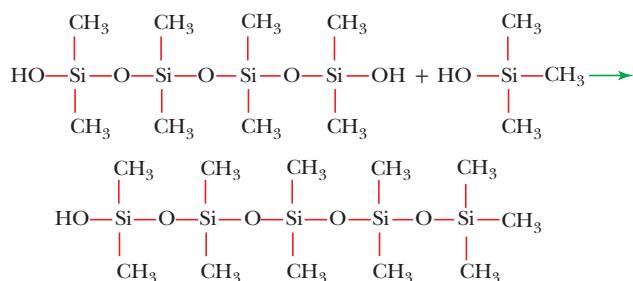
Hydrolysis under carefully controlled conditions can produce cyclic structures, with rings containing three, four, five or six Si atoms:



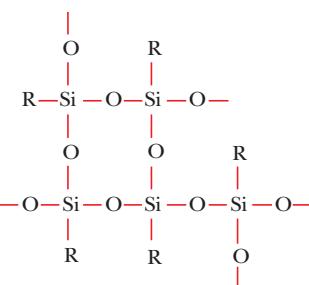
Hydrolysis of trimethylmonochlorosilane ($\text{CH}_3)_3\text{SiCl}$ yields $(\text{CH}_3)_3\text{SiOH}$ trimethylsilanol as a volatile liquid, which can condense, giving hexamethyldisiloxane. Since this compound has no OH groups, it cannot polymerize any further.



If some $(\text{CH}_3)_3\text{SiCl}$ is mixed with $(\text{CH}_3)_2\text{SiCl}_2$ and hydrolysed, the $(\text{CH}_3)_3\text{SiCl}$ will block the end of the straight chain produced by $(\text{CH}_3)_2\text{SiCl}_2$. Since there is no longer a functional OH group at this end of the chain, it cannot grow any more at this end. Eventually the other end will be blocked in a similar way. Thus $(\text{CH}_3)_3\text{SiCl}$ is a chain stopping unit, and the ratio of $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CH}_3)_2\text{SiCl}_2$ in the starting mixture will determine the average chain size.



The hydrolysis of methyl trichlorosilane RSiCl_3 gives a very complex cross-linked polymer.



In a similar way addition of a small amount of CH_3SiCl_3 to the hydrolysis mixture produces a few cross-links, or provides a site for attaching other molecules. By controlled mixing of the reactants, any given type of polymer can be produced.

Silicones are fairly expensive but have many desirable properties. They were originally developed as electrical insulators, because they are more stable to heat than are organic polymers, and if they do break down do not produce conducting materials as carbon does. They are resistant to heat, oxidation and most chemicals. They are strongly water repellent, are good electrical insulators, and have non-stick properties and anti-foaming properties. Their strength and inertness are related to two factors:

1. Their stable silica-like skeleton of $\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}$. The $\text{Si}-\text{O}$ bond energy is very high (502 kJ mol⁻¹).
2. The high strength of the $\text{Si}-\text{C}$ bond.

Uses of silicones

1. Their water repellency arises because a silicone chain is surrounded by organic side groups, and looks like an alkane from the outside. Silicone may be liquids, oils, greases, elastomers (rubbers) or resins.
2. The boiling point and viscosity increase with chain length, giving compounds ranging from watery liquids to viscous oils and greases. The fluids are used as water repellents for treating masonry and building. Glassware and fabrics. They are also included in car polish and shoe polish.

3. Silicone fluids are non-toxic and have a low surface tension. Addition of a few parts per million of a silicone greatly reduces foaming in sewage disposal, textile dyeing, beer making (fermentation) and frothing of cooking oil in making potato crisps or chips.
4. Silicone oils are used as dielectric insulating material in high voltage transformers. They are also used as hydraulic fluids.
5. Methyl silicones can be used as light duty lubricating oil, but are not suitable for heavy duty applications like gearboxes, because the oil film breaks down under high pressure. Silicones with some phenyl groups are better lubricants. These oils can be mixed with lithium stearate soaps to give greases.
6. Silicone rubbers are made of long, straight chain polymers, (dimethyl-polysiloxanes) between 6000 and 600 000 Si units long, mixed with a filler – usually finely divided SiO_2 or occasionally graphite.
7. Silicone rubbers are useful because they retain their elasticity from -90°C to $+250^\circ\text{C}$, which is a much wider range than for natural rubber. They are also good electrical insulators.

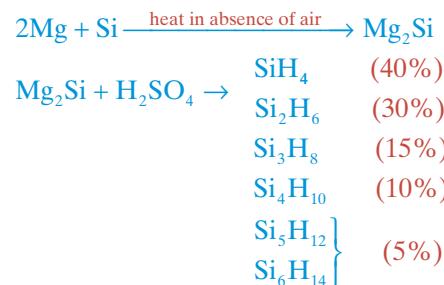
10.30 | HYDRIDES OF SILICON

All the elements form covalent hydrides, but the number of compounds formed and the ease with which they form differs greatly. Carbon forms a vast number of chain and ring compounds including:

1. The alkanes (paraffins) $\text{C}_n\text{H}_{2n+2}$
2. The alkenes (olefines) C_nH_{2n}
3. The alkynes (acetylenes) $\text{C}_n\text{H}_{2n-2}$
4. The aromatic compounds

These are the basis of organic chemistry. There is a strong tendency to catenation (forming chains) because the C–C bond is very strong.

Silicon forms a limited number of saturated hydrides, $\text{Si}_n\text{H}_{2n+2}$, called the silanes. These may exist as straight chains or branched chains, containing up to eight Si atoms. Ring compounds are very rare. No analogues of alkenes or alkynes are known. Monosilane SiH_4 is the only silicon hydride of importance. SiH_4 and SiHCl_3 were first made by treating an Al/Si alloy with dilute HCl. A mixture of silanes was prepared by hydrolysing magnesium silicide, Mg_2Si , with sulphuric or phosphoric acid. These compounds are colourless gases or volatile liquids. They are highly reactive, and catch fire or explode in air. Apart from SiH_4 they are thermally unstable. It only became possible to study them when A. Stock invented a method of handling reactive gases in a vacuum frame.



More recently monosilane has been prepared by reducing SiCl_4 with $\text{Li}[\text{AlH}_4]$, LiH or NaH in ether solution at low temperatures. This is a much better method, as it gives one product rather than a mixture and it gives a quantitative yield.

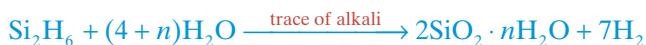




Silanes may also be prepared by direct reaction by heating Si or ferrosilicon with anhydrous HX or RX in the presence of a copper catalyst.



The silanes are much more reactive than the alkanes. The alkanes are chemically unreactive apart from reaction with the halogens, and burning in air. In contrast the silanes are strong reducing agents, ignite in air and explode in Cl₂. Pure silanes do not react with dilute acids or pure water in silica apparatus, but they hydrolyse readily in alkaline solutions, or even with the trace of alkali which leaches out from glass apparatus.



Compounds with Si—H bonds undergo an important hydrosilation reaction with alkenes, in the presence of a platinum catalyst. The reaction is similar to hydroboration, and the products may be used to make silicones.



The difference in behaviour between alkanes and silanes is attributed to several factors:

1. Pauling's electronegativity values are: C = 2.5, Si = 1.8, and H = 2.1. Thus the bonding electrons between C and H or Si and H are not equally shared, leaving a δ^- charge on C and a δ^+ charge on Si. Thus Si is vulnerable to attack by nucleophilic reagents.



2. The larger size of Si makes it easier to attack.
3. Si has low energy *d* orbitals which may be used to form an intermediate compound, and thus lower the activation energy of the process.

10.31 | COMPLEXES

The ability to form complexes is favoured by a high charge, small size and availability of empty orbitals of the right energy. Carbon is in the second period and has a maximum of eight electrons in its outer shell. In four-covalent compounds of carbon, the second shell contains the maximum of eight electrons. Because this structure resembles that of a noble gas, these compounds are stable, and carbon does not form complexes. Four-covalent compounds of the subsequent elements can form complexes due to the availability of *d* orbitals, and they generally increase their coordination number from 4 to 6.



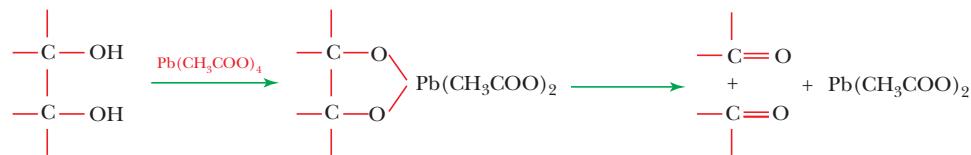
The VSEPR theory suggests that because there are six outer electron pairs these complexes will be octahedral. The valence bond theory requires that four covalent and two coordinate bonds are formed and give an octahedral structure. For example, $[\text{SiF}_6]^{2-}$:

Electronic structure of silicon atom in ground state	full inner shells	$3s$ 	$3p$ 	$3d$ 
Silicon atom in excited state				
Silicon atom having gained a share in four electrons from four fluorine atoms in the SiF_4 molecule				
$[\text{SiF}_6]^{2-}$ where two F each donate share in electron pair, forming two coordinate bonds				
six electron pairs give an octahedral structure (sp^3d^2 hybridization)				

The arguments over hybridizing d orbitals have been discussed in Chapter 3. The $[\text{SiF}_6]^{2-}$ ion is usually formed from SiO_2 and aqueous HF. The $[\text{SiF}_6]^{2-}$ complex is stable in water.



Lead tetraacetate $\text{Pb}(\text{CH}_3\text{COO})_4$ can be obtained as a colourless, solid by treating Pb_3O_4 with glacial acetic acid. It is water sensitive, and is widely used as a selective oxidizing agent in organic chemistry. Its best known application is in the cleavage of 1, 2-diols (glycols), as present, for example, in carbohydrates.



10.32 | INTERNAL π BONDING USING d ORBITALS

The compounds trimethylamine (CH_3)₃N and trisilylamine (SiH₃)₃N have similar formulae, but have totally different structures (Figure 10.25).

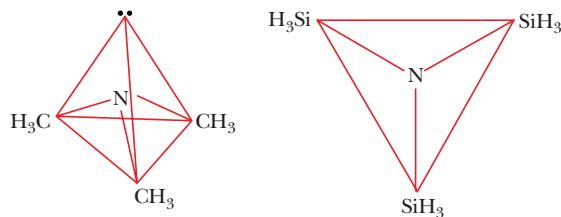


Figure 10.25 Trimethylamine $\text{N}(\text{CH}_3)_3$ and trisilylamine $\text{N}(\text{SiH}_3)_3$.

Electronic structure of nitrogen atom – ground state

1s 2s 2p

three unpaired electrons form bonds with CH_3 groups – tetrahedral arrangement of three bond pairs and one lone pair (sp^3 hybridization)

In trisilylamine, three sp^2 orbitals are used for σ bonding, giving a plane triangular structure. The lone pair of electrons occupy a p orbital at right angles to the plane triangle. This overlaps with empty d orbitals

on each of the three silicon atoms, and results in π bonding, more accurately described as $p\pi-d\pi$ bonding, because it is from a full *p* orbital to an empty *d* orbital. This shortens the bond lengths N—Si. Since the nitrogen no longer has a lone pair of electrons, the molecule has no donor properties. Similar $p\pi-d\pi$ bonding is impossible in $(\text{CH}_3)_3\text{N}$ because C does not possess *d* orbitals and hence this molecule is pyramidal. About 200 compounds are now thought to contain $p\pi-d\pi$ bonds (Figure 10.26).

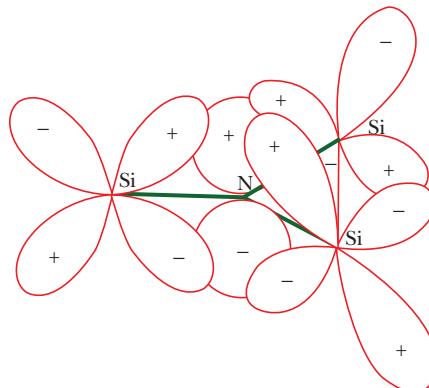


Figure 10.26 $p\pi-d\pi$ bonding in trisilylamine. (From Mackay and Mackay, *Introduction to Modern Inorganic Chemistry*, 4th ed., Blackie, 1989.)

10.33 | HALIDES

Tetrahalides

All the tetrahalides are known except PbI_4 . They are typically covalent, tetrahedral, and very volatile. The exceptions are SnF_4 and PbF_4 , which have three-dimensional structures and are high melting (SnF_4 sublimes at 705°C , PbF_4 melts at 600°C). The elements after C have *d* orbitals available, and the Si—F, Si—Cl and Si—O bonds are stronger than the corresponding bonds with C. This is thought to be due to the donation of electrons from F, Cl or O to Si, giving rise to $p\pi-d\pi$ bonding (see Figure 10.27).

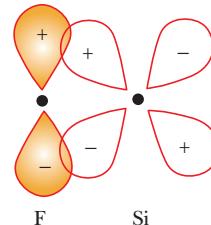
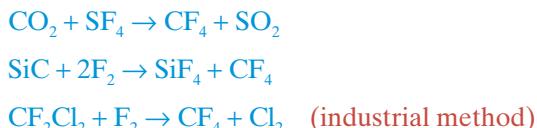


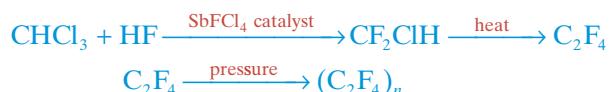
Figure 10.27 $p\pi-d\pi$ overlap in SiF_4 .

Carbon

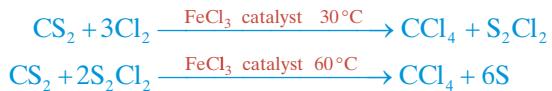
Tetrafluoromethane (carbon tetrafluoride) CF_4 is an exceptionally unreactive gas. It can be made as follows:



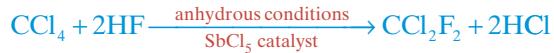
Other fluorine compounds such as hexafluoroethane C_2F_6 and tetrafluoro-ethylene C_2F_4 are known. Under pressure C_2F_4 polymerizes to $(\text{C}_2\text{F}_4)_n$, giving polytetrafluoroethylene or PTFE. This is a hard, white solid plastic with a greasy feel to the touch, and is much heavier (more dense) than one would expect. It is a good electrical insulator, and is chemically inert. It is expensive, and is used in the laboratory because of its inertness. It has a very low coefficient of friction and is used for coating non-stick pans and razor blades. Fluorocarbons are useful lubricants, solvents and insulators.



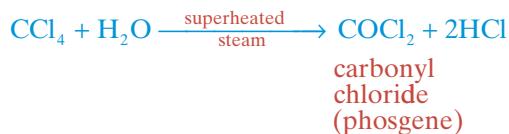
Tetrachloromethane (carbon tetrachloride) CCl_4 is manufactured mainly from carbon disulphide.



CCl_4 is extensively used as a solvent, and for the preparation of Freons. It is also used in fire extinguishers, where the heavy vapour excludes dioxygen and thus puts the fire out.



The carbon halides are not hydrolysed *under normal conditions* because they have no *d* orbitals, and cannot form a five-coordinate hydrolysis intermediate. In contrast the silicon halides hydrolyse readily. Silicon has *3d* orbitals available, and these may be used to coordinate OH^- ions or water as a first step in hydrolysis. In any atom there are always empty orbitals, but these are usually too high in energy to be used. If sufficient energy is provided by using superheated steam then CCl_4 will hydrolyse:



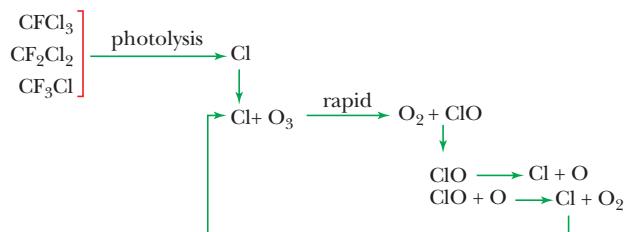
Phosgene is highly toxic, and was used as a poisonous gas in World War I. It is now made by combining CO and Cl₂ with a C catalyst in sunlight, and is used to make isocyanates for the manufacture of polyurethanes.

Freons

Mixed chlorofluorocarbons (sometimes called CFCs) such as CFCl_3 , CF_2Cl_2 and CF_3Cl are known as Freons. They are unreactive and non-toxic and are widely used as refrigeration fluids, as the propellant in aerosols, and for washing computer boards.

Freons are very much more effective 'greenhouse gases' in the atmosphere than is CO₂, though the amount of Freons present is extremely small. Much more seriously, the Freons have penetrated the upper atmosphere (5–20 miles high), and are causing damage to the ozone layer. The ozone layer is important as it filters the radiation from the sun and prevents most of the harmful UV radiation from reaching the earth. Excessive exposure to UV radiation should be avoided as it causes skin cancer (melanoma) in humans.

In the upper atmosphere Freons undergo a photolytic reaction and produce free chlorine atoms (which are radicals). These react readily with ozone. The ClO radicals formed decompose slowly, re-forming chlorine radicals, which react with more ozone and so on. The chlorine radicals do not recombine to form Cl₂, because they need a three-body collision to dissipate the energy, and such collisions are extremely rare in the upper atmosphere. There is no effective sink for chlorine radicals. Once formed they are used again and again, so a small number of radicals make a very effective scavenger for ozone.



Overall reaction: $2\text{O}_3 \rightarrow 3\text{O}_2$

Several less harmful aerosol propellants are now in use. Hydrofluorocarbons (HFCs) such as CH_2FCF_3 and hydrochlorofluorocarbons (HCFCs) such as CHCl_2CF_3 are being used as substitutes. They are also greenhouse gases, and may damage the ozone layer, but they do less damage than CFCs because they do not remain in the atmosphere for so long. The H atoms are attacked by hydroxyl radicals in the upper atmosphere, forming trifluoroacetic acid. The latter is not very toxic, and is eventually decomposed by bacteria in

the soil. CO_2 is an alternative propellant, but when cold it has a low vapour pressure and is therefore no use for windscreen de-icers. Butane also gives difficulties, since it is flammable, and cannot be used with food.

Silicon

The silicon halides can be prepared by heating either Si or SiC with the appropriate halogen. In marked contrast to the inertness of CF_4 , CCl_4 and the Freons, SiF_4 is readily hydrolysed by alkali.



The silicon halides are rapidly hydrolysed by water to give silicic acid.



In the case of the tetrafluoride, a secondary reaction occurs between the resultant HF and the unchanged SiF_4 , forming the hexafluorosilicate ion $[\text{SiF}_6]^{2-}$



SiCl_4 is commercially important. Small amounts are used to make ultra pure Si for transistors. Large quantities of SiCl_4 are hydrolysed at a high temperature (in an oxy-hydrogen flame) giving very finely powdered SiO_2 rather than $\text{Si}(\text{OH})_4$. This ultrafine SiO_2 is used as a thixotropic agent in polyester and epoxy paints and resins, and as an inert filler in silicone rubber.

Other members of the series $\text{Si}_n\text{X}_{2n+2}$ can be produced by pyrolysis (strong heating). These are either volatile liquids or solids. The longest chains known are $\text{Si}_{16}\text{F}_{34}$, $\text{Si}_6\text{Cl}_{14}$ and $\text{Si}_4\text{Br}_{10}$. The chains are longer than those formed in the hydrides. This is due to $p\pi-d\pi$ bonding from full halogen p orbitals with d orbitals on Si.



Tin and lead

Sn and Pb form two series of halides, MX_4 and MX_2 . With Sn the (+IV) oxidation state is the most stable, but with Pb the (+II) state is the most stable.

The tetrahalides are all colourless volatile liquids except for SnI_4 which is bright orange solids. Compounds formed by the main group elements are normally white. The energy absorbed causes the transfer of an electron from I to Sn. (This corresponds to the temporary reduction of Sn(IV) to Sn(III).) Since transferring an electron to another atom is transferring a charge, such spectra are called *charge transfer spectra*. This occurs in SnI_4 because the atoms have similar energy levels. This would be expected because they are close in the periodic table, and have similar sizes. Charge transfer spectra do not occur with the other halides.

SnCl_4 and PbCl_4 hydrolyse in dilute solutions, but hydrolysis is often incomplete and can be repressed by the addition of the appropriate halogen acid.



In the presence of excess acid, halides of Si, Sn and Pb increase their coordination number from 4 to 6, and form complex ions, such as $[\text{SiF}_6]^{2-}$, $[\text{SnCl}_6]^{2-}$ and $[\text{SnCl}_5]^-$. PbI_4 is not known, probably because of the oxidizing power of Pb(+ IV) and the reducing power of I^- , which results in PbI_2 always being formed.

Catenated halides

Carbon forms a number of catenated halides, perhaps the best known being Teflon or polytetrafluoroethylene, which is described above. The polymers formed have chain lengths of several hundred carbon atoms.

Silicon forms polymers $(\text{SiF}_2)_n$ and $(\text{SiCl}_2)_n$ by passing the tetrahalide over heated silicon. These polymers decompose on heating into low molecular weight polymers (or oligomers) of formula $\text{Si}_n\text{X}_{2n+2}$. The longest chains known are $\text{Si}_{16}\text{F}_{34}$, $\text{Si}_6\text{Cl}_{14}$ and $\text{Si}_4\text{Br}_{10}$. Sn and Pb do not form any catenated halides.

Dihalides

There is a steady increase in the stability of dihalides:



SiF_2 can be made by high temperature reactions, and can be trapped by cooling in liquid N_2 . When the product warms up, polymerization occurs giving a range of compounds up to $\text{Si}_{16}\text{F}_{34}$.



SnF_2 and SnCl_2 are white solids, and are obtained by heating Sn or SnO with gaseous HF or HCl. SnCl_2 partly hydrolyses in water, forming the basic chloride $\text{Sn}(\text{OH})\text{Cl}$. SnF_2 and SnCl_2 both dissolve in solutions containing halide ions.



Sn^{2+} ions do occur in perchlorate solutions, but the stannous ion is readily oxidized by air to Sn^{IV} unless precautions are taken. The compounds PbX_2 are much more stable than PbX_4 . Pb is the only element in the group with well defined cations. The salts PbX_2 can all be made from a water soluble Pb^{2+} salt and the corresponding halide ion or halogen acid.

10.34 | ORGANIC DERIVATIVES

The elements of this group have an extensive organometallic chemistry. The divalent state becomes increasingly stable and important on descending the group (the inert pair effect), yet rather surprisingly the organometallic derivatives of Sn and Pb all contain M^{IV} and not M^{II} .

The alkyl silicon chlorides are important as the starting materials for the manufacture of silicones. The silicone polymers have already been described. Tetra organic derivatives of Pb may be prepared from the halides using Grignard or organolithium reagents.



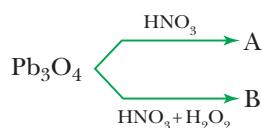
Tetraethyl lead is produced in large amounts and used as an 'anti-knock' additive to increase the octane number of petrol. The commercial preparation uses a sodium/lead alloy.



Lead is poisonous to man, and burning petrol containing PbEt_4 releases lead into the atmosphere. Hence it is banned and use of lead free petrol is increasing.

SINGLE CORRECT CHOICE TYPE QUESTIONS

- Which of the following elements was used in Biblical times on the floor in the Hanging gardens of Babylon (one of the wonders of the ancient world)?
 - Sn
 - Pb
 - Si
 - C
 - The lowest melting solid among the following elements is
 - Si
 - Pb
 - Ge
 - Sn
 - Which of the following carbides consists of C_3^{4-} type of anionic part?
 - Al_4C_3
 - CaC_2
 - B_4C
 - Mg_2C_3
 - Which of the following factors is mainly responsible for toxicity of CO gas?
- (A) It has very high calorific value.
 (B) It readily combines with O_2 to form CO_2 .
 (C) It readily forms a complex with haemoglobin in the blood, which is 300 times more stable than oxyhaemoglobin complex.
 (D) CO is sparingly soluble in water.
5. In the following reactions, the Pb compounds A and B are respectively



MULTIPLE CORRECT CHOICE TYPE QUESTIONS

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1 – 3

CO_2 is an acidic oxide and reacts with bases forming two series of salts bicarbonates and carbonates. CO_2 dissolves in water also, slightly, to form H_2CO_3 .

1. When CO_2 dissolves in water, the ions that are present in equilibrium are

 - (A) CO_3^{2-}
 - (B) HCO_3^-
 - (C) H_3O^+
 - (D) All of these

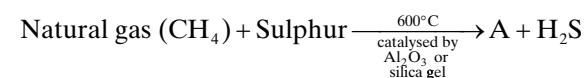
2. A hydrate of CO_2 can also be formed at 0°C under a pressure of 50 atm of CO_2 . The formula of the hydrate of CO_2 is

 - (A) $\text{CO}_2 \cdot 2\text{H}_2\text{O}$
 - (B) $\text{CO}_2 \cdot 4\text{H}_2\text{O}$
 - (C) $\text{CO}_2 \cdot 6\text{H}_2\text{O}$
 - (D) $\text{CO}_2 \cdot 8\text{H}_2\text{O}$

3. Again H_2O and CO_2 are used by plants in a different manner during photosynthesis. The products of photosynthesis are

 - (A) $\text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2$
 - (B) $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{O}_2$
 - (C) $\text{C}_{12}\text{O}_{22}\text{O}_{11} + \text{H}_2$
 - (D) $\text{C}_4\text{H}_{12}\text{O}_6 + \text{N}_2$

Passage 2: For Questions 4 – 5



Compound A can also be prepared by heating charcoal and sulphur vapour at about 850°C.

4. Which of the following properties are correct for A?

 - (A) It is highly inflammable.
 - (B) It is very poisonous, affecting brain and central nervous system.
 - (C) It is a colourless volatile liquid having very low flash point (30°C).
 - (D) All of these

5. For the following reaction, which of the following statements is incorrect regarding B and C?



- (A) Both B and C have planar anionic part.
 - (B) B and C are isoelectronic (total number of electrons).
 - (C) Both B and C are ionic compounds.
 - (D) None of these

Passage 3: For Questions 6 – 7

- I. Red solid (A) + $\text{HNO}_3 \rightarrow$ Neutral liquid (B)
+ C + D
brown ppt.
- II. C (solution) + $\text{H}_2\text{S} \rightarrow$ E
black ppt.
- III. D is a very good oxidizing agent.
- IV. D + $\text{SO}_2 \rightarrow$ white solid (F) which is insoluble in dilute mineral acid.
- V. Compound A is an oxide of lead

6. The formula of D is
(A) PbO
(B) $\text{Pb}(\text{NO}_3)_2$
(C) PbO_2
(D) $\text{PbO}\cdot\text{PbO}_2$
7. F can be converted into E when F is treated with
(A) dil. HCl
(B) H_2S
(C) coke powder (red hot)
(D) sulphur powder

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
(B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
(C) If Statement I is true but Statement II is false.
(D) If Statement I is false but Statement II is true.

1. Statement I: Ag_2CO_3 is slightly yellow or yellowish white in colour.

Statement II: Ag^+ has strong polarizing power.

2. Statement I: The IE_1 of Pb is greater than that of Sn.

Statement II: The radius of Pb is greater than that of Sn.

3. Statement I: Water gas has higher calorific value compared to producer gas.

Statement II: All constituents of producer gas may act as good fuel.

4. Statement I: $\text{I}_2\text{O}_5 + 5\text{CO} \rightarrow \text{I}_2 + 5\text{CO}_2$
 $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$

$$\begin{aligned} \text{The number of equivalent of } \text{S}_2\text{O}_3^{2-} &= \text{number of equivalent of } \text{I}_2 \\ &= \text{number of equivalent of CO} \end{aligned}$$

Statement II: The above set of reactions falls under the category of iodometry reactions.

5. Statement I: The formula for interstitial carbide formed by transition metals is MC.

Statement II: Transition metals are in general crystallized in the form of fcc or hcp pattern and all octahedral voids are occupied by carbon atom.

6. Statement I: Mg_2C_3 is a C_3 -type of ionic carbide.

Statement II: Mg_2C_3 consists of three carbon atoms in one formula unit.

7. Statement I: Silane is more reactive than methane.

Statement II: The Si and C atoms are both sp^3 hybridized in the two compounds.

8. Statement I: SiO_2 is not isostructural with CO_2 .

Statement II: The formation of $3p_\pi - 2p_\pi$ is not as effective as formation of $2p_\pi - 2p_\pi$ in CO_2 .

9. Statement I: Silicones have water repelling characteristics.

Statement II: (Si—O—Si) skeleton is covered with alkyl groups.

10. Statement I: $2\text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} + \text{O}_2$
In this reaction H_2SO_4 acts as reducing agent.

Statement II: If PbO_2 is considered as lead peroxide, then above reaction is an example of disproportionation reaction.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. Find the number of C–C linkages in C_{60} .
2. Find the number of six membered rings in C_{84} .
3. How many of the Group 14 elements have higher value of IE_1 as compared to Pb?

4. Among the following, find the number of elements that show catenation property.
C, Si, P, S, O, N, Ge
5. Find the number of Fe – C bonds in $\text{Fe}_2(\text{CO})_9$.
6. Find the difference in number of σ bonds in the reactant and products when ammonium carbonate is heated.

7. Find the number of planar species from the following.
 CO_3^{2-} , COCl_2 , SiO_4^{2-} , C_3O_2 , HCO_3^- , CS_3^{2-} , C_3S_2
8. When SnC_2O_4 is heated in absence of air, find the difference in oxidation states of carbon atoms in gaseous products.
9. Find the number of acidic oxides from the following.
 CO , GeO , SnO , PbO_2 , SnO_2 , GeO_2 , SiO_2
10. Find the number of water of crystallization in molecule of butter of tin.

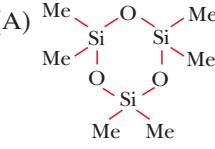
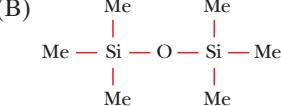
MATRIX-MATCH TYPE QUESTIONS

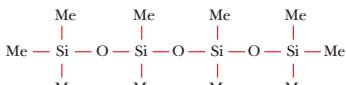
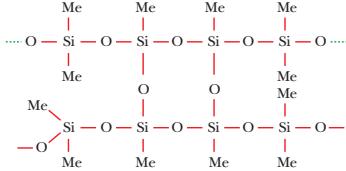
In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the type of silicon with the example.

Column I	Column II
(A) Neso-silicate	(P) $\text{Zn}_4(\text{OH})[\text{Si}_2\text{O}_7]$, Hemimorphite
(B) Phyllo-silicate	(Q) $\text{Mg}_3(\text{OH})_2[(\text{Si}_2\text{O}_5)_2]$, Tale
(C) Soro-silicate	(R) $\text{Na}_2\text{Fe}_3^{\text{II}}\text{Fe}_2^{\text{III}}[(\text{Si}_4\text{O}_{11})_2]$, Crocidolite
(D) Amphibole-silicate	(S) $\text{Be}_2[\text{Be}_2\text{SiO}_4]$, Phenacite

2. Match the chlorosilanes with the compounds they yield on hydrolysis.

Column I	Column II
(A) 	(P) Only Me_2SiCl_2
(B) 	(Q) $\text{Me}_2\text{SiCl}_2 + \text{Me}_3\text{SiCl}$

Column I	Column II
(C) 	(R) $\text{Me}_2\text{SiCl}_2 + \text{MeSiCl}_3$
(D) 	(S) Only Me_3SiCl

3. Match the reaction with the nature of the product obtained.

Column I	Column II
(A) Diamond	(P) All atoms are sp^2 hybridized.
(B) Graphite	(Q) $d_{\text{C-C}}$ is maximum.
(C) Fullerene	(R) Does not exist as discrete molecules.
	(S) Ring structure is existing.

ANSWERS

Single Correct Choice Type Questions

1. (B) 3. (D) 5. (A) 7. (D) 9. (A)
 2. (D) 4. (C) 6. (D) 8. (D)

Multiple Correct Choice Type Questions

1. (A), (C) 3. (A), (B), (C), (D) 5. (A), (C)
 2. (B), (C) 4. (A), (B), (C) 6. (B), (C), (D)

Comprehension Type Questions

1. (D) 3. (A) 5. (B) 7. (C)
 2. (D) 4. (D) 6. (C)

Assertion–Reasoning Type Questions**1.** (A)**3.** (C)**5.** (A)**7.** (B)**9.** (A)**2.** (B)**4.** (D)**6.** (B)**8.** (A)**10.** (D)**Integer Answer Type Questions****1.** 90**3.** 3**5.** 12**7.** 6**9.** 3**2.** 32**4.** 7**6.** 1**8.** 2**10.** 5**Matrix–Match Type Questions**

- 1.** (A) \rightarrow (S)
(B) \rightarrow (Q)
(C) \rightarrow (P)
(D) \rightarrow (R)

- 2.** (A) \rightarrow (P)
(B) \rightarrow (S)
(C) \rightarrow (Q)
(D) \rightarrow (R)

- 3.** (A) \rightarrow (Q), (R), (S)
(B) \rightarrow (P), (R), (S)
(C) \rightarrow (P), (S)

PART 3: THE GROUP 15 ELEMENTS

Table 10.14 Electronic structures and oxidation states

Element	Electronic structure			Oxidation states*							
Nitrogen	N	[He]	$2s^2 2p^3$	-III	-II	-I	0	I	II	III	IV
Phosphorus	P	[Ne]	$3s^2 3p^3$	III							V
Arsenic	As	[Ar]	$3d^{10} 4s^2 4p^3$	III							V
Antimony	Sb	[Kr]	$4d^{10} 5s^2 5p^2$	III							V
Bismuth	Bi	[Xe]	$4f^{14} 5d^{10} 6s^2 6p^3$	III							V

* The most important oxidation states (generally the most abundant and stable) are shown in bold. Other well-characterized but less important states are shown in normal type. Oxidation states that are unstable, or in doubt, are given in parentheses.

The elements of this group all have five electrons in their outer shell (Table 10.14). They exhibit a maximum oxidation state of five towards oxygen by using all five outer electrons in forming bonds. The tendency for the pair of *s* electrons to remain inert (the inert pair effect) increases with increasing atomic weight. Thus, only the *p* electrons are used in bonding and trivalence results. Valencies of three and five are shown with the halogens and with sulphur. The hydrides are trivalent. Nitrogen exhibits a very wide range of oxidation states: (-III) in ammonia NH_3 , (-II) in hydrazine N_2H_4 , (-I) in hydroxylamine NH_2OH , (0) in dinitrogen N_2 , (+I) in nitrous oxide N_2O , (+II) in nitric oxide NO , (+III) in nitrous acid HNO_2 , (+IV) in nitrogen dioxide NO_2 and (+V) in nitric acid HNO_3 . The negative oxidation states arise because the electronegativity of H = 2.1 and that for N = 3.0.

10.35 | GENERAL PROPERTIES AND STRUCTURES OF THE ELEMENTS

Nitrogen

The first element differs from the rest as was the case in the previous groups. Thus dinitrogen is a colourless, odourless, tasteless gas which is diamagnetic and exists as diatomic molecules N_2 . The other elements are solids and exist as several allotropic forms (Table 10.15). The N_2 molecule contains a triple bond $\text{N}\equiv\text{N}$ with a short bond length of 1.09 Å. This bond is very stable, and the dissociation energy is consequently very high (945.4 kJ mol⁻¹). Thus N_2 is inert at room temperature, though it does react with Li, forming the nitride Li_3N . Other isoelectronic species such as CO, CN^- and NO^+ are much more reactive than N_2 , and this is because the bonds are partly polar, whilst in N_2 they are not. At elevated temperatures N_2 becomes increasingly reactive, and reacts directly with elements from Groups 2, 13 and 14, with H_2 and with some of the transition metals.

Active nitrogen can be made by passing an electric spark through N_2 gas at a low pressure. This forms atomic nitrogen, and the process is associated with a yellow–pink afterglow. Active nitrogen will react with a number of elements, and breaks many normally stable molecules.

Table 10.15 Melting and boiling points

	Melting point (°C)	Boiling point (°C)
N_2	-210	-195.8
P_4	44	281
$\alpha\text{-As}$	816*	615 (sublimes)
$\alpha\text{-Sb}$	631	1587
$\alpha\text{-Bi}$	271	1564

* At 38.6 atmospheres pressure.

Phosphorus

Phosphorus is solid at room temperature. White phosphorus is soft, waxy and reactive. It reacts with moist air and gives out light (chemiluminescence). It ignites spontaneously in air at about 35°C , and is stored under water to prevent this. It is highly toxic. It exists as tetrahedral P_4 molecules, and the tetrahedral structure remains in the liquid and gaseous states. Above 800°C P_4 molecules in the gas begin to dissociate into P_2 molecules, which have a bond energy of $489.6 \text{ kJ mol}^{-1}$. (This is only half the value for N_2 because the orbitals in the third shell are much larger and give relatively poor $p\pi-p\pi$ overlap.) If white phosphorus is heated to about 250°C , or a lower temperature in the presence of sunlight, then red phosphorus is formed. This is a polymeric solid, which is much less reactive than white phosphorus. It is stable in air and does not ignite unless it is heated to 400°C . It need not be stored under water. It is insoluble in organic solvents. Heating white phosphorus under high pressure results in a highly polymerized form of P called black phosphorus. This is thermodynamically the most stable allotrope. It is inert and has a layer structure (Figure 10.28). Other more doubtful allotropes have been reported.

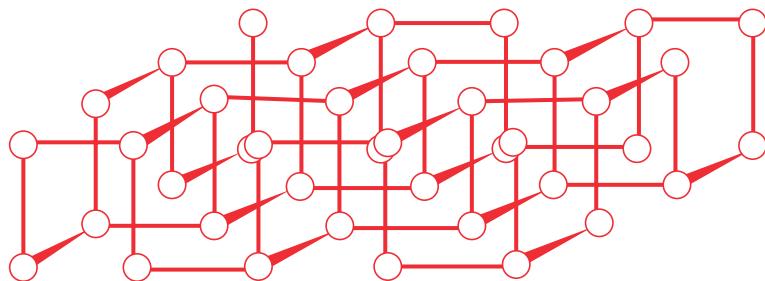


Figure 10.28 The structure of black phosphorus. The atoms are arranged in corrugated planes in crystalline black phosphorus (Van Wazer, J.R., *Phosphorus and Its Compounds*, Vol.1, Interscience, New York – London, 1958, p.121).

Bond type

The majority of compounds formed by this group are covalent.

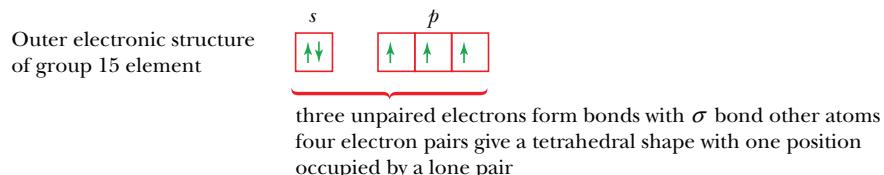


Table 10.16 Radii, ionization energies and electronegativity

Covalent radius (Å)	Ionization energies (kJ mol ⁻¹)			Pauling's electronegativity
	1st	2nd	3rd	
N	0.74	1403	2857	3.0
P	1.10	1012	1897	2.1
As	1.21	947	1950	2.0
Sb	1.41	834	1590	1.9
Bi	1.52	703	1610	1.9

A coordination number of 4 is obtained if the lone pair is donated (that is used to form a coordinate bond) to another atom or ion. An example is the ammonium ion $[H_3N \rightarrow H]^+$ (Figure 10.29).

It requires too much energy to remove all five outer electrons so M^{5+} ions are not formed. However, Sb and Bi can lose just three electrons, forming M^{3+} ions, but the ionization energy is too high for the other elements to do so (Table 10.16). Both SbF_3 and BiF_3 exist as ionic solids. The M^{3+} ions are not very stable in solution. They can exist in fairly strong acid solutions, but are rapidly hydrolysed in water to give the antimony oxide ion or bismuth oxide ion SbO^{+} and BiO^{+} . This change is reversed by adding 5M HCl.

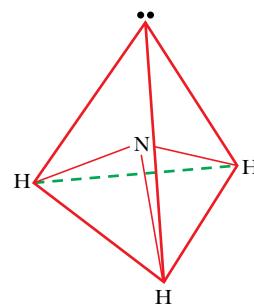
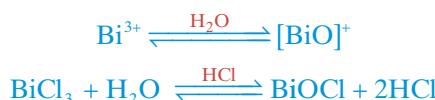


Figure 10.29 Structure of ammonia.

Nitrogen atoms may gain three electrons and so attain a noble gas configuration, forming ionic nitrides containing the N^{3-} ion. It takes 2125 kJ mol⁻¹ of energy to form N^{3-} . Thus ionic nitrides are formed only by metals which have low ionization energies and can form nitrides with high lattice energies (Li_3N , Be_3N_2 , Mg_3N_2 , Ca_3N_2). Though compounds such as Na_3P and Na_3Bi are known, these are not ionic.

Nitrogen cannot extend its coordination number beyond 4 because there are only four orbitals available in the second shell of electrons. Thus nitrogen cannot form complexes by accepting electron pairs from other ligands, but the subsequent elements can form such complexes. Thus the other elements may have coordination numbers of 5 or 6 as, for example, in PCl_5 gas and $[PCl_6]^-$. The formation of complexes may be explained by involving one or two d orbitals in bonding. Thus sp^3d or sp^3d^2 hybridization may occur. The $3d$ orbitals of an isolated phosphorus atom are much larger than the $3s$ and $3p$ orbitals. This might at first sight suggest that the use of the $3d$ orbitals for bonding is improbable. However, when electronegative ligands are placed round the phosphorus atom, the $3d$ orbitals contract to nearly the same size as the $3s$ and $3p$ orbitals. (The extent of d orbital participation in σ bonding is controversial and is discussed in Chapter 3.)

Nitrogen also differs from the other elements in that it can form strong $p\pi-p\pi$ multiple bonds. Because of this it forms several compounds which have no counterparts in the other elements. These include nitrates NO_3^- , nitrites NO_2^- , azides N_3^- , dinitrogen N_2 , oxides of nitrogen N_2O , NO , NO_2 , N_2O_4 , cyanides CN^- , and azo and diazo compounds. Because nitrogen can form multiple bonds, the oxides N_2O_3 and N_2O_5 are monomeric, whilst the trioxides and pentoxides of the other elements are dimeric.

Metallic and non-metallic character

Group 15 shows the usual trend, that metallic character increases on descending the group. Thus N and P are non-metals, As and Sb are metalloids, which show many metallic properties, and Bi is a true metal. The increasing metallic character is shown by the following:

1. In the appearance and structures of the elements.
2. By their tendency to form positive ions.
3. By the nature of their oxides. Metallic oxides are typically basic, and non-metallic oxides are acidic. Thus the normal oxides of N and P are strongly acidic, whereas those of As and Sb are amphoteric and that of Bi is largely basic.
4. The electrical resistivity of the metallic forms (α -As 33, α -Sb 39 and α -Bi 106 μ ohm cm) are much lower than for white phosphorus (1×10^{17} μ ohm cm), indicating an increase in metallic properties. However, the resistivity values are higher than the values for a good conductor such as Cu, 1.67 μ ohm cm, and higher than Sn, 11 and Pb, 20 μ ohm cm, in the adjacent group. (See Appendix J.)

Reactivity

Dinitrogen is relatively unreactive, which is why it has accumulated in such large amounts in the atmosphere.

White phosphorus catches fire when exposed to air, burning to form P_4O_{10} . It is stored under water to prevent this. Red phosphorus is stable in air at room temperature, though it reacts on heating.

10.36 | HYDRIDES

The elements all form volatile hydrides of formula MH_3 , which are all poisonous, foul smelling gases. On descending the group from NH_3 to BiH_3 :

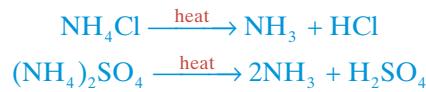
1. The hydrides become increasingly difficult to prepare.
2. Their stability decreases.
3. Their reducing power increases.
4. The ease of replacing the hydrogen atoms by other groups such as Cl or Me decreases.
5. Their ability to act as electron donors, using the lone pair of electrons for coordinate bond formation, decreases.

Ammonia NH_3

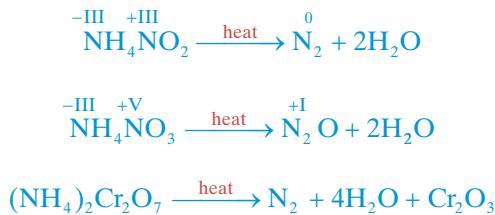
NH_3 is a colourless gas with a pungent odour. The gas is quite poisonous. It dissolves very readily in water with the evolution of heat. At $20^\circ C$ and one atmosphere pressure 53.1 g NH_3 dissolves in 100 g water. This corresponds to 702 volumes of NH_3 dissolving in 1 volume of H_2O . In solution ammonia forms ammonium hydroxide NH_4OH , and behaves as a weak base.



NH_3 and NH_4OH both react with acids, forming ammonium salts. These salts resemble potassium salts in solubility and in their crystal structures. Like the Group 1 salts, ammonium salts are typically colourless. There are some differences. Ammonium salts are usually slightly acidic if they have been formed with strong acids such as HNO_3 , HCl and H_2SO_4 , since NH_4OH is only a weak base. Ammonium salts decompose quite readily on heating. If the anion is not particularly oxidizing (e.g. Cl^- , CO_3^{2-} or SO_4^{2-}) then ammonia is evolved:



If the anion is more oxidizing (e.g. NO_2^- , NO_3^- , ClO_4^- , $Cr_2O_7^{2-}$) then NH_4^+ is oxidized to N_2 or N_2O .



NH_3 burns in dioxygen with a pale yellow flame:



The same reaction occurs in air, but the heat of reaction is insufficient to maintain combustion unless heat is supplied, for example in a gas flame. Certain mixtures of NH_3/O_2 and NH_3 /air are explosive.

NH_3 is prepared in the laboratory by heating an ammonium salt with $NaOH$. This is a standard test in the laboratory for NH_4^+ compounds.

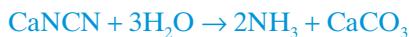


The NH_3 evolved may be detected:

1. By its characteristic smell.
2. By turning moist litmus paper blue.

3. By forming dense white clouds of NH_4Cl with the stopper from a bottle of HCl .
4. By forming a yellow-orange-brown precipitate with Nessler's solution.

Most of ammonia is manufactured synthetically from H_2 and N_2 by the Haber–Bosch process (see later). Ammonia can also be obtained from the hydrolysis of calcium cyanamide, CaCN . Calcium cyanamide is usually used as a fertilizer, and this reaction occurs slowly in the soil.



Ammonium salts

Ammonium salts are all very soluble in water. They all react with NaOH , liberating NH_3 . The NH_4^+ ion is tetrahedral. Several ammonium salts are important.

NH_4Cl is well known. At one time it was obtained by heating camel dung: NH_4Cl is easily purified by sublimation! It can be recovered as a by-product from the Solvay process. It is used in 'dry batteries' of the Leclanche type.

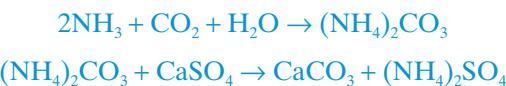
NH_4NO_3 is used in enormous amounts as a nitrogenous fertilizer. It is deliquescent. Because it can cause explosions it is often mixed with CaCO_3 or $(\text{NH}_4)_2\text{SO}_4$ to make it safe. It is also used as an explosive, since on strong heating (above 300°C), or with a detonator, very rapid decomposition occurs. The solid has almost zero volume and it produces seven volumes of gas; this causes the explosion:



At 280°C , it decomposes as follows:



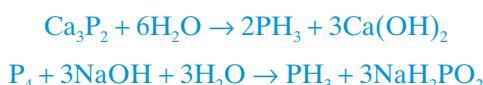
Smaller amounts of $(\text{NH}_4)_2\text{SO}_4$ are also used as a fertilizer. At one time $(\text{NH}_4)_2\text{SO}_4$ was obtained as a by-product from making coal gas (town gas). Since natural gas has become available in developed countries, town gas is no longer made. $(\text{NH}_4)_2\text{SO}_4$ is made by passing NH_3 and CO_2 gases into a slurry of CaSO_4 in water (i.e. slurry of gypsum).



Small amounts of diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ and ammonium dihydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ are used as fertilizers. They are also used for fireproofing wood, paper and textiles. NH_4ClO_4 is used as an oxidizing agent in solid fuel rocket propellants.

Phosphine PH_3

Phosphine PH_3 is a colourless and extremely toxic gas, which smells slightly of garlic or bad fish. It is highly reactive. It can be formed either by hydrolysing metal phosphides such as Na_3P or Ca_3P_2 with water, or by hydrolysing white phosphorus with NaOH solution.



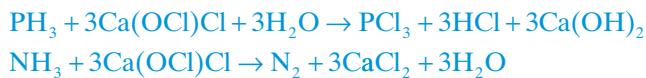
PH_3 , unlike NH_3 , is not very soluble in water: aqueous solutions are neutral. It is more soluble in CS_2 and other organic solvents. Phosphonium salts such as $[\text{PH}_4]^+ \text{Cl}^-$ can be formed, but require PH_3 and anhydrous HCl (in contrast to the ready formation of NH_4X in aqueous solution). Pure PH_3 is stable in air, but it catches fire when heated to about 150°C .



PH_3 frequently contains traces of diphosphine P_2H_4 which cause it to catch fire spontaneously. This is the origin of the flickering light called will-o'-the-wisp, which is sometimes seen in marshes.

Some important chemical properties of phosphine are:

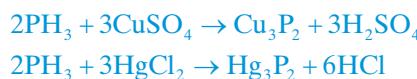
1. Some of the chemical properties of phosphine are similar to ammonia.
 - a. Phosphine is weakly basic and like ammonia gives phosphonium compounds with acids.
$$\text{PH}_3 + \text{HBr} \rightarrow \text{PH}_4\text{Br}$$
- b. Like NH_3 , PH_3 can also form addition compounds like, $\text{CuCl}_2 \cdot 2\text{PH}_3$, $\text{AlCl}_3 \cdot 2\text{PH}_3$, $\text{SnCl}_4 \cdot 2\text{PH}_3$
- c. Both NH_3 and PH_3 can be absorbed by bleaching powder.



2. Other chemical reactions are as follows:

- a. $\text{PH}_3 + \text{O}_2 \xrightarrow{150^\circ\text{C}} \text{H}_3\text{PO}_4 + \text{H}_2\text{O}$
- b. $\text{PH}_3 + 3\text{Cl}_2 \rightarrow \text{PCl}_3 + 3\text{HCl}$
- c. $\text{PH}_3 + 4\text{NO}_2 \xrightarrow[\text{spark}]{\text{electric}} 4\text{N}_2 + \text{H}_3\text{PO}_4$

- d. Formation of phosphides.



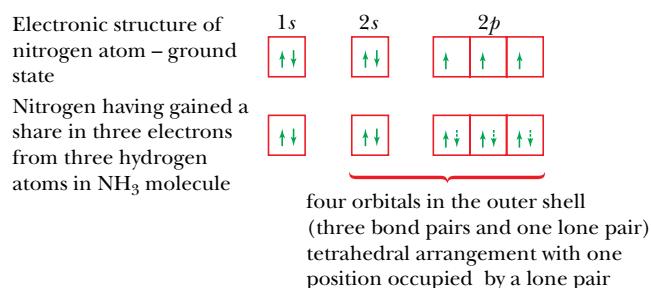
- e. $\text{PH}_3 + 6\text{AgNO}_3 \rightarrow [\text{Ag}_3\text{P} \cdot 3\text{AgNO}_3] \downarrow + 3\text{HNO}_3$
yellow ppt.
- $\text{Ag}_3\text{P} \cdot 3\text{AgNO}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{Ag} \downarrow + 3\text{HNO}_3 + \text{H}_3\text{PO}_3$
black ppt.
- f. $\text{PH}_3 + 4\text{HCHO} + \text{HCl} \rightarrow [\text{P}(\text{CH}_2\text{OH})_4]^+ \text{Cl}^-$

Arsine AsH_3 , stibine SbH_3 and bismuthine BiH_3

The bond energy (Table 10.17) and the stability of the hydrides both decrease on descending the group. Consequently, arsine AsH_3 , stibine SbH_3 and bismuthine BiH_3 are only obtained in small amounts. AsH_3 and SbH_3 are both very poisonous gases. AsH_3 , SbH_3 and BiH_3 can be prepared by hydrolysing binary metal compounds such as Zn_3As_2 , Mg_3Sb_2 or Mg_3Bi_2 with water or dilute acid. AsH_3 and SbH_3 are formed in Marsh's test for As and Sb compounds..

Structure of the hydrides

The structure of ammonia may either be described as pyramidal, or tetrahedral with one position occupied by a lone pair (Figure 10.29). This shape is predicted using the VSEPR theory since there are four electron pairs in the outer shell. These comprise three bonding pairs and one lone pair. The repulsion between a lone pair and a bond pair of electrons always exceeds that between two bond pairs. Thus the bond angles are reduced from $109^\circ 27'$ to $107^\circ 48'$, and the regular tetrahedral shape is slightly distorted.



The hydrides PH_3 , AsH_3 and SbH_3 would be expected to be similar. However, the bond pairs of electrons are much further away from the central atom than they are in NH_3 . Thus the lone pair causes even greater distortion in PH_3 , AsH_3 and SbH_3 . The bond angle decreases to $91^\circ 18'$ (Table 10.17). These bond angles suggest that in PH_3 , AsH_3 , SbH_3 and BiH_3 the orbitals used for bonding are close to pure *p* orbitals.

The melting and boiling points of the hydrides increase from PH_3 through AsH_3 to SbH_3 . The values for NH_3 seem out of line with this trend: one might have expected the boiling point of NH_3 to be -110°C or -120°C . The reason why NH_3 has a higher boiling point and is much less volatile than expected is that it is hydrogen bonded in the liquid state. The other hydrides do not form hydrogen bonds.

These hydrides are strong reducing agents and react with solutions of metal ions to give phosphides, arsenides and stibnides. They are flammable and extremely poisonous.

Table 10.17 Some properties of the hydrides

	m.p. ($^\circ\text{C}$)	b.p. ($^\circ\text{C}$)	Bond energy (kJ mol^{-1})	Bond angle	Bond length (\AA)
NH_3	-77.8	-34.5	$\text{N-H} = 389$	$\text{H-N-H} = 107^\circ 48'$	1.017
PH_3	-133.5	-87.5	$\text{P-H} = 318$	$\text{H-P-H} = 93^\circ 36'$	1.419
AsH_3	-116.3	-62.4	$\text{As-H} = 247$	$\text{H-As-H} = 91^\circ 48'$	1.519
SbH_3	-88	-18.4	$\text{Sb-H} = 255$	$\text{H-Sb-H} = 91^\circ 18'$	1.707

Donor properties

NH_3 can donate its lone pair of electrons quite strongly to form complexes. Thus ammonia forms ammonium NH_4^+ salts, and also coordination complexes with metal ions from the Co, Ni, Cu and Zn groups, for example the $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion, very readily.

PH_3 acts as an electron donor and forms numerous complexes such as $[\text{F}_3\text{B} \leftarrow \text{PH}_3]$, $[\text{Cl}_3\text{Al} \leftarrow \text{PH}_3]$ and $[\text{Cr}(\text{CO})_3(\text{PH}_3)_3]$. A variety of other trivalent phosphorus compounds such as PF_3 , PCl_3 , PEt_3 , $\text{P}(\text{OR})_3$ and PPh_3 also form complexes, which in some ways resemble complexes with CO. Thus the lone pair on P is used to form the coordinate bond to an empty orbital on the B or metal (a σ bond). In the case of metals, this original coordinate bond may be reinforced by back bonding from π overlap of a filled *d* orbital on the metal with an empty *d* orbital on P.

The donor properties of the other hydrides are very weak, and they have little or no tendency to form coordinate bonds.

In NH_3 the lone pair occupies an sp^3 hybrid orbital. In AsH_3 and SbH_3 the bond angles become close to 90° which suggests that the orbitals used for M–H bonding are almost pure *p* orbitals. If the three *p* orbitals are used for M–H bonding, the lone pair must occupy a spherical *s* orbital. This is larger, and less directional, and hence less effective for forming a coordinate bond. This means that any σ bond will be very weak. In addition the $4d$ and $5d$ orbitals are too large for effective π back bonding. These two factors account for the difference in complexing power between the hydrides.

Nitrogen forms several hydrides (see Table 10.18).

Table 10.18 Hydrides of nitrogen

Formula	Name	Oxidation state
NH_3	Ammonia	-III
N_2H_4	Hydrazine	-II
NH_2OH	Hydroxylamine	-I

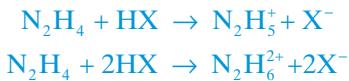
Hydrazine N_2H_4

Hydrazine is a covalent liquid, which fumes in air, and smells similar to NH_3 . Pure hydrazine burns readily in air with the evolution of a large amount of heat.

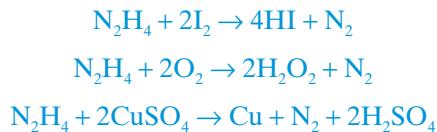


The methyl derivatives MeNH_2 and Me_2NNH_2 are mixed with N_2O_4 and used as a rocket fuel in the space shuttle, in guided missiles, and (earlier) in the Apollo lunar modules.

N_2H_4 is a weak base and reacts with acids, forming two series of salts. The salts are white ionic crystalline solids, and are soluble in water.



When dissolved in water (in neutral or basic solutions) hydrazine or its salts are powerful reducing agents. They are used to produce silver and copper mirrors and to precipitate the platinum metals. Hydrazine also reduces I_2 and O_2 .

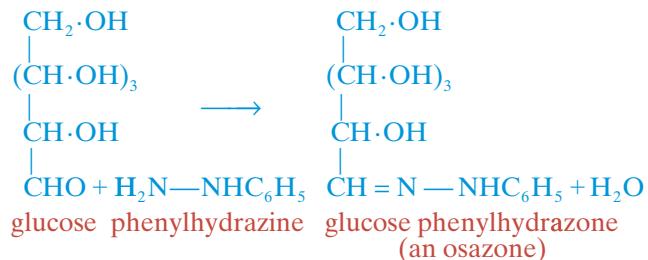


In acidic solutions, hydrazine usually behaves as a mild reducing agent, though powerful reducing agents can reduce N_2H_4 to NH_3 , thus causing N_2H_4 to be oxidized.



Hydrazine may act as an electron donor. The N atoms have a lone pair of electrons, which can form coordinate bonds to metal ions such as Ni^{2+} and Co^{2+} .

Most of hydrazine produced is used as rocket fuel. It is also used to treat the boiler feed water in power stations to prevent oxidation of the boiler and pipes. In the laboratory phenylhydrazine is used to characterize carbonyl compounds and sugars by forming crystalline derivatives called osazones.



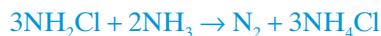
Hydrazine is still manufactured by the Raschig process, in which ammonia is oxidized by sodium hypochlorite in dilute aqueous solution.



A side reaction between chloramine and hydrazine may destroy some or all of the product.



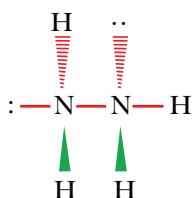
This reaction is catalyzed by heavy metal ions present in solution. For this reason distilled water is used (rather than tap water), and glue or gelatin is added to mask (i.e. complex with) the remaining metal ions. The use of excess of ammonia reduces the incidence of chloramine reacting with hydrazine. The use of a dilute solution of the reactants is necessary to minimize another side reaction:



The hydrazine is concentrated by distillation yielding $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, or by adding H_2SO_4 to precipitate the salt $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$.

Electron diffraction and infrared data indicate that the structure of hydrazine is related to that of ethane. Each N atom is tetrahedrally surrounded by one N, two H and a lone pair. The two halves of the molecule are rotated 95° about the N–N bond and adopt a gauche (non-eclipsed) conformation. The N–N bond length is 1.45 Å.

Phosphorus forms an unstable hydride P_2H_4 , which has very little chemical similarity to N_2H_4 .



Hydroxylamine NH_2OH

Hydroxylamine forms colourless crystals that melt at 33 °C. It is thermally unstable and decomposes into NH_3 , N_2 , HNO_2 and N_2O easily. It explodes if heated strongly. It is usually handled in aqueous solution, or as one of its salts, since these are more stable than free NH_2OH ,

Hydroxylamine is a weaker base than is ammonia or hydrazine. Salts contain the hydroxylammonium ion $[NH_3OH]^+$.



The appropriate reduction potentials suggest that hydroxylamine should disproportionate. It disproportionates slowly in acidic solutions:

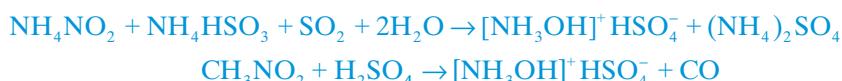


and rapidly in alkaline solutions:



Both NH_2OH and its salts are very poisonous, and they are also strong reducing agents.

Hydroxylamine is manufactured by reducing nitrites, or from nitromethane:



Hydroxylamine has donor properties (like NH_3 and N_2H_4): the N atom can form coordinate bonds, and can complex with metals. In addition it adds easily to double bonds in organic molecules, and thus provides an easy way of introducing N atoms into molecules.

NH_2OH is manufactured in large quantities to make cyclohexanone oxime, which is converted to caprolactam and then polymerized to give nylon-6 (Figure 10.30).

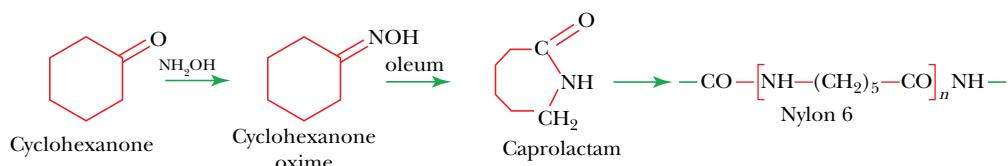
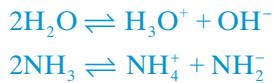


Figure 10.30 Nylon-6.

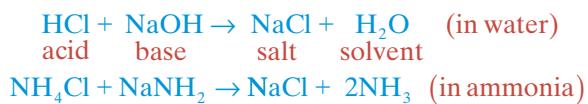
10.37 | LIQUID AMMONIA AS A SOLVENT

Ammonia gas is easily condensed (boiling point -33°C) to give liquid ammonia. Liquid ammonia is the most studied non-aqueous solvent and it resembles the aqueous system quite closely. Liquid ammonia, like water, will dissolve a wide variety of salts. Both water and ammonia undergo self ionization:

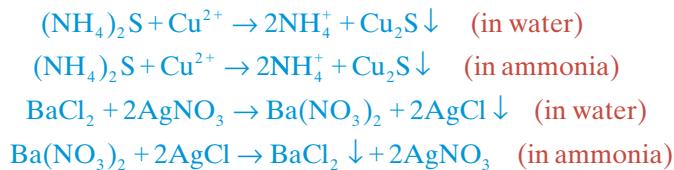


Thus, substances which produce H_3O^+ ions in water are acids, and ammonium salts are acids in liquid ammonia. Similarly, substances producing OH^- in water or NH_2^- in liquid ammonia are bases in that solvent.

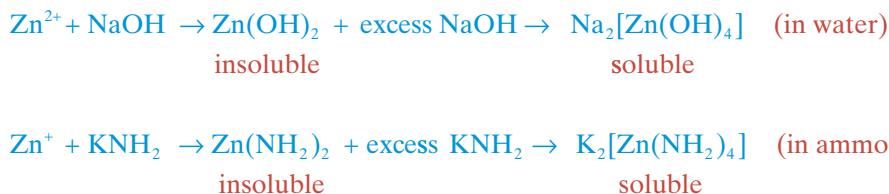
Thus acid – base neutralization reactions occur in both solvents, and phenolphthalein may be used to detect the end point in either:



In a similar way, precipitation reactions occur in both solvents. However, the direction of the reaction is a function of the solvent:



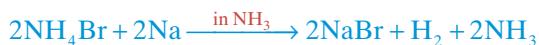
$\text{Zn}(\text{OH})_2$ is amphoteric in water and $\text{Zn}(\text{NH}_2)_2$ is amphoteric in ammonia:



Liquid ammonia is an extremely good solvent for the alkali metals and the heavier Group 2 metals Ca, Sr and Ba. The metals are very soluble and solutions in liquid ammonia have a conductivity comparable to that of pure metals. The ammonia solvates the metal ions, but is resistant to reduction by the free electrons. These solutions of metals in liquid ammonia are very good reducing agents because of the presence of free electrons.



Solutions of ammonium salts in liquid ammonia are used to clean the cooling systems in some nuclear reactors. Liquid sodium is used to cool fast breeder nuclear reactors. Liquid ammonia is a good solvent for metals, but the surfaces are left wet with NH_3 . When this evaporates it may leave a trace of finely divided sodium which is pyrophoric. Thus it is necessary to destroy the sodium by using an acid such as an ammonium salt in liquid ammonia.



Because liquid ammonia accepts protons readily, it enhances the ionization of so-called weak acids such as acetic acid.



The NH_3 removes H^+ and thus causes the reaction to proceed in the forward direction. Thus acetic acid has a $\text{p}K_a$ value of 5 in water but is almost completely ionized in liquid ammonia. Ammonia thus reduces the difference between the strengths of acids. In this respect ammonia is called a levelling solvent.

10.38 | HYDROGEN AZIDE AND THE AZIDES

Hydrogen azide HN_3 (formerly called hydrazoic acid) is a colourless liquid b.p. 37°C , which is highly poisonous and has an irritating odour. Both the liquid and the gas explode on heating or with a violent shock.

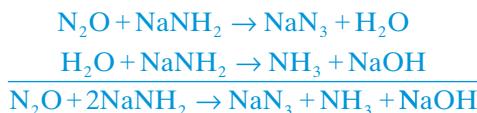


HN_3 is slightly more stable in aqueous solution, but should be treated with care. It dissociates slightly in aqueous solution ($\text{p}K_a \approx 5$). It behaves as a weak acid, of similar strength to acetic acid. It reacts with electro-positive metals, forming salts called azides, but unlike other acid + metal reactions, no hydrogen is evolved.



Covalent azides are used as detonators and explosives. Ionic azides are usually much more stable, and some are used as organic intermediates and dyestuffs.

The most important method of making azides is by passing nitrous oxide gas into fused sodamide at 190°C under anhydrous conditions. The water vapour produced reacts with more sodamide. Alternatively nitrous oxide can be passed into a solution of sodamide in liquid ammonia as a solvent.



The sodium azide so obtained may be converted to hydrogen azide by treatment with H_2SO_4 followed by distillation. Lead azide $\text{Pb}(\text{N}_3)_2$ can be precipitated from a solution of sodium azide and a soluble lead salt such as $\text{Pb}(\text{NO}_3)_2$. $\text{Pb}(\text{N}_3)_2$ is sensitive to shock and is used as a detonator to set off a high explosive charge. It is particularly reliable, and works even in damp conditions. Numerous other metal azides are known. Cyanuric triazide is a powerful explosive (Figure 10.31).

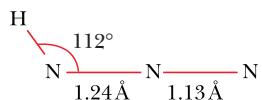
The $(\text{N}_3)^-$ ion is considered as a pseudohalide ion. It forms the extremely unstable and explosive compounds fluorazide FN_3 , chlorazide ClN_3 , bromazide BrN_3 , and iodazide IN_3 , but the dimer N_3-N_3 is unknown.

Analysis of N_3^- is by reduction with H_2S .



The N_3^- ion has 16 outer electrons and is isoelectronic with CO_2 . The N_3^- ion is linear ($\text{N}-\text{N}-\text{N}$) as is CO_2 . There is a total of two σ and two π bonds, giving $\text{N}=\text{N}=\text{N}$ and σ bond order of 2. Both $\text{N}-\text{N}$ bonds are the same length, 1.16 \AA .

The hydrogen azide molecule has a bent structure. The addition of the extra electron from H means that one electron must now occupy an antibonding MO, and hence the two $\text{N}-\text{N}$ bond lengths are different:



The bond angle $\text{H}-\text{N}-\text{N}$ is 112° , and the two $\text{N}-\text{N}$ bonds are of significantly different lengths, and the bond orders are probably 1.5 and 2 respectively.

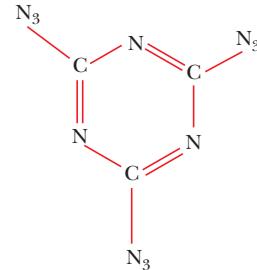


Figure 10.31 Structure of cyanuric triazide.

10.39 | NITROGEN FIXATION

There is a large amount of N_2 gas in the atmosphere, but plants are unable to utilize this because N_2 gas is so stable and unreactive. Fertile soil contains combined nitrogen, mainly in the form of nitrates, nitrites, ammonium salts or urea $CO(NH_2)_2$. These compounds are absorbed from the soil water by the roots of the plants. This reduces the fertility of the soil, though much of the nitrogen is eventually returned to the soil due to death and decay of the plants. A few species of bacteria and cyanobacteria can 'fix' atmospheric dinitrogen, that is can convert N_2 gas into combined forms. These bacteria can have a great effect on the fertility of soil by producing 'combined nitrogen'. The most important nitrogen fixing genus of bacteria is called *Rhizobium*.

Though plants require nitrates, bacteria in the soil will readily convert other nitrogenous compounds into nitrates.

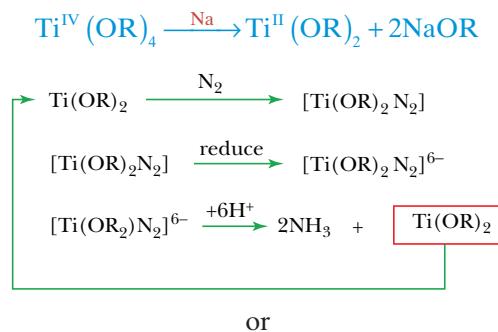


Chemical processes involving the fixation of atmospheric dinitrogen include the Haber–Bosch process for ammonia, and the formation of calcium cyanamide, which both involve the use of high temperatures and pressure. Bacteria can fix dinitrogen easily at room temperature and atmospheric pressure, yet man requires expensive plant with high temperatures and pressures to do the same.

There is considerable research interest into finding transition metal catalysed systems which will absorb dinitrogen and produce ammonia for fertilizers cheaply and without the necessity for high temperatures or pressure. The first dinitrogen complex, the pentaammine(dinitrogen)ruthenium cation, was made in 1965 by reducing ruthenium trichloride with hydrazine. Other methods have now been found, e.g. replacement of a labile ligand in a complex by N_2 . Dinitrogen complexes have now been made for almost all the transition elements.

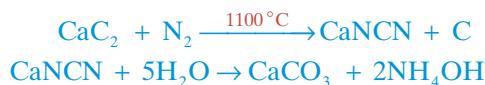


The formation of this stable dinitrogen complex led to studies with other metals. Complexes with titanium(II) are the most promising, and reduction of titanium alkoxides yields either ammonia or hydrazine. A complete cycle of reactions for fixing atmospheric dinitrogen to ammonia has been reported:



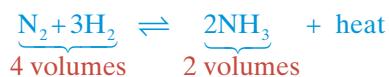
Cyanamide process

Calcium cyanamide is used in large amounts as a nitrogenous fertilizer, and as a source of organic chemicals such as melamine.



Haber–Bosch process

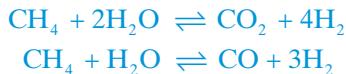
The most important commercial process is the Haber–Bosch process. Fritz Haber discovered how to make N_2 and H_2 combine directly in the laboratory. He was awarded the Nobel Prize for Chemistry in 1918. Carl Bosch was a chemical engineer who developed the plant to make ammonia using this reaction on an industrial scale. He too was awarded the Nobel Prize for Chemistry in 1931 for his work on high pressure reactions.



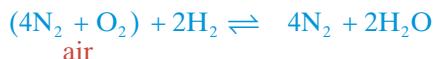
The reaction is reversible, and Le Chatelier's principle suggests that a high pressure and low temperature are required to drive the reaction to the right, and thus form NH_3 . A low temperature gives a higher percentage conversion to NH_3 , but the reaction is slow in reaching equilibrium, and a catalyst is required. In practice the conditions used are 200 atmospheres pressure, a temperature of 380–450°C and a catalyst of *promoted iron*. It is more economic to use a higher temperature, so that equilibrium will be reached much faster, even though this gives a lower percentage conversion. At a temperature of about 400°C a 15% conversion is obtained with a single pass over the catalyst. The gas mixture is cooled to condense liquid NH_3 , and the unchanged mixture of N_2 and H_2 gases is recycled. The plant is made of steel alloyed with Ni and Cr.

The catalyst is made by fusing Fe_3O_4 with KOH and a refractory material such as MgO , SiO_2 or Al_2O_3 . This is broken into small lumps and put into the ammonia convertor, where the Fe_3O_4 is reduced to give small crystals of iron in a refractory matrix. This is the active catalyst.

The actual plant is more complicated than this one-stage reaction implies, since the N_2 and H_2 must be made before they can be converted to NH_3 . The cost of H_2 is of great importance for the economy of the process. Originally the H_2 required was produced by electrolysis of water. This was expensive, and a cheaper method using coke and water was then used (water gas, producer gas). Nowadays the H_2 is produced from carbons, either naptha or CH_4 , by reacting with steam at 750°C with a Ni catalyst. All traces of S must be removed since these poison the catalyst.



Some air is added. The O_2 burns with some of the H_2 , thus leaving N_2 to give the required reaction ratio $\text{N}_2 : \text{H}_2$ of 1:3.



CO must also be removed as it too poisons the catalyst.



Finally the CO_2 is removed in a scrubber by means of a concentrated solution of K_2CO_3 , or ethanamine. About 75% of the ammonia is used as a fertilizer. Other uses include the following:

1. Making HNO_3 , which can be used to make NH_4NO_3 (fertilizer), or explosives such as nitroglycerine, nitrocellulose and TNT. HNO_3 can be used for many other purposes.
2. Making caprolactam, which on polymerization forms nylon-6 (see hydroxylamine).
3. Making hexamethylenediamine which is used in making nylon-6-6, polyurethanes and polyamides.
4. Making hydrazine and hydroxylamine.
5. Liquid NH_3 is often used as a cheaper and more convenient way of transporting H_2 than cylinders of compressed H_2 gas. The H_2 is obtained from NH_3 by heating over a catalyst of finely divided Ni or Fe.
6. Ammonia has been used as the cooling liquid in refrigerators. It has a very high heat of vaporization, and convenient boiling and freezing points. With the environmental concern over using Freons in refrigerators, this use of NH_3 could increase.

The widespread use of nitrates as fertilizers greatly boosts crop yields. Since nitrates are soluble, the run-off water into lakes and rivers also contains nitrates. This causes several problems.

1. It produces increased growth of algae and other aquatic plants, which may clog up rivers and lakes, and may make mudbanks in estuaries turn green.
 2. There is concern that nitrates are harmful in drinking water. They cause a disease in babies called methaemoglobinæmia, which reduces the amount of oxygen in the baby's blood. In extreme forms this causes the 'blue baby syndrome'. There is also concern that nitrates could be linked with stomach cancer. Because of this, the EEC have set a safety limit of 25ppm for nitrates in drinking water.
 3. There is some concern that denitrification to oxides of nitrogen, particularly N_2O , may harm the ozone layer.

10.40 | NPK FERTILIZERS

Plant fertilizers normally contain three main ingredients:

1. *Nitrogen* in a combined form (commonly as ammonium nitrate, other ammonium salts or nitrates, or as urea). Nitrogen is essential for plant growth, particularly of leaves, since it is a constituent of amino acids and proteins, which must be made to make new cells.
 2. *Phosphorus* for root growth, usually as a slightly soluble form of phosphate such as 'superphosphate' or 'triple superphosphate'. These are made from phosphate rocks such as fluoroapatite $[3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$ which are mined. Basic slag, which is a by-product from the steel industry, is also used as a phosphate fertilizer.
 3. *Potassium ions* for flowering, often provided as K_2SO_4 .

Urea

Urea is widely used as a nitrogenous fertilizer. It is very soluble, and hence quick acting, but it is easily washed away. It has a very high nitrogen content (46%). It is manufactured from NH_3 , and the reaction proceeds in two stages.

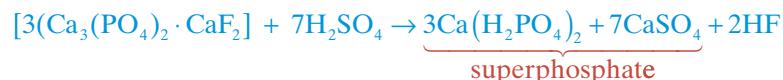


In the soil, urea slowly hydrolyses to ammonium carbonate.



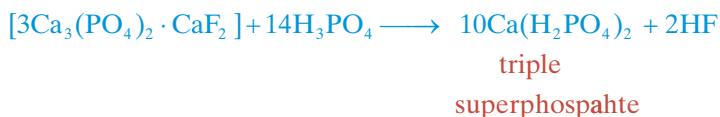
Phosphate fertilizers

Phosphate rocks such as fluoroapatite [$3\text{Ca}_3(\text{PO}_4)_2 \text{CaF}_2$] are very insoluble, and thus are of no use to plants. Superphosphate is made by treating phosphate rock with concentrated H_2SO_4 . The acid salt $\text{Ca}(\text{H}_2\text{PO}_4)_2$ is more soluble, and over a period of weeks the superphosphate will dissolve in the soil water.



The CaSO_4 is an insoluble waste product, and is of no value to plants, but is not removed from the product sold.

'Triple superphosphate' is made in a similar way, using H_3PO_4 to avoid the formation of the waste product CaSO_4 .



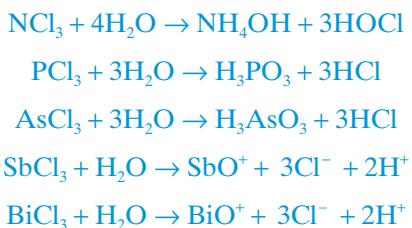
10.41 | HALIDES

Trihalides

All the possible trihalides of N, P, As, Sb and Bi are known. The nitrogen compounds are the least stable. Though NF_3 is stable, NCl_3 is explosive. NBr_3 and NI_3 are known only as their unstable ammoniates $\text{NBr}_3 \cdot 6\text{NH}_3$ and $\text{NI}_3 \cdot 6\text{NH}_3$. The latter compound can be made by dissolving I_2 in 0.880 NH_4OH . It detonates unless excess ammonia is present, and students are warned **not** to prepare this compound. The other 16 trihalides are stable.

The trihalides are predominantly covalent and, like NH_3 , have a tetrahedral structure with one position occupied by a lone pair. The exceptions are BiF_3 which is ionic and the other halides of Bi and SbF_3 which are intermediate in character.

The trihalides typically hydrolyse readily with water, but the products vary depending on the element:



They also react with NH_3 . For example,



NF_3 behaves differently from the others. It is unreactive, rather like CF_4 , and does not hydrolyse with water, dilute acids or alkali. It does react if sparked with water vapour.

PF_3 is rather less reactive towards water and is more easily handled than the other halides. The trihalides, particularly PF_3 , can act as donor molecules using their lone pair to form a coordinate bond, for example in $\text{Ni}(\text{PF}_3)_4$. In addition to this σ bond, there is π backbonding from a filled orbital on the metal to an empty d orbital on P, similar to the way CO acts as a ligand. $\text{Ni}(\text{PF}_3)_4$ can be made from nickel carbonyl $\text{Ni}(\text{CO})_4$.



Many trifluorophosphine complexes of the transition metals are known. Though most of the trihalides are made from the elements, PF_3 is made by the action of CaF_2 (or other fluoride) on PCl_3 . PF_3 is a colourless, odourless gas, which is very toxic because it forms a complex with haemoglobin in the blood, thus starving the body of oxygen.

NF_3 has little tendency to act as a donor molecule. The molecule is tetrahedral with one position occupied by a lone pair, and the bond angle $\text{F}-\text{N}-\text{F}$ is $102^\circ 30'$. However, the dipole moment is very low (0.23 Debye units) compared with 1.47D for NH_3 . The highly electronegative F atoms attract electrons, and these moments partly cancel the moment from the lone pair, and this reduces both the dipole moment and its donor power.

The trihalides also show acceptor properties, and can accept an electron pair from another ion such as F^- , forming complex ions such as $[\text{SbF}_5]^{2-}$ and $[\text{Sb}_2\text{F}_7]^-$. They also react with a variety of organometallic reagents, forming compounds MR_3 .

PCl_3 is the most important trihalide and some of it is used to make PCl_5 .



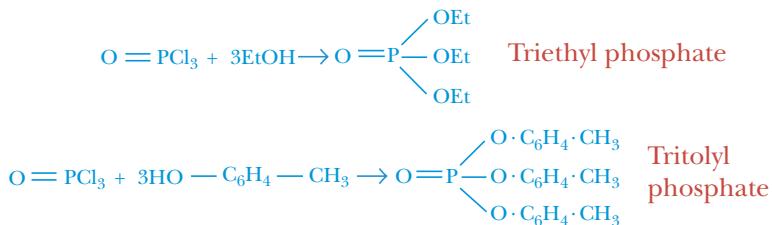
PCl_3 is widely used in organic chemistry to convert carboxylic acids to acid chlorides, and alcohols to alkyl halides.



PCl_3 can be oxidized by O_2 or P_4O_{10} to give phosphorus oxochloride POCl_3 .



POCl_3 is used in large amounts in the manufacture of trialkyl and triaryl phosphates $(\text{RO})_3\text{PO}$.

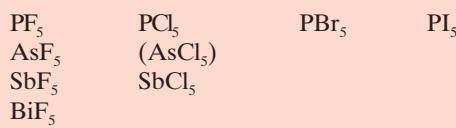


Several of these phosphate derivatives are commercially important:

1. Triethyl phosphate is used in producing systemic insecticides.
2. Tritolyl phosphate is a petrol additive.
3. Triaryl phosphates and trioctyl phosphate are used as plasticizers for polyvinyl chloride.

Pentahalides

Nitrogen is unable to form pentahalides because the second shell contains a maximum of eight electrons, i.e. four bonds. The subsequent elements have suitable *d* orbitals, and form the following pentahalides:



AsCl_5 is highly reactive and unstable, and has only a temporary existence. BiF_5 is highly reactive, and explodes with water, forming O_3 and F_2O . It oxidizes UF_4 to UF_6 , and BrF_3 to BrF_5 , and fluorinates hydrocarbons. The pentahalides are prepared as follows:



These molecules have a trigonal bipyramidal shape in the gas phase (see Figure 10.32), as expected from the VSEPR theory for five pairs of electrons.

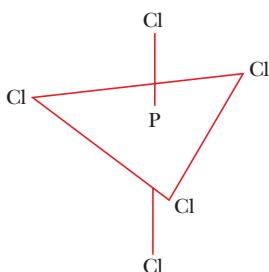
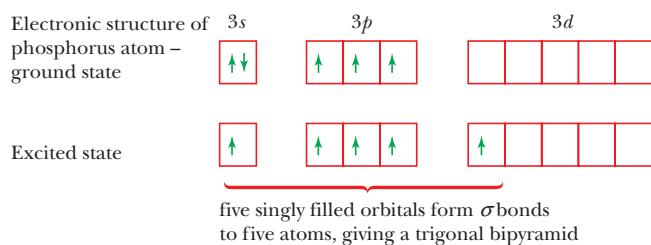


Figure 10.32 Structure of gaseous phosphorus pentachloride.

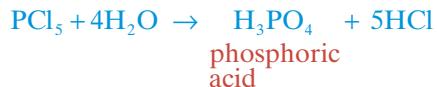
The valence bond explanation of the shape is:



The trigonal bipyramidal is not a regular structure. Electron diffraction on PF_5 gas shows that some bond angles are 90° and others are 120° , and the axial P–F bond lengths are 1.58 \AA whilst the equatorial P–F lengths are 1.53 \AA . In contrast NMR studies suggest that all five F atoms are equivalent. This paradox may be explained quite simply. Electron diffraction gives an instantaneous picture of the molecule, whilst NMR gives the picture averaged over several milliseconds. The axial and equatorial F atoms are thought to interchange their positions in less time than that needed to take the NMR. The interchange of axial and equatorial positions is called ‘pseudorotation’.

PF_5 remains covalent and keeps this structure in the solid state. However, PCl_5 is close to the ionic–covalent borderline, and it is covalent in the gas and liquid states, but is ionic in the solid state. PCl_5 solid exists as $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$: the ions have tetrahedral and octahedral structures respectively. In the solid, PBr_5 exists as $[\text{PBr}_4]^+ \text{Br}^-$, and PI_5 appears to be $[\text{PI}_4]^+$ and I^- in solution.

PCl_5 is the most important pentahalide, and it is made by passing Cl_2 into a solution of PCl_3 in CCl_4 . World production is about 20 000 tonnes/year. Complete hydrolysis of the pentahalides yields the appropriate *-ic* acid. Thus PCl_5 reacts violently with water:



If equimolar amounts are used, the reaction is more gentle and yields phosphorus oxochloride POCl_3 .



PCl_5 is used in organic chemistry to convert carboxylic acids to acid chlorides, and alcohols to alkyl halides.



It reacts with P_4O_{10} , forming POCl_3 , and with SO_2 , forming thionyl chloride SOCl_2 .



PCl_5 also reacts with NH_4Cl , forming a variety of phosphonitrilic chloride polymers (see later).



and



Despite the existence of pentahalides, no hydrides MH_5 are known. To attain the five-valent state, d orbitals must be used. Hydrogen is not sufficiently electronegative to make the d orbitals contract sufficiently, though PHF_4 and PH_2F_3 have been isolated.

10.42 | OXIDES OF NITROGEN

The oxides and oxoacids of nitrogen all exhibit $p\pi-p\pi$ multiple bonding between the nitrogen and oxygen atoms. This does not occur with the heavier elements in the group, and consequently nitrogen forms a number of compounds which have no P, As, Sb or Bi analogues. Nitrogen forms a very wide range of oxides, exhibiting all the oxidation states from (+I) to (+VI). The lower oxides are neutral, and the higher ones are acidic (Table 10.19).

Table 10.19 Oxides of nitrogen

Formula	Oxidation number	Name
N_2O	+I	Nitrous oxide
NO	+II	Nitric oxide
N_2O_3	+III	Nitrogen sesquioxide
NO_2, N_2O_4	+IV	Nitrogen dioxide, dinitrogen tetroxide
N_2O_5	+V	Dinitrogen pentoxide
NO_3, N_2O_6 (very unstable)	+VI	Nitrogen trioxide, dinitrogen hexoxide

Nitrous oxide N_2O

N_2O is a stable, relatively unreactive colourless gas. It is prepared by careful thermal decomposition of molten ammonium nitrate at about $280^\circ C$. If heated strongly it explodes. N_2O can also be made by heating a solution of NH_4NO_3 acidified with HCl.



N_2O is a neutral oxide and does not form hyponitrous acid $H_2N_2O_2$ with water nor hyponitrites with alkali. It is important in the preparation of sodium azide, and hence also of the other azides:



The largest use of N_2O is as a propellant for whipped ice-cream. Because it has no taste, and is non-toxic, it meets the strict food and health regulations.

N_2O is used as an anaesthetic, particularly by dentists. It is sometimes called 'laughing gas', because small amounts cause euphoria. It requires a partial pressure of 760 mm Hg of N_2O to anaesthetize a patient completely. Thus if dioxygen is also supplied, the patient may not be completely unconscious. If deprived of dioxygen for long, the patient will die. Plainly N_2O is unsuitable for long operations. Usually N_2O is administered to put the patient 'to sleep', and O_2 to make him recover consciousness.

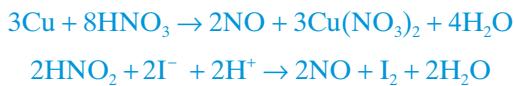
The molecule is linear as would be expected for a triatomic molecule with 16 outer shell electrons (see also N_3^- and CO_2). However, CO_2 is symmetrical ($O-C-O$), whereas in N_2O the orbital energies favour the formation of the asymmetrical molecule $N-N-O$ rather than the symmetrical molecule $N-O-N$. The bond lengths are short, and the bond orders have been calculated as $N-N$ 2.73 and $N-O$ 1.61.



Nitric oxide NO

NO is a colourless gas and is an important intermediate in the manufacture of nitric acid by the catalytic oxidation of ammonia (Ostwald process). It was also important in the obsolete Birkeland-Eyde process

which involved sparking dinitrogen and dioxygen. NO is prepared in the laboratory by the reduction of dilute HNO_3 with Cu, or reduction of HNO_2 with I^- :

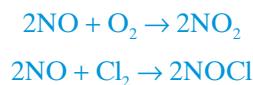


NO is a neutral oxide and is not an acid anhydride.

NO has 11 valency electrons. It is impossible for them all to be paired, and hence this is an odd electron molecule and the gas is paramagnetic. It is diamagnetic in the liquid and solid states, because the molecule dimerizes forming $\text{O}-\text{N}-\text{N}-\text{O}$. The asymmetrical dimer $\text{O}-\text{N}-\text{O}-\text{N}$ has been observed to be formed as a red solid in the presence of HCl or other Lewis acids.

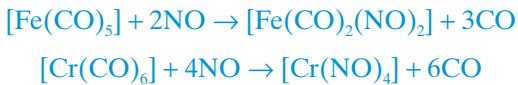
The bond length $\text{N}-\text{O}$ is 1.15 Å, which is intermediate between a double and a triple bond. Bonding is best described using the molecular orbital theory (see Chapter 3). The bonding is similar to that in N_2 and CO which both have 10 outer electrons. NO has 11 outer electrons, and the extra unpaired electron occupies an antibonding π^*2p orbital. This reduces the bond order from 3 in N_2 to $2\frac{1}{2}$ in NO. If this electron is removed by oxidizing NO, the nitrosonium ion NO^+ is formed. In NO^+ the bond order is 3, and the $\text{N}-\text{O}$ bond length contracts from 1.15 Å in NO to 1.06 Å in NO^+ .

Odd electron molecules are usually highly reactive and tend to dimerize, NO is unusually stable for an odd electron molecule. Nevertheless it reacts instantly with dioxygen to give NO_2 , and with the halogens it gives nitrosyl halides, e.g. NOCl .



NO readily forms coordination complexes with transition metal ions. These complexes are called nitrosyls. Fe^{2+} and NO form the complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$, which is responsible for the colour in the ‘brown-ring test’ for nitrates. Most nitrosyl complexes are coloured. Another example is sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$.

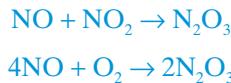
NO often acts as a three-electron donor, in contrast to most ligands which donate two electrons. Thus three CO groups may be replaced by two NO groups:



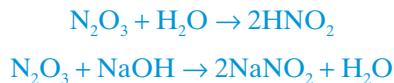
In these complexes the $\text{M}-\text{N}-\text{O}$ atoms are linear, or close to linear. However, in 1968 the $\text{M}-\text{N}-\text{O}$ angle in $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)(\text{NO})]^+$ was found to be 123° , and since then a number of other complexes have been found with bond angles in the range $120-130^\circ$. These bent bonds, which are weaker than straight bonds, are of considerable theoretical interest. NO may also act as a bridging ligand between two or three metal atoms in a similar way to CO.

Nitrogen sesquioxide N_2O_3

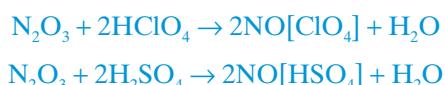
N_2O_3 can only be obtained at low temperatures. It can be made by condensing equimolar amounts of NO and NO_2 together, or by reacting NO with the appropriate amount of O_2 . This gives a blue liquid or solid, which is unstable and dissociates into NO and NO_2 at -30°C .



It is an acidic oxide and is the anhydride of nitrous acid HNO_2 . With alkali it forms nitrites.



N_2O_3 reacts with the concentrated acids, forming nitrosyl salts:



The oxide exists in two different forms (Figure 10.33). These may be interconverted by irradiation with light of the appropriate wavelength. The N–N bond length from microwave spectra is 1.864 Å in the asymmetrical form. This is exceptionally long and thus the bond is exceptionally weak compared with the N–N bond found in hydrazine (length of 1.45 Å). Solid N_2O_3 exists in the form $[\text{NO}]^+ [\text{NO}_2]^-$.

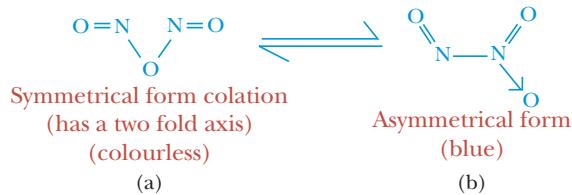


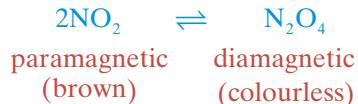
Figure 10.33 Two forms of N_2O_3 :

Nitrogen dioxide NO_2 and dinitrogen tetroxide N_2O_4

NO_2 is a red-brown poisonous gas and is produced on a large scale by oxidizing NO in the Ostwald process for the manufacture of nitric acid. In the laboratory it is prepared by heating lead nitrate:



The gaseous products O_2 and NO_2 are passed through a U-tube cooled in ice. The NO_2 (b.p. 21°C) condenses. The $Pb(NO_3)_2$ must be carefully dried, since NO_2 reacts with water. The NO_2 is obtained as a brown liquid which turns paler on cooling, and eventually becomes a colourless solid. This is because NO_2 dimerizes into colourless N_2O_4 . NO_2 is an odd electron molecule, and is paramagnetic and very reactive. It dimerizes to N_2O_4 , pairing the previously unpaired electrons. N_2O_4 has no unpaired electrons and is diamagnetic.



N_2O_4 is a mixed anhydride, because it reacts with water to give a mixture of nitric and nitrous acids:

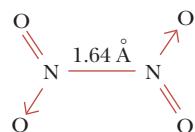


The HNO_3 formed decomposes to give NO_2 .



Thus moist NO_2 or N_2O_4 gases are strongly acidic.

The NO_2 molecule is angular with an $\text{O}=\text{N}=\text{O}$ angle of 132° . The bond length $\text{O}=\text{N}$ of 1.20 \AA is intermediate between a single and a double bond. X-ray diffraction on solid N_2O_4 shows the structure to be planar.

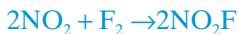


The N—N bond is very long (1.64 Å), and is therefore weak. It is much longer than the single bond N—N distance of 1.47 Å in N_2H_4 , but there is no satisfactory explanation of why it is long.

Liquid N_2O_4 is useful as a non-aqueous solvent. It self-ionizes:



The NO_2 - N_2O_4 system is a strong oxidizing agent. NO_2 reacts with fluorine and chlorine, forming nitryl fluoride NO_2F and nitryl chloride NO_2Cl . It oxidizes HCl to Cl_2 and CO to CO_2 .



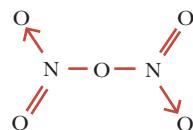
Dinitrogen pentoxide N_2O_5

N_2O_5 is prepared by carefully dehydrating HNO_3 with P_2O_5 at low temperatures. It is a colourless deliquescent solid, which is highly reactive, is a strong oxidizing agent, and is light sensitive. It is the anhydride of HNO_3 .



In the gas phase N_2O_5 decomposes into NO_2 , NO and O_2 . Nitrogen trioxide NO_3 may be formed by treating N_2O_5 with O_3 .

X-ray diffraction shows that solid N_2O_5 is ionic NO_2^+ NO_3^- : it should in reality be called nitronium nitrate. It is covalent in solution and in the gas phase, and probably has the structure:



10.43 | OXOACIDS OF NITROGEN

Nitrous acid HNO_2

Nitrous acid is unstable except in dilute solution. It is easily made by acidifying a solution of a nitrite. Barium nitrite is often used with H_2SO_4 , since the insoluble BaSO_4 can be filtered off easily.

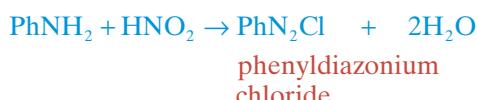


Group 1 metal nitrites can be made by heating nitrates, either on their own or with Pb.



Nitrous acid and nitrites are weak oxidizing agents and will oxidize Fe^{2+} to Fe^{3+} , and I^- to I_2 ; they themselves are reduced to N_2O or NO . However, HNO_2 and nitrites are oxidized by KMnO_4 and Cl_2 , forming nitrates NO_3^- .

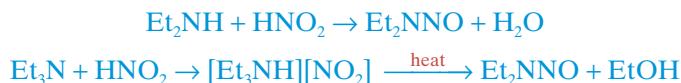
Large amounts of nitrites are used to make diazo compounds, which are converted into azo dyes, and also pharmaceutical products.



Nitrites are important in the manufacture of hydroxylamine:



Sodium nitrite is used as a food additive in cured meat, sausages, hot dogs, bacon and tinned ham. NO_2^- ions inhibit the growth of bacteria, particularly *Clostridium botulinum*, which causes botulism (a particularly unpleasant form of food poisoning). Reductive decomposition of NO_2^- gives NO , which forms a red complex with haemoglobin, and improves the look of meat. There is concern that during the cooking of meat, the nitrites may react with amines and be converted into nitrosamines $\text{R}_2\text{N}-\text{N}=\text{O}$, which are thought to cause cancer. Certainly secondary and tertiary aliphatic amines form nitrosamines with nitrites:



The nitrite ion is a good ligand and forms many coordination complexes. Since lone pairs of electrons are present on both N and O atoms, either N or O can form a coordinate bond. This gives rise to isomerism between nitro complexes $\text{M} \leftarrow \text{NO}_2$ and nitrito complexes $\text{M} \leftarrow \text{ONO}$, for example $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$. (This is discussed in Chapter 5, under 'Isomerism'.) If a solution of Co^{2+} ions is treated with NO_2^- ions, first Co^{2+} ions are oxidized to Co^{3+} , then NO_2^- ions form the complex $[\text{Co}(\text{NO}_2)_6]^{3-}$. Precipitation of potassium cobaltinitrite $\text{K}_3[\text{Co}(\text{NO}_2)_6]^{3-}$ is used to detect K^+ qualitatively. The NO_2^- ion may act as a chelating ligand, and bond to the same metal twice, or it may act as a bridging ligand joining two metal atoms.

The nitrite ion NO_2^- has a plane triangular structure, with N at the centre, two corners occupied by O atoms, and the third corner occupied by the lone pair. A three-centre bond covers the N and the two O atoms and the bond order is 1.5 for the N—O bonds, which have bond lengths in between those for a single and double bond. (More details are given in Chapter 3.)

Nitric acid HNO_3

HNO_3 is the most important oxoacid of nitrogen. (The three most important industrial acids in order of tonnages produced are (1) H_2SO_4 , (2) HNO_3 and (3) HCl .) Pure nitric acid is a colourless liquid, but on exposure to light it turns slightly brown because of slight decomposition into NO_2 and O_2 ,

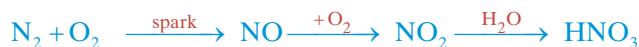


It is a strong acid and is 100% dissociated in dilute aqueous solutions into H_3O^+ and NO_3^- . It forms a large number of salts called nitrates, which are typically very soluble in water.

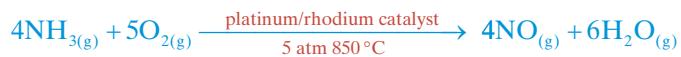
The shape of the NO_3^- ion is a planar triangle, like the CO_3^{2-} ion. The latter elements in both groups form tetrahedral oxoacid ions such as PO_4^{3-} and SiO_4^{4-} . This difference in shape is probably due to the small size of the N and C atoms and their restriction to eight electrons in their outer shell.

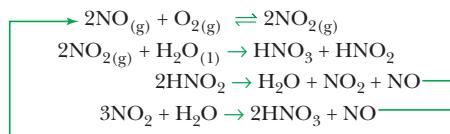
HNO_3 is an excellent oxidizing agent particularly when hot and concentrated. H^+ ions are oxidizing, but the NO_3^- ion is an even stronger oxidizing agent in acid solution. Thus metals like copper and silver which are insoluble in HCl dissolve in HNO_3 . Some metals such as gold are insoluble even in HNO_3 , but will dissolve in aqua regia, a mixture of 25% concentrated HNO_3 and 75% concentrated HCl . The enhanced ability to dissolve metals shown by aqua regia arises from the oxidizing power of HNO_3 coupled with the ability of Cl^- to form complexes with the metal ions.

HNO_3 was originally made from NaNO_3 or KNO_3 and concentrated H_2SO_4 . The first synthetic method was the Birkeland–Eyde process. This sparked N_2 and O_2 together in an electric arc furnace, and passed the gas into water. The process was started in Norway in 1903, but is now obsolete, because of the high cost of electricity.



The Ostwald process depends on the catalytic oxidation of ammonia to NO , followed by oxidation of NO to NO_2 , and conversion of NO_2 with water to HNO_3 . The first plant was set up in Germany in 1908, and Ostwald was awarded the Nobel Prize in 1909. The method is still in use. The overall process is:





Overall:



This gives a HNO_3 solution of concentration 60% by weight. Distillation only increases the concentration to 68% since a constant boiling mixture is formed. 'Concentrated' HNO_3 contains 98% acid and is produced by dehydrating with concentrated sulphuric acid.

When nitric acid is mixed with concentrated sulphuric acid, the nitronium ion NO_2^+ is formed. This is the active species in the nitration of aromatic organic compounds (Figure 10.34), this is an important step in making explosives, or the nitro compounds may be reduced to aniline and used for making dyestuffs:

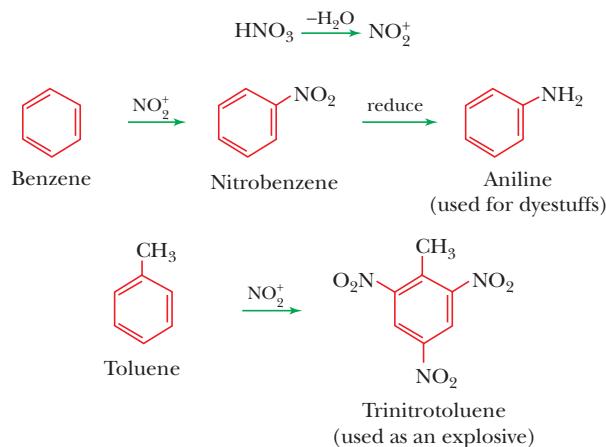


Figure 10.34 Nitration of benzene and toluene.

Covalent nitrates are less stable than ionic nitrates. (This is a similar behaviour to that of the azides.) Nitroglycerine, nitrocellulose and trinitrotoluene (TNT) are all explosive (Figure 10.35).

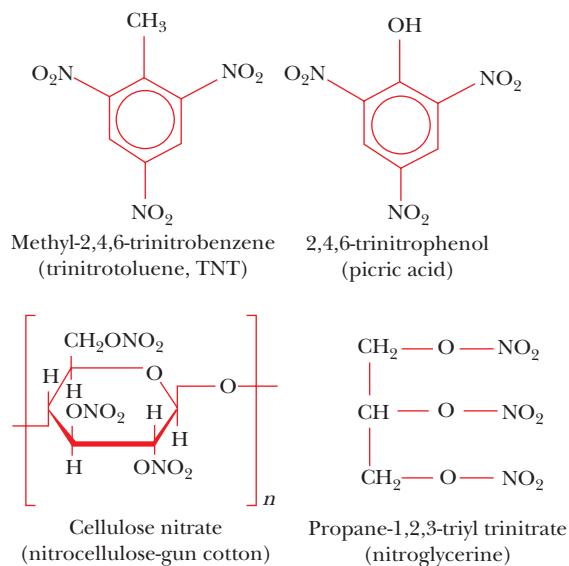
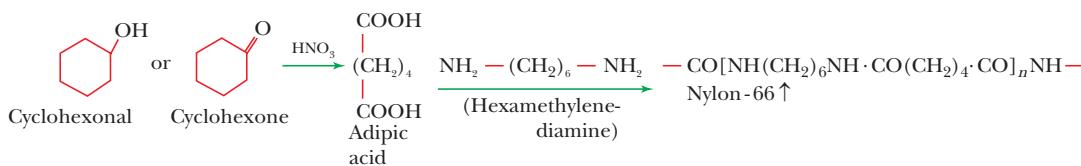


Figure 10.35 Some explosives.

HNO_3 is a strong oxidizing agent, and is used to oxidize cyclohexanol/cyclohexanone mixtures to adipic acid (which reacts with hexamethylene-diamine in the manufacture of nylon-66).



HNO_3 is also used to oxidize *p*-xylene to terephthalic acid for the manufacture of terylene.

The structure of the nitrate ion is a planar triangle. All three oxygen atoms are equivalent. In addition to the σ bonds, four-centre π molecular orbitals cover the N and the three σ atoms. Each of the N—O bonds has a bond order of $1\frac{1}{3}$, 1 from the σ bond and $\frac{1}{3}$ from the π bond. (This is described more fully in Chapter 3.)

Other Chemical Properties of HNO_3

The important oxidizing chemical properties of nitric acid are listed as follows.

- 1. Oxidation of non-metals:** Nitric acid oxidizes non-metals to their corresponding oxyacids in their highest oxidation state by means of nascent oxygen generated. Some examples are:



- 2. Oxidation of metalloids:** These are also oxidized to the corresponding oxyacids in their highest oxidation states.



- 3. Oxidation of other compounds**



- 4. Oxidation of organic compounds:** A number of organic compounds get oxidized with nitric acid, for example, toluene to benzoic acid and cane sugar to oxalic acid.



Nitric acid attacks **proteins** forming a yellow nitro compound called xanthoprotein. The skin and wool are therefore stained yellow by the acid. This reaction is used as a test for proteins.

5. Oxidation of metals: Most metals, except noble metals (gold and platinum, which dissolve in aqua regia) are oxidized by nitric acid and the nature of the product formed depends on the concentration and temperature of the acid. Some metals, like Cr and Al do not dissolve in concentrated HNO_3 due to formation of passive film on the surface.



The reactions of metals with HNO_3 can be summarized as follows in Table 10.20.

Table 10.20 Reactions of metals of different concentrations of nitric acid

Strength of HNO_3	Metal	Main products
Extremely dilute (2%)	Mg, Mn	Metal nitrate + H_2
Dilute (6%)	Fe, Zn, Sn	Metal nitrate + $\text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$
Dilute (20%)	Pb, Cu, Ag, Hg	Metal nitrate + $\text{NO} + \text{H}_2\text{O}$
	Fe, Zn	Metal nitrate + $\text{N}_2\text{O} + \text{H}_2\text{O}$
	Sn	$\text{NH}_4\text{NO}_3 + \text{Sn}(\text{NO}_3)_2$
Concentrated (70%)	Fe, Zn, Pb, Cu, Ag	Metal nitrate + $\text{NO}_2 + \text{H}_2\text{O}$
	Sn	$\text{H}_2\text{SnO}_3 + \text{NO}_2$

10.44 | OXIDES OF PHOSPHORUS

The oxides of phosphorus are mainly P_4O_6 and P_4O_{10} , where P is in the +3 and +5 oxidation states, respectively. Other oxides are also reported, like, P_4O_7 , P_4O_8 and P_4O_9 where P atom is in +3 and +5 oxidation states. They form fewer oxides than does nitrogen, presumably because of the inability of these elements to form $p\pi-p\pi$ double bonds.

Trioxides

Phosphorus trioxide is dimeric and should be written P_4O_6 , not P_2O_3 . P_4O_6 is actually not a dimer of P_2O_3 , only formula-wise it is like a dimer because P_2O_3 does not exist structurally. P_4O_6 has four P atoms at the corners of a tetrahedron, with six O atoms along the edges, each O being bonded to two P atoms. The structure of P_4O_6 is shown in Figure 10.36. Since the P—O—P angle is 127° the O atoms are strictly above the edges, but it is more convenient to draw them on the edges.

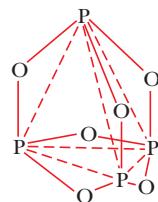


Figure 10.36 Structure of phosphorus trioxide P_4O_6 .

Because yellow phosphorus is more reactive than is N_2 , phosphorus oxides (unlike nitrogen oxides) can all be obtained by burning phosphorus in air.



P_4O_6 is formed by burning phosphorus in a limited supply of air. It is a soft white solid (m.p. 24°C, b.p. 175°C). It is removed from the reaction mixture and is purified by distillation. (Higher oxides are formed in a plentiful supply of air.) P_4O_6 will burn in air, forming P_4O_{10} .



The basicity of oxides and hydroxides usually increases on descending a group. P_4O_6 is acidic and hydrolyses in water, forming phosphorous acid.



Pentoxides

Phosphorus pentoxide is the most important oxide, and is quite common. It is dimeric and has the formula P_4O_{10} , not P_2O_5 . It is also not a true dimer because monomeric form P_2O_5 does not exist structurally. Its structure is derived from that of P_4O_6 . Each P atom in P_4O_6 forms three bonds to O atoms. There are five electrons in the outer shell of a P atom. Three electrons have been used in bonding, and the other two comprise a lone pair, which is situated on the outside of the tetrahedral unit. In P_4O_{10} the lone pairs on each of the four P atoms form a coordinate bond to an oxygen atom (Figure 10.37).

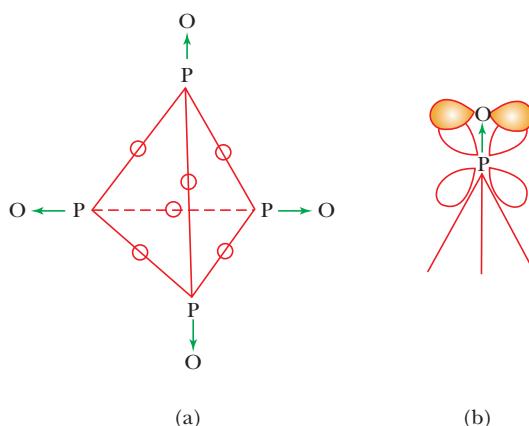


Figure 10.37 Structure of phosphorus pentoxide P_4O_{10} . (a) Formation of σ bonds, (b) Orbitals involved in back bonding.

Measurement of the P—O bond lengths shows that the bridging bonds on the edges are 1.60 Å but the coordinate bonds on the corners are 1.43 Å. The bridging bonds compare with those in P_4O_6 (1.65 Å) and are normal single bonds. The bonds on the corners are much shorter than a single bond, and are in fact double bonds. These double bonds are different in origin from the ‘usual’ double bonds such as that in ethene which arises from $p\pi-p\pi$ overlap with one electron coming from each C atom. The second bond in P=O is formed by $p\pi-d\pi$ back bonding. A full p orbital on the O atom overlaps sideways with an empty d orbital on the P atom. Thus it differs from the double bond in ethene in two respects:

1. A p orbital overlaps with a d orbital, rather than p with p .
2. Both electrons come from one atom, and hence the bond is a ‘dative bond’.

P_4O_{10} is formed by burning P in an excess of air or dioxygen. It absorbs water from the air or from other compounds, and becomes sticky. Because of this strong affinity for water, P_4O_{10} is used as a drying agent. Finely powdered P_4O_{10} is sometimes spread over glass wool and used for drying purposes. This provides a large drying surface, which is not easily covered by solid hydrolysis products. P_4O_{10} hydrolyses violently in water, forming phosphoric acid H_3PO_4 . The manufacture of pure H_3PO_4 by this route is the largest use of P_4O_{10} .



P_4O_{10} reacts with alcohols and ethers, forming phosphate esters. (The relation of these esters to phosphoric acid is shown by writing H_3PO_4 as $O=P(OH)_3$.)



10.45 | OXOACIDS OF PHOSPHORUS

Phosphorus forms two series of oxoacids:

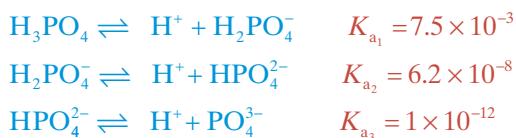
1. The phosphoric series of acids, in which the oxidation state of P is (+V), and in which the compounds have oxidizing properties.
2. The phosphorous series of acids, which contain P in the oxidation state (+III), and which are reducing agents.

In all of these, P is four-coordinate and tetrahedrally surrounded wherever possible, $p\pi-p\pi$ back bonding gives rise to P=O bonds. The hydrogen atoms in OH groups are ionizable and are acidic, but the P—H bonds found in the phosphorous acids have reducing, not acidic, properties. Simple phosphate ions can condense (polymerize) together to give a wide range of more complicated isopolyacids or their salts.

The phosphoric acid series

Orthophosphoric acids

The simplest phosphoric acid is H_3PO_4 orthophosphoric acid (Figure 10.38). The acid contains three replaceable H atoms, and is tribasic. It undergoes stepwise dissociation:



Three series of salts can be formed:

1. Dihydrogen phosphates, for example sodium dihydrogen phosphate NaH_2PO_4 , which is slightly acidic in water.
2. Monohydrogen phosphates, for example disodium hydrogen phosphate Na_2HPO_4 , which is slightly basic in water.
3. Normal phosphates such as trisodium phosphate Na_3PO_4 , which are appreciably basic in solution.

NaH_2PO_4 and Na_2HPO_4 are made industrially by neutralizing H_3PO_4 with 'soda ash' (Na_2CO_3), but $NaOH$ is required to make Na_3PO_4 . All three salts exist in the anhydrous state and also in a number of hydrated forms, and they are used extensively.

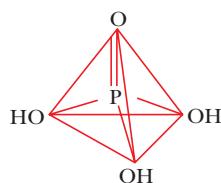
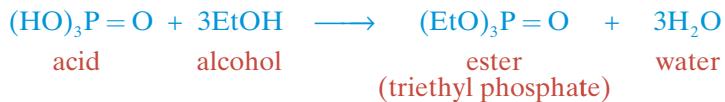
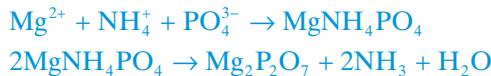


Figure 10.38 Structure of orthophosphoric acid H_3PO_4 .

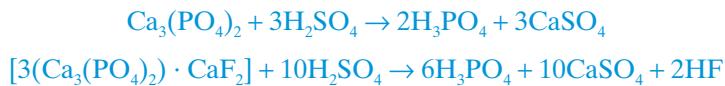
Phosphoric acid also forms esters with alcohols:



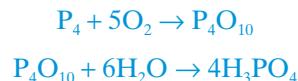
Phosphates can be estimated quantitatively by adding a solution containing Mg^{2+} and NH_4OH solution to a solution of the phosphate. Magnesium ammonium phosphate is precipitated quantitatively, and this is filtered, washed, ignited, and weighed as magnesium pyrophosphate $\text{Mg}_2\text{P}_2\text{O}_7$.



Impure orthophosphoric acid H_3PO_4 is prepared in large amounts by treating phosphate rock with H_2SO_4 . This is called the 'wet process'. The CaSO_4 is hydrated to gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which is filtered off, and the F^- is converted to $\text{Na}_2[\text{SiF}_6]$ and removed. The H_3PO_4 is concentrated by evaporation. Most of the H_3PO_4 made in this way is used to make fertilizer.



Pure H_3PO_4 is made by the 'furnace process'. Molten P is burnt in a furnace with air and steam. First P_4O_{10} is formed by reaction between P and O, and then this is immediately hydrolysed.

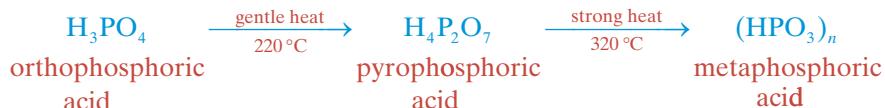


Phosphoric acid is hydrogen bonded in aqueous solution, and because of this the 'concentrated acid' is syrupy and viscous. Concentrated acid is widely used and contains about 85% by weight of H_3PO_4 (100% pure (anhydrous) H_3PO_4 is seldom used, but it can be prepared as colourless deliquescent crystals by evaporation at low pressure). Most of the acid (solution) made in this way is used in the laboratory, and in food (Kraft cheese Na_2HPO_4) and pharmaceutical preparations.

H_3PO_4 may also be made by the action of concentrated HNO_3 on P.



Orthophosphoric acid loses water steadily on heating:



Polyporphosphates

A very large number of polyphosphoric acids and their salts, the polyphosphates, arise by polymerizing acidic $[\text{PO}_4]$ units forming isopolyacids. These consist of chains of tetrahedra, each sharing the O atoms at one or two corners of the $[\text{PO}_4]$ tetrahedron, giving simple unbranched chains, in a similar way to the formation of pyroxenes by the silicates.

The hydrolysis of P_4O_{10} proceeds in stages, and an understanding of these stages leads to an understanding of the wide range of phosphoric acids (Figure 10.39).



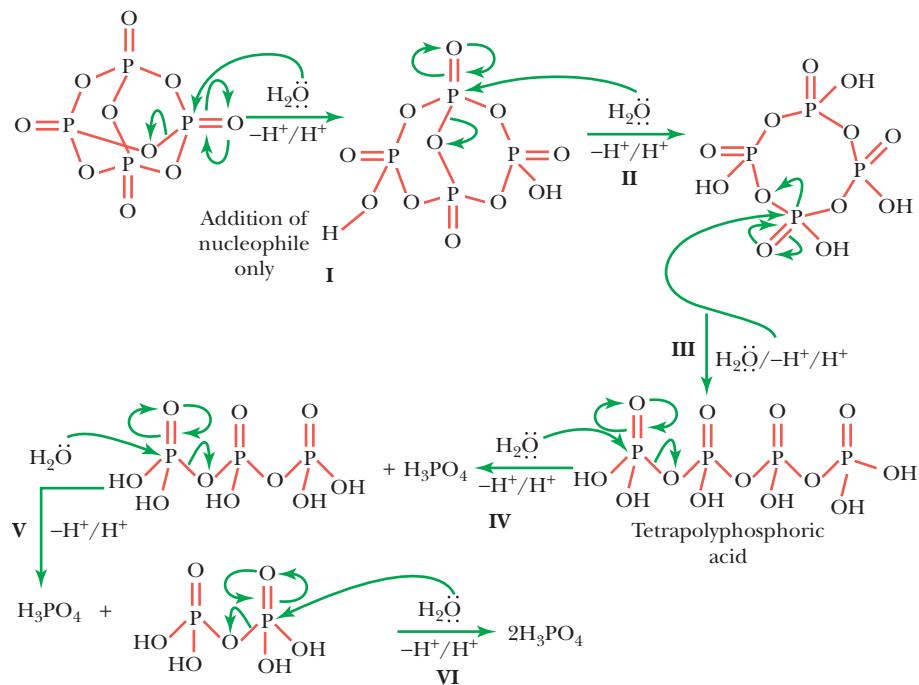


Figure 10.39 Scheme for the hydrolysis of P_4O_{10} .

Polyphosphates are straight chain compounds. The basicity of the various acids, that is the number of replaceable H atoms, can be found by drawing the structure and counting the number of OH groups. Thus orthophosphoric acid is tribasic, pyrophosphoric acid is tetrabasic, tripolyphosphoric acid is pentabasic, tetrapolyphosphoric acid is hexabasic, and tetrametaphosphoric acid is tetrabasic (Figure 10.40).

Many polyphosphates are known. Chains of different lengths with up to ten $[\text{PO}_4]$ units have been isolated, but the first four in the series are well known.

H_3PO_4	orthophosphoric acid
$\text{H}_4\text{P}_2\text{O}_7$	dipolyphosphoric acid (pyrophosphoric acid)
$\text{H}_5\text{P}_3\text{O}_{10}$	tripolyphosphoric acid
$\text{H}_6\text{P}_4\text{O}_{13}$	tetrapolyphosphoric acid

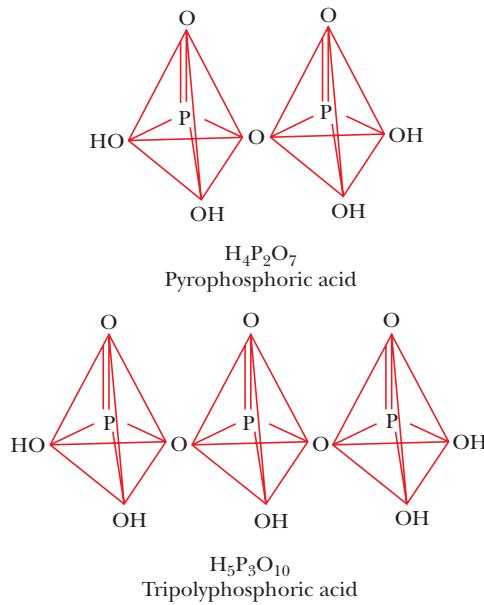


Figure 10.40 Pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$ and tripolyphosphoric acid $\text{H}_5\text{P}_3\text{O}_{10}$.

Some very long chain polymers called Graham's salt, Kurrol salt and Maddrell's salt are also known. These are named after the person who first reported them, and they are discussed later.

Disodium dihydrogenpyrophosphate $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ is mixed with NaHCO_3 and used in bread making to leaven the bread, that is to make it rise. They react and evolve CO_2 , when heated together. This is an easier way of making batches of bread than using yeast, and is used commercially.



Graham's salt

Graham's salt is the best known of these long chain polyphosphates, and is formed by quenching molten NaPO_3 . It forms a glassy solid instead of crystallizing. In industry it is incorrectly called sodium hexametaphosphate. Graham's salt is soluble in water: These solutions give precipitates with metal ions such as Pb^{2+} and Ag^+ but not with Ca^{2+} and Mg^{2+} . Graham's salt is sold commercially under the trade name Calgon. It is widely used for softening water. It sequesters Ca^{2+} and Mg^{2+} in a similar way to $\text{Na}_5\text{P}_3\text{O}_{10}$. Many of these polyphosphates are used for water softening, and also for descaling boilers and pipes.

Metaphosphates – cyclophosphates

The metaphosphates form a family of ring compounds. The old name of metaphosphates is still widely used even though according to IUPAC nomenclature cyclo- should be used to indicate the formation of rings. They can be prepared by heating orthophosphates:



There is no evidence for the existence of free monometaphosphate ions PO_3^- , or of dimetaphosphate ions. The latter would involve the sharing of two corners, that is an edge between two $[\text{PO}_4]$ tetrahedra, and would impose a great deal of strain on the structure. In contrast, tri- and tetra-metaphosphates are well known (Figure 10.41). A few larger rings have been isolated with up to eight $[\text{PO}_4]$ units, that is up to $\text{Na}_8[\text{P}_8\text{O}_{24}]$. These are obtained as mixtures, and are conveniently separated by paper chromatography or thin layer chromatography.

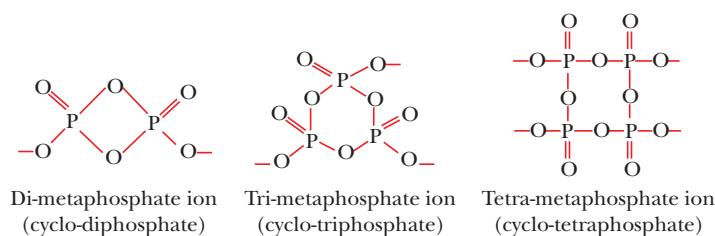
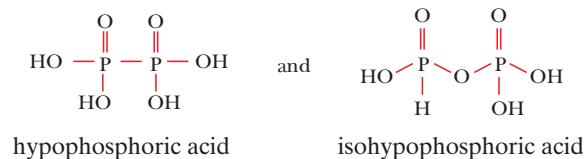


Figure 10.41 Some polyphosphate ions.

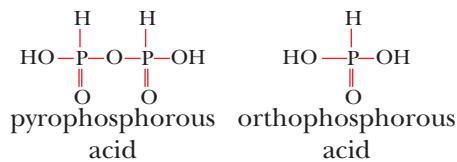
Note: $\text{H}_4\text{P}_2\text{O}_6$ exists in two forms, that is, tetrabasic hypophosphoric acid (I) and tribasic isohypophosphoric acid (II). The structures are as shown below.



The phosphorous acid series

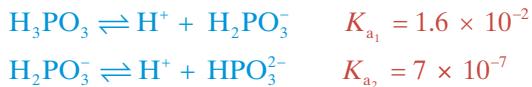
The phosphorous acids are less well known. They all contain phosphorus in the oxidation state (+III). They have P–H bonds and are therefore reducing agents.

Hydrolysis of P_4O_6 in a manner analogous to the hydrolysis of P_4O_{10} already described yields pyro- and orthophosphorous acids, which are both dibasic and reducing agents.



Orthophosphorous acid H_3PO_3

H_3PO_3 contains two acidic H atoms (the OH groups), and one reducing H (the P—H hydrogen atom). Consequently only two of the three H atoms can ionize, and the acid is dibasic.



Thus H_3PO_3 can form two series of salts:

1. Dihydrogen phosphites, for example NaH_2PO_3 ,
2. Monohydrogen phosphites, for example Na_2HPO_3 .

The phosphites are very strong reducing agents in basic solutions. In acid solutions they are converted to H_3PO_3 , which is still a moderately strong reducing agent.

Hypophosphorous acid H_3PO_2

H_3PO_2 contains P in the oxidation state (+I), and has one O atom less than the orthophosphorous acid. It is prepared by alkaline hydrolysis of phosphorus (Figure 10.42).



The acid is monobasic and a very strong reducing agent. Salts of this acid are called hypophosphites, and sodium hypophosphite NaH_2PO_2 is used industrially to bleach wood and to make paper.

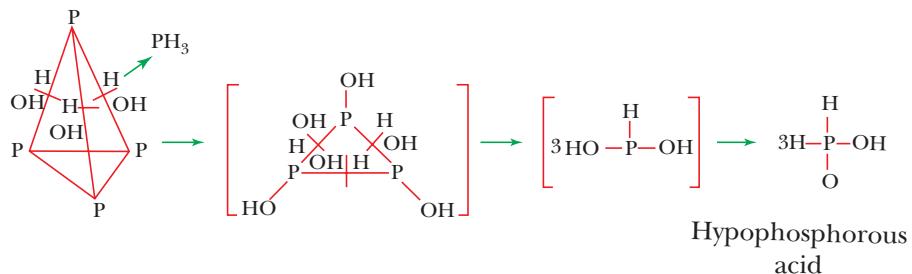


Figure 10.42 Alkaline hydrolysis of phosphorus.

Major uses of phosphates

Phosphate rock is mined on a vast scale. The minerals vary both in purity and in composition. Industry expresses the production of phosphates in terms of the P_2O_5 content. The major commercial use (85%) is for fertilizers such as superphosphate, triple superphosphate, and ammonium phosphate. These do not need to be especially pure.

SINGLE CORRECT CHOICE TYPE QUESTIONS

1. NH_3 burns in air under suitable conditions to produce
(A) N_2 (B) NO (C) N_2O (d) N_2O_3

2. Which of the following is not a covalent nitride?
(A) BN (B) AlN (C) Ge_3N_4 (d) ScN

3. In the cationic parts of solid N_2O_5 and solid N_2O_4 , the bond orders of N–O are, respectively
(A) 3 and 2
(B) 2 and 3
(C) 2.5 and 3
(D) 3 in both

4. The best reducing agent among the following is
(A) NH_3 (B) SbH_3 (C) PH_3 (D) AsH_3

5. N_2H_4 reacts with conc. H_2SO_4 to produce a salt $[\text{NH}_3 - \text{NH}_3]^{2+} \text{SO}_4^-$ in which
(A) $d_{\text{N}-\text{N}} \text{ (salt)} > d_{\text{N}-\text{N}}(\text{N}_2\text{H}_4)$
(B) $d_{\text{N}-\text{N}} \text{ (salt)} < d_{\text{N}-\text{N}}(\text{N}_2\text{H}_4)$
(C) $d_{\text{N}-\text{N}} \text{ (salt)} = d_{\text{N}-\text{N}}(\text{N}_2\text{H}_4)$
(D) Cannot be predicted.

6. Which is not correct regarding the Holme's signal?
(A) PH_3 catches fire on contact with air, spontaneously.
(B) P_2H_4 catches fire on contact with air, spontaneously.
(C) PH_3 , C_2H_2 and P_2H_4 are formed together.
(D) All the gases burn together.

7. PH_3 and NH_3 on separately reacting with bleaching powder produce respectively
(A) P and N_2
(B) PCl_3 and NCl_3
(C) PCl_3 and N_2
(D) PCl_5 and NCl_3

8. N_2 is passed through overheated CaC_2 . Which of the following options is correct for the product formed?
(I) State of hybridization of C is sp .
(II) Urea is an intermediate formed during hydrolysis of the above product.
(III) Anion present in the product is not a pseudo halide ion.
(IV) Hydrolysis of product gives rise to NH_3 gas slowly.
(A) I, II and III
(B) III and IV
(C) I, II and IV
(D) None of the above.

9. Phosphorescence shown by P is due to
(A) oxidation of P into P_2O_3 .
(B) oxidation of P into P_2O_5 .
(C) oxidation of luciferin by luciferase enzyme.
(D) reduction of P into phosphide ions.

10. Which of the following compounds consist of a P–P linkage?
(A) Hypophosphoric acid.
(B) Pyrophosphorous acid.
(C) Dipolyphosphoric acid.
(D) Metaphosphoric acid.

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. Which of the following properties decreases for MH_3 on descending the group from NH_3 to BiH_3 ?

 - (A) Thermal stability
 - (B) Reducing power
 - (C) The ease of replacing hydrogen atoms by other groups such as Cl, Me
 - (D) The lone pair donating ability

2. NH_3 gas can be detected by which of the following methods?

 - (A) By its characteristic pungent smell.
 - (B) By turning of moist litmus paper blue.
 - (C) By forming intense white clouds of NH_4Cl with stopper from bottle of conc. HCl.
 - (D) By forming a yellow-orange-brown precipitate with Nessler's solution.

3. Which of the following statements is/are true regarding N_2O ?

 - (A) It is used as anaesthetic by dentists.
 - (B) Bond orders are fractional for N-N and N-O bonds.
 - (C) It reacts with water to give HNO_3 and HNO_2 .
 - (D) It is a very good supporter of combustion.

4. Which of the following substances cannot be used for drying NH_3 ?

 - (A) Anhyd. CaCl_2
 - (B) P_2O_5
 - (C) Conc. H_2SO_4
 - (D) CaO

5. Which of the following properties of red P and white P are related to their structure?

 - (A) Large difference in melting point.
 - (B) Difference in hardness.
 - (C) Ignition behaviour.
 - (D) None of these.

COMPREHENSION TYPE QUESTIONS

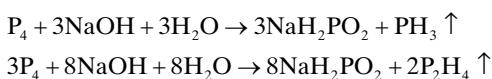
Passage 1: For Questions 1 to 3

One of the important hydrides of nitrogen is hydrazine (N_2H_4). It is mostly used as rocket fuel. It is manufactured by Raschig process.

- Which of the following mixtures of hydrazine or hydrazine derivatives act as a rocket fuel?
 - $N_2H_4 + H_2O_2$
 - $MeNNH_2 + N_2O_4$
 - $MeNNH_2 + N_2O_4$
 - All of these
- In which of the following reactions, N_2H_4 acts as an oxidizing agent?
 - $N_2H_4 + I_2 \rightarrow$
 - $N_2H_4 + O_2 \rightarrow$
 - $N_2H_4 + CuSO_4 \rightarrow$
 - $N_2H_4 + Zn/HCl \rightarrow$
- Which of the following statements is incorrect regarding N_2H_4 ?
 - It is used to characterize carbonyl compounds and sugars by forming crystalline derivative called osazones.
 - It is prepared by oxidation of NH_3 by $NaOCl$ in dilute aqueous solution.
 - In its preparation by Raschig process tap water cannot be used.
 - Structurally it exists in eclipsed form.

Passage 2: For Questions 4 to 6

When white phosphorus reacts with $NaOH$, it produces a gaseous mixture by the following parallel reactions.



- The gas mixture comes out and catches fire immediately due to the presence of
 - PH_3
 - P_2H_4
 - P_2H_6
 - H_2

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.

- The correct thermal stability order is
 - $PH_4Cl > PH_4Br > PH_4I$
 - $PH_4I > PH_4Cl > PH_4Br$
 - $PH_4Br > PH_4Cl > PH_4I$
 - $PH_4I > PH_4Br > PH_4Cl$
- The formation of PH_4^+ is difficult compared to that of NH_4^+ because
 - the lone pair of P resides at $3d$ orbital.
 - lone pair of P resides at almost pure p orbital.
 - lone pair of P resides at sp^3 hybrid orbital.
 - lone pair of P resides at almost pure s orbital.

Passage 3: For Questions 7 to 9

A white solid having garlic smell (A) $\xrightarrow[\text{Cold}]{H_2O}$ (B) $\xrightarrow[\text{heating}]{\text{on}}$ gas (C) having rotten fish smell + acid (D)

- A is
 - P (white)
 - P (red)
 - P_2O_3
 - $(CO_2H)_2$
- Gas (C) is passed through formaldehyde solution in the presence of HCl to produce a colourless solid which is used for making
 - bullet proof clothing.
 - fire proof clothing.
 - poison sensitive clothing.
 - None of these.
- With increase in temperature, following heating, acid (D) produces the following products in which correct sequence?
 - Pyroacid, metaacid, anhydride.
 - Metaacid, pyroacid, anhydride.
 - Metaacid, anhydride, pyroacid.
 - Pyroacid, anhydride, metaacid.

- If Statement I is true but Statement II is false.
- If Statement I is false but Statement II is true.

- Statement I:** White phosphorus is stored under kerosene.

- Statement II:** White phosphorus catches fire when exposed to air.

2. **Statement I:** NH_4NO_3 is used as an explosive.

Statement II: On strong heating above 300°C , it causes the formation of seven volumes of gas from almost zero volume solid.

3. **Statement I:** NH_3 can be dried by quick lime.

Statement II: Quick lime is also basic in nature and no reaction takes place with NH_3 .

4. **Statement I:** N_2O is a better supporter of combustion as compared to air.

Statement II: N_2O decomposes to $(\text{N}_2 + \frac{1}{2}\text{O}_2)$ which contains 33% O_2 as compared to 20% O_2 in air.

5. **Statement I:** Conc. HNO_3 can be stored in aluminium vessel.

Statement II: The surface of aluminium vessel gets-coated with impervious layer of Al_2O_3 on reaction with conc. HNO_3 .

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. Find the number of P–O–P linkages in P_4O_{10} .

2. Find the oxidation state of N-atom in $[\text{N}_2\text{H}_6]\text{SO}_4$.

3. Nylon-6 has the formula of $-\text{CO}[-\text{NH}-(\text{CH}_2)_3-\text{CO}]_n-\text{NH}-$.

Find the number of carbon atoms between two nitrogen atoms.

4. Find the number of linear molecule from the following:



5. In how many of the following species, the N–O bond length is greater than that in NO^+ ?



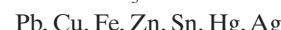
6. The difference in oxidation states of two nitrogen atoms of cationic part and anionic part of N_2O_5 is _____.

7. Find the maximum number of tribasic acids that may exist from the following formulas.



8. Find the number σ -bonds in triethyl phosphate.

9. How many of the following elements form N_2O on reaction with 20% HNO_3 solution?



10. Find the maximum number equal P–F bond lengths in PF_5 .

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labeled as (A), (B), (C) and (D), while those in Column II are labeled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the nitrogen oxides with their properties.

Column I	Column II
(A) N_2O	(P) Neutral towards water.
(B) NO	(Q) Acidic towards water.
(C) N_2O_3 (unsymmetrical)	(R) N–N linkage is present.
(D) N_2O_4	(S) Molecule having highest bond order of N–O bond.
(E) N_2O_5	

2. Match the compounds with their characteristics/ uses.

Column I	Column II
(A) NH_4Cl	(P) Used as fertilizer.
(B) NH_4NO_3	(Q) Can be obtained by heating camel dung.

Column I	Column II
(C) $(\text{NH}_4)_2\text{SO}_4$	(R) It is deliquescent in nature.
(D) NH_4ClO_4	(S) Used as solid fuel in rocket propellant.
	(T) Used in dry batteries.

3. Match the fertilizer with the compounds/reactions they are obtained from.

Column I	Column II
(A) Triple superphosphate	(P) Ammonium carbonate
(B) Urea	(Q) Gypsum slurry + $\text{NH}_3 + \text{CO}_2$
(C) Nitrolim	(R) Fluoroapatite
(D) Ammonium sulphate	(S) $\text{CaC}_2 + \text{N}_2$

ANSWERS**Single Correct Choice Type Questions**

- | | | | | |
|---------------|---------------|---------------|---------------|----------------|
| 1. (B) | 3. (B) | 5. (B) | 7. (C) | 9. (A) |
| 2. (D) | 4. (B) | 6. (A) | 8. (C) | 10. (A) |

Multiple Correct Choice Type Questions

- | | | | | |
|-------------------------|------------------------------|-------------------------|-------------------------|-------------------------|
| 1. (A), (C), (D) | 2. (A), (B), (C), (D) | 3. (A), (B), (D) | 4. (A), (B), (C) | 5. (A), (B), (C) |
|-------------------------|------------------------------|-------------------------|-------------------------|-------------------------|

Comprehension Type Questions

- | | | | | |
|---------------|---------------|---------------|---------------|---------------|
| 1. (D) | 3. (D) | 5. (D) | 7. (C) | 9. (A) |
| 2. (D) | 4. (B) | 6. (D) | 8. (B) | |

Assertion–Reasoning Type Questions

- | | | | | |
|---------------|---------------|---------------|---------------|---------------|
| 1. (D) | 2. (A) | 3. (A) | 4. (A) | 5. (A) |
|---------------|---------------|---------------|---------------|---------------|

Integer Answer Type Questions

- | | | | | |
|--------------|-------------|-------------|--------------|--------------|
| 1. 6 | 3. 6 | 5. 6 | 7. 2 | 9. 2 |
| 2. -2 | 4. 0 | 6. 0 | 8. 25 | 10. 3 |

Matrix–Match Type Questions

- | | | |
|--|--|--|
| 1. (A) → (P) (R)
(B) → (P), (S)
(C) → (Q), (R)
(D) → (Q), (R)
(E) → (Q) | 2. (A) → (Q), (T)
(B) → (P), (R)
(C) → (P)
(D) → (S) | 3. (A) → (R)
(B) → (P)
(C) → (S)
(D) → (Q) |
|--|--|--|

PART 4: THE GROUP 16 ELEMENTS – CHALCOGENS

The first four elements are non-metals. Collectively they are called ‘the chalcogens’ or ore-forming elements, because a large number of metal ores are oxides or sulphides. Several chemicals in this group are industrially important. H_2SO_4 is the most important chemical in the chemical industry.

The elements show the usual increase in metallic character on descending the group. This is shown by their reactions, the structures of the elements, and an increased tendency to form M^{2+} ions together with a decrease in stability of M^{2-} ions. O and S are totally non-metallic. Non-metallic character is weaker in Se and Te. Po is markedly metallic, and is also radioactive and short-lived.

Oxygen is a very important element in inorganic chemistry, since it reacts with almost all the other elements. Most of its compounds are covered under the other elements.

S, Se and Te are moderately reactive and burn in air to form dioxides. They combine directly with most elements, both metals and non-metals, though less readily than with O. As expected for non-metals, S, Se and Te are not attacked by acids except those which are oxidizing agents. Po shows metallic properties and is radioactive.

Oxygen shows several differences from the rest of the group. These are associated with its smaller size, higher electronegativity, and the lack of suitable *d* orbitals. Oxygen can use *p* π orbitals to form strong double bonds. The other elements can also form double bonds, but these become weaker as the atomic number increases. Thus CO_2 ($\text{O}=\text{C}=\text{O}$) is stable, CS_2 less stable, CSe_2 polymerizes rather than form double bonds and CTe_2 is unknown. Oxygen also forms strong hydrogen bonds which greatly affect the properties of water and other compounds.

Sulphur shows a much greater tendency to form chains and rings than the other elements (see Allotropic Forms).

Whereas O and S have only *s* and *p* electrons, Se follows after the first transition series and has *d* electrons too. The filling of the 3*d* shell affects the properties of Ge, As, Se and Br. The atoms are smaller, and the electrons are held more tightly. This is the reason why Se is reluctant to attain the highest oxidation state of (+VI) shown by S. Thus HNO_3 oxidizes S to H_2SO_4 (S+VI) but only oxidizes Se to H_2SeO_3 (Se+IV).

All compounds of Se, Te and Po are potentially toxic, and should be handled with care. Organo derivatives, and volatile compounds such as H_2Se and H_2Te , are 100 times more toxic than HCN.

10.46 | GENERAL PROPERTIES

Electronic structure and oxidation states

The elements all have the electronic structure s^2p^4 . They may attain a noble gas configuration either by gaining two electrons, forming M^{2-} ions, or by sharing two electrons, thus forming two covalent bonds. The electronegativity of O is very high – second only to F. The electronegativity difference between M and O is large. Thus most metal oxides are ionic and contain O^{2-} ions, and the oxidation state of O is (–II). Sulphides, selenides and tellurides are formed with the metals in Groups 1 and 2 and the lanthanides, and these compounds are some of the most stable formed. Compounds are often written as containing S^{2-} , Se^{2-} and Te^{2-} .

The elements also form compounds containing two covalent (electron-pair) bonds such as H_2O , F_2O , Cl_2O , H_2S and SCl_2 . Where the chalcogen atom is the least electronegative atom in the molecule (e.g. in SCl_2 where the electronegativity of S = 2.5 and Cl = 3.5) the S shows an oxidation state of (+II).

In addition, the elements S, Se and Te show oxidation states of IV and VI, and these are more stable than the +II state. The electronic structure and common oxidation states of Group 16 elements are given in Table 10.20.

Table 10.20 Electronic structures and oxidation states

Elements	Electronic structure			Oxidation states*			
Oxygen	O	[He]	$2s^2 2p^4$	–II	(–I)		
Sulphur	S	[Ne]	$3s^2 3p^4$	–II		(II)	IV
Selenium	Se	[Ar]	$3d^{10} 4s^2 4p4$	(–II)		II	IV
Tellurium	Te	[Kr]	$4d^{10} 5s^2 5p^4$			II	IV
Polonium	Po	[Xe]	$4f^{14} 5d^{10} 6s^2 6p^4$			II	IV

* The most important oxidation states (generally the most abundant and stable) are shown in bold. Other well-characterized but less important states are shown in normal type. Oxidation states that are unstable, or in doubt, are given in parentheses.

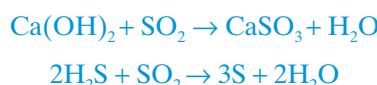
Acid rain and SO_2

Coal typically contains 2% S, and may contain up to 4%. This represents a huge potential source of S, which could be extracted as SO_2 from the flue gases. Because it is uneconomic to remove the SO_2 , only about 1% of this total tonnage is recovered as H_2SO_4 . The majority is discharged into the atmosphere, where it causes acid rain.

The atmospheric chemistry of acid rain is not fully understood. SO_2 is oxidized by ozone or hydrogen peroxide to SO_3 . This reacts with water or hydroxyl radicals to give H_2SO_4 .

Acid rain causes damage to trees, plants, fish and buildings, and causes respiratory ailments in man and animals. About 60% of atmospheric SO_2 comes from coal fired power stations. Most of the rest comes from oil refineries, oil fired power stations and smelters.

Total elimination of SO_2 pollution is not possible for both economic and technical reasons. However, we have the technology to reduce pollution to a low figure. The methods used are scrubbing the flue gases with a slurry of $\text{Ca}(\text{OH})_2$, or reducing the SO_2 to S using H_2S and an activated alumina catalyst.



Uses of sulphur

S is an essential though minor constituent of certain proteins. It is present in the amino acids cystine, cysteine and methionine.

Almost 90% of the World production of SO_2 is converted to SO_3 and finally to H_2SO_4 . Sixty per cent of the H_2SO_4 produced is used to make fertilizers. The remainder is used to make a variety of other chemicals. Sulphites SO_3^{2-} , hydrogen sulphites HSO_3^- and SO_2 are important for bleaching.

The 10% of S for non-acid purposes is used as elemental S. Some is used to make carbon disulphide CS_2 . This is important in the vulcanizing of rubber. Other uses of sulphur are in the manufacture of fungicides, insecticides and gunpowder. Gunpowder is an intimate mixture of saltpetre NaNO_3 (75%), charcoal (15%) and sulphur (10%).

10.47 | STRUCTURE AND ALLOTROPY OF THE ELEMENTS

All the elements except Te are polymorphic, that is they exist in more than one allotropic form.

Oxygen

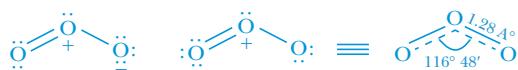
Oxygen occurs as two non-metallic forms, dioxygen O_2 and ozone O_3 . Dioxygen O_2 is stable as a diatomic molecule, which accounts for it being a gas. (S, Se, Te and Po have more complicated structures, e.g. S_8 , and are solids at normal temperatures.) The bonding in the O_2 molecule is not as simple as it might at first appear. If the molecule had two covalent bonds, then all the electrons would be paired and the molecule should be diamagnetic.



Dioxygen is paramagnetic and therefore contains two unpaired electrons. The explanation of this phenomenon was one of the early successes of the molecular orbital theory. The structure is described (see Chapter 3). Liquid dioxygen is pale blue in colour, and the solid is also blue.

Ozone

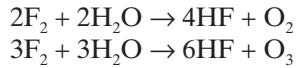
Ozone O_3 is the triatomic allotrope of oxygen. It is unstable, and decomposes to O_2 . The structure of O_3 is angular, with an O—O—O bond angle of $116^\circ 48'$. Both O—O bond lengths are 1.28 \AA , which is intermediate between a single bond (1.48 \AA in H_2O_2) and a double bond (1.21 \AA in O_2).



Preparation of ozone

O_3 is usually prepared by the action of a silent electric discharge upon dioxygen between two concentric metallized tubes in an apparatus called an ozonizer. Concentrations of up to 10% of O_3 are obtained in this way. Higher concentrations or pure O_3 can be obtained by fractional liquification of the mixture. The pure liquid is dangerously explosive. Low concentrations of O_3 can be made by UV irradiation of O_2 . This occurs in the atmosphere when photochemical smog is formed over some cities, for example over Los Angeles or Tokyo. The photochemical change is useful for producing low concentrations to sterilize food, particularly for cold storage. O_3 can also be made by heating O_2 to over $2500^\circ C$ and quenching. In all of these preparations oxygen atoms are produced, and these react with O_2 molecules to form O_3 .

Ozone can also be prepared by passing F_2 gas in H_2O . The following reactions take place:



The separation is done as usual by passing through a spiral tube kept at liquid air ($-190^\circ C$) and the process is called fractional liquefaction of the mixture.

Physical properties

O_3 is an unstable, blue diamagnetic gas, b.p. $-112^\circ C$. The colour is due to intense absorption of red light (λ 557 and 602 nm). It is dark blue in liquid state and violet-black in solid state. It also absorbs strongly in the UV region (λ 255 nm). This is particularly important since there is a layer of O_3 in the upper atmosphere which absorbs harmful UV radiation from the sun, thus protecting people on the earth. The use of chlorofluorocarbons in aerosols and refrigerators, and their subsequent escape into the atmosphere, is blamed for making holes in the ozone layer over the Antarctic and Arctic. It is feared that this will allow an excessive amount of UV light to reach the earth which will cause skin cancer (melanoma) in humans. Oxides of nitrogen (from car exhausts) and the halogens can also damage the O_3 layer.

O_3 has a characteristic fishy smell, often associated with sparking electrical equipment. The gas is toxic, and continuous exposure to concentrations of 0.1 ppm must be avoided.

Chemical properties

O_3 is thermodynamically unstable, and decomposes to O_2 . The decomposition is exothermic, and is catalysed by many materials. The solid and liquid often decompose explosively. The gas decomposes slowly, even when warmed, *providing catalysts and UV light are absent*. O_3 is an extremely powerful oxidizing agent, second only to F_2 in oxidizing power, and reacts much more readily than dioxygen. It is one of the best oxidizing agent in acid solution and can be dangerously explosive at high concentrations.



It acts as a powerful oxidizing agent due to the ease with which it can liberate atoms of nascent oxygen $O_3 \rightarrow O_2 + O$. Some of the oxidation reactions of O_3 in which O_2 is liberated are listed as follows:

1. Oxidation of metal sulphides to metal sulphates



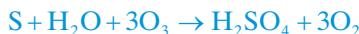
2. Oxidation of iodide ions to iodine



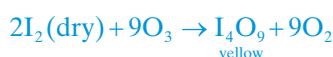
3. Oxidation of nitrites, sulphites and arsenites to sulphates, nitrates and arsenates



4. Reactions with sulphur, phosphorous and arsenic in presence of moisture



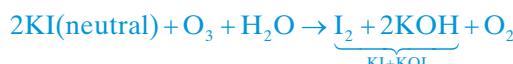
5. Reaction with iodine



6. Oxidation of transition metals to higher oxidation state in their compounds



7. Oxidation of KI under acidic, neutral and alkaline conditions



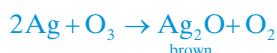
O₃ is estimated quantitatively using the above reaction, as follows.



8. Oxidation of metals



In this reaction, mercury loses its fluidity and tailing is observed.



9. $\text{BaO}_2 + \text{O}_3 \rightarrow \text{BaO} + 2\text{O}_2$





In some oxidation reactions, O_2 molecule is not liberated but consumed instead.



Uses of ozone

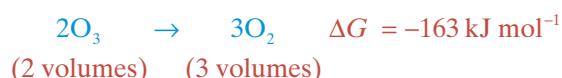
O_3 is also used as a disinfectant. For example, it is used to purify drinking water, since it destroys bacteria and viruses. Its advantage over chlorine for this purpose is that it avoids the unpleasant smell and taste of chlorine, since any excess O_3 soon decomposes to O_2 . For similar reasons it is used to treat water in swimming pools.

Estimation of ozone

The amount of O_3 in a gas mixture may be determined by passing the gas into a KI solution buffered with a borate buffer (pH 9.2). The iodine that is liberated is titrated with sodium thiosulphate.

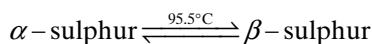


Alternatively the gas may be decomposed catalytically, and the change in volume measured.



Sulphur

Sulphur has more allotropic forms than any other element. These different forms arise partly from the extent to which S has polymerized, and partly from the crystal structures adopted. The two common crystalline forms are α or rhombic sulphur which is stable at room temperature, and β or monoclinic sulphur which is stable above 95.5 °C. These two forms change reversibly with slow heating or slow cooling. Rhombic sulphur occurs naturally as large yellow crystals in volcanic areas. A third modification known as γ -monoclinic sulphur is nacreous (looks like mother-of-pearl). It can be made by chilling hot concentrated solutions of S in solvents such as CS_2 , toluene or EtOH. All three forms contain puckered S_8 rings with a crown conformation (Figure 10.43a), and differ only in the overall packing of the rings in the crystal. This affects their densities:



α -rhombic	2.069 g cm^{-3}
β -monoclinic	$1.94\text{--}2.01 \text{ g cm}^{-3}$
γ -monoclinic	2.19 g cm^{-3}

Engel's sulphur (ϵ -sulphur) is unstable and contains S_6 rings arranged in the chair conformation (Figure 10.43b). It is made by pouring $\text{Na}_2\text{S}_2\text{O}_3$ solution into concentrated HCl and extracting the S with toluene. It can also be made as follows:

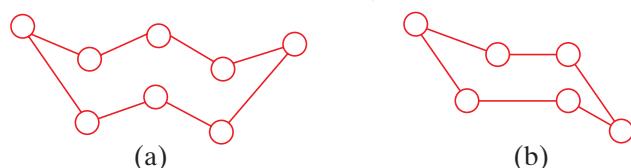


Figure 10.43 (a) Structure of S_8 molecule (b) Structure of S_6 molecule.

In all of these ring compounds the S–S distance is 2.04 – 2.06 Å, and the bond angle S–S–S is in the range 102–108°. They are all soluble in CS₂.

Sulphur melts to form a mobile liquid. As the temperature is raised the colour darkens. At 160 °C the S₈ rings break, and the diradicals so formed polymerize, forming long chains of up to a million atoms. This makes all the physical properties change discontinuously. The viscosity increases sharply, and continues to rise up to 200 °C. At higher temperatures chains break, and shorter chains and rings are formed, which makes the viscosity decrease up to 444 °C, the boiling point. The vapour at 200 °C consists mostly of S₈ rings, but contains 1–2% of S₂ molecules. At 600 °C the gas mainly consists of S₂ molecules.

The S₂ molecule is paramagnetic and blue coloured like O₂, and presumably has similar bonding. S₂ gas is stable up to 2200 °C.

10.48 | PHYSICAL PROPERTIES

The physical properties of elements of Group 16 are discussed given in Table 10.21.

Table 10.21 Physical properties of the elements

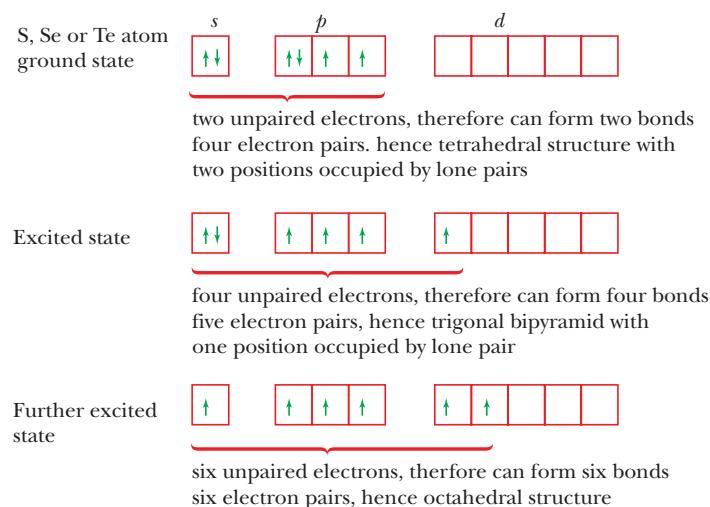
	Covalent radius (Å)	Ionic radius M ²⁻ (Å)	First ionization energy (kJ mol ⁻¹)	Pauling's electro- negativity	Melting point (°C)	Boiling point (°C)
O	0.74	1.40	1314	3.5	-229	-183
S	1.04	1.84	999	2.5	114	445
Se	1.14	1.98	941	2.4	221	685
Te	1.37	2.21	869	2.1	452	1087

Values for covalent radii are for two-coordination.

10.49 | CHEMICAL REACTIVITY

Oxidation states (+II), (+IV) and (+VI)

Oxygen is never more than divalent because when it has formed two covalent bonds it has attained a noble gas configuration, and there are no low energy orbitals which can be used to form further bonds. However, the elements S, Se, Te and Po have empty *d* orbitals which may be used for bonding, and they can form four or six bonds by unpairing electrons.



Compounds of S, Se and Te with O are typically tetravalent. The (+IV) state shows both oxidizing and reducing properties. Fluorine brings out the maximum oxidation state of (+VI). Compounds in the (+VI) state show oxidizing properties. The higher oxidation states become less stable on descending the group. These compounds are typically volatile because they are covalent.

Bond lengths and $p\pi - d\pi$ bonding

The bonds between S and O, or Se and O, are much shorter than might be expected for a single bond. In some cases they may be formulated as localized double bonds. A σ bond is formed in the usual way. In addition a π bond is formed by the sideways overlap of a p orbital on the oxygen with a d orbital on the sulphur, giving a $p\pi-d\pi$ interaction. This $p\pi-d\pi$ bonding is similar to that found in the oxides and oxoacids of phosphorus, and is in contrast to the more common $p\pi-p\pi$ type of double bond found in ethene (Figure 10.44).

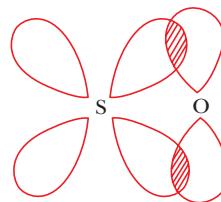


Figure 10.44 $p\pi-d\pi$ overlap.

To obtain effective $p\pi-d\pi$ overlap, the size of the d orbital must be similar to the size of the p orbital. Thus sulphur forms stronger π bonds than the larger elements in the group. On crossing a period in the periodic table, the nuclear charge is increased and more s and p electrons are added. Since these s and p electrons shield the nuclear charge incompletely, the size of the atom and the size of the d orbitals decreases from Si to P to S to Cl. The decrease in the size of the $3d$ orbitals in this series of elements leads to progressively stronger $p\pi-d\pi$ bonds. Thus in the silicates there is hardly any $p\pi-d\pi$ bonding. Thus SiO_4 units polymerize into an enormous variety of structures linked by $\text{Si}-\text{O}-\text{Si}$ σ bonds. In the phosphates, π bonding is stronger, but a large number of polymeric phosphates exist. In the oxoacids of sulphur, π bonding is even stronger and has become a dominant factor. Thus only a small amount of polymerization occurs, and only a few polymeric compounds are known with $\text{S}-\text{O}-\text{S}$ linkages. For chlorine, $p\pi-d\pi$ bonding is so strong that no polymerization of oxoanions occurs.

Differences between oxygen and the other elements

Oxygen differs from the rest of the group in that it is more electronegative and therefore more ionic in its compounds.

Hydrogen bonding is very important for O compounds, but it is only recently that weak hydrogen bonds involving S have been proved to exist.

The absence of higher valency states and the limitation to a coordination number of 4 are a consequence of the limitation of the second shell to eight electrons. The other elements can have a coordination number of 6 by using d orbitals.

Oxygen can use $p\pi$ orbitals to form strong double bonds. The other elements can also form double bonds, but these become weaker as the atomic number increases.

10.50 | GENERAL PROPERTIES OF OXIDES

Practically all of the elements react with dioxygen to form oxides. There are several ways in which oxides may be classified, depending on their structure or their chemical properties.

Classification based on structure

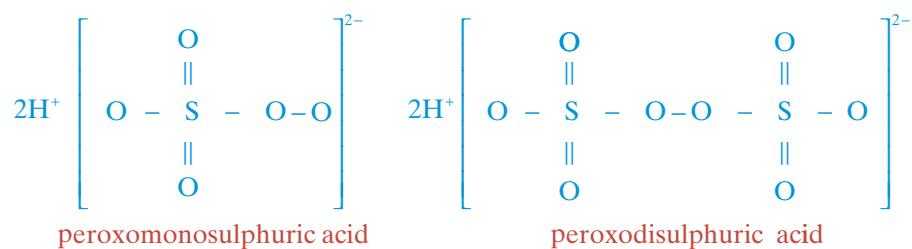
First consider the classification according to their geometric structure. In this way oxides are classified as normal oxides, peroxides or suboxides.

Normal oxides

In these, the oxidation number of M can be deduced from the empirical formula M_xO_y , taking the oxidation number of oxygen as (-II). These oxides, for example H_2O , MgO and Al_2O_3 , contain only M–O bonds.

Peroxides

These contain more oxygen than would be expected from the oxidation number of M. Some are ionic and contain the peroxide ion O_2^{2-} , for example those of Group 1 and 2 metals (Na_2O_2 and BaO_2). Others are covalently bound and contain $-O-O-$ in the structure, for example H_2O_2 ($H-O-O-H$), peroxomonosulphuric acid and peroxodisulphuric acid.



Peroxo compounds are strong oxidizing agents, and are hydrolysed by water to give H_2O_2 .



Superoxides, e.g. KO_2 , contain more oxygen than would be expected.

Suboxides

Here the formula contains less oxygen than would be expected from the oxidation number of M. They involve M—M bonds in addition to M—O bonds, for example $\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$.

Classification based on chemical properties

A second method of classifying oxides depends on their acid–base properties. Thus oxides may be acidic, basic, amphoteric or neutral, depending on the products formed when they react with water.

Basic oxides

Metallic oxides are generally basic. Most metal oxides are ionic and contain the O^{2-} ion. The oxides of the more electropositive metals, Groups 1 and 2, and the lanthanides are typical. A large amount of energy is required to form an ionic oxide. This is because the O_2 molecule must first be broken into atoms, and then the energy (the electron affinity) required to add two electrons to form O^{2-} is also large. Thus ionic oxides are formed by compounds with high lattice energy to offset this. Thus ionic oxides typically have high melting points (Na_2O 1275 °C, MgO 2800 °C, La_2O_3 2315 °C). When they react with water the O^{2-} ion is converted into OH^- .



However, many metal oxides with formulae M_2O_3 and MO_2 , though ionic, do not react with water. Examples include Tl_2O_3 , Bi_2O_3 and ThO_2 . These react with acids to form salts, and so are basic. Where a metal can exist in more than one oxidation state, and thus form more than one oxide, e.g. CrO , Cr_2O_3 , CrO_3 , PbO , PbO_2 , and Sb_4O_6 , Sb_4O_{10} , the lowest oxidation state is the most ionic and the most basic. Thus CrO is basic, Cr_2O_3 amphoteric and CrO_3 acidic.

Amphoteric oxides

Many metals yield oxides which are amphoteric, and react with both strong acids and strong bases. Examples include BeO , Al_2O_3 , Ga_2O_3 , SnO , PbO and ZnO .



Acidic oxides

Non-metallic oxides are usually covalent. Many occur as discrete molecules (CO_2 , NO_2 , SO_2 , Cl_2O) and have low melting and boiling points, though some, such as B_2O_3 and SiO_2 , form infinite ‘giant molecules’ and have high melting points. They are all acidic. There are many are the anhydrides of acids.



Others which do not react with water such as SiO_2 do react with NaOH , thus showing their acidic properties. In cases where the element exists in more than one oxidation state, e.g. N_2O_3 and N_2O_5 , SO_2 and SO_3 , the higher oxidation state is the most acidic.



N_2O_3 contains N(+III) and N_2O_5 contains N(+V). HNO_3 is a stronger acid than HNO_2 . This may be rationalized since the higher the oxidation state of the central atom the more it will attract electrons, thus weakening any O—H bonds and facilitating the release of H^+ .

Neutral oxides

A few covalent oxides have no acidic or basic properties (N_2O , NO , CO).

10.51 | OXIDES OF SULPHUR

The various oxides of sulphur are listed in Table 10.22.

Table 10.22 Oxides

Element	MO_2	MO_3
S	SO_2	SO_3

Dioxide SO_2

SO_2 is produced commercially on a vast scale:

1. By burning S in air.



2. By burning H_2S in air.



3. By roasting various metal sulphide ores with air in smelters (particularly FeS_2 , and to a smaller extent CuS and ZnS).



4. Large amounts are produced as a waste product by burning coal and, to a lesser extent, other fossil fuels, oil and gas. This undoubtedly harms the environment.

SO_2 is a colourless gas (b.p. – 10°C, m.p. –75.5°C), which has a choking smell, and is very soluble in water (39 cm³ of SO_2 gas will dissolve in 1 cm³ of water). The SO_2 in solution is almost completely present as various hydrated species such as $\text{SO}_2 \cdot 6\text{H}_2\text{O}$ and the solution contains only a minute amount of sulphurous acid H_2SO_3 . SO_2 levels above 5 ppm are poisonous to man, but plants are harmed at appreciably lower levels.

SO_2 gas forms discrete V-shaped molecules, and this structure is retained in the solid state (Figure 10.45). The bond angle is 119°30'. The bonding in SO_2 is described in Chapter 3. It is a polar molecule and overall direction of dipole is as shown in Fig. 10.45.



Figure 10.45 Structure of SO_2 .

Chemical properties

SO_2 can act as an oxidizing agent in some cases.



When SO_2 is passed into FeCl_2 and SnCl_2 solutions at very low pH, it oxidizes them into Fe^{3+} and Sn^{4+} as follows.



Estimation of SO_2

Quantitative methods for measuring SO_2 in the atmosphere are highly developed because of environmental concern over 'acid rain'. Methods include:

1. Oxidation to H_2SO_4 , followed by determination of the H_2SO_4 by titration



2. Reaction with $\text{K}_2[\text{HgCl}_4]$ to give a mercury complex which reacts with the dye pararosaniline, and is estimated colorimetrically.



Detection of SO_2

SO_2 may be detected in the laboratory:

1. By its smell.
2. Because it turns a filter paper moistened with acidified potassium dichromate solution green, due to the formation of Cr^{3+} .



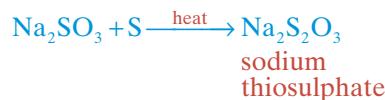
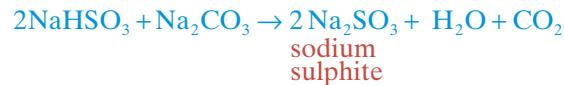
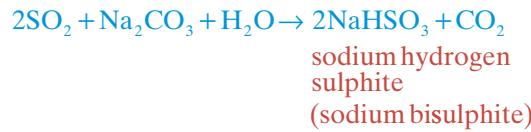
3. Because it turns starch iodate paper blue (due to starch and I_2).



Other methods for its detection based on its reducing property are already covered in Chapter 7.

Uses

1. SO_2 is used to make other products such as sulphites, bisulphites and thiosulphates.



2. SO_2 has also been used as a non-aqueous solvent. A wide range of covalent compounds, both inorganic and organic, are soluble in liquid SO_2 , and it is a useful reaction medium.
3. It is used bleaching wool and silk, as antichlor, disinfectant and preservative of food.

Trioxide SO_3

SO_3 is the only important trioxide. It is manufactured on a huge scale by the Contact process in which SO_2 reacts with O_2 in the presence of a catalyst (Pt or V_2O_5). Most of the SO_2 produced is oxidized to SO_3 by the Contact process, and used to manufacture H_2SO_4 .



The forward reaction is exothermic, and is favoured by a low temperature. Since there is a decrease in the number of moles of gas, the process is favoured by a high pressure. In practice the reaction is carried out at atmospheric pressure. The formation of SO_3 is favoured by an excess of O_2 , and removing the SO_3 from the reaction mixture. A catalyst is used to obtain a reasonable conversion in a reasonable time. In the Contact process a platinum gauze and platinized asbestos were both used at one time. Pt is an excellent catalyst, and it works at moderately low temperatures. However, it is very expensive and is susceptible to poisoning, particularly by metals such as As . Nowadays a V_2O_5 catalyst activated with K_2O is used instead, and is supported on kieselguhr or silica. This is much cheaper, and is resistant to poisoning. The catalyst is inactive below $400^\circ C$ and breaks down between $600^\circ C$ and $650^\circ C$. Dust may clog the catalyst surface, and impair its efficiency. To prevent this the gases are passed through an electrostatic precipitator. The catalyst may last for over 20 years.

The SO_3 is not usually isolated, and practically all of it is converted to H_2SO_4 . SO_3 reacts vigorously with water, evolving a large amount of heat and forming H_2SO_4 . Commercially it is not possible just to react SO_3 with water. The SO_3 reacts with water vapour and causes the formation of a dense mist of H_2SO_4 droplets, which are difficult to condense and pass out of the absorber into the atmosphere. To avoid this, it has been found best to dissolve SO_3 in 98–99% H_2SO_4 in ceramic packed towers, to give oleum or fuming sulphuric acid. This is mainly pyrosulphuric acid $H_2S_2O_7$. Water is continuously added to keep the concentration of H_2SO_4 constant.



In the gas phase SO_3 has a plane triangular structure (Figure 10.46). The bonding is best described as sulphur forming three σ -bonds, giving rise to a plane triangle, and three delocalized π bonds.

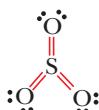


Figure 10.46 Structure of SO_3 gas.

At room temperature SO_3 is solid and exists in three distinct forms. γSO_3 is ice-like and is a cyclic trimer ($\text{SO}_3)_3$, m.p. 16.8°C . If SO_3 is kept for a long time, or if a trace of water is present, either $\beta\text{-SO}_3$ or $\alpha\text{-SO}_3$ is formed. Both look like asbestos, and comprise bundles of white silky needles. $\beta\text{-SO}_3$ (m.p. 32.5°C) is made up of infinite helical chains of tetrahedral $[\text{SO}_4]$ units each sharing two corners. This structure is similar to that of chain phosphates. $\alpha\text{-SO}_3$ (m.p. 62.2°C) is the most stable form, and is made of chains cross-linked into sheets (Figure 10.47).

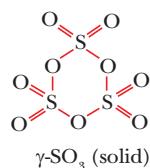
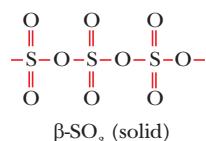


Figure 10.47 Structure of SO_3 chains and SO_3 cyclic trimer.

SO_3 is a powerful oxidizing agent, especially when hot. It oxidizes HBr to Br_2 and P to P_4O_{10} . Commercially, SO_3 is important in the manufacture of H_2SO_4 .

SO_3 is used to make sulphamic acid $\text{NH}_2\text{SO}_3\text{H}$



Sulphamic acid is the only strong acid that exists as a solid at room temperature. It is used for cleaning the plant at sugar refineries and breweries.

10.52 | OXOACIDS OF SULPHUR

The oxoacids of sulphur are more numerous and more important than those of Se and Te. Many of the oxoacids of sulphur do not exist as free acids, but are known as anions and salts. Acids ending in -ous have S in the oxidation state (+IV), and form salts ending in -ite. Acids ending in -ic have S in the oxidation state (+VI) and form salts ending in -ate.

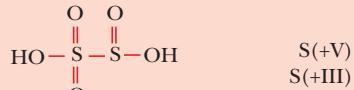
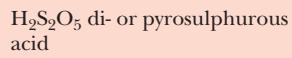
As discussed previously under bond lengths and $p\pi-d\pi$ bonding, the oxoanions have strong π bonds and so they have little tendency to polymerize compared with the phosphates and silicates. To emphasize structural similarities the acids are listed in four series:

1. sulphurous acid series
 2. sulphuric acid series
 3. thionic acid series
 4. peroxyacid series.

1. Sulphurous acid series

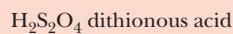


S(+IV)



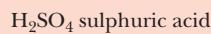
S(+V)

S(+III)

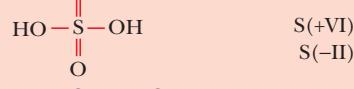
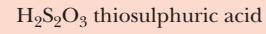


S(+III)

2. Sulphuric acid series

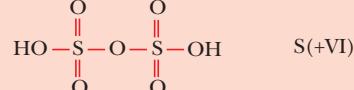
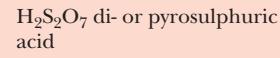


S(+VI)



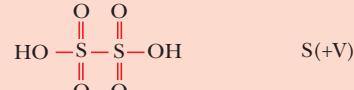
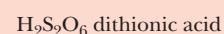
S(+VI)

S(-II)

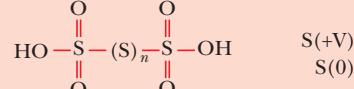
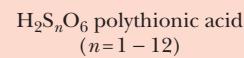


S(+VI)

3. Thionic acid series



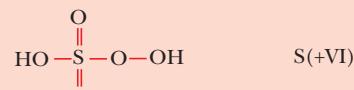
S(+V)



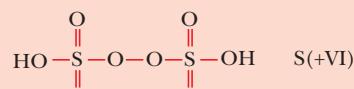
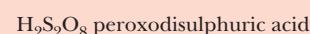
S(+V)

S(0)

4. Peroxoacid series



S(+VI)



S(+VI)

Sulphurous acid

Though SO_2 is very soluble in water, most is present as hydrated $\text{SO}_2 \cdot \text{H}_2\text{O}$. Sulphurous acid H_2SO_3 may exist in the solution in minute amounts, or not at all, though the solution is acidic. Its salts, the sulphites SO_3^{2-} , form stable crystalline solids. Many sulphites are insoluble or are sparingly soluble in water, e.g. CaSO_3 , BaSO_3 or Ag_2SO_3 . However, those of the Group 1 metals and ammonium are soluble in water, and in dilute solutions the hydrogen sulphite (bisulphite) ion HSO_3^- is the predominant species. Crystals of hydrogen sulphites have only been formed with a few large metal ions, e.g. RbHSO_3 and CsHSO_3 . Most attempts to isolate hydrogen sulphites lead to internal dehydration with the formation of disulphites $\text{S}_2\text{O}_5^{2-}$:



Na_2SO_3 is an important industrial chemical. It is made by passing SO_2 into an aqueous solution of Na_2CO_3 to give aqueous NaHSO_3 , then treating the solution with more Na_2CO_3 .



The main use of Na_2SO_3 is as a bleach for wood pulp in the paper making industry. Some is used to treat boiler feed water (it removes O_2 and thus reduces corrosion of pipes and boilers). Small amounts are used in photographic developer.

Sulphites and hydrogen sulphites liberate SO_2 on treatment with dilute acids:



Sulphites and hydrogen sulphites both contain S in the oxidation state (+IV) and are moderately strong reducing agents. Sulphites are determined by reaction with I_2 , and determination of the excess I_2 with sodium thiosulphate.



The sulphite ion exists in crystals and has a pyramidal structure (Figure 10.48), that is tetrahedral with one position occupied by a lone pair. The bond angles $\text{O}-\text{S}-\text{O}$ are slightly distorted (106°) due to the lone pair, and the bond lengths are 1.51 \AA . The π bond is delocalized, and hence the $\text{S}-\text{O}$ bonds have a bond order of 1.33.

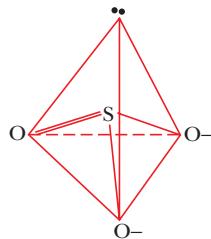
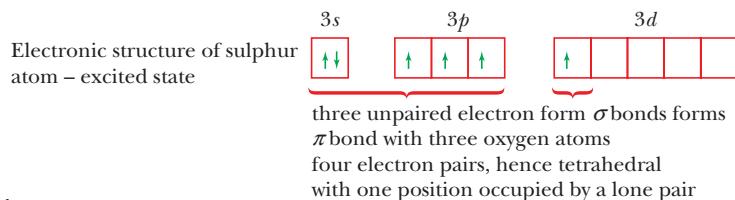


Figure 10.48 Structure of sulphite ion SO_3^{2-} .



Sulphuric acid series

H_2SO_4 is the most important acid used in the chemical industry. By far the most important commercial process for its manufacture is the Contact process, in which SO_2 is oxidized by air to SO_3 , using a catalytic surface. Formerly a platinum gauze or platinized asbestos was used as catalyst. This has now been replaced by vanadium pentoxide, which is slightly less efficient but is cheaper and less easily poisoned. The SO_3 could be mixed with water to give H_2SO_4 , but the reaction is violent and produces a dense chemical mist which is difficult to condense. Instead, the SO_3 is passed into 98% H_2SO_4 , forming pyrosulphuric acid $\text{H}_2\text{S}_2\text{O}_7$, sometimes called oleum or fuming sulphuric acid. (Some trisulphuric acid $\text{H}_2\text{S}_3\text{O}_{10}$ is also formed.) This solution may be sold as oleum, or diluted with water to give concentrated sulphuric acid which is a 98% mixture with water (an 18 M solution).



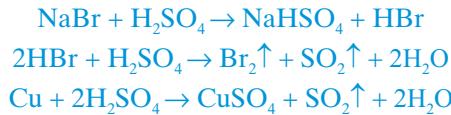
Physical properties

Pure sulphuric acid melts at 10.5°C , forming a viscous liquid. It is strongly hydrogen bonded, and in the absence of water it does not react with metals to produce H_2 . Many metals reduce H_2SO_4 (S + VI) to SO_2 (S + IV), especially if heated. If pure H_2SO_4 is heated, a little SO_3 is evolved, and an azeotropic mixture of 98.3% H_2SO_4 and 1.7% water is produced. This boils at 338°C . Pure H_2SO_4 is used as a non-aqueous solvent and as a sulphonating agent.

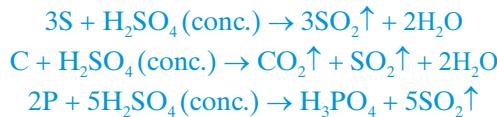
Chemical properties

Anhydrous H_2SO_4 and concentrated H_2SO_4 mix with water in all proportions, and evolve a great deal of heat (880 kJ mol^{-1}). If water is poured into concentrated acid, the heat evolved leads to boiling of the drops of water and causes violent splashing. *The safe way to dilute strong acids is to carefully pour the acid into the water with stirring.*

Concentrated H_2SO_4 has quite strong oxidizing properties. Thus when NaBr is dissolved in concentrated H_2SO_4 , HBr is formed but in addition some Br^- ions are oxidized to Br_2 . Cu does not react with acids because it is lower than H in the electrochemical series. However, several noble metals such as Cu dissolve in concentrated H_2SO_4 due to its oxidizing properties. The oxidizing properties of SO_4^{2-} convert Cu into Cu^{2+} .



It oxidizes some non-metals also.



In dilute aqueous solution H_2SO_4 acts as a strong acid. The first proton dissociates very readily, and hence hydrogen sulphates HSO_4^- formed. The second proton dissociates much less readily, to form sulphates SO_4^{2-} . Because of this, solutions of hydrogen sulphates are acidic.

The SO_4^{2-} ion is tetrahedral. The bond lengths are all equal (1.49 \AA) and are all rather short. The bond order of the S—O bonds is approximately 1.5. The bonding is best explained as four σ bonds between S and the O atoms, with two π bonds delocalized over the S and the four O atoms.

Dehydrating properties

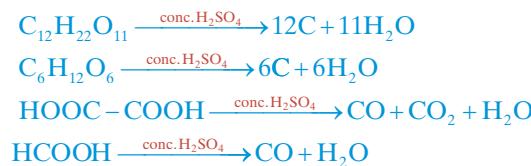
Concentrated H_2SO_4 absorbs water avidly, and is an effective drying agent for gases. It is sometimes used as a drying agent in desiccators. It dehydrates HNO_3 , forming the nitronium ion NO_2^+ , which is very important in the nitration of organic compounds.



H_2SO_4 can also remove the elements of water, for example in the preparation of ethers.



It removes water so strongly from some organic compounds that they char, and only the carbon remains. Paper and cloth are completely destroyed.



Uses of sulphuric acid

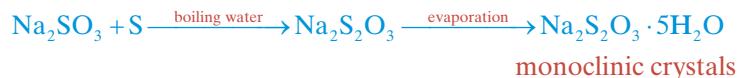
1. The largest use is in converting calcium phosphate into superphosphate, which is used as a fertilizer.
2. Fatty acids are sulphonated to make detergents.
3. Pickling is the removal of oxides and scale from the surface of metals.
4. H_2SO_4 has an important electrochemical use as the electrolyte in lead storage batteries.

Thiosulphuric acid and thiosulphates

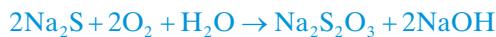
Thiosulphuric acid $\text{H}_2\text{S}_2\text{O}_3$ cannot be formed by adding acid to a thiosulphate because the free acid decomposes in water into a mixture of S, H_2S , H_2S_x , SO_2 and H_2SO_4 . It can be made in the absence of water (e.g. in ether) at low temperatures (-78°C).



In contrast, the salts which are called thiosulphates are stable and numerous. Thiosulphates are made by boiling alkaline or neutral sulphite solutions with S.



Here, Na_2SO_3 is prepared by passing SO_2 through a solution containing Na_2CO_3 in excess. It is also prepared by oxidizing polysulphides with air.



Other methods of preparation of sodium thiosulphate include the following.

1. $\text{Na}_2\text{SO}_4 + 4\text{C} \xrightarrow{\text{roasting}} \text{Na}_2\text{S} + 4\text{CO}$
 $2\text{Na}_2\text{S} + 3\text{SO}_2 \rightarrow 2\text{Na}_2\text{S}_2\text{O}_3 + \text{S}$
2. $2\text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + 4\text{SO}_2 \rightarrow 3\text{Na}_2\text{S}_2\text{O}_3 + \text{CO}_2$
3. $6\text{NaOH} + 4\text{S} \rightarrow 3\text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S} + 3\text{H}_2\text{O}$
4. $3\text{Ca}(\text{OH})_2 + 12\text{S} \rightarrow \text{CaS}_2\text{O}_3 + 2\text{CaS}_5 + 3\text{H}_2\text{O}$
5. $\text{Na}_2\text{SO}_3 + \text{Na}_2\text{S} + \text{I}_2 \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaI}$

The thiosulphate ion is structurally similar to the sulphate ion (Figure 10.49).

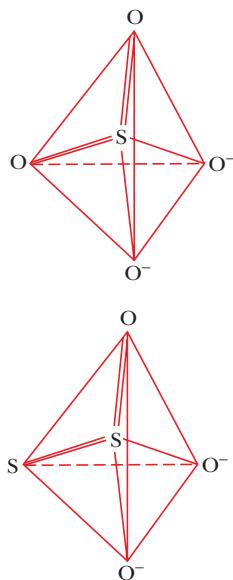
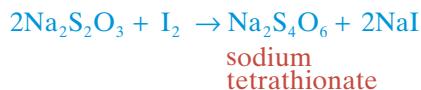


Figure 10.49 Structure of sulphate and thiosulphate ions.

Hydrated sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is called 'hypo'. It forms very large colourless hexagonal crystals, m.p. 48°C . It is readily soluble in water and solutions are used for iodine titrations in volumetric analysis. Iodine very rapidly oxidizes thiosulphate ions $\text{S}_2\text{O}_3^{2-}$ to tetrathionate ions $\text{S}_4\text{O}_6^{2-}$, and the I_2 is reduced to I^- ions.

$\text{Na}_2\text{S}_2\text{O}_3$ is used in the bleaching industry to destroy any excess Cl_2 on fabrics after they have been through a bleach bath. Similarly $\text{Na}_2\text{S}_2\text{O}_3$ is sometimes used to remove the taste from heavily chlorinated drinking water. Since Cl_2 is a stronger oxidizing agent than I_2 , hydrogensulphate ions are formed rather than tetrathionate ions.



Hypo is used in photography for 'fixing' films and prints. Photographic emulsions are made of AgNO_3 , AgCl and AgBr . Parts of the film exposed to light begin to decompose to Ag , thus forming a negative image. The process is enhanced by the developer solution. After developing, the film or print is put in a solution of hypo ($\text{Na}_2\text{S}_2\text{O}_3$). This forms a soluble complex with silver salts, thus dissolving any unchanged silver salts in the photographic emulsion. When there is no photographic emulsion left, the film or print can safely be exposed to light.



Note: Other properties of $\text{S}_2\text{O}_3^{2-}$ are already covered in Chapter 7.

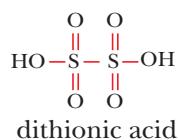
Pyrosulphates

Pyrosulphates can be made by heating hydrogen sulphates strongly, or by dissolving SO_3 in H_2SO_4 . Some trisulphuric acid $\text{H}_2\text{S}_3\text{O}_{10}$ is also formed, but polysulphuric acids higher than this are not known.



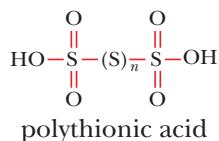
Thionic acid series

Dithionic acid $\text{H}_2\text{S}_2\text{O}_6$ is known only in solution. The acid is dibasic, and salts called dithionates are known, e.g. $\text{Na}_2\text{S}_2\text{O}_6$. No acid salts exist. The acid and its salts contain S in the oxidation state (+V).



The dithionate ion has a structure similar to that of ethane, but the two SO_3 groups adopt an almost eclipsed conformation. The S–S length is 2.15 \AA and the S–O bonds are 1.43 \AA – again rather short. The bond angles S–S–O are close to tetrahedral (103°).

A range of polythionates have been known as salts since the early work of Wackenroder on the effect of H_2S on aqueous solutions of SO_2 . Ions such as trithionate $\text{S}_3\text{O}_6^{2-}$, tetrathionate $\text{S}_4\text{O}_6^{2-}$, pentathionate $\text{S}_5\text{O}_6^{2-}$ and hexathionate $\text{S}_6\text{O}_6^{2-}$ are named according to the total number of S atoms present. It is only in recent times that the parent acids have been made.

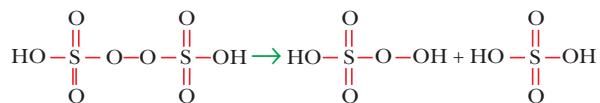


Peroxoacid series

The name peroxyo indicates that the compound contains an $-\text{O}-\text{O}-$ linkage. Two peroxyoacids of sulphur are known: peroxyomonosulphuric acid H_2SO_5 and peroxydisulphuric acid $\text{H}_2\text{S}_2\text{O}_8$. No peroxyoacids

of Se and Te are known. $\text{H}_2\text{S}_2\text{O}_8$ is a colourless solid, m.p. 65°C . It is obtained by electrolysis of sulphates at high current density. It is soluble in water, and is a powerful and useful oxidizing agent. It will convert Mn^{2+} to permanganate and Cr^{3+} to chromate. The most important salts are $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{S}_2\text{O}_8$.

Hydrolysis of peroxodisulphuric acid gives peroxomonosulphuric acid, H_2SO_5 , which is often called Caro's acid.



H_2SO_5 can also be made from chlorosulphuric acid:



It forms colourless crystals, m.p. 45°C , but must be handled with care since it may explode.

10.53 | OXOHALIDES

Thionyl compounds

The following thionyl compounds are known



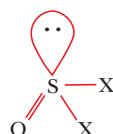
Thionyl chloride SOCl_2 is a colourless fuming liquid, b.p. 78°C , and is usually prepared as follows:



Most thionyl compounds are readily hydrolysed by water, though SOF_2 only reacts slowly.

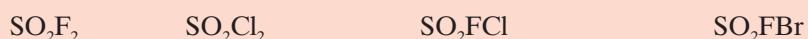


The structure of these oxohalides is tetrahedral with one position occupied by a lone pair.



Sulphuryl compounds

The following sulphuryl halides are known



Sulphuryl chloride SO_2Cl_2 is a colourless fuming liquid, b.p. 69°C , and is made by direct reaction of SO_2 and Cl_2 in the presence of a catalyst. It is used as a chlorinating agent. Sulphuryl fluoride is a gas and is not hydrolysed by water, but the chloride fumes in moist air and is hydrolysed by water. The sulphuryl halides have a distorted tetrahedral structure. They may be regarded as derivatives of H_2SO_4 , where both OH groups have been replaced by halogens. If only one group is replaced, halosulphuric acids are obtained.

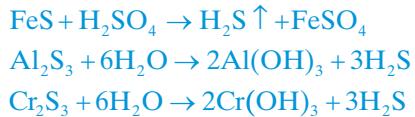


Fluorosulphuric acid forms many salts, but chlorosulphuric acid forms none and is used as a chlorinating agent in organic chemistry.

10.54 | HYDRIDES

The elements all form covalent hydrides. These are water H_2O , hydrogen sulphide H_2S , hydrogen selenide H_2Se , hydrogen telluride H_2Te and hydrogen polonide H_2Po . Water is liquid at room temperature, but the others are all colourless, foul smelling toxic gases.

Our point of interest is H_2S which can be prepared by the action of mineral acids on metal sulphides or hydrolysis.



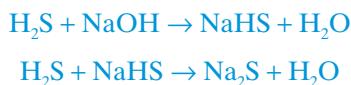
This gas can be dried by anhydrous CaCl_2 or P_2O_5 . Concentrated sulphuric acid is also a very good drying agent but cannot be used for this purpose because it oxidizes H_2S to S.



H_2S is soluble in water and burns in air with a blue flame.



H_2S is about twice as soluble in water as CO_2 , and 1 volume of water can absorb 4.6 volumes of H_2S at 0°C and 2.6 volumes at 20°C . A saturated solution is used as a laboratory reagent, but it does not keep well since air slowly oxidizes it and sulphur is deposited. H_2S is a very weak dibasic acid. Most metal sulphides can be regarded as salts of H_2S , and since it is dibasic two series of salts can be derived from it, the hydrogen sulphides, e.g. NaHS , and the normal sulphides, e.g. Na_2S .



The alkali metal sulphides are all soluble in water and hydrolyse strongly (a 1M solution is about 90% hydrolysed), so they are strongly basic.



Most of the sulphides of the heavy metals are insoluble in water and so do not hydrolyse. If a dilute solution of ammonia is saturated with H_2S then ammonium hydrogen sulphide NH_4HS is formed, not $(\text{NH}_4)_2\text{S}$. The latter only exists at low temperatures in the absence of water. Solutions of NH_4HS are colourless, and when mixed with an equimolar amount of NH_3 it is used as a laboratory reagent. More commonly 'yellow ammonium sulphide' $[(\text{NH}_4)_2\text{S}_2]$ is used as a laboratory reagent, for example to precipitate metal sulphides in qualitative analysis. Yellow ammonium sulphide is really a mixture of ammonium polysulphides, and is made by dissolving sulphur in colourless $\text{NH}_4\text{HS}/\text{NH}_3$ solution.

H_2S can be identified by the following methods:

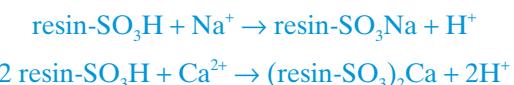
1. It has rotten eggs smell.
2. It can turn moist $\text{Pb}(\text{OAc})_2$ or $\text{Cd}(\text{OAc})_2$ paper black and yellow, respectively.
3. It gives violet colouration with alkaline solution of sodium nitroprusside.
4. Using its strong reducing properties, it can also be identified by several methods which are already discussed in Chapter 7.

Water

Water is the most abundant chemical compound, and the oceans cover almost 71% of the earth's surface. For this reason we have no need to prepare water. However, sea water contains many dissolved salts, and less than 3% of the earth's water is fresh water, and most of that is present as polar ice. The preparation of

pure water for drinking and laboratory use is a major industry. The human body is more tolerant of some impurities than is industry.

Very pure water is required for laboratory and industrial use. The only way to remove all solid solutes is distillation. This is expensive since water has a high boiling point and high latent heat of evaporation. During distillation the water tends to dissolve appreciable amounts of CO_2 from the atmosphere, which make it acidic. A cheaper method is to produce deionized water. This is done by passing the water down two different ion-exchange columns one after the other. (Alternatively a 'mixed bed' may be used, i.e. a single column made up of two different ion-exchange materials.) Ion-exchange resins are insoluble polymeric solids, containing a reactive group. They are manufactured in bead form, and are permeable to water. The first column contains a sulphonic acid resin, that is an organic resin with acidic groups — SO_3H . This removes all metal ions from solution and replaces them with H^+ :



The second column contains a resin with basic groups — $\text{NR}_4^+ \text{OH}^-$, which removes negative ions.



Water produced in this way usually contains soluble silicates and CO_2 . When all the reactive sites on the resin have been used, the resins can be regenerated by treating the first one with dilute H_2SO_4 , and the second one with a Na_2CO_3 solution.

Drinking water is usually much less pure, and water with no dissolved salts does not taste very nice. The World Health Organization recommends a maximum desirable content of not more than 0.5 grams of dissolved solids per litre, though the maximum permissible level is three times this. If the fresh water source contains silt, this is allowed to settle out. Light Suspended particles and colloidal particles which discolour the water are removed by treating with Al(OH)_3 or Fe(OH)_3 . These coagulate suspended particles, thus clarifying the water. (Alum is the most widely used coagulating agent.) If necessary some water softening may be performed by ion-exchange, or by mixing water from different sources. The water is then chlorinated, or treated with ozone to kill bacteria. These are present because of drainage from fields into rivers and lakes, and also from the disposal of partly treated and untreated sewage. Failure to treat drinking water is the major cause of enteritis. In some underdeveloped parts of the world up to half the children under the age of five die from this cause or other waterborne diseases.

Sea water has a high salt content. The production of drinking water and water for crops from sea water is called desalination. It requires a large amount of energy, and is therefore expensive. It is only carried out when the shortage of fresh water is severe, but it has become increasingly important in arid regions like the Persian Gulf. Distillation, ion-exchange, electrodialysis, reverse osmosis and the freezing out of ice have all been used.

Apart from water, the other hydrides are all poisonous and have unpleasant odours. The hydrides decrease in stability from H_2O to H_2S to H_2Se to H_2Te . (This is shown by the decrease in their enthalpies of formation — Table 10.23.) They become less stable because the bonding orbitals become larger and more diffuse: hence overlap with the hydrogen 1s orbital is less effective.

Table 10.23 Some properties of H_2O , H_2S , H_2Se and H_2Te

	Enthalpies of formation (kJ mol ⁻¹)	Bond angle	Boiling point (°C)
H_2O	-242	$\text{H}-\text{O}-\text{H} = 104^\circ 28'$	100
H_2S	-20	$\text{H}-\text{S}-\text{H} = 92^\circ$	-60
H_2Se	+81	$\text{H}-\text{Se}-\text{H} = 91^\circ$	-42
H_2Te	+154		-2.3

The $\text{H}-\text{O}-\text{H}$ bond angle in water is $104^\circ 28'$, in accordance with the VSEPR prediction of slightly less than tetrahedral due to the presence of lone pairs of electrons. Thus the orbitals used for bonding by O are

close to sp^3 hybrids. In H_2S , H_2Se and H_2Te the bond angles become close to 90° . This suggests that almost pure p orbitals on Se and Te are used for bonding to hydrogen.

In a series of similar compounds, the boiling points usually increase as the atoms become larger and heavier. If the boiling points increase, then the volatility decreases. This trend is shown by the boiling points of H_2S , H_2Se , H_2Te and H_2Po , but the boiling point of water is anomalous.

Water has an abnormally low volatility because its molecules are associated with each other by means of hydrogen bonds in both the solid and liquid states. The structure of liquid water is not known for certain, but probably consists of groups of two or three molecules hydrogen bonded together. The structure of ordinary hexagonal ice is known. At high pressures other more dense structures are formed. A total of nine different forms of ice are known. X-ray studies do not often reveal the positions of H atoms. In this case the H positions were found by neutron diffraction on solid deuterium oxide D_2O . The structure is similar to wurtzite ZnS (see Chapter 3), with O atoms occupying both the Zn^{2+} and the S^{2-} positions. The H atoms are located just off the line joining two O atoms, and the $O-H \dots O$ angle is $104^\circ 28'$. The strength of a hydrogen bond is about 20 kJ mol^{-1} . This association is responsible for the abnormally high boiling point and melting point of water.

The H bonding is the main reason why covalent compounds have a very low solubility in water. When two substances mix there is an increase in entropy since the order decreases. Thus mixing is always favoured. However, in the case of water, dissolving something means that hydrogen bonds must be broken. Unless there is an interaction between the dissolved material and water greater than the energy lost through breaking hydrogen bonds, then the material will not dissolve. Covalent materials have little interaction with water, and so are insoluble. Ionic materials become hydrated, and polar materials take part in the hydrogen bonding, so they are soluble.

A unique property of water is that the solid is less dense than the liquid. This is why lakes and the sea freeze from the top downwards. The ice at the top makes it difficult to cool the water underneath, so even at the North Pole there is water underneath the ice. But for this the sea would freeze solid and the polar ice-caps would cover much more of the earth's surface. The maximum density of water occurs at 4°C . On melting, the hydrogen bonded network in the solid partly breaks down. Ice has a rather open structure, with quite large cavities. On partial melting some 'free' water molecules occupy some of these cavities, and hence the density increases. This effect outweighs the effect of thermal expansion up to 4°C , but above this temperature expansion is the larger effect so the density decreases.

Other hydrides

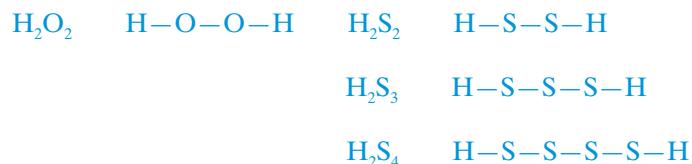
The hydrides dissociate to a varying degree, forming H^+ ions. They are all very weak acids and there is an increase in acidic strength from H_2O to H_2Te . In the compounds H_2O , H_2S , H_2Se and H_2Te the most important factor is the enthalpy of formation, the values being -120 , -10 , $+43$ and $+77 \text{ kJ mol}^{-1}$. The stability decreases (the last two are in fact thermodynamically unstable), thus accounting for the greater dissociation of H_2Te .



The more acidic the hydrogen atom in the hydrides, the more stable will be the salts formed from them, i.e. oxides, sulphides, selenides and tellurides.

Peroxides and polysulphides

Oxygen, and to a greater extent sulphur, differ from the remainder in their ability to catenate and form polyoxides and polysulphides, which are less stable than the normal salts. Unbranched polysulphane chains containing up to eight sulphur atoms have been prepared.



H_2O_2 and H_2S_2 have similar ‘skew’ structures. The dimensions of H_2O_2 gas are shown in Figure 10.50. H_2O_2 is the smallest molecule known to show restricted rotation, in this case about the O—O bond. A similar structure is retained in the liquid and solid, but the bond lengths and angles are slightly changed because of hydrogen bonding.

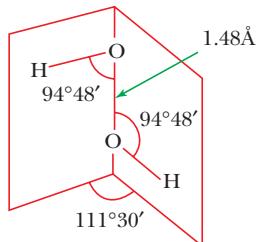


Figure 10.50 Structure of H_2O_2 in gas phase.

Hydrogen peroxide

Preparation

1. H_2O_2 can be prepared by the addition of acid to peroxide.



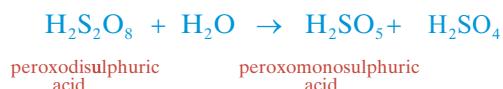
Now-a-days instead of conc. H_2SO_4 , H_3PO_4 is used because H_2SO_4 catalyzes the decomposition of H_2O_2 .



Then H_3PO_4 is regenerated as follows, so indirectly H_2SO_4 is used.



2. At one time H_2O_2 was obtained by electrolysis of H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ at a high current density to form peroxosulphates, which were then hydrolysed.



3. H_2O_2 is now produced on an industrial scale by a cyclic process (Figure 10.51). 2-Ethyl anthroquinol is oxidized by air to the corresponding quinone and H_2O_2 . The anthraquinone is reduced back to anthraquinol with hydrogen at a moderate temperature using platinum, palladium or Raney nickel as catalyst. The cycle is then repeated. The reaction is carried out in a mixture of organic solvents (ester/hydrocarbon or octanol/methylnaphthalene). The solvent must:

- a. dissolve the quinol and quinone
 - b. resist oxidation
 - c. be immiscible with water.

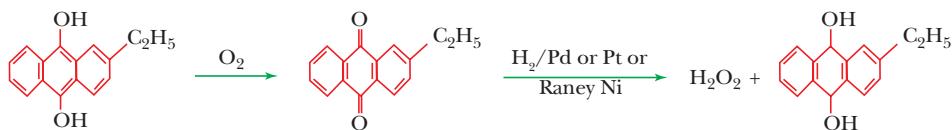


Figure 10.51 Production of H_2O_2 .

The H_2O_2 is extracted with water as a 1% solution. This is concentrated by distillation under reduced pressure, and sold as a 30% (by weight) solution which has a pH of about 4.0 (85% solutions are also produced). H_2O_2 solutions are stored in plastic or wax coated glass vessels, often with negative catalysts such as urea or sodium stannate added as stabilizers. Solutions keep quite well, but must be handled with care since they may explode with traces of organic material or dust.

Physical properties

Pure H_2O_2 is a colourless liquid which resembles water quite closely. It is more hydrogen bonded than is water and so has a higher boiling point (b.p. 152 °C, m.p. –0.4 °C). It is more dense than water (density 1.4 g cm⁻³), though it has a high dielectric constant.

Chemical properties

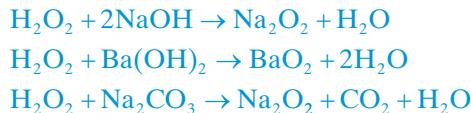
H_2O_2 is unstable, and the rate at which it decomposes (disproportionates) depends on the temperature and concentration. Many impurities catalyse the decomposition, which may become very violent, especially concentrated solutions. Catalysts include metal ions Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , metal surfaces such as Pt or Ag, MnO_2 , charcoal or alkali –even the small amount leached from glass.



However, it decomposes only slowly in the absence of catalysts.

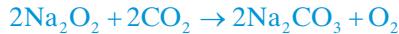


It has some acidic properties also.



In most of its reactions H_2O_2 acts as a strong oxidizing agent. In acidic solutions these reactions are often slow, but in basic solution they are usually fast. H_2O_2 will oxidize Fe^{2+} to Fe^{3+} , $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ (ferrocyanide) to $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ (ferricyanide), NH_2OH to HNO_3 and SO_3^{2-} to SO_4^{2-} .

Ionic peroxides such as Na_2O_2 give H_2O_2 with water or dilute acids. Na_2O_2 reacts with gaseous CO_2 .



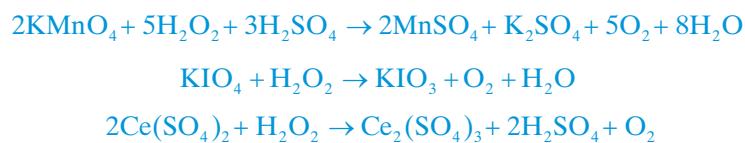
Heating Na_2O_2 with many organic compounds results in their oxidation to carbonates. Fusing Na_2O_2 with Fe^{2+} salts gives sodium ferrate $\text{Na}_2[\text{FeO}_4]$ which contains Fe(+VI).

Some important reactions of H_2O_2 as oxidizing agent are listed as follows.

1. $\text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$
2. $\text{NaNO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$
3. $\text{Na}_2\text{SO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
4. $\text{Na}_3\text{AsO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{Na}_3\text{AsO}_4 + \text{H}_2\text{O}$
5. $2\text{KI} + \text{H}_2\text{O}_2 \rightarrow 2\text{KOH} + \text{I}_2$

6. $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S} \downarrow + 2\text{H}_2\text{O}$
7. $\text{H}_2\text{SO}_4 + 2\text{FeSO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$
8. $2\text{K}_4[\text{Fe}(\text{CN})_6] + \text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow 2\text{K}_3[\text{Fe}(\text{CN})_6] + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$
9. $2[\text{Cr}(\text{OH})_4]^- + 3\text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + 8\text{H}_2\text{O}$
10. $\text{CrO}_4^{2-} + 2\text{H}^+ + 2\text{H}_2\text{O}_2 \rightarrow \text{CrO}_5 \downarrow + 3\text{H}_2\text{O}$
 $4\text{CrO}_5 + 12\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 7\text{O}_2 + 6\text{H}_2\text{O}$
11. $\text{Mn}^{2+} + \text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$

With stronger oxidizing agents H_2O_2 is oxidized, that is H_2O_2 is forced to act as a reducing agent, and in such cases O_2 is always evolved. For example,



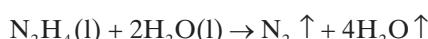
Some important reactions of H_2O_2 as reducing agent are listed as follows.

1. $\text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{Ag} + \text{H}_2\text{O} + \text{O}_2$
2. $\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 2\text{O}_2$
3. $\text{MnO}_3 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{O}_2$
4. $\text{PbO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{PbO} + \text{H}_2\text{O} + \text{O}_2$
5. $\text{Pb}_3\text{O}_4 + \text{H}_2\text{O}_2 + 6\text{HNO}_3 \rightarrow 3\text{Pb}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + \text{O}_2$
6. $\text{X}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{HX} + \text{O}_2$ (where $\text{X} = \text{Cl, Br}$)
7. $2\text{KMnO}_4 + 3\text{H}_2\text{O}_2 \rightarrow 2\text{KOH} + 2\text{MnO}_2 + 2\text{H}_2\text{O} + 3\text{O}_2$
 $2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 5\text{O}_2 + 8\text{H}_2\text{O}$
8. $2[\text{Fe}(\text{CN})_6]^{3-} + 2\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow 2[\text{Fe}(\text{CN})_6]^{4-} + 2\text{H}_2\text{O} + \text{O}_2$
9. $\text{NaOCl} + \text{H}_2\text{O}_2 \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{O}_2$
10. $\text{NaIO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{NaIO}_3 + \text{H}_2\text{O} + \text{O}_2$

Uses

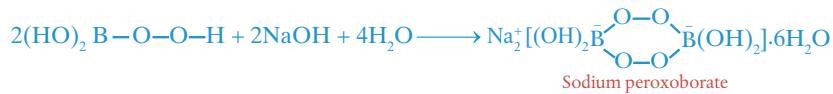
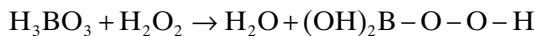
Important uses of hydrogen peroxide are listed as follows.

1. H_2O_2 is a major industrial chemical, and is used extensively as a mild bleaching agent for textiles and paper/wood pulp.
2. It is used for several environmental purposes: to restore aerobic conditions in sewage waters, and to oxidize cyanides and sulphides.
3. It is an important rocket fuel. When it is mixed with N_2H_4 in 1:2 proportion, its reaction is highly exothermic as well as associated with large increase in volume.

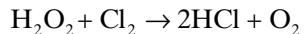


Three mole liquid produces five moles of gas, which causes huge volume expansion.

4. It is also used for making other chemicals, particularly sodium peroxoborate $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 6\text{H}_2\text{O}$, which is used as a brightener in washing powders.



5. Smaller amounts of H_2O_2 are used to bleach hair, feathers, fats and waxes.
6. It is used as an oxidizing agent in the laboratory, and as an antiseptic to treat wounds.
7. It is useful to counteract chlorine, and in this reaction H_2O_2 behaves as a reducing agent.



The H_2O_2 is extracted with water as a 1% solution. This is concentrated by distillation under reduced pressure, and sold as a 30% (by weight) solution which has a pH of about 4.0 (85% solutions are also produced). H_2O_2 solutions are stored in plastic or wax coated glass vessels, often with negative catalysts such as urea or sodium stannate added as stabilizers. Solutions keep quite well, but must be handled with care since they may explode with traces of organic material or specs of dust.

10.55 | HALIDES

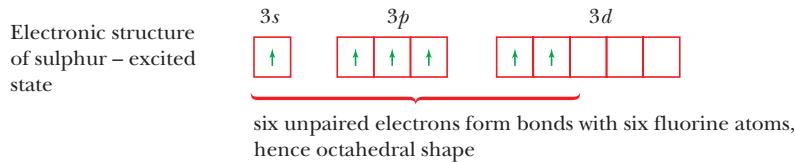
Compounds with the halogens are listed in Table 10.24. Since F is more electronegative than O, binary compounds are oxygen fluorides, whereas similar chlorine compounds are chlorine oxides. Some of these compounds including the oxides of iodine, are therefore described in under 'Halogen oxides'.

Table 10.24 Compounds with the halogens

	MX_6	MX_4	MX_2	M_2X_2	M_2X	Others
O			OF_2 Cl_2O Br_2O	O_2F_2	ClO_2 BrO_2	$\text{O}_3\text{F}_2, \text{O}_4\text{F}_2$ $\text{Cl}_2\text{O}_6, \text{Cl}_2\text{O}_7$ BrO_3 $\text{I}_2\text{O}_4, \text{I}_4\text{O}_9, \text{I}_2\text{O}_5$
S	SF_6	SF_4 SCl_4	SF_2 SCl_2	S_2F_2 S_2Cl_2 S_2Br_2		$\text{SSF}_2, \text{S}_2\text{F}_4, \text{S}_2\text{F}_{10}$
Se	SeF_6	SeF_4 SeCl_4 SeBr_4		Se_2Cl_2 Se_2Br_2		
Te	TeF_6	TeF_4 TeCl_4 TeBr_4 Tel_4	TeCl_2 TeBr_2 TeI_2			
Po		PoCl_4 PoBr_4 PoI_4	PoCl_2 PoBr_2 (PoI_2)			

Compounds shown in parentheses are unstable.

Fluorine brings out the maximum valency of six with S, Se and Te; and SF_6 , SeF_6 and TeF_6 are all formed by direct combination. They are all colourless gases and have an octahedral structure as predicted by the VSEPR theory. The low boiling point indicates a high degree of covalency.



SF_6 is a colourless, odourless, non-flammable gas, which is insoluble in water and extremely inert. SeF_6 is slightly more reactive and TeF_6 is hydrolyzed by water. This is possibly due to the larger size of Te which permits the larger coordination number necessary in the first stage of hydrolysis.



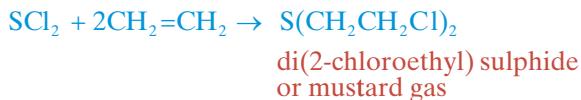
SF_4 is highly reactive, but is more stable than the lower fluorides. In contrast to the relatively stable hexafluorides, the tetrahalides are very sensitive to water.



SF_4 is a powerful fluorinating agent.

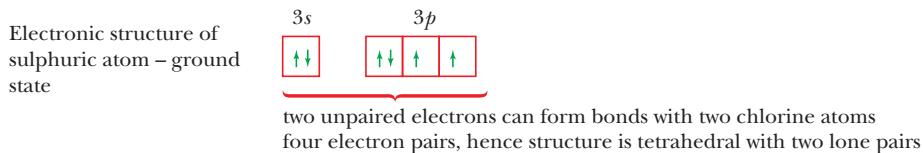


SCl_2 is commercially important since it readily adds across double bonds in alkenes. It has been used to produce the notorious ‘mustard gas’, first used in World War I, and more recently in 1988 in the Iran–Iraq war.



Mustard gas is not a gas but a volatile liquid (m.p. 13°C , b.p. 215°C). It was sprayed as a mist that stayed close to the ground, and was blown by gentle winds onto the enemy. It causes severe blistering of the skin and death. In living cells it is converted into the divinyl compound $(\text{CH}_2\text{CH})_2\text{S}$ which reacts with and disrupts proteins in the cell.

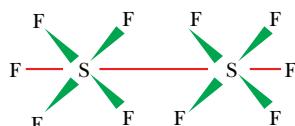
The dihalides form angular molecules, based on a tetrahedron with two positions occupied by lone pairs. The lone pairs distort the tetrahedral angle of $109^\circ 28'$ to 103° in SCl_2 , 101.5° in F_2O and 98° in TeBr_2 .



Dimeric monohalides such as S_2F_2 and S_2Cl_2 are formed by direct action between S and the halogens. S_2Cl_2 is a toxic yellow liquid (m.p. -76°C , b.p. 138°C), with a revolting smell. The structure of S_2Cl_2 and the other monohalides is similar to that of H_2O_2 , with a bond angle of 104° which is due to distortion by two lone pairs.

S_2F_2 is an unstable compound. It exists in two different isomeric forms, $\text{F}-\text{S}-\text{S}-\text{F}$ (like $\text{Cl}-\text{S}-\text{S}-\text{Cl}$ and $\text{H}-\text{O}-\text{O}-\text{H}$), and thiothionyl fluoride $\text{S}=\text{SF}_2$.

The compound S_2F_{10} has an unusual structure, of two octahedra joined together.



SINGLE CORRECT CHOICE TYPE QUESTIONS

- Which of the following is incorrect regarding O_3 ?
 - It is an allotrope of oxygen.
 - d_{O-O} is in between that of O_2 and H_2O_2 .
 - It is an angular-shaped molecule.
 - It is paramagnetic like O_2 .
- Fluidity of Hg is lost on reaction with O_3 due to the formation of
 - Hg_2O
 - Hg_2O_2
 - HgO_2
 - HgO
- Dry I_2 and moist I_2 on reaction with O_3 produces compounds A and B, respectively. Then A and B are
 - HIO_3 and I_4O_9
 - I_4O_9 and HIO_3
 - HIO_3 and HIO_4
 - HIO_4 and HIO_3
- The compounds of sulphur obtained by reaction of sulphur and conc. hot KOH, when reacted separately with dil. HCl produce
 - different gases, SO_2 and H_2S .
 - the same gas SO_2 .
 - sulphur back.
 - the same gas H_2S .
- The best yield of H_2O_2 is obtained from BaO_2 on acidification with which of the following acids?
 - H_2SO_4
 - HNO_3
 - H_3PO_4
 - $HOCl$
- H_2O_2 is used for detection of Ti^{4+} ions and the yellow solution obtained has the formula and oxidation state as
 - H_2TiO_4 and + 6
 - H_2TiO_3 and + 4
 - H_2TiO_4 and + 4
 - $TiSO_4$ and + 2
- Which of the following species does not contain S–S linkage?
 - $S_2O_2^{2-}$
 - $S_2O_3^{2-}$
 - $S_2O_5^{2-}$
 - None of these.

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

- Oxygen shows several differences from the rest of the elements of the group. This is because
 - it has small size.
 - it has high electronegativity.
 - of the lack of suitable d -orbitals.
 - it can form strong π -bonds.
- The weaker π -bond formation is responsible for the non-existence of which of the following compounds as discrete molecule?
 - CO_2
 - CS_2
 - CSe_2
 - CTe_2
- SO_2 pollution (from coal fired power station) can be controlled by
 - passing the flue gas through slurry of $Ca(OH)_2$.
 - reduction of SO_2 into S using H_2S and activated Al_2O_3 catalyst.
 - passing through saturated solution of SO_2 .
 - passing through acidified $KMnO_4$ solution.
- Gun powder is a mixture of
 - $NaNO_3$
 - KNO_3
 - charcoal powder
 - sulphur
- The final product obtained from the electrolysis of 50% H_2SO_4 with high current density has a
 - S–O–O–S linkage.
 - O–O–linkage.
 - S–S linkage.
 - S–O–S linkage.
- In which of the following cases, the element is oxidized into its highest oxidation state when it reacted with O_3 under moist conditions?
 - S
 - I_2
 - P
 - As
- Which of the following compounds can be used for drying of H_2S gas?
 - Conc. H_2SO_4
 - P_2O_5
 - Fused $CaCl_2$
 - Anhydrous Al_2O_3
- Ozone gas can be absorbed by
 - olive oil.
 - turpentine oil.
 - mustard oil.
 - oil of cinnamon

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1 to 3

Ozone is an allotrope of oxygen. It can be prepared by several methods but always a very small amount of conversion is observed. It forms an important layer in the upper atmosphere as it can absorb UV rays from sun. It is also a powerful oxidizing agent.

- Which of the following substances can cause depletion of O_3 layer?
 (A) Chlorofluorocarbons
 (B) Oxides of nitrogen like NO
 (C) Halogens
 (D) All of these
- O_3 can be prepared by
 (A) action of silent electric discharge upon O_2 in an ozonizer.
 (B) UV irradiation of O_2 .
 (C) passing F_2 in water.
 (D) All of these.
- In which of following cases, the products formed are incorrect considering the oxidizing properties of O_3 ?
 (A) $2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_3$
 (B) $2Ag + O_3 \rightarrow Ag_2O + O_2$
 (C) $SO_2 + O_3 \rightarrow SO_3 + O_2$
 (D) $PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$

Passage 2: For Questions 4 and 5

SO_2 can act as oxidizing agent as well as reducing agent and the major source of obtaining SO_2 is roasting of sulphide ores and by burning sulphur.

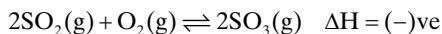
- SO_2 is very soluble in water; 39 cc of SO_2 gas is dissolved in 1 cc of water. In this solution SO_2 is mostly present as

- (A) H_2SO_3
 (B) various hydrates like $SO_2 \cdot 6H_2O$.
 (C) Both (A) and (B) in equal amount.
 (D) H_2SO_4

- Which of the following statements is incorrect regarding SO_2 ?
 (A) It can be detected by turning of moist starch iodate paper blue.
 (B) It can be estimated calorimetrically by reacting with $K_2[HgCl_4]$ followed by the reaction with the dye pararosaniline.
 (C) SO_2 can be used to bleach wool and silk.
 (D) SO_2 reduces $FeCl_2$ into Fe in strongly acidic medium.

Passage 3: For Questions 6 and 7

Contact process is used to convert SO_2 into SO_3 in the presence of platinum catalyst and the reaction is exothermic.



- Now-a-days a cheaper catalyst is used instead of platinum and that catalyst is
 (A) V_2O_3 and K_2O
 (B) V_2O_4 and K_2O
 (C) V_2O_5 and K_2O
 (D) VO_3 and K_2O
- During the conversion of SO_3 into H_2SO_4 on commercial scale, the intermediate compound is
 (A) $H_2S_2O_3$
 (B) $H_2S_2O_5$
 (C) $H_2S_2O_6$
 (D) $H_2S_2O_7$

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
 (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I
 (C) If Statement I is true but Statement II is false.
 (D) If Statement I is false and Statement II is true.

- Statement I:** HNO_3 oxidizes S to H_2SO_4 while Se is oxidized to H_2SeO_3 .

Statement II: The presence of ten electrons in $3d$ -subshell, causes poor shielding and finally attracts the outermost electron more strongly for Se.

- Statement I:** Conc. H_2SO_4 can be used for drying H_2S gas.

Statement II: Conc. H_2SO_4 shows very good dehydrating property.

- Statement I:** H_2O_2 can be used as good rocket propellant when mixed with N_2H_4 .

Statement II: H_2O_2 and N_2H_4 both exist in the gauche form.

- Statement I:** O_3 has a fishy smell.

Statement II: It absorbs red part of the visible light.

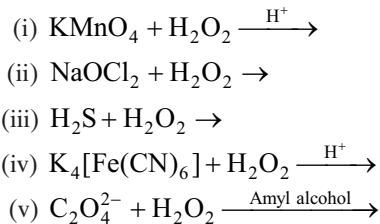
- Statement I:** In most of the reactions of O_3 , O_2 is one of the products formed.

Statement II: Only one O atom comes out easily from O_3 when it undergoes reduction accepting two electrons.

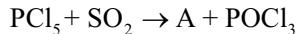
INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following is a non-negative integer.

- The sum of the oxidation states of sulphur atoms in $\text{H}_2\text{S}_2\text{O}_5$ is ____.
- When SO_2 is dissolved in water, then number of ions that will be in equilibrium is ____.
- The sum of oxidation states of sulphur atoms in $\text{H}_2\text{S}_n\text{O}_6$ is ____.
- Find the number of reactions, among the following, where H_2O_2 acts as reducing agent.



- In the following reaction, find the number of d -orbitals involved in bonding of compound A.



- H_2S gas can be dried by how many of the following reagents?
Anhydrous CaCl_2 , conc. H_2SO_4 , P_2O_5 , KOH solution, Na_2CO_3 solution.
- How many of the following properties increase regularly from H_2O to H_2Te ?
 - Acidic strength
 - Bond angle
 - Boiling point
 - Bond length
- The oxidation state of sulphur atom in $\text{H}_2\text{S}_2\text{O}_7$ is ____.
- The number of lone pairs in O_3 molecule is ____.
- The sum of oxidation state of all sulphur atoms in pentathionate ion is ____.

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

- Match the compounds with their uses.

Column I	Column II
(A) O_3	(P) Very good fluorinating agent.
(B) H_2O_2	(Q) Used for preparing mustard gas.
(C) SF_4	(R) Used as rocket fuel.
(D) SCl_2	(S) Used to purify drinking water.

- Match the compounds with the correct statement about them.

Column I	Column II
(A) γSO_3	(P) Consists of S–O–S linkage.
(B) $\text{Na}_2\text{S}_4\text{O}_6$	(Q) S is in the maximum oxidation state.

Column I	Column II
(C) Caro's acid (H_2SO_5)	(R) Peroxy linkage is present.
(D) Oleum ($\text{H}_2\text{S}_2\text{O}_7$)	(S) S–S linkage is present.
	(T) It is not a ring system.

- Match the compounds with their properties.

Column I	Column II
(A) O_3	(P) Acts as reducing agent.
(B) H_2O_2	(Q) Acts as oxidising agent.
(C) SO_2	(R) Molecule is polar.
(D) H_2S	(S) Molecule is planar.

ANSWERS**Single Correct Choice Type Questions**

- | | | | |
|--------|--------|--------|--------|
| 1. (D) | 3. (B) | 5. (C) | 7. (D) |
| 2. (A) | 4. (A) | 6. (C) | |

Multiple Correct Choice Type Questions

- | | | | |
|-----------------------|------------------|------------------|------------------|
| 1. (A), (B), (C), (D) | 3. (A), (B) | 5. (A), (B) | 7. (B), (C), (D) |
| 2. (C), (D) | 4. (A), (C), (D) | 6. (A), (C), (D) | 8. (B), (D) |

Comprehension Type Questions

- | | | | |
|--------|--------|--------|--------|
| 1. (D) | 3. (C) | 5. (D) | 7. (D) |
| 2. (D) | 4. (B) | 6. (C) | |

Assertion–Reasoning Type Questions

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (A) | 2. (D) | 3. (B) | 4. (B) | 5. (A) |
|--------|--------|--------|--------|--------|

Integer Answer Type Questions

- | | | | | |
|------|-------|------|------|--------|
| 1. 8 | 3. 10 | 5. 1 | 7. 2 | 9. 6 |
| 2. 3 | 4. 2 | 6. 2 | 8. 6 | 10. 10 |

Matrix–Match Type Questions

- | | | |
|---|---|--|
| 1. (A) → (S)
(B) → (R)
(C) → (P)
(D) → (Q) | 2. (A) → (P), (Q)
(B) → (S), (T)
(C) → (Q), (R), (T)
(D) → (P), (Q), (T) | 3. (A) → (Q), (R), (S)
(B) → (P), (Q), (R)
(C) → (P), (Q), (R), (S)
(D) → (P), (R), (S) |
|---|---|--|

PART 5: THE GROUP 17 ELEMENTS – THE HALOGENS

Table 10.25 Electronic structures and oxidation states

Element		Electronic configuration	Oxidation states*
Fluorine	F	[He]	$2s^2 2p^5$
Chlorine	Cl	[Ne]	$3s^2 3p^5$
Bromine	Br	[Ar]	$3d^{10} 4s^2 4p^5$
Iodine	I	[Kr]	$4d^{10} 5s^2 5p^5$
Astatine	At	[Xe]	$4f^{14} 5d^{10} 6s^2 6p^5$

* The most important oxidation states (generally the most abundant and stable) are shown in bold. Other well-characterized but less important states are shown in normal type.

The name halogen comes from the Greek, and means salt former. The elements all react directly with metals to form salts, and they are also very reactive with non-metals. Fluorine is the most reactive element known.

The elements all have seven electrons in their outer shell. The $s^2 p^5$ configuration is one p electron less than that of the next noble gas. Thus atoms complete their octet either by acquiring an electron (i.e. through forming an ionic bond, giving X^-), or by sharing an electron with another atom (thus forming a covalent bond). Compounds with metals are typically ionic, whilst those with non-metals are covalent.

The halogens show very close group similarities. Fluorine (the first element in the group) differs in several ways from the rest of the group. The first element of each of the main groups all show differences from the subsequent elements. The reasons for the difference are:

1. The first element is smaller than the rest, and holds its electrons more firmly.
2. It has no low-lying d orbitals which may be used for bonding.

The properties of chlorine and bromine are closer than those between the other pairs of elements because their sizes are closer. The ionic radius of Cl^- is 38% larger than that of F^- , but the radius of Br^- is only 6.5% larger than that of Cl^- . The relatively small change in size occurs because Br^- contains ten $3d$ electrons, which shield the nuclear charge ineffectively. This also results in the electronegativity values being particularly close for these two elements. Thus there is little difference in polarity of the bonds formed by Cl and Br with other elements.

The oxidation states ($\pm I$) are by far the most common (Table 10.25). Whether it is ($-I$) or ($+I$) depends on whether the halogen is the most electronegative element. Higher oxidation states exist for all of the elements except F. The lack of low-lying empty d orbitals in the second shell prevents F from forming more than one normal covalent bond.

Fluorine is a very strong oxidizing agent, and this together with its small size allows it to form compounds that bring out the highest oxidation state of other elements. Examples include IF_7 , PtF_6 , SF_6 and many other hexafluorides, BiF_5 , SbF_5 , TbF_4 and $K[Ag^{III}F_4]$.

The elements all exist as diatomic molecules, and they are all coloured. Gaseous F_2 is light yellow, Cl_2 gas is yellow-green. Br_2 gas and liquid are dark red-brown, and I_2 gas is violet. The colours arise from the absorption of light on promoting an electron from the ground state to a higher state. On descending the group the energy levels become closer, so the promotion energy becomes less and the wavelength of the band becomes longer.

I_2 solid crystallizes as black flakes, and has a slightly metallic lustre. Though the X-ray structure shows discrete I_2 molecules, the colour is reminiscent of charge transfer compounds, and the properties are different from those of other molecular solids. The solid conducts electricity to a small extent, and the conductivity increases when the temperature is raised. This behaviour is like that of an intrinsic semiconductor, and different from metals. However, liquid I_2 conducts very slightly. This is ascribed to self-ionization:



10.56 | EXTRACTION AND USES OF THE ELEMENTS

Fluorine

Fluorine is extremely reactive, and this causes great difficulties in the preparation and handling of the element. The first preparation of fluorine was by Moissan in 1886. He was subsequently awarded the Nobel Prize for Chemistry in 1906 for this work. Fluorine is obtained by treating CaF_2 with concentrated H_2SO_4 to give an aqueous mixture of HF. This is distilled, yielding anhydrous liquid HF. Then a cooled solution of KHF_2 in anhydrous HF is electrolyzed, giving F_2 and H_2 (Figure 10.52).

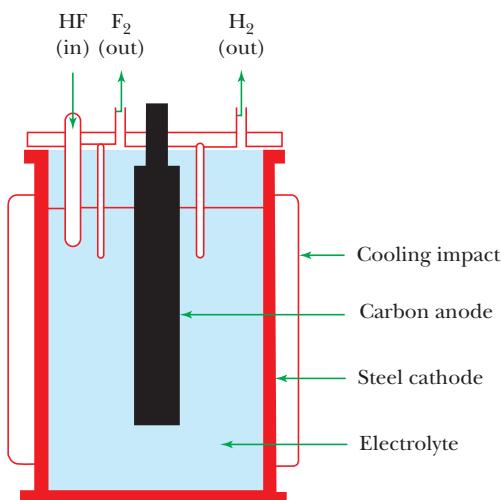


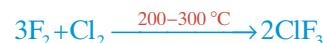
Figure 10.52 Fluorine cell.

There are many difficulties in obtaining fluorine.

1. HF is corrosive, and etches glass and also causes very painful skin wounds. These arise partly by dehydrating the tissue, and partly from the acidic nature of HF. The wounds are slow to heal because F^- ions remove Ca^{2+} ions from the tissues.
2. Gaseous HF is also very toxic (3 ppm) compared with HCN (10 ppm).
3. Anhydrous HF is only slightly ionized and is therefore a poor conductor of electricity. Thus a mixture of KF and HF is electrolysed to increase the conductivity. Moissan used a solution of KF in HF with a mole ratio of 1:13. This has the disadvantage that the vapour pressure of HF is high, and this gives problems with toxicity and corrosion, even when the reaction mixture is cooled to -24°C . Modern methods use medium temperature fluorine generators. These use a mole ratio of 1:2 of KF: HF so that the vapour pressure of HF is much lower. This mixture melts at about 72°C which is a much easier temperature to maintain. Note that KF and HF react to form the acid salt $\text{K}^+[\text{F}-\text{H}-\text{F}]^-$.
4. Water must be rigorously excluded or the fluorine produced will oxidize it to dioxygen.
5. The hydrogen liberated at the cathode must be separated from the fluorine liberated at the anode by a diaphragm, otherwise they will react explosively.
6. Fluorine is extremely reactive. It catches fire, for example with traces of grease or with crystalline silicon. Glass and most metals are attacked. It is difficult to find suitable materials from which to make the reaction vessels. Moissan used a platinum U-tube, since platinum is very unreactive (but it is very expensive). Copper or Monel metal (Cu/Ni alloy) are now used instead, because they cost less. A protective fluoride film forms on the surface of the metal and slows down further attack.

7. The cathodes are made of steel, the anodes are carbon, and teflon is used for electrical insulation (Figure 10.61). Graphite anodes must not be used, since graphite reacts with fluorine, forming graphite compounds CF . In these, fluorine atoms progressively invade the space between the sheets of graphite, forcing them apart, and buckling them. This gradually stops the graphite from conducting, the current needed increases, more heat is produced, and eventually an explosion may occur. Ungraphitized carbon is used to avoid this. It is made from powdered coke compacted and impregnated with copper.

Cylinders of F_2 are now commercially available. However, for many purposes F_2 is converted to ClF_3 (b.p. 12°C), which though very reactive is less unpleasant and easier to transport.



Production of fluorine first became important for the manufacture of inorganic fluorides such as AlF_3 and synthetic $\text{Na}_3[\text{AlF}_6]$. Both are used in the extraction of aluminium.

The fluorocarbons are a very interesting and useful group of compounds, derived from hydrocarbons by substituting F for H. Tetrafluoromethane CF_4 is the fluorocarbon corresponding to methane. Completely fluorinated compounds $\text{C}_n\text{F}_{2n+2}$ are called perfluoro compounds. Thus CF_4 is perfluoromethane. Perfluoro compounds have very low boiling points for their molecular weight: this is associated with very weak intermolecular forces. Fluorocarbons are extremely inert. Unlike methane, CF_4 can be heated in air without burning. Fluorocarbons are inert to concentrated HNO_3 and H_2SO_4 , to strong oxidizing agents such as KMnO_4 or O_3 , and to strong reducing agents such as $\text{Li}[\text{AlH}_4]$ or C at 1000°C . They are attacked by molten Na. When pyrolysed at very high temperatures the C—C bonds break rather than the C—F bonds.

Tetrafluoroethene $\text{F}_2\text{C}=\text{CF}_2$ (b.p. -76.6°C) can be made:



Fluoroalkenes of this type can be polymerized either thermally, or using a free radical initiator. Depending on the degree of polymerization, that is on the molecular weight produced, the products may be oils, greases or a solid of high molecular weight called polytetrafluoroethylene. This is similar to ethene (formerly called ethylene) polymerizing to give polyethylene (polythene). Polytetrafluoroethylene is known commercially as PTFE or Teflon. It is a very inert solid plastic material, and is useful because it is completely resistant to chemical attack and is an electrical insulator. Though expensive, it is used in laboratories. It is also used as a coating for non-stick pans.

Freons are mixed chlorofluorocarbons. Compounds such as CClF_3 , CCl_2F_2 and CCl_3F are important as non-toxic refrigerating fluids and aerosol propellants. They too are very inert, and are discussed later. CF_3CHBrCl is used as an anaesthetic called Fluothane.

Another use of F_2 is to make SF_6 , which is a very inert gas used as a dielectric (insulating) medium for high voltage equipment. F_2 is also used to make other fluorinating agents ClF_3 , BrF_3 and IF_5 and SbF_5 . The earlier use of liquid F_2 as an oxidizing agent in rocket motors has now been discontinued. Anhydrous HF has many uses.

Traces of fluoride ions F^- in drinking water (about 1 ppm) greatly reduce the incidence of dental caries (tooth decay). The F^- ions make the enamel on teeth much harder, by converting hydroxyapatite $[\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2]$ (the enamel on the surface of teeth) into the much harder fluoroapatite $[\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$. However, F^- concentrations above 2 ppm cause discolouration, the brown mottling of teeth, and higher concentrations are harmful. In some places NaF and $\text{H}_2[\text{SiF}_6]$ are added to drinking water, where the natural water is very soft and contains insufficient naturally occurring F^- ions. NaF is now used in fluoride toothpaste. (The original fluoride toothpaste contained SnF_2 and $\text{Sn}_2\text{P}_2\text{O}_7$.)

Chlorine

Chlorine was first prepared by Scheele by oxidizing HCl with MnO_2 . This method was used as a laboratory preparation, but chlorine is now readily available in cylinders.

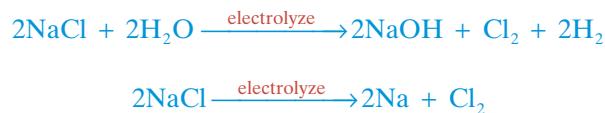


Gas prepared from MnO_2 in this way must be purified. First it is passed through water to remove HCl , and then through concentrated H_2SO_4 to remove water. It may be further dried by passing it over CaO and P_4O_{10} .

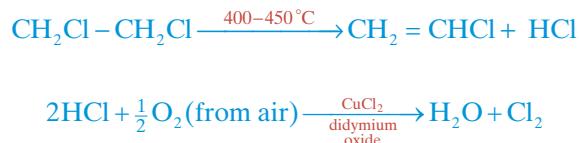
Chlorine is produced commercially on a vast scale by two main methods.

1. By the electrolysis of aqueous NaCl solutions in the manufacture of NaOH .
2. By electrolysis of fused NaCl in the manufacture of sodium.

Before 1960 chlorine was a by-product from these processes. Since then there has been a great increase in the use of chlorine, mainly in the manufacture of plastics such as polyvinyl chloride. Thus chlorine is now the major product.



At one time chlorine was produced by oxidizing HCl with air, using the Deacon process. This process became obsolete (and now a modified Deacon process is now used to a small extent. It utilizes HCl obtained as a by-product from the pyrolysis of 1,2-dichloroethane to vinyl chloride, and uses an improved catalyst (CuCl_2 with didymium oxide as promoter; didymium is an old name meaning 'twin', and it consists of two lanthanide elements praseodymium and neodymium). This works at a slightly lower temperature than the original process.



Chlorine gas is toxic. It was used as a poison gas in World War I. The gas is detectable by smell at a concentration of 3 ppm, and 15 ppm causes a sore throat and running eyes. Higher concentrations cause coughing, lung damage, and death.

About two thirds of World production of chlorine is used to make organic chloro compounds, one fifth for bleaching, and the rest for the manufacture of a variety of inorganic chemicals. The main two organic compounds produced are:

1,2-dichloroethane

vinyl chloride monomer

Both are used in the plastics industry.

Large amounts of chlorine are used for bleaching textiles, wood, pulp and paper. Chlorine is widely used throughout the developed world to purify drinking water, because it kills bacteria. It is also used to make a wide variety of inorganic chemicals including:

bleaching powder

sodium hypochlorite NaOCl

chlorine dioxide ClO_2

sodium chlorate NaClO_3

many metal and non-metal chlorides

organic compounds like CCl_4 , CHCl_3 , DDT

It is also used to prepare poisonous gases like phosgene (COCl_2), tear gas (Cl_3CNO_2) and mustard gas ($\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$).

Bromine

Bromine is obtained from sea water and brine lakes. Sea water contains about 65 ppm Br^- . Thus 15 tonnes of sea water contain about 1 kg of bromine. Bromine is extracted from sea water, but it is more economic to use more concentrated brine sources which contain 2000–5000 ppm of Br^- . First H_2SO_4 is added to adjust

the pH to about 3.5. Then Cl_2 gas is passed through the solution to oxidize the Br^- to Br_2 . This is an example of displacement of one element by another higher in the electrochemical series.



The Br_2 is removed by a stream of air, because Br_2 is quite volatile. The gas is passed through a solution of Na_2CO_3 , when the Br_2 is absorbed, forming a mixture of NaBr and NaBrO_3 . Finally the solution is acidified and distilled to give pure bromine.



1,2-dibromoethane is added to petrol to act as a lead scavenger. Tetraethyl lead is added to petrol to improve its octane rating, but when it burns it forms lead deposits. 1,2-dibromoethane is added to prevent the build-up of lead deposits on the sparking plug and in the engine. The lead passes out with the exhaust gases, mainly as PbClBr . The use of PbEt_4 as an anti-knock additive to petrol has already declined, and will decline further because of legislation against its use, and environmental concern over the toxic effects of lead. Therefore the use of 1,2-dibromoethane has also declined.

Iodine

There are two different commercial methods of obtaining iodine. The method used depends on whether the source is Chile saltpetre or natural brines.

Chile saltpetre is mainly NaNO_3 , but it contains traces of sodium iodate NaIO_3 and sodium periodate NaIO_4 . Pure NaNO_3 is obtained by dissolving saltpetre in water and crystallizing NaNO_3 . The iodate residues thus accumulate and concentrate in the mother liquor. Eventually, this concentrate is divided into two parts. One part is reduced with NaHSO_3 to give I^- . This is mixed with the untreated part, giving I_2 , which is filtered off as a solid and then purified by sublimation.



There is no one dominant use. Half of the iodine produced is used to make a variety of organic compounds including iodoform CHI_3 (used as an antiseptic), and methyl iodide CH_3I . AgI is used for photographic films, and for seeding clouds to produce rain. Small amounts of iodine are required in the human diet, so traces (10 ppm) of NaI are added to table salt. KI is added to animal and poultry feeds. The thyroid gland produces a growth regulating hormone called thyroxine which contains iodine. The deficiency of iodine causes disease goitre. Iodine has limited use as an antiseptic; tincture of iodine is an aqueous solution of I_2 in KI, and French iodine is a solution in alcohol. In the laboratory iodides and iodates are used in volumetric analysis, and Nessler's reagent $\text{K}_2[\text{HgI}_4]$ is used to detect ammonia.

10.57 | GENERAL PROPERTIES

Size of atoms and ions

The ionic and covalent radii of Group 17 elements are listed in Table 10.26.

Table 10.26 Ionic and covalent radii

	Covalent radius (\AA)	Ionic radius X^- (\AA)
F	0.72	1.33
Cl	0.99	1.84
Br	1.14	1.96
I	1.33	2.20

Ionization energy

The ionization energies of the halogens show the usual trend to smaller values as the atoms increase in size (Table 10.27). The values are very high, and there is little tendency for the atoms to lose electrons and form positive ions.

Table 10.27 Ionization and hydration energies, electron affinity

	First ionization energy (kJ mol ⁻¹)	Electron affinity (kJ mol ⁻¹)	Hydration energy X ⁻ (kJ mol ⁻¹)
F	1681	-333	-513
Cl	1256	-349	-370
Br	1143	-325	-339
I	1009	-296	-274
At	-	-270	-

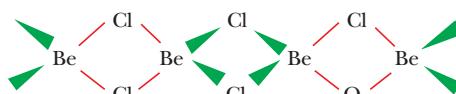
The ionization energy for F is appreciably higher than for the others, because of its small size. F always has an oxidation state of (-I) except in F₂. It forms compounds either by gaining an electron to form F⁻, or by sharing an electron to form a covalent bond.

Hydrogen has an ionization energy of 1311 kJ mol⁻¹, and it forms H⁺ ions. It is at first surprising that the halogens Cl, Br and I have lower ionization energies than H, yet they do not form simple X⁺ ions. The ionization energy is the energy required to produce an ion from a single isolated gaseous atom. Usually we have a crystalline solid, or a solution, so the lattice energy or hydration energy must also be considered. Because H⁺ is very small, crystals containing H⁺ have a high lattice energy, and in solution the hydration energy is also very high (1091 kJ mol⁻¹). The negative ions also have a hydration energy. Thus H⁺ ions are formed because the lattice energy, or the hydration energy, exceeds the ionization energy. In contrast the halogen cation X⁺ would be large and thus have low hydration and lattice energies. Since the ionization energy would be larger than the lattice energy or hydration energy, these ions are not normally formed. However, a few compounds are known where I⁺ is stabilized by forming a complex with a Lewis base, for example [I(pyridine)₂]⁺NO₃⁻.

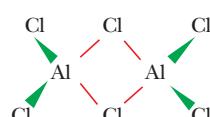
The electron affinities for the halogens are all negative. This shows that energy is evolved when a halogen atom gains an electron, and X → X⁻. Thus, the halogens all form halide ions.

Type of bonds formed and oxidation states

Most compounds formed by the halogens and metals are ionic. However covalent halides are formed in a few cases where the metal ions are very small and have a high charge. The structures of BeCl₂ and AlCl₃ are unusual (Figure 10.53).



(a)



(b)

Figure 10.53 Structure of (a) BeCl₂ and (b) AlCl₃.

The halogens all have very high electronegativity values. When they react with metals there will be a large electronegativity difference: hence they form ionic bonds.

When two halogen atoms form a molecule, they form a covalent bond. Most compounds between the halogens and non-metals are also covalent. Fluorine is always univalent, and since it is the most electronegative element it always has the oxidation number (-I). With Cl, Br and I, a covalence of one is the most common. The oxidation state may be either (-I) or (+I) depending on which atom in the molecule has the greater electronegativity.

Cl, Br and I also exhibit higher valencies, with oxidation numbers of (+III), (+V) and (+VII). These higher valency states are covalent, and arise quite logically by promoting electrons from filled p and s levels to empty d levels. The unpaired electrons then form three, five or seven covalent bonds. There are numerous examples of higher valency states in the interhalogens and halogen oxides.

Electronic structure of halogen atom – ground state	full inner shell	ns	np	nd
<i>(Only one unpaired electron, so can only form one covalent bond)</i>				
Electronic structure of halogen atom – excited state	full inner shell			
<i>(Three unpaired electron, so can form three covalent bonds)</i>				
Electronic structure of halogen atom – further excited state	full inner shell			
<i>(Five unpaired electron, so can form five covalent bonds)</i>				
Electronic structure of halogen atom – still further excited	full inner shell			
<i>(Seven unpaired electron, so can form seven covalent bonds)</i>				

The oxidation states (+IV) and (+VI) occur in the oxides ClO_2 , BrO_2 , Cl_2O_6 and BrO_3 .

Melting and boiling points

The melting and boiling points of the elements increase with increased atomic number (Table 10.28). At room temperature, fluorine and chlorine are gases, bromine is liquid, and iodine is a solid. In temperate climates, only two elements are liquid at room temperature, bromine and mercury. (In very hot climates caesium and thallium are also liquid.) At atmospheric pressure I_2 solid sublimes without melting.

Table 10.28 Melting and boiling points

	Melting point (°C)	Boiling point (°C)
F_2	-219	-188
Cl_2	-101	-34
Br_2	-7	60
I_2	114	185

Bond energy in X_2 molecules

The elements all form diatomic molecules. It would be expected that the bond energy in the X_2 molecules would decrease as the atoms become larger, since increased size results in less effective overlap of

orbitals. Cl_2 , Br_2 and I_2 show the expected trend (Table 10.29), but the bond energy for F_2 does not fit the expected trend. Hence the order is $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$.

Table 10.29 Bond energy and bond lengths of X_2

	Bond energy (free energy of dissociation) (kJ mol^{-1})	Bond length X_2 (\AA)
F	126	1.43
Cl	210	1.99
Br	158	2.28
I	118	2.66

The bond energy in F_2 is abnormally low (126 kJ mol^{-1}), and this is largely responsible for its very high reactivity. (Other elements in the first row of the periodic table also have weaker bonds than the elements which follow in their respective groups. For example in Group 15 the N–N bond in hydrazine is weaker than P–P, and in Group 16 the O–O bond in peroxides is weaker than S–S.) Two different explanations have been suggested for the low bond energy:

1. Mulliken postulated that in Cl_2 , Br_2 and I_2 *some* *pd* hybridization occurred, allowing *some* multiple bonding. This would make the bonds stronger than in F_2 in which there are no *d* orbitals available.
2. Coulson suggested that since fluorine atoms are small, the F–F distance is also small (1.48 \AA), and hence internuclear repulsion is appreciable. The large electron – electron repulsions between the lone pairs of electrons on the two fluorine atoms weaken the bond.

It seems unnecessary to invoke multiple bonding to explain these facts, and the simpler Coulson explanation is widely accepted.

Oxidizing power

Electron affinity is the tendency of the atoms to gain electrons. This reaches a maximum at chlorine. (See Table 10.27) Oxidation may be regarded as the removal of electrons, so that an oxidizing agent gains electrons. Thus the halogens act as oxidizing agents. The strength of an oxidizing agent (that is, its oxidation potential) depends on several energy terms and is best represented by a Born–Haber type of energy cycle (Figure 10.54).

The oxidation potential is the energy change between the element in its standard state, and in its hydrated ions. Thus for iodine the change is from $\frac{1}{2}\text{I}_{2(\text{solid})}$ to $\text{I}_{(\text{hydrated})}^-$. Thus the oxidation potential is equal to the sum of the energy put in as the enthalpies of fusion, vaporization and dissociation, less the energy evolved as the electron affinity and enthalpy of hydration.

In a similar cycle the oxidation potential for bromine can be calculated for the change from $\frac{1}{2}\text{Br}_{2(\text{liquid})}$ to $\text{Br}_{(\text{hydrated})}^-$. (Note that since in its standard state bromine is liquid, the enthalpy of fusion must be omitted. Similarly in calculating the oxidation potential for chlorine and fluorine, since they are gases, both the enthalpies of fusion and vaporization must be omitted.)

Chlorine has the highest electron affinity, so gaseous Cl atoms accept electrons most readily. However, Cl is *not* the strongest oxidizing agent. Table 10.30 shows that, summing all the energy terms in the cycle, fluorine has the most negative ΔH° value. Since the difference between ΔG° and ΔH° is not significant, it follows that fluorine accepts electrons more readily than chlorine, so fluorine is the strongest oxidizing agent. There are two main reasons for this change of order:

1. F_2 has a low enthalpy of dissociation (arising from the weakness of the F–F bond).
2. F_2 has a high free energy of hydration (arising from the smaller size of the F^- ion).

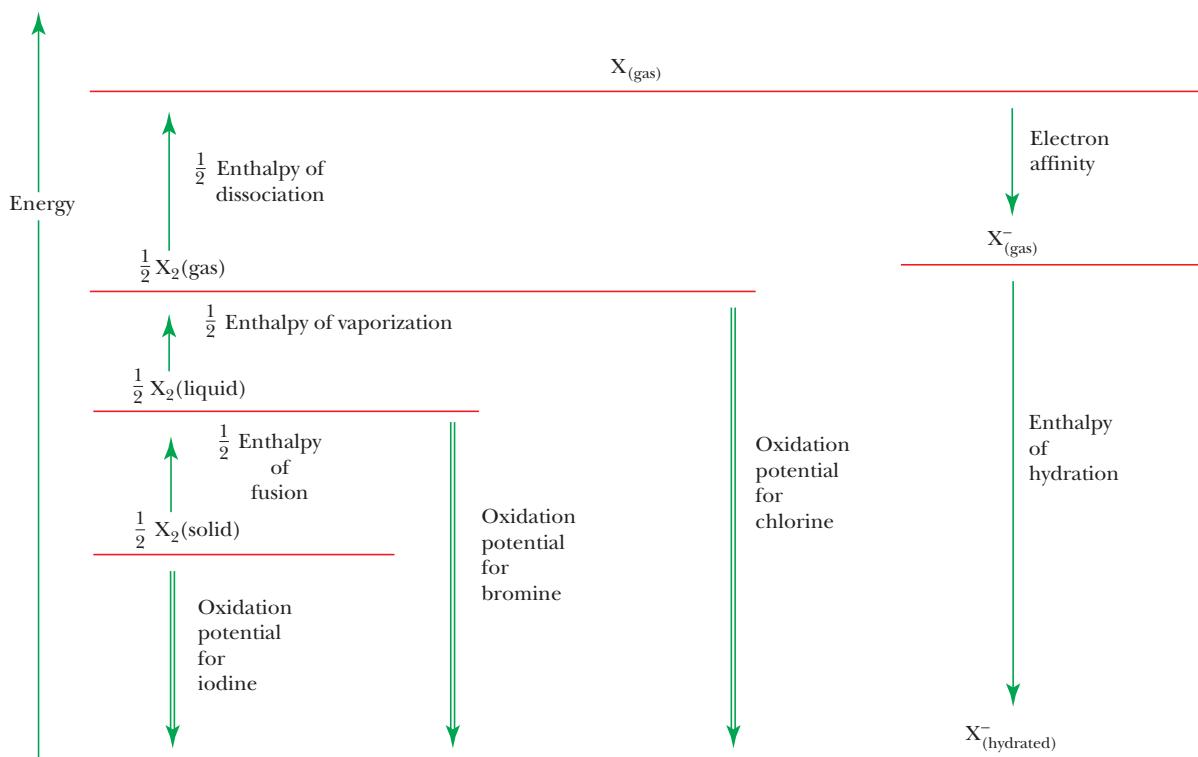


Figure 10.54 Energy cycle showing the oxidation potentials of the halogens. (Oxidation potential is used here in preference to reduction potential to stress that the halogens are strong oxidizing agents. Note $\Delta G^\circ = -nFE^\circ$).

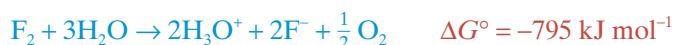
Table 10.30 Enthalpy (ΔH°) values for $\frac{1}{2} X_2 \rightarrow X_{(\text{hydrated})}$ (all values in kJ mol^{-1})

	$\frac{1}{2}$ Enthalpy of fusion	$\frac{1}{2}$ Enthalpy of vaporization	$\frac{1}{2}$ Enthalpy of dissociation	Electron affinity	Enthalpy of hydration	Sum of ΔH°
F_2	–	–	+ 159/2	–333	–513	–836
Cl_2	–	–	+ 243/2	–349	–370	–597.5
Br_2	–	+ 30/2	+ 193/2	–325	–339	–552.5
I_2	+ 15/2	+ 42/2	+ 151/2	–296	–274	–466

Fluorine is a very strong oxidizing agent, and it will replace Cl^- both in solution and also when dry. Similarly, chlorine gas will displace Br^- from solution. (This is the basis of the commercial extraction of bromine from sea water.) In general any halogen of low atomic number will oxidize halide ions of higher atomic number.

10.58 | REACTION WITH WATER

The halogens are all soluble in water, but the extent to which they react with the water, and the reaction mechanism that is followed, vary. Fluorine is so strong an oxidizing agent that it oxidizes water to dioxygen. The reaction is spontaneous and strongly exothermic. (The free energy change is large and negative.) Oxidation may be regarded as the removal of electrons, so that an oxidizing agent gains electrons. Thus the fluorine atoms are reduced to fluoride ions.



A similar reaction between chlorine and water is thermodynamically possible, but the reaction is very slow because the energy of activation is high.



With chlorine an alternative disproportionation reaction occurs rapidly:

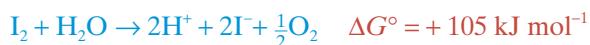


A similar disproportionation reaction occurs to a very limited extent with Br_2 and I_2 . Thus a saturated aqueous solution of Cl_2 at 25°C contains about two thirds hydrated X_2 and one third OCl^- . Solutions of Br_2 and I_2 contain only a very small amount of OBr^- , and a negligible amount of OI^- , respectively (Table 10.31).

Table 10.31 Concentrations in saturated aqueous solutions at 25°C

	Solubility (mol L^{-1})	Concentration X_2 (hydrated) (mol L^{-1})	Concentration HOX (mol L^{-1})
Cl_2	0.091	0.061	0.030
Br_2	0.21	0.21	1.1×10^{-3}
I_2	0.0013	0.0013	6.4×10^{-6}

Iodine is an even weaker oxidizing agent. The free energy change is positive, which shows that energy must be supplied to make it oxidize water.



It follows that for the reverse reaction ΔG° would be -105 kJ mol^{-1} , so the reverse reaction should occur spontaneously. This is the case. Atmospheric dioxygen oxidizes iodide ions to iodine. At the end point of an iodine titration with sodium thiosulphate, the iodine originally present is all converted to iodide ions. Thus the bluish colour produced by the starch indicator with iodine disappears, and the solution becomes colourless.



If the titration flask is allowed to stand for two or three minutes, the indicator turns blue again. This is because some atmospheric oxidation has taken place, forming I_2 , which reacts with the starch to give the blue colour again.



The end point of the titration is usually taken as being when the colour disappears *and the solution remains colourless for half a minute*.

10.59 | REACTIVITY OF THE ELEMENTS

Fluorine is the most reactive of all the elements in the periodic table. It reacts with all the other elements except the lighter noble gases He, Ne and Ar. It reacts with xenon under mild conditions to form xenon fluorides. Reactions with many elements are vigorous, and often explosive. In the massive form a few metals such as Cu, Ni, Fe and Al acquire a protective fluoride coating. However, if these metals are in powdered form (with a large surface area), or if the reaction mixture is heated, then the reaction is vigorous. The reactivity of the other halogens decreases in the order $\text{Cl} > \text{Br} > \text{I}$. Chlorine and bromine react with most of the elements, though less vigorously than does fluorine. Iodine is less reactive and does not combine with some elements such as S and Se. Fluorine and chlorine often oxidize elements further than do bromine and iodine, by this means bringing out higher valencies, for example in PBr_3 and PCl_5 , and in S_2Br_2 , SCl_2 and SF_6 .

The great reactivity of fluorine is attributable to two factors:

1. The low dissociation energy of the F–F bond (which results in a low activation energy for the reaction).
2. The very strong bonds which are formed.

Both of these properties arise from the small size of fluorine. The weak F–F bond arises because of repulsion between the lone pairs of electron on the two atoms. Strong bonds arise because of the high coordination number and high lattice energy.

Some bond energies are shown in Table 10.32. These explain why the halogens form very strong bonds. Many are stronger than the C–C bond, which is itself regarded as a very strong bond. (The C–C bond energy is 347 kJ mol⁻¹.)

Table 10.32 Some bond energies of halogen compounds (all values in kJ mol⁻¹)

	HX	BX ₃	AlX ₃	CX ₄	NX ₃	X ₂
F	566	645	582	439	272	126
Cl	431	444	427	347	201	210
Br	366	368	360	276	243	158
I	299	272	285	238	*	118

* Unstable and explosive.

Some important reactions of halogens are given in Table 10.33.

Table 10.33 Some reactions of the halogens

Reaction	Comment
2F ₂ + 2H ₂ O → 4H ⁺ + 4F ⁻ + O ₂	Vigorous reaction with F
2I ₂ + 2H ₂ O ← 4H ⁺ + 4X ⁻ + O ₂	I reaction in reverse direction
X ₂ + H ₂ O → H ⁺ + X ⁻ + HOX	Cl > Br > I (F not at all)
X ₂ + H ₂ → 2HX	All the halogens
nX ₂ + 2M → 2MX _n	Most metals form halides F the most vigorous
X ₂ + CO → COX ₂	Cl and Br form carbonyl halides
3X ₂ + 2P → PX ₃	All the halogens form trihalides
5X ₂ + 2P → PX ₅	As, Sb and Bi also form trihalides F, Cl and Br form pentahalides AsF ₅ , SbF ₅ , BiF ₅ , SbCl ₅
X ₂ + 2S → S ₂ X ₂	Cl and Br
2Cl ₂ + S → SCl ₄	Cl only
3F ₂ + S → SF ₆	F only
X ₂ + H ₂ S → 2HX + S	All the halogens oxidize S ²⁻ to S
X ₂ + SO ₂ → SO ₂ X ₂	F and Cl
3X ₂ + 8NH ₃ → N ₂ + 6NH ₄ X	F, Cl and Br
X ₂ + X' → 2XX'	Interhalogen compounds formed higher
X ₂ + X'X → X'X ₃	interhalogen compounds

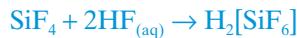
10.60 | HYDROGEN HALIDES HX

It is usual to refer to pure anhydrous HX compounds as hydrogen halides, and their aqueous solutions as hydrohalic acids or simply halogen acids.

The halogens all react with hydrogen and form hydrides HX, though except for HCl this is not the usual way of preparing them. Reactivity towards hydrogen decreases down the group. Hydrogen and fluorine react violently. The reaction with chlorine is slow in the dark, faster in daylight, and explosive in sunlight. The reaction with iodine is slow at room temperature.

HF

Industrially HF is made by heating CaF_2 with strong H_2SO_4 . The reaction is endothermic: hence the need for heating. It is important that SiO_2 impurities are removed from the CaF_2 , as otherwise they consume much of the HF produced.



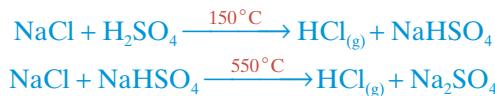
The HF is purified by successive washing, cooling and fractional distillation, giving a product that is 99.95% pure.

HF is used to prepare CFCs, AlF_3 and artificial cryolite (used in electrolytic extraction of aluminium). Aqueous solution of HF is used for pickling steel and etching glass.

HCl

HCl is produced on a very large scale. There are several different preparative methods:

1. At one time HCl was made exclusively by the ‘salt cake’ method. In this method, concentrated H_2SO_4 was added to rock salt (NaCl). The reaction was endothermic, and was performed in two stages at different temperatures. The first of the reactions was carried out at about 150°C . The solid NaCl reacted with H_2SO_4 and became coated with insoluble NaHSO_4 . This prevented further reaction, and accounts for the name ‘salt cake’. In the second stage, the mixture was heated to about 550°C , when further reaction with H_2SO_4 occurred and Na_2SO_4 was formed. This by-product was sold, mostly for paper making (Kraft process).



2. Large amounts of impure HCl have become available in recent years as a by-product from the heavy organic chemical industry. For example, HCl is produced in the conversion of 1,2-dichloethane $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ to vinyl chloride $\text{CH}_2 = \text{CHCl}$, and in the manufacture of chlorinated ethanes and chlorinated fluorocarbons. This is now the largest source of HCl.
3. High purity HCl is made by direct combination of the elements. A gaseous mixture of H_2 and Cl_2 is explosive. However, the reaction proceeds quietly if the gases are burnt in a hydrogen–chlorine flame in a special combustion chamber. The process is strongly exothermic.
4. HCl is conveniently made in the laboratory by treating NH_4Cl with concentrated H_2SO_4 . NH_4Cl costs more than NaCl (which was used in the ‘salt cake’ process). However, NH_4Cl is preferred because

NH_4HSO_4 is soluble, and the reaction does not stop at the halfway stage.



Hydrogen chloride gas is very soluble in water. Aqueous solutions of HCl are sold as *hydrochloric acid*. A saturated solution at 20°C contains 42% HCl by weight, and ‘concentrated’ acid normally contains about 38% HCl by weight (approx. 12M). Pure hydrochloric acid is colourless, but technical grades are sometimes yellow because of contamination by Fe(III). The largest use is for ‘pickling’ metals, that is removing oxide layers from the surface. It is also used to make metal chlorides, in the manufacture of dyestuffs, and in the sugar industry.

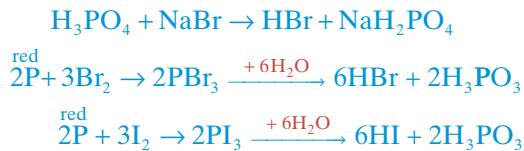
Gaseous HCl is conveniently prepared in the laboratory from concentrated HCl and concentrated H_2SO_4 .

HBr and HI

HBr and HI are made by the reaction of concentrated phosphoric acid H_3PO_4 on metal bromides or iodides, in a similar reaction to the 'salt cake' process for HCl. Note that a non-oxidizing acid such as phosphoric acid must be used. Concentrated H_2SO_4 is a strong oxidizing agent and would oxidize HBr to Br_2 and HI to I_2 .



The usual laboratory preparation involves reducing bromine or iodine with red phosphorus in water. Thus HBr is made by adding bromine to a mixture of red phosphorus and water. For HI, water is added to a mixture of phosphorus and iodine.



HF is only just liquid at room temperature (b.p. 19.9°C), and HCl to HBr and HI are gases. The boiling points increase regularly from HCl, HBr to HI, but the value for HF is completely out of line with the others (Table 10.34).

Table 10.34 Some properties of HX compounds

	Melting point (°C)	Boiling point (°C)	Density (g cm ⁻³)	pK _a values	Composition of azeotrope (weight %)
HF	-83.1	19.9	0.99	3.2	35.37
HCl	-114.2	-85.0	1.19	-7	20.24
HBr	-86.9	-66.7	2.16	-9	47.0
HI	-50.8	-35.4	2.80	-10	57.0

The unexpectedly high boiling point of HF arises because of the hydrogen bonds formed between the F atom of one molecule and the H atom of another molecule. This links the molecules together as $(\text{HF})_n$, and they form zig-zag chains in both the liquid and the solid (Figure 10.55). Some hydrogen bonding also occurs in the gas, which consists of a mixture of cyclic $(\text{HF})_6$ polymers, dimeric $(\text{HF})_2$, and monomeric HF. HCl, HBr and HI are not hydrogen bonded in the gas and liquid, though HCl and HBr are weakly hydrogen bonded in the solid.

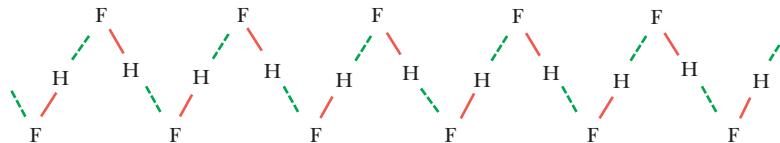


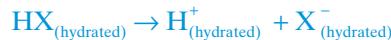
Figure 10.55 Hydrogen-bonded chain in solid HF.

Hydrogen bonds are generally weak ($5\text{--}35\text{ kJ mol}^{-1}$) compared with normal covalent bonds (C--C 347 kJ mol⁻¹), but their effect is highly significant. The most electronegative elements fluorine and oxygen (and to a lesser extent chlorine) form the strongest hydrogen bonds. (The bond energy of the hydrogen bond in $\text{F--H} \dots \text{F}$ is 29 kJ mol⁻¹ in $\text{HF}_{(g)}$).

In the gaseous state the hydrides are essentially covalent. However, in aqueous solutions they ionize. H^+ are not produced since the proton is transferred from HCl to H_2O , thus giving $[\text{H}_3\text{O}]^+$. HCl, HBr and HI ionize almost completely and are therefore strong acids. HF only ionizes slightly and is therefore a weak acid.



It is at first paradoxical that HF is the weakest acid in water, since HF has a greater electronegativity difference than the other hydrides, and therefore has more ionic character. However, acidic strength is the tendency of hydrated molecules to form hydrogen ions:



This may be represented in stages: dissociation, ionization and hydration in an energy cycle.

The acid strength is equal to the sum of all the energy terms round the energy cycle in Figure 10.56.

acid strength = enthalpy of dehydration

- + enthalpy of dissociation
- + ionization energy of H^+
- + electron affinity X^-
- + enthalpy of hydration of H^+ and X^-

The factors which make HF the weakest halogen acid in water become apparent if the various thermodynamic terms are examined in more detail. The dissociation constant k for the change is given by the equation:



$$\Delta G^\circ = -RT \ln k$$

(where ΔG° is the Gibbs standard free energy, R the gas constant and T the absolute temperature). However, ΔG depends on the change in enthalpy ΔH and the change in entropy ΔS

$$\Delta G = \Delta H - T\Delta S$$

Table 10.35 shows the enthalpy changes (ΔH) for the various stages in the above energy cycle.

Consider first the total enthalpy change ΔH for the dissociation of $\text{HX}_{(\text{hydrated})}$ into $\text{H}^+_{(\text{hydrated})} + \text{X}^-_{(\text{hydrated})}$. The ΔH values for the various halogen acids are all negative which means that energy is evolved in the process,

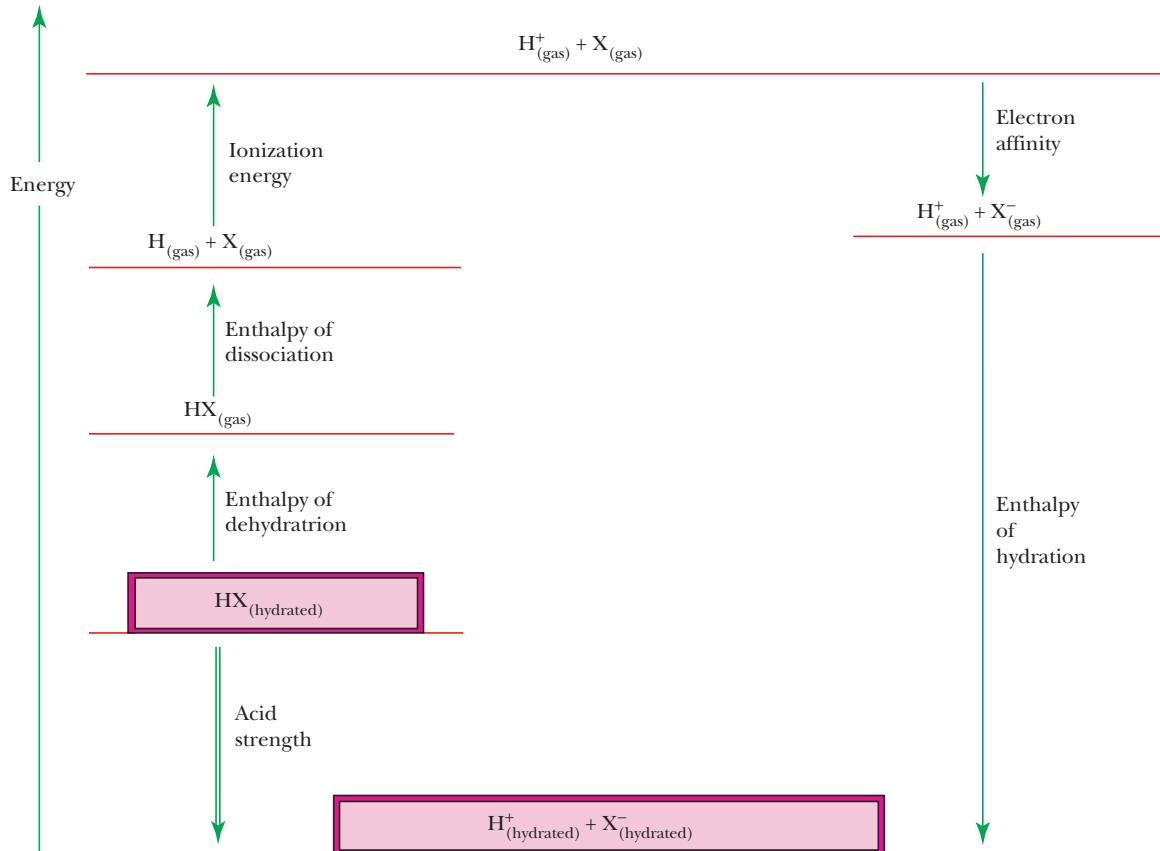


Figure 10.56 Energy cycle showing the acid strengths of the halogens.

Table 10.35 Energy cycle. (All values in kJ mol^{-1} .)

	Enthalpy dehydration	Enthalpy dissociation	Ionization energy $\text{H} \rightarrow \text{H}^+$	Electron affinity of X	Enthalpy hydration		Total ΔH	$T\Delta S$	$\Delta G =$ $(\Delta H - T\Delta S)$
					H^+	H^-			
HF	48	574	1311	-338	-1091	-513	-18	51	-69
HCl	18	428	1311	-355	-1091	-370	-68	56	-124
HBr	21	363	1311	-331	-1091	-339	-75	59	-134
HI	23	295	1311	-302	-1091	-394	-167	62	-229

so the change is thermodynamically possible. However, the value for HF is small compared with the values for HCl, HBr and HI. Thus HF is only slightly exothermic in aqueous solution whereas the others evolve a considerable amount of heat.

The low total ΔH value for HF is the result of several factors.

1. The enthalpies of dissociation show that the H—F bond is much stronger than the H—Cl, H—Br or H—I bonds. Thus the dissociation energy of HF is nearly twice that required to dissociate HI. (The strength of the HF bond is also shown by the short bond length of 1.0 Å compared with 1.7 Å in HI.)
2. The enthalpy of dehydration for the step $\text{HX}_{(\text{hydrated})} \rightarrow \text{HX}_{(\text{gas})}$ is much higher for HF than for the others. This is because of the strong hydrogen bonding which occurs in aqueous HF solutions.
3. The unexpectedly low value for the electron affinity of F^- also contributes, and though the enthalpy of hydration of F^- is very high, it is not enough to offset these other terms.

If allowance is made for the $T\Delta S$ term, the ΔH values can be converted into corresponding ΔG values. From these the dissociation constants are obtained: HF $k = 10^{-3}$, HCl $k = 10^8$, HBr $k = 10^{10}$ and HI $k = 10^{11}$.

The dissociation constants show quite clearly that HF is only very slightly ionized in water, and is therefore a weak acid. In a similar way, the others are almost totally dissociated, and are therefore strong acids.

Liquid HF has been used as a non-aqueous solvent. It undergoes self-ionization:



Acid–base reactions occur in this solvent system. However, the solvent itself has a very strong tendency to donate protons. Thus when the familiar mineral acids HNO_3 , H_2SO_4 and HCl are dissolved in HF, the mineral acids are forced to accept protons from the HF. Thus the so-called mineral acids are actually behaving as bases *in this solvent*. The very strong proton donating powers of HF mean that very few substances act as acids in HF. Perchloric acid is an exception, and it does behave as an acid. The only other known acids in liquid HF are fluoride acceptors such as SbF_5 , NbF_5 , AsF_5 and BF_3 . Many compounds react with HF, thus limiting its usefulness as a solvent. It is a useful medium for preparing fluoro complexes such as $[\text{SbF}_6]^-$, and fluorides.

10.61 | HALIDES

Ionic halides

Most halides where the metal has an oxidation state of (+I), (+II), or +(III) are ionic. This includes Group 1, Group 2 (except Be), the lanthanides, and *some* of the transition metals. Most ionic halides are soluble in water, giving hydrated metal ions and halide ions. A few are insoluble: LiF , CaF_2 , SrF_2 , BaF_2 , and the chlorides, bromides and iodides of Ag(+I), Cu(+I), Hg(+I) and Pb(+II).

Molecular (covalent) halides

Among the metals which show variable valency, the highest oxidation state is usually found with the fluorides. For a metal with variable oxidation states, the higher oxidation states will be covalent and the lower ones ionic. For example, PbCl_4 is covalent and PbCl_2 is ionic. Most of the more electronegative elements also form covalent halides, sometimes called molecular halides. For example, BCl_3 , SiCl_4 , PCl_5 , etc.

Bridging halides

Halide bridges are sometimes formed between two atoms. (Less commonly they are formed between three atoms.) Thus AlCl_3 forms a dimeric structure whereas BeF_2 and BeCl_2 form infinite chains. The bridges are depicted as the halogen forming one normal covalent bond, and donating a lone pair of electrons to form a second (coordinate) bond. Both bonds are identical. The bridge may be described in molecular orbital terms as a three-centre four-electron bond, which is already discussed in Chapter 3.

10.62 | HALOGEN OXIDES

The compounds with oxygen probably show greater differences between the different halogens than any other class of compound. Differences between F and the others arise for the usual reasons (small size, lack of d orbitals and high electronegativity). In addition oxygen is less electronegative than F, but more electronegative than Cl, Br and I. Thus binary compounds of F and O are fluorides of oxygen rather than oxides of fluorine. The other halogens are less electronegative than oxygen and thus form oxides. There is only a small difference in electronegativity between the halogens and oxygen, so the bonds are largely covalent. Rather surprisingly I_2O_4 and I_4O_9 are stable and ionic.

Most of the halogen oxides are unstable, and tend to explode when subjected to shock, or sometimes even when exposed to light. The iodine oxides are the most stable, then the chlorine oxides, but the bromine oxides all decompose below room temperature. The higher oxidation states are more stable than the lower states. Of the compounds shown in Table 10.36, ClO_2 , Cl_2O , I_2O_5 and OF_2 are the most important.

Table 10.36 Compounds of the halogens with oxygen (and their oxidation states)

Oxidation state	(-I) (+I)	(+IV)	(+V)	(+VI)	(+VIII)	Others
Fluorides	OF_2 (-I) O_2F_2 (-I)					O_4F_2
Oxides	Cl_2O (+I)	ClO_2		Cl_2O_6 ClO_3	Cl_2O_7	ClClO_4
	Br_2O (+I)	BrO_2	I_2O_5			I_4O_9 I_2O_4

Oxygen difluoride OF_2

OF_2 is a pale yellow gas, formed by passing F_2 into dilute (2%) NaOH .



OF_2 is a strong oxidizing agent, and has been used as a rocket fuel. It dissolves in water and gives a neutral solution, so it is not an acid anhydride. With NaOH it gives fluoride ions and dioxygen.

Dioxygen difluoride O_2F_2

O_2F_2 is an unstable orange-yellow solid, and is a violent oxidizing and fluorinating agent. It is formed by passing an electric discharge through a mixture of F_2 and O_2 at very low pressure and at liquid air temperature. It decomposes at -95°C . Its structure is similar to that of H_2O_2 , except that the O—O bond length of 1.22 Å is much shorter than the O—O distance of 1.48 Å in H_2O_2 . The O—F bond lengths are 1.58 Å, which is much longer than in OF_2 . Other oxyfluorides reported are: O_4F_2 , O_5F_2 and O_6F_2 .

Dichlorine monoxide Cl_2O

Cl_2O is a yellow-brown gas. It is commercially important. Both laboratory and commercial preparations are by heating freshly precipitated (yellow) mercuric oxide with the halogen gas diluted with dry air.



Cl_2O explodes in the presence of reducing agents, or NH_3 , or on heating.



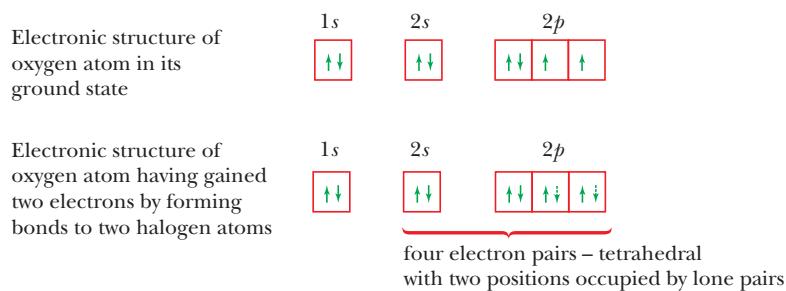
Cl_2O gas is very soluble in water (144 g Cl_2O dissolves in 100 g H_2O at -9°C), forming hypochlorous acid, and the two are in equilibrium.



Cl_2O dissolves in NaOH solution, forming sodium hypochlorite.



The structures of OF_2 , Cl_2O and Br_2O are all related to a tetrahedron with two positions occupied by lone pairs of electrons.



Repulsion between the lone pairs reduces the bond angle in F_2O from the tetrahedral angle of $109^\circ 28'$ to 103° (Figure 10.57). In Cl_2O (and presumably Br_2O) the bond angle is increased because of steric crowding of the larger halogen atoms.

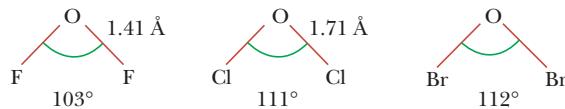


Figure 10.57 Bond angles in F_2O , Cl_2O and Br_2O .

Bleaching powder

Most of the Cl_2O produced is used to make hypochlorites. NaOCl is sold in aqueous solution. $\text{Ca}(\text{OCl})_2$ is a solid. An impure form mixed with $\text{Ca}(\text{OH})_2$ and CaCl_2 is sold as 'bleaching powder'. The latter is also made by passing Cl_2 into $\text{Ca}(\text{OH})_2$. These are used to bleach wood pulp and fabrics, and as disinfectants.

When allowed to stand for long, bleaching powder undergoes the following reactions.



Some important reactions depicting oxidizing property of bleaching powder are as follows.

1. $\text{Ca}(\text{OCl})\text{Cl} + \text{H}_2\text{S} \rightarrow \text{S} + \text{CaCl}_2 + \text{H}_2\text{O}$
2. $\text{Ca}(\text{OCl})\text{Cl} + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{CaCl}_2 + \text{H}_2\text{O}$
3. $\text{Ca}(\text{OCl})\text{Cl} + \text{KNO}_2 \rightarrow \text{CaCl}_2 + \text{KNO}_3$
4. $3\text{Ca}(\text{OCl})\text{Cl} + 2\text{NH}_3 \rightarrow \text{CaCl}_2 + 3\text{H}_2\text{O} + \text{N}_2$
5. $\text{Ca}(\text{OCl})\text{Cl} + 2\text{KI} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{KCl} + \text{H}_2\text{O} + \text{I}_2$



CaOCl_2 also reacts with acids to liberate chlorine.



Chlorine dioxide ClO_2

ClO_2 is a yellow gas which condenses to a deep red liquid, b.p. 11°C. In spite of its high reactivity (or perhaps because of this) ClO_2 is of commercial importance, and is the most important of the oxides. ClO_2 is a powerful oxidizing and chlorinating agent. Large quantities are used for bleaching wood pulp and cellulose, and for purifying drinking water. It is 30 times as effective as chlorine in bleaching flour (to make white bread).

ClO_2 liquid explodes above – 40°C. The gas detonates readily when concentrated above 50 mm Hg partial pressure. It explodes when mixed with reducing agents. Because of this, it is made in situ, and is used diluted with air or CO_2 . The safest laboratory preparation is from sodium chlorate and oxalic acid, as this automatically dilutes the gas with CO_2 .



The gas is made commercially from NaClO_3 . A pure product is formed using SO_2 . Using HCl causes contamination with Cl_2 , but this may be unimportant or even useful for bleaching and sterilization.



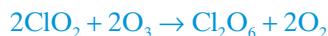
ClO_2 dissolves in water, evolving heat, and giving a dark green solution. This decomposes very slowly in the dark, but rapidly if illuminated.



It is also used to manufacture sodium chlorite NaClO_2 , which is also used for bleaching textiles and paper.



Some other reactions are:



The ClO_2 molecule is paramagnetic and contains an odd number of electrons. Odd electron molecules are generally highly reactive and ClO_2 is typical. Odd electron molecules often dimerize in order to pair the electrons, but ClO_2 does not. This is thought to be because the odd electron is delocalized. The molecule is angular with an O–Cl–O angle of 118°. The bond lengths are both 1.47 Å and are shorter than for single bonds.

Chlorine perchlorate $\text{Cl} \cdot \text{ClO}_4$

This can be made by the following reaction at – 45°C.



It is less stable than ClO_2 , and decomposes to O_2 , Cl_2 and Cl_2O_6 at room temperature.

Dichlorine hexoxide Cl_2O_6

Cl_2O_6 is a dark red liquid, which freezes to give a yellow solid at -180°C . Cl_2O_6 is in equilibrium with the monomer ClO_3 , and is made from ClO_2 and O_3 . The structure of neither the liquid nor the solid is known. Both are diamagnetic, and so have no unpaired electrons. Possible structures are shown in Figure 10.58.

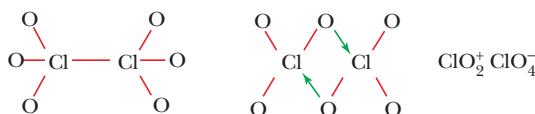


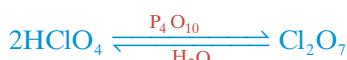
Figure 10.58 Possible structures of Cl_2O_6 .

Cl_2O_6 is a strong oxidizing agent and explodes on contact with grease. Hydrolysis of Cl_2O_6 with water or alkali gives chlorate and perchlorate. Reaction with anhydrous HF is reversible.



Dichlorine heptoxide Cl_2O_7

Cl_2O_7 is a colourless oily liquid. It is moderately stable and is the only exothermic oxide of chlorine, but it is shock sensitive. It is made by carefully dehydrating perchloric acid with phosphorus pentoxide, or H_3PO_4 at -10°C , followed by distillation at -35°C and a pressure of 1 mm Hg. Its structure is $\text{O}_3\text{Cl}-\text{O}-\text{ClO}_3$, with a bond angle of $118^\circ 36'$ at the central oxygen. It is less reactive than the lower oxides, and does not ignite organic materials. It reacts with water, forming perchloric acid.



10.63 | OXOACIDS

Table 10.37 The oxoacids of halogens

	HOX	HXO_2	HXO_3	HXO_4
Oxidation states of the halogens	(+I)	(+III)	(+V)	(+VII)
	* HOF			
	HOCl	HClO_2	HClO_3	HClO_4
	HOBr		HBrO_3	HBrO_4
	HOI		HIO_3	HIO_4

*F is in (-I) oxidation state.

Four series of oxoacids are known (Table 10.37). The structures of the ions formed are shown in Figure 10.59. All these structures are based on a tetrahedron. The sp^3 hybrid orbitals used for bonding form only weak σ bonds, because the s and p levels differ appreciably in energy. The ions are stabilized by strong $p\pi - d\pi$ bonding between full $2p$ orbitals on oxygen with empty d orbitals on the halogen atoms. Even so, many of the oxoacids are known only in solution, or as their salts.

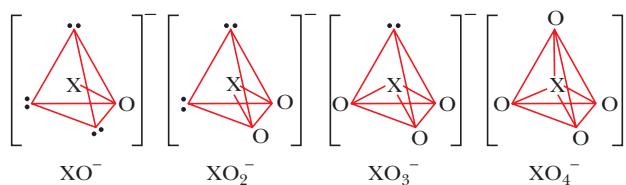


Figure 10.59 Structures of the oxoacids (skeleton only).

Fluorine has no *d* orbitals, and thus cannot form $p\pi - d\pi$ bonds. For a long time it was thought that F could not form any oxoacids. It is now known that HOF can be made under special conditions, but it is very unstable. No other oxoacids of F are known.

Hypohalous acids HOX

The hypohalous acids HOF, HOCl, HOBr and HOI are all known, and the halogen has the oxidation state (+I) except HOF where F is in -I, hydrogen is in +I and oxygen atom is in zero oxidation state.

HOF is a colourless unstable gas, first made in 1968. More recently HOF has been made by passing F_2 over ice at $0^\circ C$, and removing the product into a cold trap.



HOF is unstable, and decomposes on its own to HF and O_2 . It is a strong oxidizing agent and oxidizes H_2O to H_2O_2 quite readily. HOF should be a stronger acid than HOCl.

HOCl, HOBr and HOI are not very stable, and are known only in aqueous solutions. They are very weak acids, but they are good oxidizing agents especially in acidic solutions. They can be prepared by shaking the halogen with freshly precipitated HgO in water, for example:



Hypochlorous acid is the most stable. Sodium hypochlorite $NaOCl$ is well known, and is used extensively for bleaching cotton fabric, and as a domestic bleach. It is also used as a disinfectant and sterilizing agent. The halogens Cl_2 , Br_2 and I_2 all dissolve to some extent in water, forming hydrated X_2 molecules and X^- and OX^- ions.

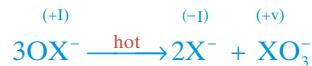


In a saturated solution of chlorine, about two thirds exists as hydrated molecules, and the rest as hydrochloric and hypochlorous acids. A much smaller amount of HOBr and a negligible amount of HOI are formed by similar means.

Dissolving the halogens in $NaOH$ can in principle be used to make all the hypohalite ions.



However, the hypohalite ions tend to disproportionate, particularly in basic solutions. The rate of the disproportionation reaction increases with temperature. Thus when Cl_2 dissolves in $NaOH$ at or below room temperature, a reasonably pure solution of $NaOCl$ and $NaCl$ is obtained. However, in hot solutions ($80^\circ C$) the sodium hypochlorite disproportionates rapidly, and a good yield of sodium chlorate is obtained.



Hypobromites can only be made at about $0^\circ C$: at temperatures above $50^\circ C$ quantitative yields of BrO_3^- are obtained.



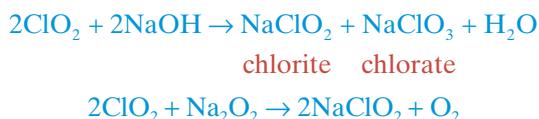
Hypoiodites disproportionate rapidly at all temperatures, and IO_3^- is produced quantitatively.

Halous acids HXO_2

The only halous acid known for certain is chlorous acid HClO_2 . This only exists in solution. It is a weak acid, but is stronger than HOCl . The chlorine atom exists in the oxidation state (+III). HClO_2 is made by treating barium chlorite with H_2SO_4 , and filtering off the BaSO_4 precipitate.



Salts of HClO_2 are called chlorites, and are made either from ClO_2 and sodium hydroxide, or ClO_2 and sodium peroxide.



Chlorites are used as bleaches. They are stable in alkaline solution even when boiled, but in acid solution they disproportionate, particularly when heated.

Halic acids HXO_3

Three halic acids are known: HClO_3 , HBrO_3 and HIO_3 . The halogen has the oxidation state (+V). HClO_3 and HBrO_3 are not very stable, but are known in solution, and as salts. HClO_3 and HBrO_3 detonate if attempts are made to evaporate them to dryness. The main reaction is:



In contrast, iodic acid HIO_3 is reasonably stable, and exists as a white solid. The halic acids all behave as strong oxidizing agents and strong acids.

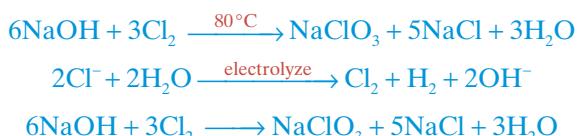
HIO_3 can be made by oxidizing I_2 with concentrated HNO_3 or O_3 . HClO_3 and HBrO_3 are made by treating the barium halates with H_2SO_4 , and filtering off the BaSO_4 .



Chlorates may be made in two ways:

1. Passing Cl_2 into a hot solution of NaOH .
2. Electrolysing hot chloride solutions that are vigorously stirred.

Only one sixth of the chlorine is converted to ClO_3^- , which appears very inefficient. However, the NaCl produced is electrolysed again, and is thus not wasted.



Chlorates and bromates decompose on heating, but the way they decompose is complex and is not fully understood. KClO_3 may decompose in two different ways, depending on the temperature.

1. Heating KClO_3 to 400–500°C is the well known laboratory experiment to produce dioxygen. It also gives a trace of Cl_2 or ClO_2 (though this is seldom mentioned). Decomposition occurs at 150°C if a catalyst such as MnO_2 or powdered glass is present to provide a surface from which O_2 can escape.



When $\text{Zn}(\text{ClO}_3)_2$ is heated it decomposes to O_2 and Cl_2 .



2. In the absence of a catalyst, especially at a lower temperature, KClO_3 tends to disproportionate to perchlorate and chloride.



Chlorates are much more soluble than bromates and iodates.

Chlorates are used to make fireworks and matches. Sodium chlorate is widely used as a powerful weedkiller. Its effects remain for some time, and it prevents growth for one growing season. Solid chlorates, bromates and iodates should be handled with care. Chlorates can explode on grinding, on heating, or if they come into contact with easily oxidized substances such as organic matter or sulphur. They are particularly dangerous in the solid form, but are much safer in solution. Solid sodium chlorate has been used by terrorists in making bombs.

Perhalic acids HXO_4

Perchloric and periodic acids and their salts are well known. Perbromates were unknown until 1968, and are not common.

NaClO_4 is made by electrolysing aqueous NaClO_3 using smooth platinum anodes in a steel container which also acts as the cathode. The platinum electrode gives a high oxygen overpotential, and thus prevents the electrolysis of water.



All other perchlorates and perchloric acid HClO_4 are made from NaClO_4 .

- NH_4ClO_4 is a white solid and was formerly used as a blasting compound in mining. It is now used in the booster rockets in the Challenger Space Shuttle to oxidize the fuel (Al powder). NH_4ClO_4 will absorb sufficient ammonia to liquefy itself.
- HClO_4 is used mostly to make other perchlorates. HClO_4 is a colourless liquid and can be made from NH_4ClO_4 and dilute nitric acid, or from NaClO_4 and concentrated hydrochloric acid.



In principle perchlorates could be made from the disproportionation of chlorates, but the reaction is slow and of little use.



HClO_4 is one of the strongest acids known. The anhydrous compound is a powerful oxidizing agent which explodes on contact with organic material (wood, paper, cloth, grease, rubber or chemicals), and sometimes on its own.

- Magnesium perchlorate MgClO_4 is used as the electrolyte in so-called 'dry batteries'. It is very hygroscopic, and is a very effective desiccant called 'anhydron'.
- KClO_4 is used in fireworks and flares.

Virtually all metal perchlorates, except those with the larger Group 1 ions K^+ , Rb^+ and Cs^+ , are soluble in water. The sparing solubility of KClO_4 is used to detect potassium in qualitative analysis. (A solution of NaClO_4 is added to the solution containing K^+ , and KClO_4 is precipitated.)

Strength of the oxoacids

HClO_4 is an extremely strong acid, whilst HOCl is a very weak acid. The dissociation of an oxoacid involves two energy terms:

- Breaking an O—H bond to produce a hydrogen ion and an anion.
- Hydrating both ions.

Plainly the ClO_4^- ion is larger than the OCl^- ion, so the hydration energy of ClO_4^- is less than that for OCl^- . This would suggest that HOCl should ionize more readily than HClO_4 . Since we know the reverse to be true, the reason must be the energy required to break the O—H bond.

Oxygen is more electronegative than chlorine. In the series of oxoacids HOCl , HClO_2 , HClO_3 , HClO_4 , an increasing number of oxygen atoms are bonded to the chlorine atom. The more oxygen atoms that are bonded, the more the electrons will be pulled away from the $\text{O}-\text{H}$ bond, and the more this bond will be weakened. Thus HClO_4 requires the least energy to break the $\text{O}-\text{H}$ bond and form H^+ . Hence HClO_4 is the strongest acid.

In general, for any series of oxoacids, the acid with the most oxygen (that is the one with the highest oxidation number) is the most dissociated. Thus the acid strengths decrease $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$. In exactly the same way, H_2SO_4 is a stronger acid than H_2SO_3 , and HNO_3 is a stronger acid than HNO_2 .

10.64 | INTERHALOGEN COMPOUNDS

The halogens react with each other to form interhalogen compounds. These are divided into four types AX , AX_3 , AX_5 and AX_7 . Some important interhalogen compounds are listed in Table 10.38.

Table 10.38 Interhalogen compounds, and their physical state at 25°C

AX	AX_3	AX_5	AX_7
ClF(g) Colourless			
BrF(g) Pale brown	$\text{ClF}_3(\text{g})$ Colourless		
BrCl(g) Red-brown	$\text{BrF}_3(\text{l})$ Pale yellow	$\text{ClF}_5(\text{g})$ Colourless	
ICl(s) Ruby red	$(\text{ICl}_3)_2(\text{s})$ Bright yellow	$\text{BrF}_5(\text{l})$ Colourless	$\text{IF}_7(\text{g})$ Colourless
IBr(s) Black	$(\text{IF}_3)(\text{s})$ (unstable) Yellow	$\text{IF}_5(\text{l})$ Colourless	
<u>(IF)* (unstable)</u>			

*Disproportionates rapidly into IF_5 and I_2 .

There are never more than two different halogens in a molecule. The bonds are essentially covalent because of the small electronegativity difference and the melting and boiling points increase as the difference in electronegativity increases.

The compounds formed in the AX and AX_3 groups are those where the electronegativity difference is not too great. The higher valencies AX_5 and AX_7 are shown by large atoms such as Br and I associated with small atoms such as F. This is because it is possible to pack more small atoms round a large one.

The interhalogens are generally more reactive than the halogens (except F_2). This is because the $\text{A}-\text{X}$ bond in interhalogens is weaker than the $\text{X}-\text{X}$ bond in the halogens. The reactions of interhalogens are similar to those of the halogens. Hydrolysis gives halide and oxohalide ions. Note that the oxohalide ion is always formed from the larger halogen present.



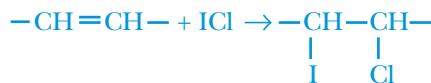
Interhalogen compounds will fluorinate many metal oxides, metal halides and metals.



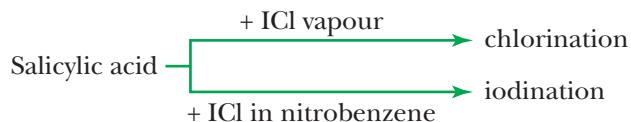
AX, AX₃ and AX₅ compounds

- Iodine monochloride ICl is well known. It is used as Wij's reagent in the estimation of the iodine number of fats and oils. The iodine number is a measure of the number of double bonds, i.e. the degree of unsaturation of the fat. The ICl adds to double bonds in the fat. The ICl solution is brown coloured,

and when it is added to an unsaturated fat the colour disappears until all the double bonds have reacted. The iodine number is simply the volume (ml) of a standard solution of ICl which reacts with a fixed weight of fat.



2. When ICl reacts with organic compounds it often iodinates them, though chlorination may occur depending on the conditions.



It is thought that the attacking species is I^+ , since the I atoms substitute in positions where there is an excess of electrons. Both ICl and IBr are partially ionized in the fused state. Conductivity measurements show that ICl ionizes to the extent of about 1%. Rather than form the simple ions I^+ and Cl^- , the ions are solvated.



3. The order of reactivity of the interhalogens is:



4. ICl_3 does not exist, but the dimer I_2Cl_6 is a bright yellow solid. Its structure (Figure 10.60) is planar. The terminal I—Cl bonds are normal single bonds of length 2.38 Å and 2.39 Å. The bridging I—Cl bonds are appreciably longer (2.68 Å and 2.72 Å), suggesting delocalized bonding rather than simple halogen bridges formed by coordinate bonds from Cl to I. The liquid has an appreciable electrical conductivity, due to self-ionization:

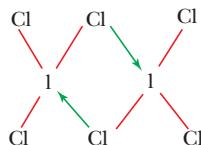


Figure 10.60 Structure of I_2Cl_6 .



It has been less studied as an ionizing solvent than the others because the gas decomposes into ICl and Cl_2 .

5. Liquid IF_5 self-ionizes, and therefore conducts electricity.



10.65 | POLYHALIDES

Halide ions often react with molecules of halogens or interhalogens and form polyhalide ions. Iodine is only slightly soluble in water (0.34 g l^{-1}). Its solubility is greatly increased if some iodide ions are present in the solution. The increase in solubility is due to the formation of a polyhalide ion, in this case the triiodide ion I_3^- . This is stable both in aqueous solution and in ionic crystals.

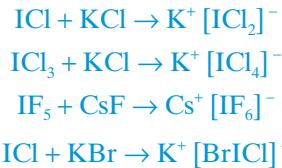


The I-I distances in $[\text{Me}_4\text{N}]^+[\text{I}_3^-]$ are 2.92 Å. If the bond length of 2.66 Å in I_2 is taken as a normal single bond, the bonds in I_3^- are very weak.

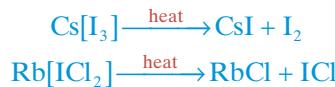
More complex ions such as pentaiodide I_5^- , heptaiodide I_7^- and enneaiodide I_9^- have also been prepared. Crystalline compounds containing the larger polyiodide ions generally contain large metal ions such as Cs^+ or large complex cations such as R_4N^+ . This is because a large anion together with a large cation give a high coordination number and hence a high lattice energy. Polyhalides such as $\text{KI}_3 \cdot \text{H}_2\text{O}$, RbI_3 , NH_4I_5 , $[(\text{C}_2\text{H}_5)_4\text{N}]\text{I}_7^-$ and $\text{RbI}_9 \cdot 2\text{C}_6\text{H}_6$ may be formed by the direct addition of I_2 to I^- , either with or without a solvent.

The Br_3^- ion is much less stable and less common than I_3^- . A few unstable Cl_3^- compounds are known, and the ion is formed in concentrated solution. F_3^- compounds are also known now-a-days (see Molecular Orbital Theory).

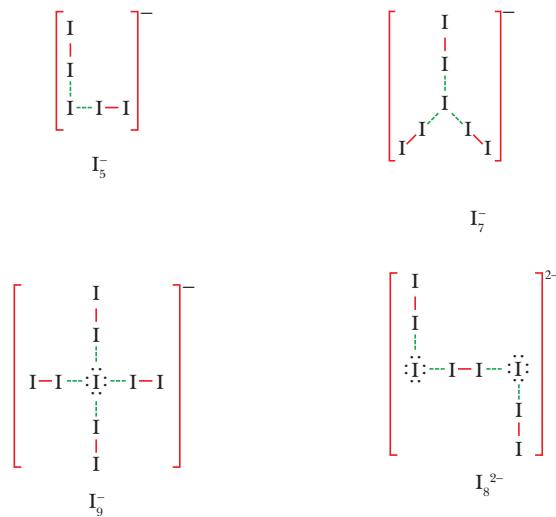
Many polyhalides are known which contain two or three different halogens, for example $\text{K}[\text{ICl}_2]$, $\text{K}[\text{ICl}_4]$, $\text{Cs}[\text{IBrF}]$ and $\text{K}[\text{IBrCl}]$. These are formed from interhalogens and metal halides.



Polyhalides are typical ionic compounds (crystalline, stable and soluble in water, conduct electricity when in solution), though they tend to decompose on heating. The products of the decomposition (that is which halogen remains attached to the metal) are governed by the lattice energy of the products. The lattice energy of the alkali metal halides is highest for the smaller halide ions, so the smaller halogen remains bonded to the metal.



The structures of the polyhalides are known. The trihalides $\text{K}[\text{I}_3]$, $\text{K}[\text{ICl}_2]$ and $\text{Cs}[\text{IBrF}]$ all contain a linear trihalide ion. Structure of I_5^- , I_7^- , I_8^{2-} are given as follows.



10.66 | PSEUDOHALOGENS AND PSEUDOHALIDES

A few ions are known, consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. They are therefore called pseudohalide ions (Table 10.39). Pseudohalide ions are univalent, and these form salts resembling the halide salts. For example, the sodium salts are soluble in water, but the silver salts are insoluble. The hydrogen compounds are acids like the halogen acids HX .

Table 10.39 The important pseudohalogens

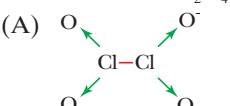
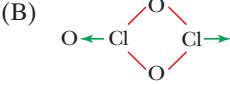
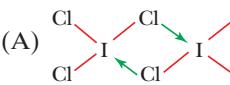
Anion	Acid	Dimer	
CN^-	Cyanide ion	HCN	Hydrogen cyanide
SCN^-	Thiocyanate ion	HSCN	Thiocyanic acid
SeCN^-	Selenocyanate ion		
OCN^-	Cyanate ion	HO CN	Cyanic acid
NCN^{2-}	Cyanamide ion	H_2NCN	Cyanamide
ONC^-	Fulminate ion	HONC	Fulminic acid
N_3^-	Azide ion	HN_3	Hydrogen azide

Some of the pseudohalide ions combine to form dimers comparable with the halogen molecules X_2 . These include cyanogen (CN_2), thiocyanogen (SCN_2) and selenocyanogen (SeCN_2).

The best known pseudohalide is CN^- . This resembles Cl^- , Br^- and I^- in the following respects:

1. It forms an acid HCN.
2. It can be oxidized to form a molecule cyanogen (CN_2).
3. It forms insoluble salts with Ag^+ , Pb^{2+} and Hg^+ .
4. Interpseudohalogen compounds ClCN , BrCN and ICN can be formed.
5. AgCN is insoluble in water but soluble in ammonia, as is AgCl .
6. It forms a large number of complexes similar to halide complexes, e.g. $[\text{Cu}(\text{CN})_4]^{2-}$ and $[\text{CuCl}_4]^{2-}$, and $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{CoCl}_6]^{3-}$

SINGLE CORRECT CHOICE TYPE QUESTIONS

1. The state of hybridization in anionic part of solid Cl_2O_6 is
(A) sp^3d^2 (B) sp^3d (C) sp^3 (D) sp^2
2. The structure of Cl_2O_4 is
(A) 
(B) 
(C) $\text{Cl}^+\text{ClO}_4^-$
(D) None of these
3. Liquid I_2Cl_6 has the structure
(A) 
(B) $[\text{ICl}_2]^+[\text{ICl}_4]^-$
(C) monomeric T-shaped
(D) None of these
4. Which of the following processes is not feasible spontaneously?
(A) $\text{H}_2\text{O} + \text{F}_2 \rightarrow \text{HF} + \text{HOF}$
(B) $\text{H}_2\text{O} + \text{Cl}_2 \rightarrow \text{HCl} + \text{HOCl}$
(C) $\text{H}_2\text{O} + \text{Br}_2 \rightarrow 2\text{HBr} + [\text{O}]$
(D) $\text{H}_2\text{O} + \text{I}_2 \rightarrow 2\text{HI} + [\text{O}]$
5. Etching action of HF does not involve
(A) formation of SiF_4 .
(B) corrosion of vessel wall.
(C) formation of H_2SiF_6 .
(D) white marking on laboratory ware.
6. In the following statements, which combination of **true (T)** and **false (F)** options is correct?
I. All oxoacids of chlorine undergo disproportionation on heating.
II. ClO_2 does not dimerize but Cl_2O_4 exists.
III. Six Cl–O bonds in Cl_2O_7 are the same.
IV. $\text{Rb}[\text{ClI}_2]$ on heating produces $\text{RbI} + \text{Cl}_2$.
(A) FTTF
(B) FTTT
(C) TTTF
(D) FFTF
7. Salicylic acid reacts with ICl vapour to produce
(A) iodinated product.
(B) chlorinated product.
(C) mixture of both.
(D) virtually no reaction.
8. In the following statements, which combination of **true (T)** and **false (F)** options is correct?
I. Ionic mobility is the highest for I^- in water as compared to other halides.
II. Stability order is: $\text{Cl}_3^- > \text{Br}_3^- > \text{I}_3^-$
III. Reactivity order is: $\text{F} < \text{Cl} < \text{Br} < \text{I}$
IV. Oxidizing power order is: $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$

- (A) TFTF
(B) TFFF
(C) TFFT
(D) FTFT
9. Which of the following has the maximum vapour pressure?
(A) HCl
(B) HBr
(C) HF
(D) HI
10. Halogens are coloured because
(A) they are diamagnetic.
(B) they are paramagnetic.
(C) HOMO-LUMO transition takes place by absorption of visible light.
(D) HOMO-LUMO transition takes place by absorption of any kind of light.

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. For purification of Cl_2 obtained from MnO_2 , it is passed through
(A) water to remove HCl.
(B) HCl to remove water.
(C) conc. H_2SO_4 to remove water.
(D) CaO or P_4O_{10} to remove water.
2. Which of following properties decrease(s) down the group from F to I?
(A) X^- radius
(B) Hydration energy of X^-
(C) Electron affinity magnitude of X
(D) IE_1 of X
3. Which of the following orders is/are correct?
(A) Thermal stability order: $\text{HOX} < \text{H}X\text{O}_2 < \text{H}X\text{O}_3 < \text{H}X\text{O}_4$
(B) Oxidizing power order: $\text{HOX} < \text{H}X\text{O}_2 < \text{H}X\text{O}_3 < \text{H}X\text{O}_4$
- (C) Bond angle order: $\text{ClO}_2 > \text{Cl}_2\text{O} > \text{H}_2\text{O} > \text{Cl}_2\text{S}$
(D) Intensity of colour order: $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$
4. Which of the following reactions is/are the proof for the existence of ion pair in Cl_2O_6 in solid state?
(A) $\text{Cl}_2\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{HClO}_3 + \text{HClO}_4$
(B) $\text{Cl}_2\text{O}_6 + \text{HF} \rightarrow \text{ClO}_2\text{F} + \text{HClO}_4$
(C) $\text{Cl}_2\text{O}_6 + \text{NO}_2 \rightarrow \text{ClO}_2 + [\text{NO}_2]^+[\text{ClO}_4]^-$
(D) None of these
5. Which of the following processes can give Cl_2 gas as a product?
(A) Electrolysis of aq. NaCl.
(B) Oxidation of conc. HCl by K_2CrO_4 .
(C) Electrolysis of very dilute aq. NaCl.
(D) Oxidation of conc. HCl by MnO_2 .

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1 to 3

Preparation of F_2 by Moissan's method faces a lot of difficulties of different kinds and one of the main reason for this is the high reactivity of F_2 .

1. The purpose of addition of KF in the electrolyte is
(A) to lower down the melting temperature of the mixture.
(B) to increase the melting temperature of the mixture.
(C) to lower down the electrical conductivity of the mixture.
(D) to increase the electrical conductivity of the mixture.
2. Initially Moissan used the HF:KF in the ratio of 13 : 1. But there was a serious drawback with this due to high vapour pressure of HF which causes problems of toxicity and corrosion. To solve this problem, which of the following steps were followed?
(A) The temperature was decreased to -24°C .
(B) Mole ratio is changed into 2 : 1
(C) (A) and (B) were both done together
(D) None of the above.

3. Which of the following precautions is/are taken for this process?
(A) Container of electrolysis must not be made of glass.
(B) HF produced must be free from water by which it is distilled to prepare anhydrous HF before putting into electrolyte.
(C) The liberated H_2 at cathode must be separated from the fluorine liberated at the anode by a diaphragm.
(D) All of the above

Passage 2: For Questions 4 and 5

All the halogens react with hydrogen to form hydrogen halides HX but in general this not the method of preparation.

4. Preparation of which HX is not associated with conc. H_2SO_4 ?
(A) HF (B) HCl (C) HBr (D) HI
5. Which of the following statements is incorrect regarding HX ?

- (A) HCl and HBr are liquid at room temperature.
 (B) HI is the most acidic among HX.
 (C) HF is the only liquid at room temperature.
 (D) HF shows hydrogen bonding in its vapour state also.

Passage 3: For Questions 6 and 7

When Cl_2 gas is heated with freshly precipitated HgO in the presence of dry air, a yellow-brown gas (A) is formed. Gas A explodes in presence of NH_3 and it is highly soluble in H_2O .

6. Gas A is
 (A) Cl_2O
 (B) ClO_2
 (C) ClO_3
 (D) Cl_2O_7
7. The product(s) on explosion of gas A with NH_3 is/are
 (A) NH_4Cl
 (B) H_2O
 (C) N_2
 (D) All of these

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
 (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
 (C) If Statement I is true but Statement II is false.
 (D) If Statement I is false and Statement II is true.

1. **Statement I:** 1, 2-Dibromoethane is added to petrol to act as lead scavenger.

Statement II: 1, 2-Dibromoethane prevents the buildup of lead deposits on the sparking plug and in the engine.

2. **Statement I:** Br_2 gas is passed through Na_2CO_3 solution for its purification.

Statement II: NaBr and NaOBr produced are acidified to get back Br_2 .

3. **Statement I:** Fluorine has highest oxidizing power.

Statement II: Electron affinity of chlorine is higher than that of fluorine.

4. **Statement I:** $\text{I}_2 + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{I}^- + \frac{1}{2}\text{O}_2$ (Spontaneous)

Statement II: Atmospheric dioxygen oxidizes iodide ions to iodine.

5. **Statement I:** F_3^- is known.

Statement II: F^- ion donates its lone pair into the vacant $\sigma_{2p_x}^+$ orbital of F_2 molecule.

INTEGER ANSWER TYPE QUESTIONS

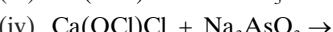
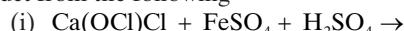
The answer to each of the following is a non-negative integer.

1. The number of oxides present in didymium oxide used for modified Deacon process as a catalyst is ____

2. Find the number of identical angles in Cl_2O_7 .

3. The sum of the oxidation states of Cl atoms in bleaching powder of formula $\text{Ca}(\text{OCl})\text{Cl}$ is ____

4. Find the number of reactions where CaCl_2 is the product from the following



5. How many of the following oxides exist in ion pair form?



6. How many of the following oxides have higher bond angle than F_2O ?
 $\text{H}_2\text{O}, \text{Cl}_2\text{O}, \text{ClO}_2, \text{Br}_2\text{O}$

7. When SiF_4 reacts with HF, in the product formed how many of the d -orbitals from its valence shell are not used?

8. Find the number of H-bonds present in cyclic $(\text{HF})_6$ molecule in its gas phase.

9. Find the number of π -bonds in $(\text{CN})_2$.

10. Find the number of pseudohalide ions from the following.



11. The number of equivalent Cl–O bonds in Cl_2O_7 is ____.

12. HF is a weak acid but on addition of AsF_5 , it becomes a very strong acid. The number of 90° angles in the anionic part of the product is ____.

MATRIX MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as **(A)**, **(B)**, **(C)** and **(D)**, while those in Column II are labelled as **(P)**, **(Q)**, **(R)**, **(S)** and **(T)**. Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the compounds with the characteristics..

Column I	Column II
(A) F_2	(P) Diamagnetic in nature.
(B) Cl_2	(Q) Coloured substance but not gaseous at room temperature.
(C) Br_2	(R) Reacts with water and produces acid.
(D) I_2	(S) X_2 which cannot oxidize any of the halide ions.

2. Match the reactions with the compounds which are prepared by these.

Column I	Column II
(A) $Ba(ClO_2)_2 + H_2SO_4 \rightarrow$	(P) ClO_2
(B) $F_2 + H_2O \xrightarrow{-40^\circ C} \rightarrow$	(Q) ClO_3

Column I	Column II
(C) $HClO_4 \xrightarrow[-10^\circ C]{P_2O_{10}}$	(R) Cl_2O_7
(D) $NaClO_5 + SO_2 + H_2SO_4 \xrightarrow{\text{trace of NaCl}}$	(S) HOF
	(T) $HClO_2$

3. Match the hydrogen halides with their properties.

Column I	Column II
(A) HF	(P) Most volatile compound.
(B) HCl	(Q) Strongest reducing agent.
(C) HBr	(R) Compound shows H-bonding.
(D) HI	(S) On reaction with conc. H_2SO_4 produces X_2 type of molecule.

ANSWERS**Single Correct Choice Type Questions**

- 1.** (C) **3.** (B) **5.** (A) **7.** (B) **9.** (A)
2. (C) **4.** (D) **6.** (A) **8.** (B) **10.** (C)

Multiple Correct Choice Type Questions

- 1.** (A), (C), (D) **2.** (B), (D) **3.** (A), (C), (D) **4.** (A), (B), (C) **5.** (A), (B), (D)

Comprehension Type Questions

- 1.** (D) **3.** (D) **5.** (B), (C), (D) **7.** (D)
2. (B) **4.** (C), (D) **6.** (A)

Assertion–Reasoning Type Questions

- 1.** (A) **2.** (C) **3.** (B) **4.** (D) **5.** (A)

Integer Answer Type Questions

- 1.** 2 **3.** 0 **5.** 2 **7.** 3 **9.** 4 **11.** 6
2. 6 **4.** 3 **6.** 4 **8.** 6 **10.** 4 **12.** 12

Matrix–Match Type Questions

- 1.** (A) \rightarrow (P) (R)
(B) \rightarrow (P), (R)
(C) \rightarrow (P), (Q), (R)
(D) \rightarrow (P), (Q), (T)
2. (A) \rightarrow (T)
(B) \rightarrow (S)
(C) \rightarrow (R)
(D) \rightarrow (P)
3. (A) \rightarrow (R)
(B) \rightarrow (P)
(C) \rightarrow (S)
(D) \rightarrow (Q), (S)

PART 6: THE GROUP 18 ELEMENTS – NOBLE GASES

The elements of Group 18 have been called ‘the inert gases’ and ‘the rare gases’. Both are misnomers, since the discovery of the xenon fluorides in 1962 shows that xenon is not inert, and argon makes up 0.9% by volume of the atmosphere. The name ‘noble gases’ implies that they tend to be unreactive, in the same way that the noble metals are often reluctant to react and are the least reactive metals.

Table 10.40 Electronic structures

Element	Symbol	Electronic structure	
Helium	He		$1s^2$
Neon	Ne	[He]	$2s^2 2p^6$
Argon	Ar	[Ne]	$3s^2 3p^6$
Krypton	Kr	[Ar]	$3d^{10} 4s^2 4p^6$
Xenon	Xe	[Kr]	$4d^{10} 5s^2 5p^6$
Radon	Rn	[Xe]	$4f^{14} 5d^{10} 6s^2 6p^6$

Helium has two electrons which form a complete shell $1s^2$. The other noble gases have a closed octet of electrons in their outer shell $ns^2 np^6$ (Table 10.40). This electronic configuration is very stable and is related to their chemical inactivity. These atoms have an electron affinity of zero (or slightly negative), and have very high ionization energies – higher than any other elements. Under normal conditions the noble gas atoms have little tendency to gain or lose electrons. Thus they have little tendency to form bonds, and so they exist as single atoms.

10.67 | OCCURRENCE AND RECOVERY OF THE ELEMENTS

The gases He, Ne, Ar, Kr and Xe all occur in the atmosphere. A mixture of the noble gases was first obtained by Cavendish in 1784. Cavendish removed N_2 from air by adding excess O_2 and sparking. The NO_2 formed was absorbed in $NaOH$ solution. The excess O_2 was removed by burning with S, and absorbing the SO_2 in $NaOH$ solution. This gave a small volume of unreactive gas.

Ar is quite abundant and can be recovered by fractional distillation of liquid air. It constitutes 0.93% by volume of air (i.e. 9300 ppm). It originates in the air mostly from electron capture (β^+ decay) of potassium:



The other noble gases are much less abundant. The non-radioactive noble gases are all produced industrially by fractional distillation of liquid air. This gives large amounts of dinitrogen and dioxygen, and only a small amount of the noble gases. (The dioxygen is mainly used for steel making.) Of the noble gases, Ar is obtained in the largest amounts, and it is the cheapest.

10.68 | USES OF THE ELEMENTS

The largest use of Ar is to provide an inert atmosphere for metallurgical processes.

Helium has the lowest boiling point of any liquid, and it is used in cryoscopy to obtain the very low temperatures required for superconductivity, and lasers. It is used in weather balloons and airships. Though H_2 has a lower density and is cheaper and more readily available than He, H_2 is highly flammable. Thus on safety grounds He is used in preference to H_2 in airships. He is much less dense than air. One cubic metre of He gas at atmospheric pressure can lift 1 kg. Helium is used in preference to dinitrogen to dilute dioxygen in the gas cylinders used by divers. This is because dinitrogen is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of N_2 in the blood. This causes the painful (or fatal) condition called ‘bends’. Helium is only slightly soluble so the risk of ‘bends’ is reduced.

Small amounts of Ne are used in neon discharge tubes which give the familiar reddish orange glow of ‘neon’ signs. The other gases are also used in discharge tubes to give different colours.

10.69 | PHYSICAL PROPERTIES

The elements are all colourless, odourless monatomic gases. The enthalpy of vaporization is a measure of the forces holding the atoms together. The values are very low because the only forces between the atoms are very weak van der Waals forces. The enthalpy of vaporization increases down the group as the polarizability of the atoms increases.

Because the interatomic forces are very weak, the melting points and boiling points are also very low. The boiling point of He is the lowest of any element, only four degrees above absolute zero.

The atomic radii of the elements are all very large, and increase on descending the group. It must be noted that these are non-bonded radii, and should be compared with the van der Waals radii of other elements rather than with covalent (bonded) radii. (See Table 10.41.)

Table 10.41 Physical properties of the noble gases

	First ionization energy (kJ mol ⁻¹)	Enthalpy of vaporization (kJ mol ⁻¹)	Melting point (°C)	Boiling point (°C)	Atomic radii (Å)	Abundance in atmosphere (% volume)
He	2372	0.08		-269.0	1.20	5.2×10^{-4}
Ne	2080	1.7	-248.6	-246.0	1.60	1.5×10^{-3}
Ar	1521	6.5	-189.4	-186.0	1.91	0.93
Kr	1351	9.1	-157.2	-153.6	2.00	1.1×10^{-4}
Xe	1170	12.7	-111.8	-108.1	2.20	8.7×10^{-6}
Rn	1037	18.1	-71	-62		

The noble gases are all able to diffuse through glass, rubber and plastic materials, and some metals. This makes them difficult to handle in the laboratory, particularly since glass Dewar flasks cannot be used for low temperature work.

10.70 | SPECIAL PROPERTIES OF HELIUM

Helium is unique. It has the lowest boiling point of any substance known. All other elements become solids on cooling, but cooling only produces helium liquid. It only forms a solid under high pressure (about 25 atmospheres). There are two different liquid phases. Helium I is a normal liquid, but helium II is a superfluid. A superfluid is a most unusual state of matter. Normally atoms are free to move in a gas, can move in a more restricted way in a liquid, and can only vibrate about fixed positions in a solid. As the temperature decreases, the amount of thermal motion of atoms decreases, and gases become liquids, and eventually solids. When the temperature of helium gas is lowered to 4.2 K it liquifies as helium I. Rather surprisingly the liquid continues to boil vigorously. At 2.2 K, the liquid suddenly stops boiling (which with normal materials is when a solid is formed). In this case helium II is formed. This is still a liquid because the interatomic forces are not strong enough to form a solid, but thermal motion of the atoms has actually stopped. Helium I is a normal liquid, and when it changes to helium II at the λ -point temperature, many physical properties change abruptly. The specific heat changes by a factor of 10. The thermal conductivity increases by 10^6 and becomes 800 times greater than for copper. It becomes a superconductor (i.e. shows zero electrical resistance). The viscosity becomes effectively zero and 1/100th of that of gaseous hydrogen. It spreads to cover all surfaces at temperatures below the λ -point. Thus *the liquid can actually flow up the sides of the vessel* and over the edge until the levels on both sides are the same. The surface tension and compressibility are also anomalous.

10.71 | CHEMICAL PROPERTIES OF THE NOBLE GASES

The noble gases were isolated and discovered because of their lack of reactivity. For a long time it was thought that they really were chemically inert. Before 1962, the only evidence for compound formation by the noble gases was some molecular ions formed in discharge tubes, and clathrate compounds.

Molecular ions formed under excited conditions

Several molecular ions such as He_2^+ , HeH^+ , HeH^{2+} and Ar_2^+ are formed under high energy conditions in discharge tubes. They only survive momentarily and are detected spectroscopically. Neutral molecules such as He_2 are unstable.

Clathrate compounds

Clathrate compounds of the noble gases are well known. Normal chemical compounds have ionic or covalent bonds. However, in the clathrates atoms or molecules of the appropriate size are trapped in cavities in the crystal lattice of other compounds. *Though the gases are trapped, they do not form bonds.*

If an aqueous solution of quinol (1,4-dihydroxybenzene) is crystallized under a pressure of 10–40 atmospheres of Ar, Kr or Xe, the gas becomes trapped in cavities of about 4 Å diameter in the β -quinol structure. When the clathrate is dissolved, the hydrogen bonded arrangement of β -quinol breaks down and the noble gas escapes. Other small molecules such as O_2 , SO_2 , H_2S , MeCN and CH_3OH form clathrates as well as Ar, Kr and Xe. The smaller noble gases He and Ne do not form clathrate compounds because the gas atoms are small enough to escape from the cavities. The composition of these clathrate compounds corresponds to 3 quinol: 1 trapped molecule, though normally all the cavities are not filled.

The gases Ar, Kr and Xe may be trapped in cavities in a similar way when water is frozen under a high pressure of the gas. These are clathrate compounds, but are more commonly called ‘the noble gas hydrates’. They have formulae approximating to $6\text{H}_2\text{O}:1$ gas atom. He and Ne are not trapped because they are too small. The heavier noble gases can also be trapped in cavities in synthetic zeolites, and samples have been obtained containing up to 20% of Ar by weight. Clathrates provide a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.

10.72 | CHEMISTRY OF XENON

The first real compound of the noble gases was made in 1962. Bartlett and Lohman had previously used the highly oxidizing compound platinum hexafluoride to oxidize dioxygen.



The first ionization energy for $\text{O}_2 \rightarrow \text{O}_2^+$ is 1165 kJ mol⁻¹, which is almost the same as the value of 1170 kJ mol⁻¹ for $\text{Xe} \rightarrow \text{Xe}^+$. It was predicted that xenon should react with PtF_6 . Experiments showed that when deep red PtF_6 vapour was mixed with an equal volume of Xe, the gases combined immediately at room temperature to produce a yellow solid. They (incorrectly) thought the product obtained was xenon hexafluoroplatinate(V), $\text{Xe}^+ [\text{PtF}_6]^-$. The reaction has since been shown to be more complicated, and the product is really $[\text{XeF}]^+ [\text{Pt}_2\text{F}_{11}]^-$.



Soon after this it was found that Xe and F_2 reacted at 400 °C to give a colourless volatile solid XeF_4 . This has the same number of valency electrons as, and is isostructural with, the polyhalide ion $[\text{ICl}_4]^-$. Following these discoveries there was a rapid extension of the chemistry of the noble gases, and in particular of xenon.

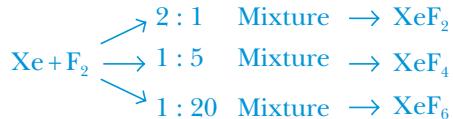
The ionization energies of He, Ne and Ar are much higher than for Xe, and are too high to allow the formation of similar compounds. The ionization energy for Kr is a little lower than for Xe, and Kr does form KrF_2 . The ionization energy of Rn is less than for Xe, and Rn might be expected to form compounds similar to those of Xe. Rn is radioactive, has no stable isotopes, and all the isotopes have short half lives. This has limited work on radon compounds, and only RnF_2 and a few complexes are known.

Xe reacts directly only with F_2 . However, oxygen compounds can be obtained from the fluorides. There is some evidence for the existence of XeCl_2 and XeCl_4 , and one compound is known with a Xe–N bond. Thus there is quite an extensive chemistry of Xe. The principal compounds are listed in Table 10.42.

Table 10.42 Structures of some xenon compounds

Formula	Name	Oxidation state	M.p. (°C)	Structure
XeF ₂	Xenon difluoride	(+II)	129	Linear (RnF ₂ and XeCl ₂ are similar)
XeF ₄	Xenon tetrafluoride	(+IV)	117	Square planar (XeCl ₄ is similar)
XeF ₆	Xenon hexafluoride	(+VI)	49.6	Distorted octahedron
XeO ₃	Xenon trioxide	(+VI)	Explodes	Pyramidal (tetrahedral with one corner unoccupied)
XeO ₂ F ₂		(+VI)	30.8	Trigonal bipyramidal (with one position unoccupied)
XeOF ₄		(+VI)	-46	Square pyramidal (octahedral with one position unoccupied)
XeO ₄	Xenon tetroxide	(+VIII)	-35.9	Tetrahedral
XeO ₃ F ₂		(+VIII)	-54.1	Trigonal bipyramidal
Ba ₂ [XeO ₆] ⁴⁻	Barium perxenate	(+VIII)	dec. > 300	Octahedral

Xenon reacts directly with fluorine when the gases are heated at 400 °C in a sealed nickel vessel, and the products depend on the F₂/Xe ratio.



The compounds XeF₂, XeF₄ and XeF₆ are all white solids. They can be sublimed at room temperature, and can be stored indefinitely in nickel or Monel containers. The lower fluorides form higher fluorides when heated with F₂ under pressure. The fluorides are all extremely strong oxidizing and fluorinating agents. They react quantitatively with hydrogen follows:



They oxidize Cl⁻ to Cl₂, I⁻ to I₂ and cerium(III) to cerium(IV):



They fluorinate compounds:



XeF₂ is now commercially available and is quite widely used in synthetic organic chemistry. It can oxidize and fluorinate the 'hetero element' in an organometallic compound, but does not attack the alkyl or aryl groups.



If XeF_2 is mixed with anhydrous HF its reactivity is greatly increased, possibly due to the formation of XeF^+ .



The fluorides differ in their reactivity with water. XeF_2 is soluble in water, but undergoes slow hydrolysis. Hydrolysis is more rapid with alkali.



XeF_4 reacts violently with water, giving xenon trioxide XeO_3 .



XeF_6 also reacts violently with water, but slow hydrolysis by atmospheric moisture gives the highly explosive solid XeO_3 .



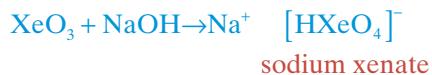
With small quantities of water, partial hydrolysis occurs, giving a colourless liquid xenon oxofluoride XeOF_4 . The same product is formed when XeF_6 reacts with silica or glass:



XeO_3 is an explosive white hygroscopic solid. It reacts with XeF_6 and XeOF_4 .



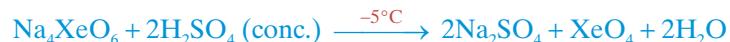
XeO_3 is soluble in water, but does not ionize. However, in alkaline solution above pH 10.5 it forms the xenate ion $[\text{HXeO}_4]^-$.



Xenates contain Xe(+VI) and they slowly disproportionate in solution to perxenates (which contain Xe(+VIII)) and Xe.



Several perxenates of Group 1 and 2 metals have been isolated, and the crystal structures of $\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_4\text{XeO}_6 \cdot 8\text{H}_2\text{O}$ have been determined by X-ray crystallography. The solubility of sodium perxenate in 0.5 M NaOH is only 0.2 grams per litre, so precipitation of sodium perxenate could be used as a gravimetric method of analysis for sodium. Perxenates are extremely powerful oxidizing agents, which will oxidize HCl to Cl_2 , H_2O to O_2 , and Mn^{2+} to MnO_4^- . With concentrated H_2SO_4 they give xenon tetroxide XeO_4 , which is volatile and explosive.



Xenon fluoride complexes

XeF_2 acts as a fluoride donor and forms complexes with covalent pentafluorides including PF_5 , AsF_5 , SbF_5 and the transition metal fluorides NbF_5 , TaF_5 , RuF_5 , OsF_5 , RhF_5 , IrF_5 and PtF_5 . These are thought to have the structure



and



The structures of some of the XeF_2 complexes in the solid state are known. In the complex $\text{XeF}_2 \cdot 2\text{SbF}_5$ (Figure 10.61), the two $\text{Xe}-\text{F}$ distances differ greatly (1.84 Å and 2.35 Å). This suggests the formulation $[\text{XeF}]^+ [\text{Sb}_2\text{F}_{11}]^-$. However, the $\text{Xe}-\text{F}$ distance of 2.35 Å is much less than the van der Waals (non-bonded) distance of 3.50 Å. This suggests that one fluorine atom forms a fluorine bridge between Xe and Sb . In fact the structure is intermediate between that expected for the ionic structure, and that for the fully covalent bridge structure.

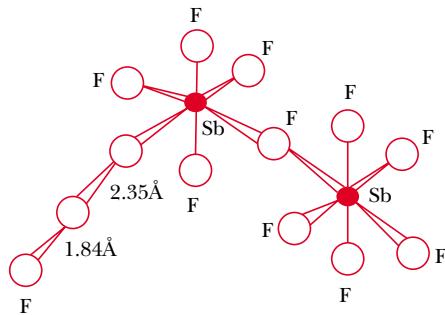


Figure 10.61 Structure of $\text{XeF}_2 \cdot 2\text{SbF}_5$. (From Mackay and Mackay, Introduction to Modern Inorganic Chemistry, 4th ed., Blackie, 1989.)

XeF_4 forms only a few complexes, for example those with PF_5 , AsF_5 and SbF_5 . XeF_6 can act as a fluoride donor, forming complexes such as:



XeF_6 may also act as a fluoride acceptor. With RbF and CsF it reacts as follows:



On heating, the $[\text{XeF}_7]^-$ ion decomposes:



10.73 | STRUCTURE AND BONDING IN XENON COMPOUNDS

The structures of the more common xenon halides, oxides and oxoions are given in Table 10.43. The nature of the bonds and the orbitals used for bonding in these compounds are of great interest and have been the subject of considerable controversy.

Table. 10.43 Possible explanation of structures

Formula	Structure	Number of electron pairs	Number of lone pairs	VSEPR explanation of structure
XeF_2	Linear	5	3	Five electron pairs form trigonal bipyramidal with three lone pairs in equatorial positions
XeF_4	Square planar	6	2	Six electron pairs form an octahedron with two positions occupied by lone pairs
XeF_6	Distorted octahedron	7	1	Pentagonal bipyramidal, or capped octahedron with one lone pair

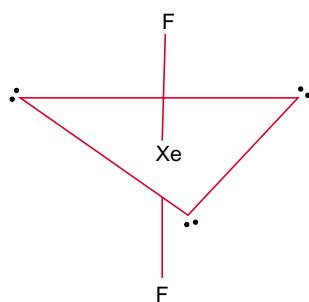
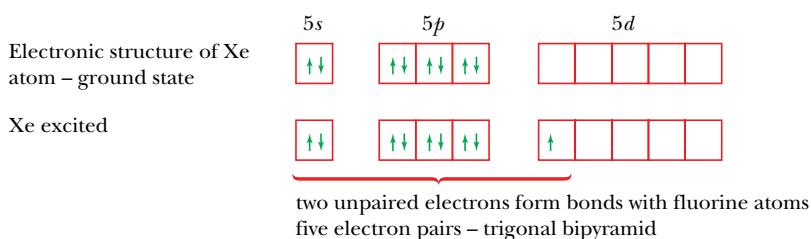
(Continued)

Table. 10.43 (Continued)

Formula	Structure	Number of electron pairs	Number of lone pairs	VSEPR explanation of structure
XeO ₃	Pyramidal	7	1	Three π bonds so the remaining four electron pairs form a tetrahedron with one corner occupied by a lone pair
XeOF ₂	T-shaped	6	2	One π bond, three sigma bonds and two lone pairs constitute the T-shape
XeO ₂ F ₂	See-saw	7	1	Two π bonds so remaining five electron pairs form trigonal bipyramidal with one equatorial position occupied by a lone pair
XeOF ₄	Square pyramidal	7	1	One π bond so remaining six electron pairs form an octahedron with one position occupied by a lone pair
XeO ₄	Tetrahedral	8	0	Four π bonds so remaining four electron pairs form a tetrahedron
XeO ₃ F ₂	Trigonal bipyramidal	8	0	Three π bonds so remaining five electron pairs form a trigonal bipyramidal
Ba ₂ [XeO ₆] ⁴⁻	Octahedral	8	0	Two π bonds so remaining six electron pairs form an octahedron

XeF₂

XeF₂ is a linear molecule with both Xe–F distances 2.00 Å. The bonding may be explained quite simply by promoting an electron from the 5p level of Xe to the 5d level. The two unpaired electrons form bonds with fluorine atoms. The five electron pairs point to the corners of a trigonal bipyramidal. Of these, three are lone pairs and occupy the equatorial positions, and two are bond pairs and occupy the apical positions. The atoms thus form a linear molecule (Figure 10.62).

Figure 10.62 XeF₂ molecule.

This explains the observed structure, but an objection is that the 5d orbitals of Xe appear to be too large for effective overlap of orbitals. The maximum in the radial electron distribution function for a 5d

orbital in a Xe atom occurs at a distance of 4.9 Å from the nucleus. It has been noted in Chapter 3 in the section 'The extent of d orbital participation in molecular bonding' that highly electronegative atoms like fluorine cause a large contraction in the size of d orbitals. If this contraction is big enough, the valence bond explanation will suffice.

A second objection is over the mixing of orbitals (sp^3d hybridization). Mixing is only effective between orbitals of similar energy, and the Xe 5d orbitals would seem too high in energy to contribute to such a scheme of hybridization. (The difference in energy between a 5p and a 5d level is about 960 kJ mol⁻¹.)

XeF₄

The structure of XeF₄ is square planar, with Xe–F distances of 1.95 Å (Figure 10.63). The valence bond theory explains this by promoting two electrons as shown:

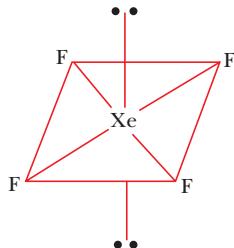
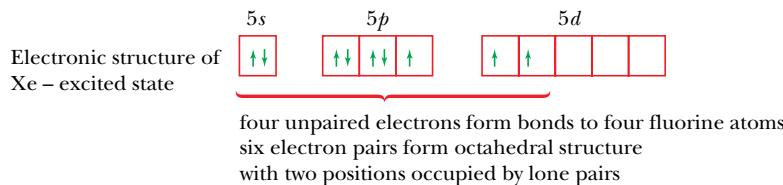


Figure 10.63 XeF₄ molecule.



The problem of whether the size of the xenon 5d orbitals will allow effective overlap, or their energy will allow mixing and hybridization, is the same as in XeF₂. The molecular orbital explanation of XeF₄ is similar to that for XeF₂. The Xe atom bonds to four F atoms.

XeF₆

The structure of XeF₆ is a distorted octahedron (Figure 10.64). The bonding in XeF₆ has caused considerable controversy which is not completely resolved. The structure may be explained in valence bond terms by promoting three electrons in Xe:

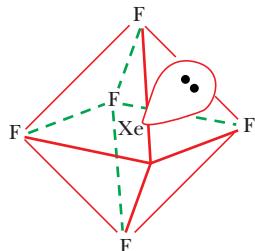


Figure 10.64 Capped octahedron.



The six unpaired electrons form bonds with fluorine atoms. The distribution of seven orbitals gives either a capped octahedron or a pentagonal bipyramidal (as in IF₇). (A capped octahedron has a lone pair pointing through one of the faces of the octahedron.) Since there are six bonds and one lone pair, a capped

octahedron would give a distorted octahedral molecule. The molecular orbital approach fails with XeF_6 , since three three-centre molecular orbital systems mutually at right angles would give a regular octahedral shape.

10.74 | STRUCTURES OF SOME XENON COMPOUNDS

Structures of some xenon compounds are shown in Figure 10.65 (skeleton only).

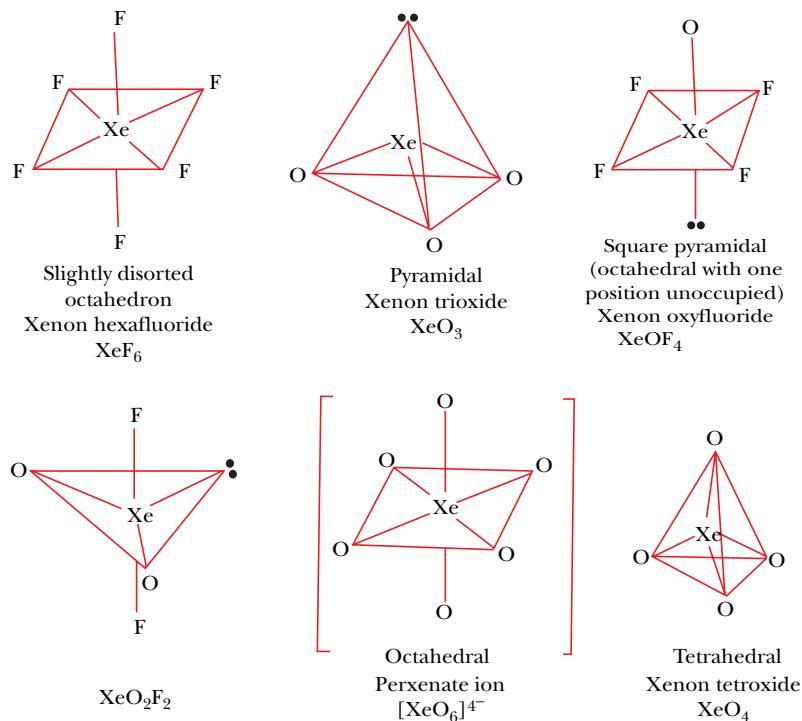


Figure 10.65 Structures of some xenon compounds.

SINGLE CORRECT CHOICE TYPE QUESTIONS

- Which of the following elements has the highest ionization energy?
 (A) He
 (B) Ne
 (C) F
 (D) H
- The most abundant inert gas element is
 (A) Ne
 (B) Ar
 (C) He
 (D) Xe
- Which of the following elements is used in cryoscopic study for superconductivity?
 (A) Liquid bromine
 (B) Mercury liquid
- (C) Liquid nitrogen
 (D) Liquid helium
- Which of the following properties does not increase from helium to xenon?
 (A) Boiling point
 (B) Atomic radius
 (C) Rate of diffusion through glass
 (D) None of these
- When XeO_3 reacts with XeOF_4 , the product formed is
 (A) XeO_4
 (B) XeO_2F_2
 (C) XeOF_2
 (D) XeO_3F_2

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

- When liquid helium is cooled below the λ - point temperature, which of the following abrupt changes is/are observed in the properties?
 - Increase in thermal conductivity
 - The viscosity becomes zero
 - It becomes a superconductor and shows zero electrical resistance.
 - The liquid can flow up the sides of the vessel.
 - Which of the following statements is/are true for XeOF_4 molecule?
 - It is planar.
 - It has a total of 15 lone pairs.
 - It hydrolyses to produce XeO_3 .
 - The shape is square pyramidal.
 - Which of the following properties are a consequence of the small size of the noble gases?
 - $\text{Xe}^+[\text{MF}_6]^-$
 - Clathrate compounds are not formed by helium.
 - Rate of diffusion through glass is very high for helium.
 - Extent of London force is the lowest for helium.
 - Abundance in atmosphere is poor.
- Which of the following momentarily occurring species have fractional bond order?
 - He_2^+
 - HeH_2^+
 - HeH^{2+}
 - Ar_2^+
 - How many of the following molecules have trigonal bipyramidal electronic geometry for their central atom?
 - XeO_3F_2
 - XeF_2
 - XeF_4
 - XeOF_2

COMPREHENSION TYPE QUESTIONS**Passage 1: For Questions 1 and 2**

In 1962, Bartlett coined the new branch of chemistry of noble gas Xe and the first compound of Xe detected (wrongly) was $\text{Xe}^+[\text{MF}_6]^-$.

- What was the concept involved behind the idea that xenon can combine with other elements to form compounds when the experiment was started?
 - IE_1 of Xe is close to that of O atom.
 - IE_1 of Xe $\approx \text{IE}_1$ of O_2 molecule.
 - ΔH_{egl} of Xe $\approx \Delta H_{\text{egl}}$ of O-atom.
 - ΔH_{egl} of Xe $\approx \Delta H_{\text{egl}}$ of O_2 molecule.
- IE_1 of noble gases is in the order $\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe} > \text{Rn}$.
Accordingly, which of the following statements is correct?
 - Rn should form compounds more easily than Xe.
 - Kr should form compounds more easily than Xe.
 - Rn and Kr both should form compounds with equal ease.
 - None of the above prediction is correct.

Passage 2: For Questions 3 to 5

Xenon fluorides are very good oxidizing agent, fluorinating agents and also can act as F donors and F acceptors.

- When XeF_4 donates its fluoride to SbF_5 , then the states of hybridization of central atoms of cationic part and anionic part of the product formed are:
 - sp^3d, sp^3d^2
 - sp^3d^2, sp^3d
 - sp^3d, sp^3d
 - sp^3d^2, sp^3d^2
- XeO_4 is obtained when
 - Xe reacts with O_2 directly.
 - XeF_4 is hydrolyzed and disproportionated to give XeO_4 .
 - XeF_6 is hydrolyzed in alkaline medium followed by treatment with conc. H_2SO_4 at low temperature.
 - XeF_6 is hydrolyzed in neutral medium followed by reaction with O_2 .
- The state of hybridization in the Xe compound obtained in alkaline hydrolysis product of XeF_6 is
 - sp^3d^2
 - sp^3d^3
 - d^2sp^3
 - sp^3d

ASSERTION–REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.

- (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I
 (C) If Statement I is true but Statement II is false.
 (D) If Statement I is false and Statement II is true.

1. Statement I: Helium is used in preference to N_2 to dilute O_2 in the gas cylinder used by divers.

Statement II: Helium has lower solubility in blood as compared to N_2 ; thus minimising the risk of bend.

2. Statement I: In the adduct $[XeF_6 \cdot ASF_5]$, XeF_6 acts as fluoride donor.

Statement II: XeF_6 acts as a Lewis base.

3. Statement I: When Pt is fluorinated with XeF_2 , it is mixed with anhydrous HF.

Statement II: Reactivity of XeF_2 increases greatly due to the formation of XeF^+ .

4. Statement I: XeO_4 with oxidation state of Xe as +8 is formed, but XeF_8 does not form.

Statement II: Steric crowding is more for XeF_8 than in XeO_4 .

5. Statement I: The variable oxidation state of Xe is observed by jump of two units.

Statement II: The valence shell electronic configuration is $5s^25p^6$ and on excitation it always produces an even number of unpaired electrons.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following is a non-negative integer.

- Find the number lone pairs in XeO_2F_2 .
- Find the number of d -orbitals used for bonding of $XeOF_4$.
- When XeF_2 fluorinates Ph_2S , the product is $Ph_2SF_2 + Xe$. Find the difference in the number of d -orbitals involved in bonding of reactants to product.

4. In the following reaction, find the difference in oxidation state of Xe in the underlined species (numerical value only).



5. Find the number of molecules that can form clathrate compounds from the following:



6. The maximum number of identical angles in $[XeF_8]^{2-}$ is ____.

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as **(A)**, **(B)**, **(C)** and **(D)**, while those in Column II are labelled as **(P)**, **(Q)**, **(R)**, **(S)** and **(T)**. Any given statement in Column I can have correct matching with *one or more* statements in Column II.

- 1.** Match the compounds with their properties.

Column I	Column II
(A) XeO_3	(P) Powerful explosive.
(B) XeF_2	(Q) Acts as fluoride donor.
(C) XeO_4	(R) Central atom carries at least one lone pair.
(D) $XeOF_4$	(S) It is formed by the reaction between XeO_3 and XeF_6
	(T) It is formed by the reaction of Na_4XeO_6 with conc. H_2SO_4 at $-9^\circ C$

- 2.** Match the compounds with their properties.

Column I	Column II
(A) XeO_6^{4-}	(P) Central atom is sp^3d^2 hybridized.
(B) XeF_4	(Q) On treatment with conc. H_2SO_4 produces XeO_4 .
(C) XeO_3	(R) Only one lone pair is present on the central atom.
(D) XeO_2F_2	(S) Central atom of the molecule has four surrounding atoms.

ANSWERS**Single Correct Choice Type Questions**

1. (A)

2. (B)

3. (D)

4. (C)

5. (B)

Multiple Correct Choice Type Questions

1. (A), (B), (C), (D)

2. (B), (C), (D)

3. (A), (B), (C)

4. (A), (C), (D)

5. (A), (B), (D)

Comprehension Type Questions

1. (B)

2. (A)

3. (A)

4. (C)

5. (A)

Assertion–Reasoning Type Questions

1. (A)

2. (C)

3. (A)

4. (A)

5. (A)

Integer Answer Type Questions

1. 11

2. 3

3. 0

4. 2

5. 8

6. 8

Matrix–Match Type Questions

1. (A) \rightarrow (P), (R)
 (B) \rightarrow (Q), (R)
 (C) \rightarrow (P), (T)
 (D) \rightarrow (R), (S)

2. (A) \rightarrow (P), (Q)
 (B) \rightarrow (P), (S)
 (C) \rightarrow (R)
 (D) \rightarrow (R), (S)

Miscellaneous Questions**SINGLE CORRECT CHOICE TYPE QUESTIONS**

1. The fluoride which is soluble in water is

- (A) CaF_2
 (B) BaF_2
 (C) SrF_2
 (D) BeF_2

2. Which of the following pair of species is non-linear?

- (A) OCN^- and Br_3^-
 (B) $(\text{SCN})_2$ and I_5^-
 (C) NCN^{2-} and N_3^-
 (D) HN_3 and $(\text{CN})_2$

3. Substance A

- I. reacts with H_2S to produce white turbidity.
 II. changes light green solution of FeSO_4 into yellow colour.
 III. reacts with moisture to give pungent smelling gas.
 Then A is
 (A) KMnO_4
 (B) $\text{K}_2\text{Cr}_2\text{O}_7$
 (C) SO_2
 (D) $\text{Ca}(\text{OCl})\text{Cl}$

4. $\text{A} + \text{SbF}_5 \rightarrow \text{B}$ $\text{B} + \text{tert-butane} \rightarrow [\text{tert-butyl}]^+ + \text{X}^- + \text{H}_2$

Then A is

- (A) HCl
 (B) HF
 (C) HBr
 (D) HI

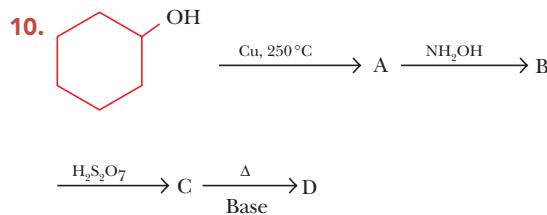
5. Which of the following represents the correct increasing order of pK_a values of the given acids?

- (A) $\text{HClO}_4 < \text{HNO}_3 < \text{H}_2\text{CO}_3 < \text{B}(\text{OH})_3$
 (B) $\text{HNO}_3 < \text{HClO}_4 < \text{B}(\text{OH})_3 < \text{H}_2\text{CO}_3$
 (C) $\text{HClO}_4 > \text{HNO}_3 > \text{H}_2\text{CO}_3 > \text{B}(\text{OH})_3$
 (D) $\text{HClO}_4 < \text{HNO}_3 < \text{B}(\text{OH})_3 < \text{H}_2\text{CO}_3$.

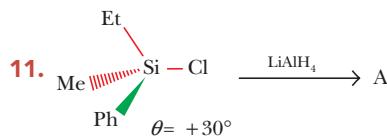
6. Which of the following options are incorrect?

- I. $\alpha - \text{S} \rightleftharpoons \beta - \text{S}; \Delta H = (-) \text{ ve}$
 II. $\alpha - \text{S} \rightleftharpoons \beta - \text{S}; \Delta H = (+) \text{ ve}$
 III. Red P \rightleftharpoons Black P; $\Delta H = (-) \text{ ve}$
 IV. Black P \rightleftharpoons White P; $\Delta H = (-) \text{ ve}$
 V. Graphite \rightleftharpoons Diamond; $\Delta H = (+) \text{ ve}$
 (A) II, IV and V
 (B) II, III and V
 (C) I and IV
 (D) I and III

7. SO_2 is passed through a strongly acidic solution of SnCl_2 . The precipitate obtained consists of S and the oxidation state of S in the precipitate is
 (A) -1
 (B) zero
 (C) -2
 (D) the precipitate does not contain S.
8. White compound A $\xrightarrow{\text{HNO}_3}$ B $\xrightarrow{\text{I}_2}$ C (used to estimate CO). The compound A is
 (A) P_2O_5
 (B) I_2O_5
 (C) I_4O_9
 (D) S_3O_9
9. $\text{Fe}(\text{CO})_5 + \text{NO} \rightarrow \text{M}$ (complex). M is
 (A) $\text{Fe}(\text{NO})_5$
 (B) $\text{Fe}(\text{CO})_5(\text{NO})_2$
 (C) $\text{Fe}(\text{CO})_2(\text{NO})_2$
 (D) $\text{Fe}(\text{CO})_2(\text{NO})_3$

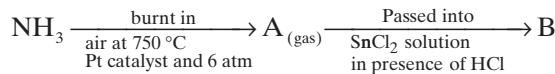


- In the given reaction, compound C is
 (A) nylon-6.
 (B) caprolactum.
 (C) nylon-66.
 (D) lactone.



- A will have the optical rotation of
 (A) $+30^\circ$.
 (B) -30° .
 (C) zero.
 (D) Cannot be predicted.

12. In the reaction



- The compound B is:
 (A) NH_2OH
 (B) NH_3
 (C) N_2O
 (D) $\text{NH}_2\text{---NH}_2$

13. FeSO_4 is a very good absorber for NO. The number of unpaired electrons in the new compound formed by this process is
 (A) 4
 (B) 5
 (C) 3
 (D) 6

14. Which of the following compounds give NH_3 on heating?

- NH_4NO_3
 - NH_4NO_2
 - $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
 - $(\text{NH}_4)_2\text{CO}_3$
 - $\text{Mg}(\text{NH}_4)\text{PO}_4$
- (A) I and IV
 (B) II and V
 (C) IV only
 (D) IV and V

15. $\text{Mg}(\text{NH}_4)\text{PO}_4$ and $\text{Na}(\text{NH}_4)\text{HPO}_4$ are heated separately. Which of the following statements is/are completely incorrect regarding the product obtained in the above processes?

- Same gas is evolved.
 - Same type of phosphate is formed.
 - Different types of gases are formed.
 - Different types of phosphates are formed.
- (A) I and II
 (B) II and IV
 (C) I and IV
 (D) II and III

16. A mixture of two gases, AsH_3 , and SbH_3 , is passed through a tube heated at the middle position. Two mirror-like depositions are observed of which (I) is before the hot position and (II) is after the hot position.

- These depositions I and II are of
 (A) Sb and As
 (B) As and Sb
 (C) Both As
 (D) Both Sb

17. Which of the following reagents does not produce any gaseous product on reaction with PbO_2 ?
 (A) HCl (hot conc.)
 (B) $\text{HNO}_3 + (\text{CO}_2\text{H})_2$
 (C) NaOH
 (D) H_2SO_4

18. Which of following options is correct for the given statement?

- In the discharge reaction of lead storage cell, the number of Faradays used is equal to
 I. twice the number of moles of PbO_2 consumed.
 II. half the number of moles of H_2SO_4 consumed.
 III. the number of moles of H_2SO_4 produced.
 IV. the number of moles of H_2O produced.
 (A) I and II
 (B) I and IV
 (C) II and IV
 (D) II and III

19. Reaction of PbO_2 with hot conc. HCl and cold conc. HCl (saturated with Cl_2) separately produces

- PbCl_2 and PbCl_4
- PbCl_2 and H_2PbCl_6
- PbCl_4 and PbCl_2
- H_2PbCl_6 and PbCl_2

20. Choose the incorrect statement from the following.
- (A) Hydrolysis of SnCl_4 is affected by the presence of HCl vapours.
- (B) Ammonolysis of SnCl_4 is not affected by the presence of NH_4Cl vapours.

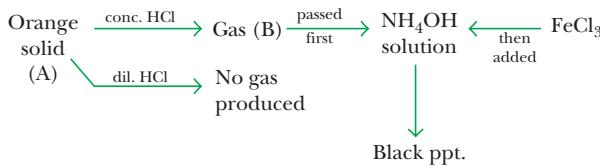
- (C) Piece of Sn kept with SnCl_2 prevents its oxidation.
- (D) SnCl_2 , SnCl_4 , and PbCl_4 all form complex acid with conc. HCl .

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

1. An element (E) + $\text{NaOH} \xrightarrow{\text{acidification}}$ disproportionated product $\xrightarrow{\text{acidification}}$ (E) comes back. The above process is true for which of the following pairs?
- (A) Cl_2 and Br_2
 (B) S and Br_2
 (C) P and F_2
 (D) S and I_2
2. When F_2 is passed into water, the products obtained are
- (A) F_2O
 (B) O_3
 (C) O_2
 (D) HF
3. Which of the following statements are true for Na in liquid NH_3 ?
- (A) It is blue in colour due to solvated electrons.
 (B) $\text{K}_2[\text{Ni}(\text{CN})_4]$ changes its structure from square planar to tetrahedral when added to it.
 (C) It conducts electricity.
 (D) None of these.
4. Which of the following statements is/are correct?
- (A) NO is a diamagnetic liquid.
 (B) B_2 and C_2 are diamagnetic.
 (C) N_2O_4 is diamagnetic.
 (D) BH_3 loses its planarity on dimerization.
5. Which of the following statements is/are correct?
- (A) Cl_2 reacts with liquid NH_3 (excess) to give N_2 .
 (B) The product obtained by the absorption of N_2 by calcium carbide is a good fertilizer.
 (C) Brown-coloured oxide of nitrogen reacts with O_3 to give another oxide with lowest oxidation state of N .
 (D) HNO_2 reacts with H_2S to produce a paramagnetic gas.
6. Choose the correct options from the following orders.
- (A) Basicity order: $\text{NH}_3 > \text{NH}_2-\text{NH}_2 > \text{NH}_2\text{OH} > \text{NF}_3$
 (B) Melting point order: $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
 (C) Boiling point order: $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
 (D) Thermal stability order: $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$
7. N_2O_4 reacts with NaOH to produce a colourless solution. Which are the correct statements among the following for this reaction?
- (A) It can give the brown ring test for nitrate.
 (B) It reacts with AgNO_3 to give white ppt.
 (C) It decolorises KMnO_4 solution.
 (D) After treatment with AgNO_3 , ppt is filtered and filtrate is treated with $\text{Zn} + \text{AcOH}$, and the resulting solution does not respond towards Grises–Illosvay test.
8. Sn^{2+} can be distinguished from Sn^{4+} by
- (A) passing H_2S .
 (B) adding $\text{Fe}[\text{Fe}(\text{CN})_6]$.
 (C) adding CuCl_2 solution.
 (D) none of these.
9. Catenation property can be shown by which of the following elements?
- (A) Carbon
 (B) Silicon
 (C) Phosphorus
 (D) Sulphur
10. Allotropism is shown by which of the following elements?
- (A) Arsenic
 (B) Tin
 (C) Oxygen
 (D) Nitrogen

COMPREHENSION TYPE QUESTIONS

Passage 1: For Questions 1–4



1. The black precipitate is
- (A) FeS
 (B) Fe_2S_3
 (C) $(\text{FeS} + \text{S})$
 (D) $(\text{FeS} + \text{Fe}_2\text{S}_3)$

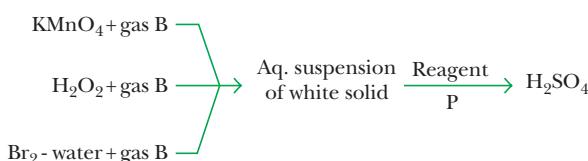
2. The orange solid is

- (A) As_2S_3
 (B) Sb_2S_3
 (C) Sb_2O_3
 (D) SbOCl

3. The metal(s) which reacts with gas B under hot condition to produce H_2 is/are

- (A) Na
 (B) Cu
 (C) Pb
 (D) All of the above.

4. In the following reactions

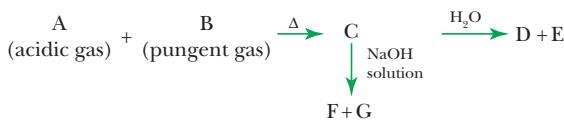


Which of the following options is correct regarding P among the following?

- I. O₃
 - II. excess Cl₂ water
 - III. HNO₃ (conc.)
 - IV. HCl
 - V. H₂O₂
- (A) I, II and V
 (B) I, II and III
 (C) III, IV and V
 (D) I and V

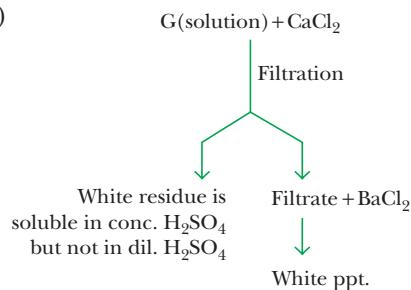
Passage 2: For Questions 5–7

In the following reactions



- (i) D and E are both acids and F and G are both salts.
 (ii) F(solution) + conc. H₂SO₄ + K₂Cr₂O₇ $\xrightarrow{\Delta}$ reddish brown vapour which is passed into NaOH solution to give yellow solution.

(iii)



5. The gas B is
 (A) SO₂
 (B) CO₂
 (C) CO
 (D) Cl₂
6. The compound C is
 (A) COCl₂
 (B) SOCl₂
 (C) SO₂Cl₂
 (D) CSCl₂
7. The hybridization state of central atom of the compound present in reddish brown vapour is

- (A) sp^3
 (B) sp^3d
 (C) d^3s
 (D) sp^2

Passage 3: For Questions 8–10

Conc. H₂SO₄ can act as a solvent, dehydrating agent and oxidizing agent.

8. When 1 mole of N₂O₅ is added to conc. H₂SO₄, it shows ____ fold freezing point depression.

- (A) four
 (B) six
 (C) eight
 (D) two

9. The nitrating mixture used for nitration of benzene is expected to show ____ fold freezing point depression.

- (A) six
 (B) two
 (C) three
 (D) four

10. In which of the following reactions conc. H₂SO₄ does not act as a dehydrating agent?

- (A) $\text{HCO}_2\text{H} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{CO} + \text{HSO}_4^-$
 (B) $\text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{SO}_4 \rightarrow 5\text{H}_2\text{O} + 6\text{C} + \text{H}_3\text{O}^+ + \text{HSO}_4^-$
 (C) $\text{P}_2\text{O}_5 + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_3 + 2\text{HPO}_3$
 (D) $\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^- + \text{CO} + \text{CO}_2$

Passage 4: For Questions 11 – 13

CuSO₄ is allowed to react separately with white P (1), PH₃ (2), H₃PO₃ (3) and H₃PO₂ (4).

11. In which of the following cases observations are the same?

- (A) 1, 2, 4
 (B) 2, 3
 (C) 1, 3, 4
 (D) 2, 4

12. In which of the following cases reduction products are the same?

- (A) 1, 3
 (B) 1, 2, 3
 (C) 3, 4
 (D) 2, 4

13. Distinction between H₃PO₃ and H₃PO₂ can be made by

- (A) treating with CuSO₄ only.
 (B) treating with CuSO₄ followed by addition of water.
 (C) treating with CuSO₄ followed by addition of dil. HCl.
 (D) treating with NaOH solution.

Passage 5: For Questions 14–16

Metallic Sn is reacted with NH_4Cl and the resulting solution is treated with sulphur.

14. The gaseous product(s) is/are
 (A) NH_3 only.
 (B) $\text{NH}_3 + \text{H}_2$.
 (C) H_2 only.
 (D) No gaseous product.
15. The colour of the final precipitate obtained is
 (A) dark brown. (C) yellow.
 (B) white. (D) pink.

16. The above resulting solution is added to AuCl_3 solution resulting in a purple colour solution, which is called as 'purple of cassius.' It consists of
 (A) colloidal solution of gold.
 (B) colloidal solution of $\text{Sn}(\text{OH})_4$ with finely divided gold particles adsorbed on it.
 (C) colloidal solution of $\text{Sn}(\text{OH})_4$.
 (D) mixture of precipitates of Au and $\text{Sn}(\text{OH})_4$.

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
 (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
 (C) If Statement I is true but Statement II is false.
 (D) If Statement I is false but Statement II is true.

1. **Statement I:** C_3O_2 and N_5^+ are isosteric yet they are not isostructural.

Statement II: C_3O_2 is linear while N_5^+ is bent.

2. **Statement I:** P_2O_5 is a stronger dehydrating agent than H_2SO_4 .

Statement II: P is more electronegative than S.

3. **Statement I:** YAS and AS are both oxidizing agents.

Statement II: S(-I) is reduced to S(-II) easily in YAS.

4. **Statement I:** The bleaching action of SO_2 is not permanent while that of H_2O_2 or Cl_2 is permanent.

Statement II: Bleaching action by SO_2 is due to reduction of the substance which undergoes further oxidation by air; while that of H_2O_2 or Cl_2 is due to oxidation of the substance.

5. **Statement I:** P_2O_5 is a stronger dehydrating agent than conc. H_2SO_4 .

Statement II: P_2O_5 dehydrates conc. H_2SO_4 into SO_3 .

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. Among the following, the number of compounds that can act as dehydrating agent is _____.

Conc. H_2SO_4 , anhyd. CaCl_2 , conc. HNO_3 , CaO , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, P_2O_5 .

2. Among the following, the number of compounds/ions having a linear structure is _____.

C_5O_2 , H_2O_5 , N_3^- , CN_2^{2-} , N_5^+ , H_2S_3 , $[\text{I}(\text{CN})_2]^-$, $(\text{CN})_2$, $(\text{SCN})_2$.

3. The number of 90° angles (approximately) in PHF_4 is _____.

4. TlI_3 is isomorphic with CsI_3 and then the oxidation state of Tl in TlI_3 is _____.

5. Among the following, the number of ions/molecules having at least one atom *sp* hybridized is _____.

C_3S_2 , NO_2^- , NO_2^+ , benzene, benzyne, diazonium cation, C_6H_5^+ , C_3^{4-} , $\text{Cr}_2\text{O}_7^{2-}$, CaC_2 , $(\text{SCN})_2$

6. When $\text{K}_2[\text{Ni}(\text{CN})_4]$ is reduced by K in liquid NH_3 , the change in co-ordination number is _____.

7. According to Drago's rule, the P atom in PH_3 is not hybridized and formation of PH_4^+ is difficult. The number of identical HPH angles in PH_4^+ ion is _____.

8. The ratio of number of lone pairs on the central atom of ClF_3 and XeF_4 is _____.

9. How many of the following are in the correct order with respect to the given property?
- (i) $H_2 > He$: Boiling point order
 (ii) $He > Ne > Ar > Kr > Xe$: Boiling point order
 (iii) $S > O > Se > Te$: Electron affinity order
 (iv) Diamond > graphite : Electrical conductivity order
 (v) $HCl < HBr < HF < HI$: Melting point order
10. How many of the following compounds are matched with the incorrect formula?
- (i) Butter of tin : $SnCl_4 \cdot 4H_2O$
 (ii) Gypsum : $CaSO_4 \cdot 2H_2O$
 (iii) Plaster of Paris : $2CaSO_4 \cdot 4H_2O$
 (iv) Mustard gas : $S(CH_2CH_2-Cl)_2$
 (v) Thionyl chloride : $COCl_2$
 (vi) Sulphuryl chloride : $SeCl_2$

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as (A), (B), (C) and (D), while those in Column II are labelled as (P), (Q), (R), (S) and (T). Any given statement in Column I can have correct matching with *one or more* statements in Column II.

1. Match the compounds with effects on heating

Column I	Column II
(A) NH_4NO_3	(P) Leaves no residue on heating.
(B) NH_4NO_2	(Q) Leaves residue on heating.
(C) $(NH_4)_2CO_3$	(R) Produces N_2 on heating.
(D) $(NH_4)_2Cr_2O_7$	(S) Produces NH_3 on heating.
(E) $Mg(NH_4)PO_4$	

2. Match the oxides with their properties.

Column I	Column II
(A) ClO_2	(P) The free electron is present in a hybrid orbital.
(B) NO_2	(Q) Produces the mixed acid on reaction with water.
(C) ClO_3	(R) Molecule is planar.
	(S) Molecule having the lowest possible O–X–O angle.

3. Match the oxides with solutions in which they are absorbed.

Column I	Column II
(A) CO	(P) Absorbed by ethanol amine.
(B) CO_2	(Q) Absorbed by $FeSO_4$ solution.
(C) NO	(R) Absorbed by aqueous suspension of Cu_2Cl_2 .
	(S) Absorbed by KOH solution.

4. *Match the compounds with their common names and uses.

Column I	Column II	Column III
(A) $SnCl_4 \cdot 5H_2O$	(P) Mosaic gold	(J) Used as fertilizer.
(B) $(NH_4)_2SnCl_6$	(Q) Nitrolim	(K) Used in calico printing.
(C) SnS_2	(R) Butter of tin	(L) Used in gilding purpose.
(D) $CaCN_2 + C$	(S) Pink salt	(M) Used as mordant in dye.

*Choose only one option from Column II and Column III for each option of Column I.

5. Match the reagent/ characteristic with their use in the detection of compounds.

Column I	Column II
(A) $Pb(OAC)_2$	(P) NH_3
(B) Nessler's reagent	(Q) PH_3
(C) Rotten fish smell	(R) H_2S
(D) Violet layer	(S) I_2

ANSWERS**Single Correct Choice Type Questions**

- | | | | | |
|---------------|---------------|----------------|----------------|----------------|
| 1. (D) | 5. (A) | 9. (C) | 13. (C) | 17. (C) |
| 2. (B) | 6. (C) | 10. (B) | 14. (D) | 18. (B) |
| 3. (D) | 7. (C) | 11. (D) | 15. (D) | 19. (B) |
| 4. (B) | 8. (A) | 12. (A) | 16. (A) | 20. (B) |

Multiple Correct Choice Type Questions

- | | | | | |
|-------------------------|-------------------------|-------------------------|-------------------------|------------------------------|
| 1. (A), (B), (D) | 3. (A), (B), (C) | 5. (A), (B), (D) | 7. (B), (C) | 9. (A), (B), (C), (D) |
| 2. (B), (C), (D) | 4. (A), (C), (D) | 6. (A), (B) | 8. (A), (B), (C) | 10. (A), (B), (C) |

Comprehension Type Questions

- | | | | |
|---------------|---------------|----------------|----------------|
| 1. (C) | 5. (D) | 9. (D) | 13. (C) |
| 2. (B) | 6. (C) | 10. (C) | 14. (B) |
| 3. (D) | 7. (C) | 11. (C) | 15. (C) |
| 4. (B) | 8. (B) | 12. (A) | 16. (B) |

Assertion–Reasoning Type Questions

- | | | | | |
|---------------|---------------|---------------|---------------|---------------|
| 1. (A) | 2. (C) | 3. (D) | 4. (A) | 5. (A) |
|---------------|---------------|---------------|---------------|---------------|

Integer Answer Type Questions

- | | | | | |
|-------------|-------------|-------------|-------------|--------------|
| 1. 4 | 3. 6 | 5. 6 | 7. 6 | 9. 2 |
| 2. 5 | 4. 1 | 6. 0 | 8. 1 | 10. 4 |

Matrix–Match Type Questions

- | | | |
|---|--|--|
| 1. (A) → (P)
(B) → (P), (R)
(C) → (P), (S)
(D) → (Q), (R)
(E) → (Q), (S) | 3. (A) → (R)
(B) → (P), (S)
(C) → (Q) | 5. (A) → (R)
(B) → (P)
(C) → (Q)
(D) → (S) |
| 2. (A) → (Q), (R)
(B) → (P), (Q), (R)
(C) → (P), (Q), (S) | 4. (A) → (R), (M)
(B) → (S), (K)
(C) → (P), (L)
(D) → (Q), (J) | |

11

The *d*-Block Elements and some of their Compounds

Transition elements										Post transition elements
3	4	5	6	7	8	9	10	11	12	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	
Ac	Rf	Db	Sg	Bh	Hs	Mt				

d-block elements.

Three series of elements are formed by filling the $3d$, $4d$ and $5d$ shells of electrons. Together these comprise the *d*-block elements. They are often called ‘transition elements’ because their position in the periodic table is between the *s*-block and *p*-block elements. Their properties are transitional between the highly reactive metallic elements of the *s*-block, which typically form ionic compounds, and the elements of the *p*-block, which are largely covalent. In the *s*- and *p*-blocks, electrons are added to the outer shell of the atom. In the *d*-block, electrons are added to the penultimate shell, expanding it from 8 to 18 electrons. Typically, the transition elements have an incompletely filled *d* level. The elements make up three complete rows of ten elements and an incomplete fourth row (Table 11.1). Group 12 (the zinc group) has a d^{10} configuration and since the *d* shell is complete, compounds of these elements (Zn, Cd, Hg,) are not typical and show some differences from other elements of the series. In the present days, transition elements are only those with incompletely filled *d* orbitals. So Zn, Cd and Hg are excluded from the transition series elements. However, they are *d*-block elements.

In the *d*-block elements the penultimate shell of electrons is expanding. Thus they have many physical and chemical properties in common. Thus all the transition elements are metals. They are therefore good conductors of electricity and heat, have a metallic lustre and are hard, strong and ductile. They also form alloys with other metals.

Contents

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- 11.2** Complexes
- 11.3** Size of Atoms and Ions
- 11.4** Density
- 11.5** Melting and Boiling Points
- 11.6** Reactivity of Metals
- 11.7** Ionization Energies
- 11.8** Colour
- 11.9** Magnetic Properties
- 11.10** Catalytic Properties
- 11.11** Nonstoichiometry
- 11.12** Abundance
- 11.13** Chromate and Dichromate
- 11.14** Manganate and Permanganate
- 11.15** Silver and its Compounds
- 11.16** Zinc Compounds
- 11.17** Copper Compounds
- 11.18** Iron Compounds

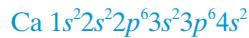
Table 11.1 The elements

Group											
3	4	5	6	7	8	9	10	11	12		
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		
Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc		
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		
Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium		
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		
Lanthanum	Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury		
Ac											
Actinium											

11.1 | VARIABLE OXIDATION STATE

One of the most striking features of the transition elements is that the elements usually exist in several different oxidation states. Furthermore, the oxidation states change in units of one, e.g. Fe^{3+} and Fe^{2+} , Cu^{2+} and Cu^+ .

The oxidation states shown by the transition elements may be related to their electronic structures. Calcium, the *s*-block element preceding the first row of transition elements, has the electronic structure:



It might be expected that the next ten transition elements would have this electronic arrangement with one to ten *d* electrons added in a regular way: $3d^1$, $3d^2$, $3d^3$... $3d^{10}$. This is true except in the cases of Cr and Cu. In these two cases, one of the *s* electrons moves into the *d* shell, because of the additional stability when the *d* orbitals are exactly half filled or completely filled (Table 11.2).

Table 11.2 Oxidation states

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic structure	d^1s^2	d^2s^2	d^3s^2	$\cancel{d^4s^2}$ d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2	$\cancel{d^9s^2}$ $d^{10}s^1$	$d^{10}s^2$
Oxidation states				I					I	
	II	II	II	II	II	II	II	II	II	II
	III	III	III	III	III	III	III	III	III	III
	IV	IV	IV	IV	IV	IV	IV	IV	IV	
		IV	V	V	V	V				
			VI	VI	VI					
				VII						

Thus Sc could have an oxidation number of (+II) if both *s* electrons are used for bonding and (+III) when two *s* and one *d* electrons are involved. Ti has an oxidation state (+II) when both *s* electrons are used for bonding, (+III) when two *s* and one *d* electrons are used and (+IV) when two *s* and two *d* electrons are used. Similarly, V shows oxidation numbers (+II), (+III), (+IV) and (+V). In the case of Cr, by using the single *s* electron for bonding, we get an oxidation number of (+I); hence by using varying numbers of *d* electrons oxidation states of (+II), (+III), (+IV), (+V) and (+VI) are possible. Mn has oxidation states (+II), (+III), (+IV), (+V), (+VI) and (+VII). Among these first five elements, the correlation between electronic structure and minimum and maximum oxidation states in simple compounds is complete. In the highest oxidation states of these first five elements, all of the *s* and *d* electrons are being used for bonding. Thus the properties depend only on the size and valency, and consequently show some similarities with elements of the main groups in similar oxidation states. For example, SO_4^{2-} (Group 16) and CrO_4^{2-} (Group 6) are isostructural, as are SiCl_4 (Group 14) and TiCl_4 (Group 4).

Once the d^5 configuration is exceeded, i.e. in the last five elements, the tendency for all the d electrons to participate in bonding decreases. Thus Fe has a maximum oxidation state of (+VI). However, the second and third elements in this group attain a maximum oxidation state of (+VIII) in RuO_4 and OsO_4 . This difference between Fe and the other two elements Ru and Os is attributed to the increased size.

These facts may be conveniently memorized, because the oxidation states form a regular 'pyramid' as shown in Table 11.2. Only Sc(+II) and Co(+V) are doubtful. The oxidation number of all elements in the elemental state is zero. In addition, several of the elements have zero-valent and other low-valent states in complexes. Low oxidation states occur particularly with π bonding ligands such as carbon monoxide and dipyridyl. Similar but not identical pyramids of oxidation states are found in the second and third rows of transition elements. The main differences are as follows:

1. In Group 8 (the iron group) the second and third row elements show a maximum oxidation state of (+VIII) compared with (+VI) for Fe.
2. The electronic structures of the atoms in the second and third rows do not always follow the pattern of the first row. The structures of Group 10 elements (the nickel group) are:

Ni	$3d^8$	$4s^2$
Pd	$4d^{10}$	$5s^0$
Pt	$5d^9$	$6s^1$

Since a full shell of electrons is a stable arrangement, the place where this occurs is of importance. The d levels are complete for copper, palladium and gold in their respective series.

Ni		Cu	$3d^{10}$	$4s^1$	Zn	$3d^{10}$	$4s^2$
Pd	$4d^{10}$	$5s^0$	Ag		Cd	$3d^{10}$	$4s^2$
Pt			Au	$5d^{10}$	$6s^1$	Hg	$3d^{10}$

Even though the ground state of the atom has a d^{10} configuration, Pd and the coinage metals Cu, Ag and Au behave as typical transition elements. This is because in their most common oxidation states, Cu(II) has a d^9 configuration and Pd(II) and Au(III) have d^8 configurations, i.e. they have an incompletely filled d level. However, in zinc, cadmium and mercury the ions Zn^{2+} , Cd^{2+} and Hg^{2+} have a d^{10} configuration. Because of this, these elements do not show the properties characteristic of transition elements.

Stability of the various oxidation states

Compounds are regarded as stable if they exist at room temperature, are not oxidized by the air, are not hydrolysed by water vapour and do not disproportionate or decompose at normal temperatures. Within each of the transition Groups 3–12, there is a difference in stability of the various oxidation states that exist. In general, the second and third row elements exhibit higher coordination numbers, and their higher oxidation states are more stable than the corresponding first row elements. This gives the known oxides and halides of the first, second and third row transition elements. Stable oxidation states form oxides, fluorides, chlorides, bromides and iodides. Strongly reducing states probably do not form fluorides and/or oxides, but may as well form the heavier halides. Conversely, strongly oxidizing states form oxides and fluorides, but not iodides.

11.2 | COMPLEXES

The transition elements have an unparalleled tendency to form coordination compounds with Lewis bases, i.e. with groups which are able to donate an electron pair. These groups are called ligands. A ligand may be a neutral molecule such as NH_3 , or an ion such as Cl^- or CN^- . Cobalt forms more complexes than any other element, and forms more compounds than any other element except carbon.



This ability to form complexes is in marked contrast to the *s*- and *p*-block elements which form only a few complexes. The reason transition elements are so good at forming complexes is that they have small, highly charged ions and have vacant low energy orbitals to accept lone pairs of electrons donated by other groups or ligands. Complexes where the metal is in the (+III) oxidation state are generally more stable than those where the metal is in the (+II) state.

11.3 | SIZE OF ATOMS AND IONS

The covalent radii of the elements (Table 11.3) decrease from left to right across a row in the transition series, until near the end when the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra orbital electrons are added. The orbital electrons shield the nuclear charge incompletely (*d* electrons shield less efficiently than *p* electrons, which in turn shield less effectively than *s* electrons). Because of this poor screening by *d* electrons, the nuclear charge attracts all of the electrons more strongly; hence a contraction in size occurs.

Atoms of the transition elements are smaller than those of the Group 1 or 2 elements in the same horizontal period. This is partly because of the usual contraction in size across a horizontal period discussed above, and partly because the orbital electrons are added to the penultimate *d* shell rather than to the outer shell of the atom.

Table 11.3 Covalent radii of the transition elements (Å)

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
2.03	1.74	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
2.16	1.91	1.62	1.45	1.34	1.29	—	1.24	1.25	1.28	1.34	1.41
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
2.35	1.98	1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44

14 Lanthanide elements

The transition elements are divided into vertical groups of three (triads) or sometimes four elements, which have similar electronic structures. On descending one of the main groups of elements in the *s*- and *p*-blocks, the size of the atoms increases because extra shells of electrons are present. The elements in the first group in the *d*-block (Group 3) show the expected increase in size Sc → Y → La. However, in the subsequent Groups (3–12) there is an increase in radius of 0.1 → 0.2 Å between the first and second member, but hardly any increase between the second and third elements. This trend is shown both in the covalent radii (Table 11.3) and in the ionic radii (Table 11.4). Interposed between lanthanum and hafnium are the 14 lanthanide elements, in which the antepenultimate 4*f* shell of electrons is filled.

Table 11.4 The effect of the lanthanide contraction on ionic radii

Ca ²⁺ 1.00	Sc ³⁺ 0.745	Ti ⁴⁺ 0.605	V ³⁺ 0.64
Sr ²⁺ 1.18	Y ³⁺ 0.90	Zr ⁴⁺ 0.72	Nb ³⁺ 0.72
Ba ²⁺ 1.35	La ³⁺ 1.032	Hf ⁴⁺ 0.71	Ta ³⁺ 0.72

14 Lanthanides

11.4 | DENSITY

The atomic volumes of the transition elements are low compared to elements in neighbouring Groups 1 and 2. This is because the increased nuclear charge is poorly screened and so attracts all the electrons more strongly. In addition, the extra electrons added occupy inner orbitals. Consequently the

densities of the transition metals are high. Practically all have a density greater than 5 g cm^{-3} . (The only exceptions are Sc 3.0 g cm^{-3} and Y and Ti 4.5 g cm^{-3} .) The densities of the second row are high and third row values are even higher. (See Appendix D.) The two elements with the highest densities are osmium 22.57 g cm^{-3} and iridium 22.61 g cm^{-3} . To get some feel for how high this figure really is, it is found that a football made of osmium or iridium measuring 30 cm in diameter would weigh 320 kg or almost one third of a tonne!

11.5 | MELTING AND BOILING POINTS

The melting and boiling points of the transition elements are generally very high (see Appendices B and C). Transition elements typically melt above 1000°C . Ten elements melt above 2000°C and three melt above 3000°C (Ta 3000°C , W 3410°C and Re 3180°C). There are a few exceptions. The melting points of La and Ag are just under 1000°C (920°C and 961°C respectively). Other notable exceptions are Zn (420°C), Cd (321°C) and Hg which is liquid at room temperature and melts at -38°C . The last three behave a typically because the d shell is complete, and d electrons do not participate in metallic bonding. The high melting points are in marked contrast to the low melting points for the s -block metals Li (181°C) and Cs (29°C). (See Table 11.5.)

The trend in melting points can be explained on the basis that more the number of unpaired electrons involved in the metallic bonding, higher will be the melting point. In case of Cr, Mo and W, there are six unpaired electrons in their ground state which provide strongest metallic bonding. While in case of Zn, Cd, Hg, the number of unpaired electrons is zero and these have weakest metallic bonding and hence lowest melting points.

Table 11.5 Melting points of transition elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
m.p. ($^\circ\text{C}$)	1539	1667	1915	1903	1244	1535	1495	1453	1083	419
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
m.p. ($^\circ\text{C}$)	1523	1857	2468	2620	2172	2310	1966	1554	962	321
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	
m.p. ($^\circ\text{C}$)	920	2227	3000	3410	3180	3045	2410	1772	1064	-38
↓ Maxima in the respective series (Vanadium is an exception)						↓ Minima in the respective series				

11.6 | REACTIVITY OF METALS

Many of the metals are sufficiently electropositive to react with mineral acids, liberating H_2 . A few have low standard electrode potentials and remain unreactive or noble. Noble character is favoured by high enthalpies of sublimation, high ionization energies and low enthalpies of solvation. The high melting points indicate high heats of sublimation. The smaller atoms have higher ionization energies, but this is offset by small ions having high solvation energies. This tendency to favour noble character is most pronounced for the platinum metals (Ru, Rh, Pd, Os, Ir, Pt) and gold.

11.7 | IONIZATION ENERGIES

The ease with which an electron may be removed from a transition metal atom (that is, its ionization energy) is intermediate between those of the s - and p -blocks. Values for the first ionization energies vary over a wide range from 541 kJ mol^{-1} for lanthanum to 1007 kJ mol^{-1} for mercury. These are comparable with the values for lithium and carbon respectively. This would suggest that the transition elements are less electropositive than Groups 1 and 2 and may form either ionic or covalent bonds depending on the conditions. Generally, the lower valence states are ionic and the higher valence states are covalent. The first row elements have many more ionic compounds than elements in the second and third rows.

11.8 | COLOUR

Many ionic and covalent compounds of transition elements are coloured. In contrast, compounds of the *s*- and *p*-block elements are almost always white. When light passes through a material, it is deprived of those wavelengths that are absorbed. If absorption occurs in the visible region of the spectrum, the transmitted light is coloured with the colour complementary to the colour of the light absorbed. Absorption in the visible and UV regions of the spectrum is caused by changes in electronic energy. Thus the spectra are sometimes called electronic spectra. (These changes are often accompanied by much smaller changes in vibrational and rotational energies.) It is always possible to promote an electron from one energy level to another. However, the energy jumps are usually so large that the absorption lies in the UV region. Special circumstances can make it possible to obtain small jumps in electronic energy which appear as absorption in the visible region.

Polarization

NaCl, NaBr and NaI are all ionic, and are all colourless; AgCl is also colourless. Thus the halide ions, Cl^- , Br^- and I^- , and the metal ions Na^+ and Ag^+ are typically colourless. However, AgBr is pale yellow and AgI is yellow. The colour arises because the Ag^+ ion polarizes the halide ions. This means that it distorts the electron cloud, and implies a greater covalent contribution. The polarizability of ions increases with size, thus I^- is the most polarized, and is the most coloured. For the same reason, Ag_2CO_3 and Ag_3PO_4 are yellow, and Ag_2O and Ag_2S are black.

Incompletely filled *d* or *f* shell

Colour may arise from an entirely different cause in ions with incomplete *d* or *f* shells. This source of colour is very important in most of the transition metal ions.

In a free isolated gaseous ion the five *d* orbitals are degenerate, i.e. they are identical in energy. In real-life situations, the ion will be surrounded by solvent molecules if it is in solution; by other ligands if it is in a complex; or by other ions if it is in a crystal lattice. The surrounding groups affect the energy of some *d* orbitals more than others. Thus the *d* orbitals are no longer degenerate, and they form two groups of orbitals of different energies. Thus in transition element ions with a partly filled *d* shell, it is possible to promote electrons from one *d* level to another *d* level of higher energy. This corresponds to a fairly small energy difference, and so light is absorbed in the visible region. The colour of a transition metal complex is dependent on how big the energy difference is between the two *d* levels. This in turn depends on the nature of the ligand, and on the type of complex formed. Thus the octahedral complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is blue, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green and $[\text{Ni}(\text{NO}_2)_6]^{4-}$ is brown-red. The colour changes with the ligand used. The colour also depends on the number of ligands and the shape of the complex formed.

The source of colour in the lanthanides and the actinides is very similar, arising from $f \rightarrow f$ transitions. With the lanthanides, the $4f$ orbitals are deeply embedded inside the atom, and are well shielded by the $5s$ and $5p$ electrons. The f electrons are practically unaffected by complex formation; hence the colour remains almost constant for a particular ion regardless of the ligand. The absorption bands are also very narrow.

Some compounds of the transition metals are white, for example ZnSO_4 and TiO_2 . In these compounds it is not possible to promote electrons within the *d* level. Zn^{2+} has a d^{10} configuration and the *d* level is full. Ti^{4+} has a d^0 configuration and the *d* level is empty. In the series Sc(+III), Ti(+IV), V(+V), Cr(+VI) and Mn(+VII), these ions may all be considered to have an empty *d* shell; hence *d*-*d* spectra are impossible and they should be colourless. However, as the oxidation number increases these states become increasingly covalent. Rather than form highly charged simple ions, oxoions are formed TiO^{2+} , VO_2^+ , VO_4^{3-} , CrO_4^{2-} and MnO_4^- . VO_2^+ is pale yellow, but CrO_4^{2-} is strongly yellow coloured, and MnO_4^- has an intense purple colour in solution though the solid is almost black. The colour arises by charge transfer. In MnO_4^- an electron is momentarily transferred from O to the metal, thus momentarily changing O^{2-} to O^- and reducing the oxidation state of the metal from Mn(VII) to Mn(VI). Charge transfer requires that the energy levels on the two different atoms are fairly close. Charge transfer always produces intense colours since the restrictions of the Laporte and spin selection rules do not apply to transitions between atoms. The colour of aquated complexes of some transition metal ions are listed here.

Sc^{3+}	→ colourless
Ti^{4+}	→ colourless
Ti^{3+}	→ purple
V^{4+}	→ blue
V^{3+}	→ green
V^{2+}	→ violet
Cr^{2+}	→ blue
Cr^{3+}	→ green
Mn^{3+}	→ violet
Mn^{2+}	→ light pink
Fe^{2+}	→ light green
Fe^{3+}	→ yellow
Co^{2+}	→ pink
Ni^{2+}	→ green
Cu^{2+}	→ blue
Zn^{2+}	→ colourless

The *s*- and *p*-block elements do not have a partially filled *d* shell so there cannot be any *d-d* transition. The energy to promote an *s* or *p* electron to a higher energy level is much greater and corresponds to ultraviolet light being absorbed. Thus compounds of *s*- and *p*-block elements typically are not coloured.

11.9 | MAGNETIC PROPERTIES

When a substance is placed in a magnetic field of strength H , the intensity of the magnetic field in the substance may be greater than or less than H .

If the field in the substance is greater than H , the substance is paramagnetic. It is easier for magnetic lines of force to travel through a paramagnetic material than through vacuum. Thus paramagnetic materials attract lines of force and if it is free to move, a paramagnetic material will move from a weaker to a stronger part of the field. Paramagnetism arises as a result of unpaired electron spins in the atom.

If the field in the substance is less than H , the substance is diamagnetic. Diamagnetic materials tend to repel lines of force. It is harder for magnetic lines of force to travel through diamagnetic materials than through vacuum, and such materials tend to move from stronger to weaker part of a magnetic field. In diamagnetic compounds all the electron spins are paired. The paramagnetic effect is much larger than the diamagnetic effect.

It should be noted that Fe, Co and Ni are ferromagnetic. These ferromagnetic materials may be regarded as a special case of paramagnetism in which the moments on individual atoms become aligned and all point in the same direction. When this happens, the magnetic susceptibility is greatly enhanced compared with what it would be if all the moments behaved independently. Alignment occurs when materials are magnetised, and Fe, Co and Ni can form permanent magnets. Ferromagnetism is found in several of the transition metals and their compounds. It is also possible to get antiferromagnetism by pairing the moments on adjacent atoms which point in opposite directions. This gives a magnetic moment less than would be expected for an array of independent ions. It occurs in several simple salts of Fe^{3+} , Mn^{2+} and Gd^{3+} . Since ferromagnetism and antiferromagnetism depend on orientation, they disappear in solution.

Many compounds of the transition elements are paramagnetic, because they contain partially filled electron shells. If the magnetic moment is measured, the number of unpaired electrons can be calculated. The magnetochemistry of the transition elements shows whether the *d* electrons are paired. This is of great importance in distinguishing between *high-spin* and *low-spin* octahedral complexes.

11.10 | CATALYTIC PROPERTIES

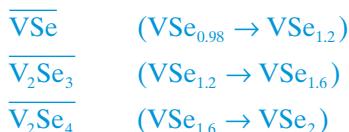
Many transition metals and their compounds have catalytic properties. Some of the more important ones are listed here:

TiCl_3	Used as the Ziegler–Natta catalyst in the production of polythene.
V_2O_5	Converts SO_2 to SO_3 in the Contact process for making H_2SO_4 .
MnO_2	Used as a catalyst to decompose KClO_3 to give O_2 .
Fe	Promoted iron is used in the Haber–Bosch process for making NH_3 .
FeSO_4 and H_2O_2	Used as Fenton's reagent for oxidizing alcohols to aldehydes.
PdCl_2	Wacker process for converting $\text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{PdCl}_2$ to $\text{CH}_3\text{CHO} + 2\text{HCl} + \text{Pd}$.
Pd	Used for hydrogenation (e.g. phenol to cyclohexanone).
$\text{PtO}_2 \cdot \text{H}_2\text{O}$	Adams catalyst, used for reductions.
Pt	Formerly used for $\text{SO}_2 \rightarrow \text{SO}_3$ in the Contact process for making H_2SO_4 .
Pt/Rh	Formerly used in the Ostwald process for making HNO_3 to oxidize NH_3 to NO .
Cu	Direct process for manufacture of $(\text{CH}_3)_2\text{SiCl}_2$ used to make silicones.
CuCl_2	Deacon process of making Cl_2 from HCl .
Ni	Raney nickel, numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of H_2 from NH_3 , reducing anthraquinone to anthraquinol in the production of H_2O_2). Reppe synthesis (polymerization of alkynes, e.g. to give benzene or cyclooctatetraene).

In some cases, the transition metals with their variable valency may form unstable intermediate compounds. In other cases the transition metal provides a suitable reaction surface.

11.11 | NONSTOICHIOMETRY

A further feature of the transition elements is that they sometimes form nonstoichiometric compounds. These are compounds of indefinite structure and proportions. For example, iron(II) oxide FeO should be written with a bar over the formula FeO to indicate that the ratio of Fe and O atoms is not exactly 1:1. Analysis shows that the formula varies between $\text{Fe}_{0.94}\text{O}$ and $\text{Fe}_{0.84}\text{O}$. Vanadium and selenium form a series of compounds ranging from $\text{VSe}_{0.98}$ to VSe_2 . These are given in the formulae:



Nonstoichiometry is shown particularly among transition metal compounds of the Group 16 elements (O, S, Se, Te). It is mostly due to the variable valency of transition elements. For example, copper is precipitated from a solution containing Cu^{2+} by passing in H_2S . The sulphide is completely insoluble, but this is not used as a gravimetric method for analysing Cu because the precipitate is a mixture of CuS and Cu_2S . Sometimes, nonstoichiometry is caused by defects in the solid structures.

11.12 | ABUNDANCE

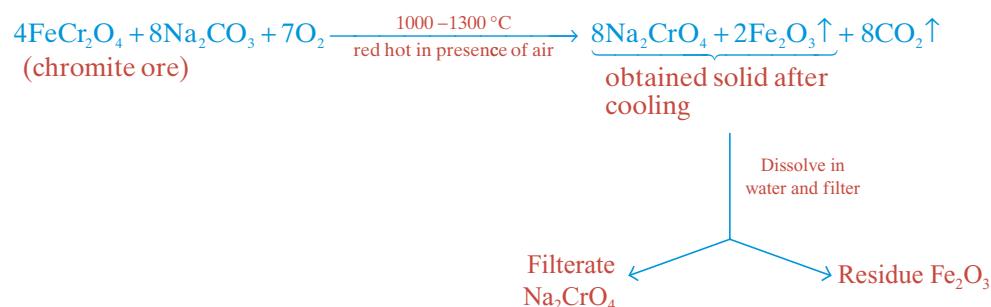
Three of the transition metals are very abundant in the earth's crust. Fe is the fourth most abundant element by weight, Ti the ninth and Mn the twelfth (Table 11.6). The first row of transition elements largely follow Harkins' rule that elements with an even atomic number are in general more abundant than their neighbours with odd atomic numbers. Manganese is an exception. The second and third row elements are much less abundant than the first row. Tc does not occur in nature. Of the last six elements in the second and third rows (Tc, Ru, Rh, Pd, Ag, Cd; Re, Os, Ir, Pt, Au, Hg) none occurs to an extent of more than 0.16 parts per million (ppm) in the earth's crust.

Table 11.6 Abundance of the transition elements in the earth's crust, in ppm by weight

Sc 25	Ti 6320	V 136	Cr 122	Mn 1060	Fe 60 000	Co 29	Ni 99	Cu 68	Zn 76
Y 31	Zr 162	Nb 20	Mo 1.2	Tc -	Ru 0.0001	Rh 0.0001	Pd 0.015	Ag 0.08	Cd 0.16
La 35	Hf 2.8	Ta 1.7	W 1.2	Re 0.0007	Os 0.005	Ir 0.001	Pt 0.01	Au 0.004	Hg 0.08

11.13 | CHROMATE AND DICHROMATE

Preparation



Lime (CaO) is added with Na_2CO_3 which keeps the mass porous so that air becomes accessible to all parts of reaction mixture and prevents fusion. Then, chromate is converted to dichromate using sulphuric acid.



The solubility of Na_2SO_4 increases up to 32°C and then decreases. Hence, a suitable temperature is to be employed to crystallize out Na_2SO_4 first. Then $\text{Na}_2\text{Cr}_2\text{O}_7$ is crystallized out as $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (red crystals) on evaporation.

Potassium dichromate is obtained by double decomposition reaction using hot concentrated $\text{Na}_2\text{Cr}_2\text{O}_7$ solution and potassium chloride



$\text{K}_2\text{Cr}_2\text{O}_7$ and NaCl both are water soluble and hence fractional crystallization is carried out. NaCl crystallizes out first and is filtered off. Then $\text{K}_2\text{Cr}_2\text{O}_7$ is crystallized out further.

Properties

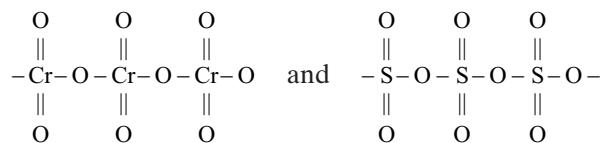
The important properties of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ such as solubility and chemical reactivity towards different reagents have been discussed in Chapter 7 (Section 7.12).

Hexavalent chromium shows similarities in properties with hexavalent sulphur compounds because both the elements have the same number of valence shell electrons. These similar properties are listed as follows:

1. SO_3 and CrO_3 are both acidic.
2. S forms SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$ and similarly Cr forms CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$.
3. K_2CrO_4 and K_2SO_4 are isomorphous.
4. $\text{SO}_2\text{Cl}_2 \xrightarrow{\text{OH}^-} \text{SO}_4^{2-}$ and $\text{CrO}_2\text{Cl}_2 \xrightarrow{\text{OH}^-} \text{CrO}_4^{2-}$



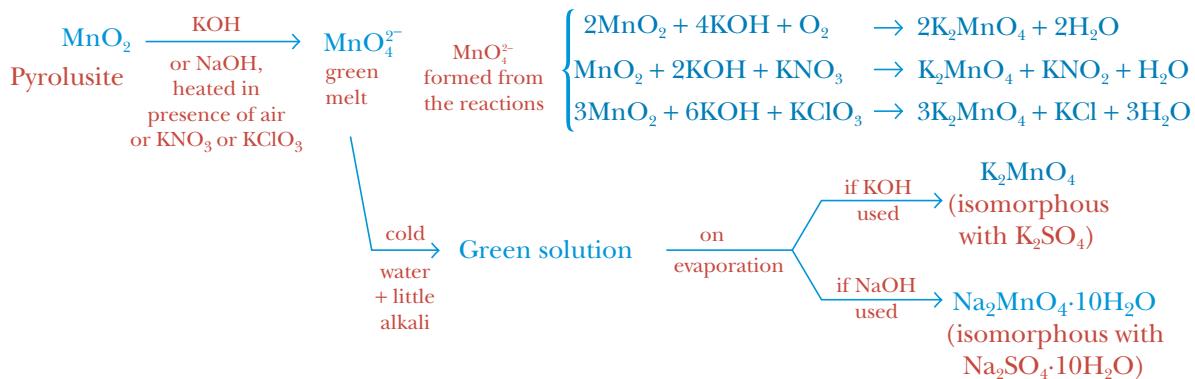
6. CrO_3 and $\beta(\text{SO}_3)$ have the same structures



11.14 | MANGANATE AND PERMANGANATE

Preparation

1.



This reaction is faster in the presence of KClO_3 and KNO_3 because these on decomposition provide oxygen easily in all parts of the reaction mixture.

2. Manganate is also obtained when KMnO_4 is boiled with conc. KOH.



The above green solution is quite stable in alkali, but decomposes in pure water and in the presence of acids, depositing MnO_2 and giving a purple solution of permanganate.



This reaction is also a method of preparation of KMnO_4 .

In this reaction one-third of Mn is lost as MnO_2 but when oxidised either by Cl_2 or by O_3 , unwanted MnO_2 is not formed.



or



Properties

1. **Oxidizing properties of KMnO_4 in acidic medium:** The oxidizing properties of KMnO_4 in acidic medium have been discussed in Chapter 7 (Section 7.13). For use as an oxidizing agent, KMnO_4 should be stored in dark bottles and standardized just before use due to the following reasons:

- a. It is not a primary standard since it is difficult to get it in a high degree of purity and free from traces of MnO_2 .
- b. It is slowly reduced to MnO_2 especially in the presence of light or acid.



- 2. Oxidizing properties of KMnO_4 in alkaline medium:** The reactions involved are



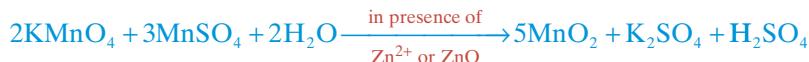
Some examples,

- a. $2\text{KMnO}_4 + \text{H}_2\text{O} + \text{KI} \rightarrow 2\text{MnO}_2 + 2\text{KOH} + \text{KIO}_3$
- b. $2\text{KMnO}_4 + 3\text{HCO}_3\text{K} \rightarrow 2\text{MnO}_2 + \text{KHCO}_3 + 2\text{K}_2\text{CO}_3 + \text{H}_2\text{O}$
- c. $2\text{KMnO}_4 + 3\text{H}_2\text{O}_2 \rightarrow 2\text{KOH} + 2\text{MnO}_2 + 2\text{H}_2\text{O} + 3\text{O}_2$

- 3. Oxidizing properties of KMnO_4 in neutral or weak acidic medium:** The reaction in neutral medium is



For example,



In absence of Zn^{2+} ions, some of Mn^{2+} ions may escape oxidation through the formation of insoluble manganous permanganate $\text{Mn}^{\text{II}}[\text{Mn}^{\text{IV}}\text{O}_3]$.

The reaction in weak acidic medium is



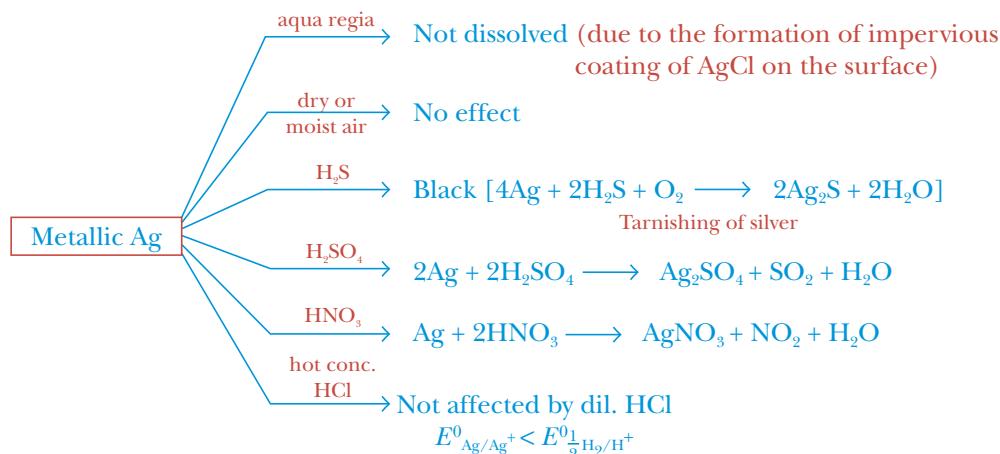
- 4. Heating effect:** The effect of heating on KMnO_4 is discussed in Chapter 7 (Section 7.13).



K_2MnO_4 is soluble in water and obtained as green filtrate. MnO_2 is insoluble in water and obtained as black residue.

11.15 | SILVER AND ITS COMPOUNDS

The reactivity of metallic silver towards different reagents is described as follows:



However, in presence of O_2 , Ag reacts with dil. HCl



Similarly, in the presence of O_2 , Ag forms complex with NaCN/KCN



Silver nitrate (AgNO_3)

It is called as lunar caustic because on contact with skin it produces a burning sensation like that with caustic soda along with the formation of finely divided silver (black colour).

Preparation

When metallic Ag is dissolved in conc. HNO_3 it produces AgNO_3 .



Properties

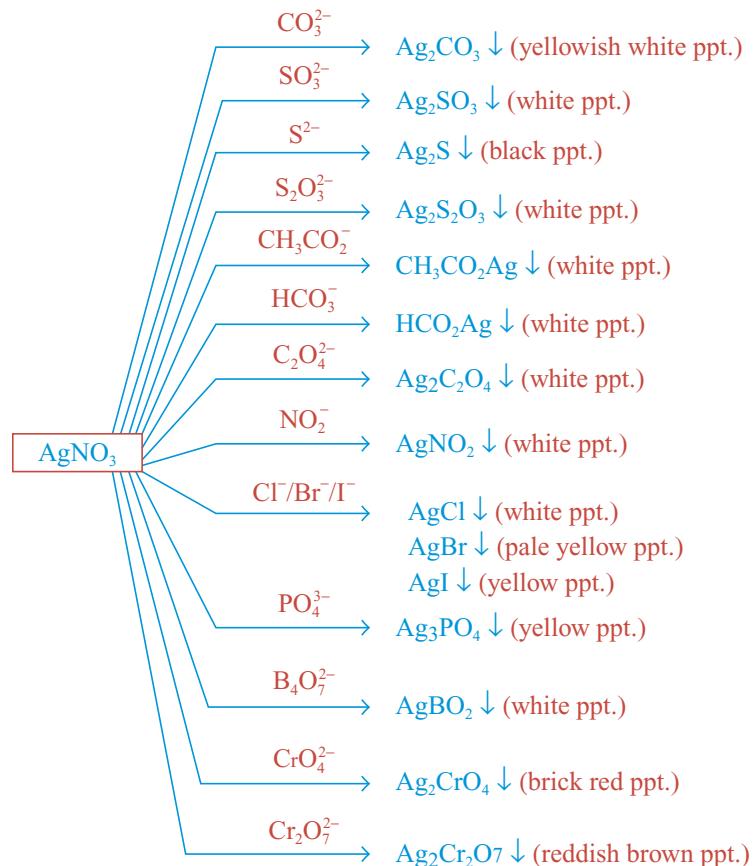
1. Thermal decomposition:



Ag is obtained as black metallic residue.

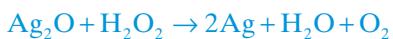
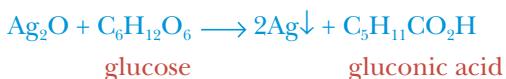
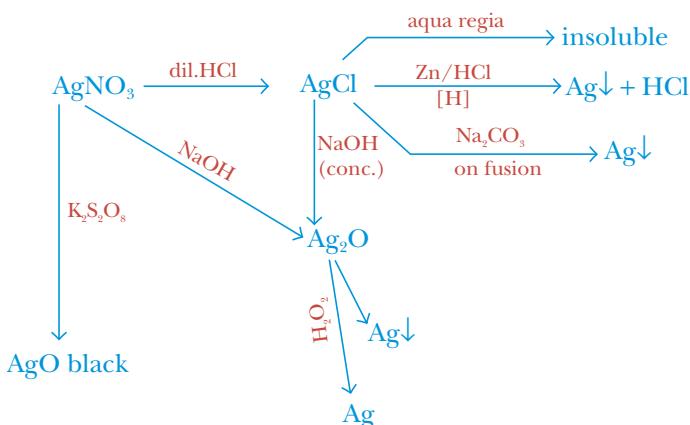
2. $6\text{AgNO}_3 + 3\text{I}_2 + 3\text{H}_2\text{O} \rightarrow 5\text{AgI} + \text{AgIO}_3 + 6\text{HNO}_3$
(excess)

3. The reactions of AgNO_3 towards different acid radicals are summarized as follows:



Note: Preparation of AgCl , AgBr , AgI , $\text{Ag}_2\text{S}_2\text{O}_3$ can be done very easily by the reaction of AgNO_3 with KCl , KBr , KI and $\text{Na}_2\text{S}_2\text{O}_3$ solution (reactions are shown above). Properties of all these compounds are also discussed at different places in Chapter 7.

4.



5. AgO is expected to be paramagnetic due to d^0 configuration. But actually it is diamagnetic and exists as $\text{Ag}^{\text{I}}[\text{Ag}^{\text{III}}\text{O}_2]$.

Use

AgCl and AgBr are used in photography.

11.16 | ZINC COMPOUNDS

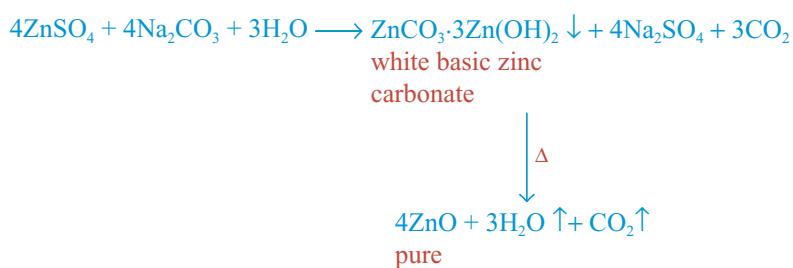
Zinc oxide (ZnO)

It is called philosopher's wool due to its wooly flock type appearance.

Preparation

1. $2\text{Zn} + \text{O}_2 \xrightarrow[\text{air}]{\text{burnt in}} 2\text{ZnO}$
 2. $\text{ZnCO}_3 \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2$
 3. $2\text{Zn}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{ZnO} + 4\text{NO}_2 + \text{O}_2$
 4. $\text{Zn}(\text{OH})_2 \xrightarrow{\Delta} \text{ZnO} + \text{H}_2\text{O}$

The purest form of ZnO is obtained by



Properties

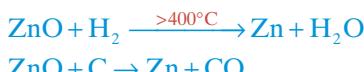
1. On heating white ZnO turns yellow in colour and this is due to the formation of f-centre.



2. It is insoluble in water.
 3. It sublimes at 400 °C.
 4. It is an amphoteric oxide, as indicated by the following reactions:



5. ZnO can be reduced to metallic zinc using hydrogen gas or carbon.



6. It forms Rinmann's green with $\text{Co}(\text{NO}_3)_2$.



Uses

1. ZnO is used as a white pigment. It is superior to white lead because it does not turn black when it comes in contact with air.
 2. Rinmann's green is used as a green pigment.
 3. It is used as zinc ointment in medicine.

Zinc chloride (ZnCl_2)

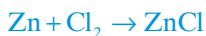
Preparation

1. $\text{ZnCO}_3 + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O} + \text{CO}_2$
 2. $\text{ZnO} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$
 3. $\text{Zn}(\text{OH})_2 + 2\text{HCl} \rightarrow \text{ZnCl}_2 + 2\text{H}_2\text{O}$

In all of the above reactions, zinc chloride crystallizes as $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$. Anhydrous ZnCl_2 cannot be made by direct heating of $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ because



However, anhydrous ZnCl_2 can be prepared by the following ways:



Properties

1. It is a deliquescent white solid (when anhydrous).
 2. $\text{ZnCl}_2 + \text{H}_2\text{S} \rightarrow \text{ZnS}$
 3. $\text{ZnCl}_2 + \text{NaOH} \rightarrow \text{Zn}(\text{OH})_2 \xrightarrow{\text{excess}} \text{Na}_2[\text{Zn}(\text{OH})_4]_{\text{whit ppt.}}$
$$\text{ZnCl}_2 + \text{NH}_4\text{OH} \rightarrow \text{Zn}(\text{OH})_2 \xrightarrow{\text{excess}} [\text{Zn}(\text{NH}_3)_4]^{2+}_{\text{whit ppt.}}$$

Other properties of ZnCl_2 have already been discussed in Chapter 7 (Sections 7.16 and 7.17).

Uses

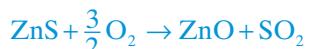
1. For impregnating timber to prevent destruction by insects.
2. As dehydrating agent when anhydrous.
3. $\text{ZnO} \cdot \text{ZnCl}_2$ is used in dental fillings.

Zinc sulphate (ZnSO_4)**Preparation**

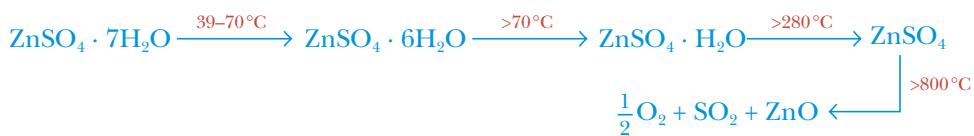
ZnSO_4 can be prepared by the following ways:

1. $\text{Zn} + \text{dil. H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$
2. $\text{ZnO} + \text{dil. H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$
3. $\text{ZnCO}_3 + \text{dil. H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2\text{O} + \text{CO}_2$
4. $\text{ZnS} + 2\text{O}_2 \rightarrow \text{ZnSO}_4$

This proceeds through the following parallel reactions:

**Properties**

1. Thermal decomposition:

**Uses**

1. In eye lotions.
2. Lithophone ($\text{ZnS} + \text{BaSO}_4$) is used as white pigment and prepared as follows:

**11.17 | COPPER COMPOUNDS****Copper oxide (CuO)****Preparation**

CuO can be prepared by the following processes:

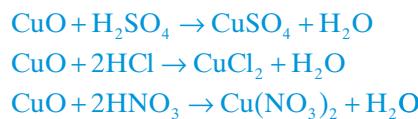
1. $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \xrightarrow{\Delta} 2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2$
Malachite green
(native copper carbonate)

This is the commercial process for the manufacture of CuO .

2. $2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}$ and $\text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuO}$
3. $\text{Cu}(\text{OH})_2 \xrightarrow{\Delta} \text{CuO} + \text{H}_2\text{O}$
4. $2\text{Cu}(\text{NO}_3)_2 \xrightarrow{250^\circ\text{C}} 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$

Properties

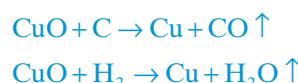
1. It is insoluble in water.
2. It readily dissolves in dilute acids by the following reactions:



3. It decomposes when heated above 1100°C .



4. It is reduced to Cu by hydrogen or carbon under hot conditions.

**Copper chloride (CuCl_2)****Preparation**

CuCl_2 can be prepared by following ways:

1. $\text{CuO} + 2\text{HCl}(\text{conc.}) \rightarrow \text{CuCl}_2 + \text{H}_2\text{O}$
2. $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3 + 4\text{HCl} \rightarrow 2\text{CuCl}_2 + 3\text{H}_2\text{O} + \text{CO}_2$

Properties

1. It is crystallized as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ which is emerald green in colour.
2. Dilute solution of CuCl_2 in water is blue in colour due to the formation of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ complex.
3. When conc. HCl or KCl is added to dilute solution of CuCl_2 , the colour changes into yellow owing to the formation of $[\text{CuCl}_4]^{2-}$.
4. The concentrated aqueous solution of CuCl_2 is green in colour having the following two complex ions in equilibrium:



5. CuCl_2 can be converted into CuCl by using the following reagents:

- $\text{CuCl}_2 + \text{copper turnings} \xrightarrow{\Delta} 2\text{CuCl}$
- $2\text{CuCl}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{CuCl} + 2\text{HCl} + 2\text{H}_2\text{SO}_4$
- $2\text{CuCl}_2 + \text{Zn/HCl} \rightarrow 2\text{CuCl} + \text{ZnCl}_2$
- $\text{CuCl}_2 + \text{SnCl}_2 \rightarrow \text{CuCl} + \text{SnCl}_4$

6. Anhydrous CuCl_2 is a dark brown mass obtained by heating $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at 150°C in the presence of HCl vapours.

**Copper sulphate (CuSO_4)****Preparation**

CuSO_4 can be prepared by the following ways:

1. $\text{CuO} + \text{H}_2\text{SO}_4(\text{dil.}) \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$
2. $\text{Cu}(\text{OH})_2 + \text{dil. H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 2\text{H}_2\text{O}$

3. $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3 + \text{dil. H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 3\text{H}_2\text{O} + \text{CO}_2$
4. $\text{Cu} + \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$

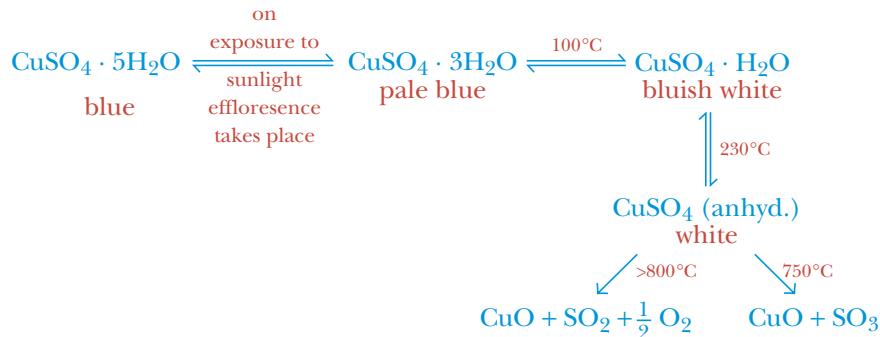
This process is used for the manufacture of CuSO_4 .

Note: $\text{Cu}(\text{scrap}) + \text{dil. H}_2\text{SO}_4 \rightarrow \text{no reaction}$

This is because copper lies below hydrogen in electrochemical series.

Properties

1. It is crystallized as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and is called as blue vitriol.



2. The other properties of CuSO_4 have already been discussed in Chapter 7 (Section 7.16).

11.18 | IRON COMPOUNDS

Iron sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

Preparation

Iron sulphate can be prepared by the following ways:

1. $\text{Fe}(\text{scrap}) + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2\uparrow$
2. From Kipp's apparatus waste
 $\text{FeS} + \text{dil. H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2\text{S}\uparrow$
3. $\text{FeS}_2 + 2\text{H}_2\text{O} + \frac{7}{2}\text{O}_2 \rightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4$

Properties

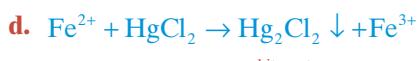
1. It undergoes oxidation forming basic ferric sulphate.



3. Its aqueous solution is acidic due to hydrolysis.



4. It acts as a reducing agent.



On further addition of FeCl_2 , it does not turn Hg_2Cl_2 into metallic Hg as in case of addition of SnCl_2 .

- It forms double salts. For example, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$
- It is crystallized as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (known as green vitriol) which is isomorphous with $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsom salt) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (white vitriol).
- Its aqueous solution is used for absorption of NO gas.

Iron oxide (FeO)

Preparation

Iron oxide is prepared by the following reaction:



Properties

It is stable at high temperatures and on cooling slowly disproportionates into Fe_3O_4 and Fe.



Iron chloride (FeCl_2)

Preparation

Iron chloride can be prepared by the following ways:

- $\text{Fe} + 2\text{HCl} \xrightarrow[\text{a current of HCl}]{\text{heated in}} \text{FeCl}_2 + \text{H}_2$
- $2\text{FeCl}_3 + \text{H}_2 \xrightarrow{\Delta} 2\text{FeCl}_2 + 2\text{HCl}$

Properties

- It is deliquescent in air.
- It is soluble in water, alcohol and ether because it is sufficiently covalent in nature.
- It volatilizes at about 1000°C and vapour density indicates the presence of Fe_2Cl_4 . Above 1300°C density becomes normal.
- It is oxidized on heating in air.



- H_2 is evolved on heating FeCl_2 with steam.



- It can exist in different hydrated forms.



- Other properties of Fe^{2+} cation have been discussed in Chapter 7(Sections 7.16 and 7.17).

Uses

- It is used to prepare writing ink.
- It is used as mordant in dying.
- It is used as weed killer in agriculture.
- It is used as a reducing agent.

SINGLE CORRECT CHOICE TYPE QUESTIONS

1. Which of the following statements is wrong regarding copper sulphate?
 (A) It reacts with KI to give I_2 .
 (B) It reacts with KCl to give Cl_2 .
 (C) Its tartarate complex reacts with NaOH and glucose followed by heating to give Cu_2O .
 (D) It gives CuO on strong heating in air.
2. ZnO shows yellow colour on heating due to
 (A) $d-d$ transition.
 (B) charge transfer spectra.
 (C) higher polarization caused by Zn^{2+} ion.
 (D) presence of F-center.
3. Malachite and azurite are used respectively as
 (A) blue and green pigment.
 (B) red and green pigment.
 (C) green and blue pigment.
 (D) green and red pigment.
4. Choose the correct options (true or false) for the following statements.
 (i) FeO is stable enough at room temperature.
 (ii) $FeCl_2$ on heating in air and in steam produces the same iron oxide.
 (iii) The colour of $FeCl_2$ depends upon the number of water of crystallization.
 (A) TTF
 (B) FTF
 (C) FFT
 (D) TFT
5. The elements with maximum and minimum melting points in the second transition series respectively are
 (A) Cr and Zn.
 (B) Cr and Cd.
 (C) Cr and Hg.
 (D) Mo and Cd.
6. (i) $BaCO_3 + Na_2CrO_4 + AcOH \rightarrow M$
 aq. suspension ppt.
 (ii) $BaCO_3 + Na_2CrO_4 + HCN \rightarrow N$
 aq. suspension ppt.
 Which is the correct option regarding the above reactions?
 (A) M and N are the same and characterized as $BaCrO_4$.
 (B) M is $BaCrO_4$ and N stands for no precipitate.
 (C) M is $BaCrO_4$ and N is $BaCO_3$.
 (D) M stands for no precipitate and N is $BaCrO_4$.
7. Which of the following statements is incorrect regarding the similarities between hexavalent Cr and S compounds?
 (A) SO_3 and CrO_3 both are acidic.
 (B) SO_2Cl_2 and CrO_2Cl_2 on alkaline hydrolysis produce similar type of products.
- (C) CrO_3 and $\gamma-SO_3$ have the same structure.
 (D) Both can form $X_2O_7^{2-}$ type of compounds.
8. $E_{MnO_4^-/MnO_2}^0 = 2.26\text{ V}$ and $E_{MnO_4^-/MnO_4^{2-}}^0 = 0.56\text{ V}$
 Which of the following reactions will be spontaneous?
 (A) $MnO_4^{2-} \rightarrow MnO_4^-$
 (B) $MnO_4^- \rightarrow MnO_2 + MnO_4^{2-}$
 (C) $MnO_4^{2-} \rightarrow MnO_2 + MnO_4^-$
 (D) None of these.
9. For the preparation of $KMnO_4$ from K_2MnO_4 which of the following reagents is the best?
 (A) Dil. H_2SO_4
 (B) $SnCl_2$ (acidified)
 (C) CO_2 is passed
 (D) Cl_2 is passed
10. When $KMnO_4$ reacts with H_2O_2 in a slightly alkaline and acidic medium, the respective products obtained are
 (A) K_2MnO_4 and Mn^{2+} (B) MnO_2 and MnO_2
 (C) MnO_2 and Mn^{2+} . (D) Mn^{2+} and MnO_2
11. AgO actually exists as $Ag [AgO_2]$, which is diamagnetic in nature. Then which of the following statements is true regarding AgO ?
 (A) The arrangement of O^{2-} ions around Ag^+ ion is square planar.
 (B) The arrangement of O^{2-} ions around Ag^{3+} ion is tetrahedral.
 (C) The arrangement of O^{2-} ions around Ag^{3+} ion is square planar.
 (D) Both (B) and (C) are correct.
12. Total number of d -orbitals involved in the hybridization of central metal ion in complex ion $[MnO_4]^-$ is
 (A) 6 (B) 4 (C) 2 (D) 3
13. Which of the following metal ions is expected to be coloured?
 (A) Zn^{2+} (B) Ti^{3+} (C) Sc^{3+} (D) Ti^{4+}
14. When Cu^{2+} solution reacts with excess KI, which of the following statements is correct?
 (A) White ppt. of Cu_2I_2 is obtained.
 (B) A clear brown solution is obtained.
 (C) A dark brown solution is obtained in which ppt. of Cu_2I_2 is invisible.
 (D) A blue solution is obtained.
15. When $KMnO_4$ is heated with fused KOH, then the product formed is
 (A) $KMnO_4$, purple
 (B) K_2MnO_4 , green
 (C) MnO_2 , black
 (D) Mn_2O_3 , brown

MULTIPLE CORRECT CHOICE TYPE QUESTIONS

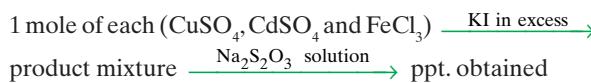
- Measurement of magnetic moment helps to predict
 - whether the compound is paramagnetic or diamagnetic.
 - whether the compound is coloured or not.
 - the number of unpaired electrons in the system.
 - whether the compound is low spin or high spin, wherever it is applicable.
- Which of the following properties of a substance disappear in solution?
 - Paramagnetism.
 - Diamagnetism.
 - Ferromagnetism.
 - Antiferromagnetism.
- The colour of a compound may be due to
 - polarization.
 - $d-d$ transition.
 - $f-f$ transition.
 - charge transfer spectra.
- The colour of a metal ion depends upon
 - the nature of the ligand.
 - the number of ligands.
 - the shape of the complex.
 - None of these.
- Which of the following statements are correct regarding Mohr's salt?
 - It does not dissolve in water completely.
 - It is one of the primary standard substances used in the laboratory.
 - The oxidation state of Fe in it is +III.
 - It produces NH_3 when NaOH is added into it.
- K_2MnO_4 is unstable in solution and the green solution obtained is changed into purple colouration. Correct statements regarding the above change are:
 - It is a disproportionation reaction.
 - It produces KMnO_4 .
- Overall solution becomes alkaline.
- It produces black precipitate of hydrated MnO_2 .
- When chromite ore is heated with Na_2CO_3 powder in the presence of air
 - one gaseous product is formed.
 - one product is water insoluble which is dark brown in colour.
 - one product is water soluble which is red in colour.
 - one product is water soluble which is yellow in colour.
- Choose incorrect options from the following statements.
 - O_2 is evolved during the hydrolysis of XeF_2 , XeF_4 , XeF_6 .
 - $\text{K}_2\text{Cr}_2\text{O}_7$ is not a deliquescent substance.
 - All C–C bonds are ruptured in glucose when it is treated with alkaline solution of AgNO_3 .
 - $\text{K}_2\text{Cr}_2\text{O}_7$ reacts with cold conc. H_2SO_4 to produce a green compound.
- For the standardization of hypo solution
 - standard KMnO_4 can be used which is prepared fresh.
 - standard $\text{K}_2\text{Cr}_2\text{O}_7$ can be used which is prepared one month before.
 - Both can be used.
 - None is suitable.
- Consider the following reaction:

$$\text{Metal M} + \text{aq. KCN} + \text{air} \rightarrow ? \xrightarrow[\text{(Impure)}]{\text{Zn}} [\text{Zn}(\text{CN})_4]^{2-} + \text{M} \downarrow_{(\text{Pure})}$$
 Then M is:
 - Au
 - Ag
 - Both
 - None

COMPREHENSION TYPE QUESTIONS

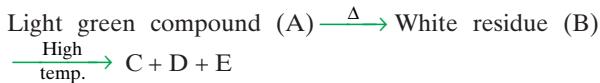
Passage 1: For Questions 1–3

A mixture is treated with KI as follows:

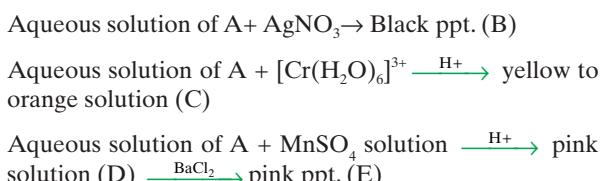


- How many moles of $\text{Na}_2\text{S}_2\text{O}_3$ are required in the above process?
 - $\frac{1}{2}$ mole
 - 2 moles
 - 1 mole
 - $1\frac{1}{2}$ moles

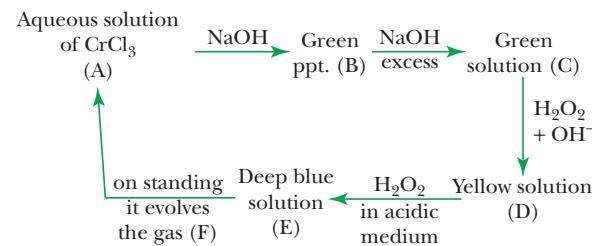
- How many moles of KI are consumed to obtain the product mixture?
 - 4 moles
 - $6\frac{1}{2}$ moles
 - 7 moles
 - $5\frac{1}{2}$ moles
- The precipitate obtained is:
 - $\text{CdI}_2 + \text{Cu}_2\text{I}_2$
 - Cu_2I_2
 - $\text{Cu}_2\text{I}_2 + \text{FeI}_2$
 - None of these.

Passage 2: For Questions 4–6

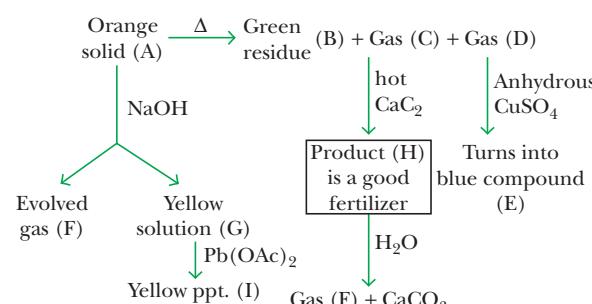
- D and E are acidic gases.
 - D is passed through HgCl_2 solution to give yellow precipitate.
 - When E is passed through water first and then H_2S is passed, white turbidity is obtained.
 - A is water soluble and on addition of HgCl_2 in it, a white precipitate is obtained which does not turn grey on addition of excess solution of A.
4. D and E are respectively
 (A) SO_2 and SO_3 .
 (B) SO_3 and SO_2 .
 (C) SO_2 and CO_2 .
 (D) CO_2 and CO .
5. The yellow precipitate in the above reaction is
 (A) mercuric oxide.
 (B) basic mercury(II) sulphite.
 (C) basic mercury (II) sulphate.
 (D) mercuric iodide.
6. C is soluble in
 (A) dil. HCl .
 (B) dil. H_2SO_4 .
 (C) conc. H_2SO_4 under hot conditions.
 (D) boiled conc. HCl .

Passage 3: For Questions 7–9

7. The black precipitate is
 (A) AgO
 (B) Ag_2O
 (C) Ag_2S
 (D) Ag
8. The true oxidation state of Ag in the black precipitate is/are
 (A) +2
 (B) +1 and +3
 (C) +1
 (D) None of these.
9. The formula of pink precipitate (E) is
 (A) BaSO_4
 (B) $\text{Ba}(\text{MnO}_4)_2$
 (C) MnO_2
 (D) MnSO_4

Passage 4: For Questions 10–12

10. The evolved gas F is
 (A) O_2
 (B) O_3
 (C) H_2
 (D) N_2
11. In which of the following compounds will chromium have the same oxidation state (VI)?
 (A) A, B, C
 (B) B, D, E
 (C) D, E
 (D) B, C, D
12. For the conversion of C \rightarrow D, which other reagent can be used?
 (A) $\text{NaBO}_3 + \text{NaOH}$
 (B) $\text{Br}_2 + \text{NaOH}$
 (C) $\text{Na}_2\text{S}_2\text{O}_8 + \text{H}^+$
 (D) All of these.

Passage 5: For Questions 13–16

13. The evolved gas F is
 (A) N_2
 (B) H_2
 (C) NH_3
 (D) O_2
14. The product H is
 (A) $\text{Ca}(\text{CN})_2$
 (B) CaCN_2
 (C) CaH_2
 (D) $\text{CaCN}_2 + \text{C}$

15. The number of water of crystallization present in compound E is
 (A) 4
 (B) 5
 (C) 2
 (D) 6
16. The oxidation state of the metal present in A is the same as that of the metal present in
 (A) G and I
 (B) G and E
 (C) B and E
 (D) B and G

ASSERTION-REASONING TYPE QUESTIONS

In the following set of questions, a Statement I is given and a corresponding Statement II is given below it. Mark the correct answer as:

- (A) If both Statement I and Statement II are true and Statement II is the correct explanation of Statement I.
- (B) If both Statement I and Statement II are true but Statement II is not the correct explanation for Statement I.
- (C) If Statement I is true but Statement II is false.
- (D) If Statement I is false but Statement II is true.

1. **Statement I:** Cu^{2+} is more stable than Cu^+ .

Statement II: Ligand field effects in the complexes are more important than electron configuration in determining stable oxidation state.

2. **Statement I:** Concentrated solution of CuCl_2 in water is yellow in colour.

Statement II: The concentrated solution contains $[\text{CuCl}_4]^{2-}$ ion and $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ion.

3. **Statement I:** Anhydrous ZnCl_2 cannot be made by heating $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$.

Statement II: It undergoes hydrolysis to produce $\text{Zn}(\text{OH})_2$ and HCl .

4. **Statement I:** FeCl_2 is a secondary standard substance.

Statement II: The weight of FeCl_2 changes with time by any means.

5. **Statement I:** CuI_2 does not exist.

Statement II: I^- ions are very susceptible towards oxidation by Cu^{2+} ions.

6. **Statement I:** $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is isomorphous with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Statement II: Both molecules have the same number of water molecules of crystallization.

7. **Statement I:** Lithophone is preferred over white lead as white pigment.

Statement II: In the presence of H_2S in air, white lead turns black.

8. **Statement I:** CO_3^{2-} and HCO_3^- ions are distinguished by using AgNO_3 .

Statement II: CO_3^{2-} gives white (yellowish) ppt. with AgNO_3 and no ppt. with HCO_3^- .

9. **Statement I:** Ag does not liberate H_2 with dil. HCl .

Statement II: $E_{\text{Ag}/\text{Ag}^+}^0 > E_{\frac{1}{2}\text{H}_2/\text{H}^+}^0$

10. **Statement I:** On addition of alkali to the yellow solution of chromate, it turns orange.

Statement II: CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are present in equilibrium and their relative concentrations depend upon the pH of the medium.

INTEGER ANSWER TYPE QUESTIONS

The answer to each of the following questions is a non-negative integer.

1. How many non-axial d -orbitals are involved in the hybridization of CrO_2Cl_2 ?
2. The sum of the oxidation states of Mn in KMnO_4 , K_2MnO_4 and K_3MnO_4 is _____.
3. The number of equivalent Cr–O bonds in CrO_4^{2-} is _____.

4. The number of the following reagents that produce ppt. with ZnSO_4 solution is _____.

NaOH , Na_2CO_3 , NaCl , Na_2HPO_4 , Na_2S , $\text{CH}_3\text{CO}_3\text{Na}$.

5. The change in the magnetic moment value when $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ is converted to $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is _____.

6. The change in the number of unpaired electrons when $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is changed into $[\text{Fe}(\text{CN})_6]^{4-}$ is _____.

MATRIX-MATCH TYPE QUESTIONS

In each of the following questions, statements are given in two columns, which have to be matched. The statements in Column I are labelled as **(A)**, **(B)**, **(C)** and **(D)**, while those in Column II are labelled as **(P)**, **(Q)**, **(R)**, **(S)** and **(T)**. Any given statement in Column I can have correct matching with *one or more* statements in Column II.

- 1.** Match the names with their chemical formulae.

Column I	Column II
(A) Kipp's apparatus waste	(P) HgCl_2
(B) Corrosive sublimate	(Q) $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$
(C) Azurite	(R) FeSO_4 solution
(D) Bordeaux mixture	(S) $\text{Ca}(\text{OH})_2 + \text{CuSO}_4$

- 2.** Match the compounds with their chemical properties.

Column I	Column II
(A) KMnO_4	(P) Acts as oxidizing agent.
(B) $\text{K}_2\text{Cr}_2\text{O}_7$	(Q) All X-O bonds are equivalent.
(C) Na_2SO_4	(R) d^3s hybridization for the central atom (s)

- 3.** Match the reaction with the nature of the product obtained.

Column I	Column II
(A) $\text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow$	(P) Redox reaction
(B) $\text{CrO}_5 + \text{H}^+ \rightarrow$	(Q) Evolution of O_2 takes place.
(C) $\text{Cr}^{3+} + \text{K}_2\text{S}_2\text{O}_8 + \text{H}^+ \rightarrow$	(R) A green solution is obtained.
(D) $\text{KMnO}_4 + \text{conc. KOH} \rightarrow$	(S) A blue solution is obtained.

- 4.** Match the isolated gaseous ions with the number of unpaired electrons.

Column I	Column II
(A) Cr^{3+}	(P) 2
(B) Fe^{3+}	(Q) 3
(C) Ni^{2+}	(R) 4
(D) Mn^{3+}	(S) 5

- 5.** Match the ore with its formula and the use to which it is put.

Column I	Column II	Column III
(A) Chromite ore	(M) $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$	(P) For preparing KMnO_4
(B) Colemanite ore	(N) MnO_2	(Q) For preparing borax
(C) Pyrolusite ore	(O) FeCr_2O_4	(R) For preparing $\text{K}_2\text{Cr}_2\text{O}_7$.

ANSWERS**Single Correct Choice Type Questions**

- | | | | | |
|---------------|---------------|---------------|----------------|----------------|
| 1. (B) | 4. (C) | 7. (C) | 10. (C) | 13. (B) |
| 2. (D) | 5. (D) | 8. (C) | 11. (C) | 14. (C) |
| 3. (C) | 6. (C) | 9. (D) | 12. (D) | 15. (B) |

Multiple Correct Choice Type Questions

- | | | | | |
|-------------------------|------------------------------|------------------------------|-------------------------|--------------------------|
| 1. (A), (C), (D) | 3. (A), (B), (C), (D) | 5. (B), (D) | 7. (A), (B), (D) | 9. (A), (B), (C) |
| 2. (C), (D) | 4. (A), (B), (C) | 6. (A), (B), (C), (D) | 8. (A), (C) | 10. (A), (B), (C) |

Comprehension Type Questions

- | | | | |
|---------------|---------------|----------------|----------------|
| 1. (B) | 5. (C) | 9. (A) | 13. (C) |
| 2. (A) | 6. (D) | 10. (A) | 14. (D) |
| 3. (B) | 7. (A) | 11. (C) | 15. (B) |
| 4. (B) | 8. (B) | 12. (D) | 16. (A) |

Assertion–Reasoning Type Questions

- | | | | | |
|---------------|---------------|---------------|---------------|----------------|
| 1. (A) | 3. (C) | 5. (A) | 7. (A) | 9. (C) |
| 2. (D) | 4. (A) | 6. (B) | 8. (A) | 10. (D) |

Integer Answer Type Questions

- | | | | | | |
|-------------|--------------|-------------|-------------|-------------|-------------|
| 1. 3 | 2. 18 | 3. 4 | 4. 4 | 5. 0 | 6. 4 |
|-------------|--------------|-------------|-------------|-------------|-------------|

Matrix–Match Type Questions

- | | | |
|--|--|--|
| 1. (A) → (R)
(B) → (P)
(C) → (Q)
(D) → (S) | 3. (A) → (P)
(B) → (P), (Q), (R)
(C) → (P)
(D) → (P), (Q), (R) | 5. (A) → (O), (R)
(B) → (M), (Q)
(C) → (N), (P) |
| 2. (A) → (P), (Q), (R)
(B) → (P), (R)
(C) → (Q) | 4. (A) → (Q)
(B) → (S)
(C) → (P)
(D) → (R) | |

12

The *f*-Block Elements and their Properties

The elements in which the additional electron enters $(n - 2)$ *f* orbital are called as *f*-block elements. They are also called as inner transition elements. These are placed at the bottom of the periodic table to make the table compact.

There are two series of *f*-block elements:

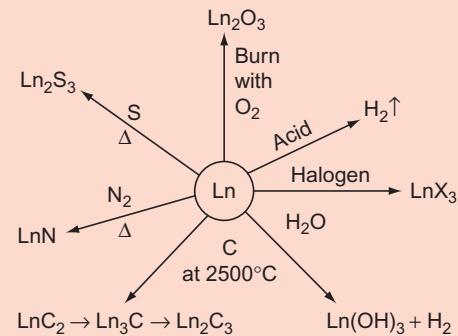
- Lanthanoids (4f-series):** These are 14 elements between lanthanum(La) and Hf in which 4*f* orbitals are successively filled; starting from Ce (At. no. 58) to Lu (At. no. 71).
- Actinoids (5f-series):** These are 14 elements, after actinium (Ac), in which 5*f* orbitals are successively filled, starting Th (At. no. 90) to Lr (At. no. 103).

12.1 | LANTHANOIDS

The 14 elements that fill up the antepenultimate 4*f* energy levels are called lanthanoids. They are extremely similar to each other in properties and until 1907, they were thought to be a single element.

The names, atomic numbers, symbols of elements and electronic configuration of atoms and M^{3+} ions are given in Table 12.1.

Lanthanum(*d*-block element preceding the 4*f*-series) has electronic structure [Xe] 5*d*¹ 6*s*². It is energetically favourable to move single 5*d* electron to 4*f* level in most of lanthanoids except Ce, Gd and Lu. Gd has a 5*d*¹ arrangement because it leads to stable half-filled configuration and in case of Lu to a stable filled *f*-shell configuration.



Important reactions of lanthanoids.

Contents

- 12.1** Lanthanoids
- 12.2** Actinoids
- 12.3** Comparison between Lanthanoids and Actinoids

Table 12.1 Electronic structures and oxidation states

Element	Atomic number	Symbol	Electronic structure of atoms	Electronic structure of M^{3+}	Oxidation states ^a
Cerium	58	Ce	[Xe] $4f^1 5d^1 6s^2$	[Xe] $4f^1$	+3 (+4)
Praseodymium	59	Pr	[Xe] $4f^3 6s^2$	[Xe] $4f^2$	+3 (+4)
Neodymium	60	Nd	[Xe] $4f^4 6s^2$	[Xe] $4f^3$	(+2) +3
Promethium	61	Pm	[Xe] $4f^5 6s^2$	[Xe] $4f^4$	(+2) +3
Samarium	62	Sm	[Xe] $4f^6 6s^2$	[Xe] $4f^5$	(+2) +3
Europium	63	Eu	[Xe] $4f^7 6s^2$	[Xe] $4f^6$	(+2) +3
Gadolinium	64	Gd	[Xe] $4f^7 5d^1 6s^2$	[Xe] $4f^7$	+3
Terbium	65	Tb	[Xe] $4f^9 6s^2$	[Xe] $4f^8$	+3 (+4)
Dysprosium	66	Dy	[Xe] $4f^{10} 6s^2$	[Xe] $4f^9$	+3 (+4)
Holmium	67	Ho	[Xe] $4f^{11} 6s^2$	[Xe] $4f^{10}$	+3
Erbium	68	Er	[Xe] $4f^{12} 6s^2$	[Xe] $4f^{11}$	+3
Thulium	69	Tm	[Xe] $4f^{13} 6s^2$	[Xe] $4f^{12}$	(+2) +3
Ytterbium	70	Yb	[Xe] $4f^{14} 6s^2$	[Xe] $4f^{13}$	(+2) +3
Lutetium	71	Lu	[Xe] $4f^{14} 5d^1 6s^2$	[Xe] $4f^{14}$	+3

^aThe most important oxidation states (generally the most abundant and stable) shown in bold. Oxidation states that are unstable, or in doubt, are given in parentheses.

Some important points to be noted are as follows:

1. The general electronic configuration for lanthanoids is $[Xe] 4f^{1-14} 5d^{0-1} 6s^2$.
2. The $4f$ electrons in the antepenultimate shell are effectively shielded from the chemical environment outside the atom by $5s$ and $5p$ electrons. Consequently, they do not take part in bonding.
3. Lanthanoids are characterized by the uniform (+3) oxidation shown by all the metals.
4. Pm (promethium) is the only synthetic radioactive lanthanoid.

Properties of lanthanoids and their ions

Atomic and ionic radii

The atomic radius decreases gradually from Ce (187 pm) to Lu (171 pm) by nearly 20 pm. This contraction in radius is due to lanthanoid contraction which results because the extra orbital electrons are incompletely shielded by the extra nuclear charge. Thus, all the electrons are pulled in closer. However, this regular decrease in radius is not followed by Eu (At. no. 63) and Yb (At. no. 70). This fact can be attributed to the electronic configuration of lanthanoids which is $[Xe] 4f^{1-14} 5d^1 6s^2$.

It can be seen from Table 12.1 that the number of electrons participating in the metallic bonding is three for all the lanthanoid elements except Eu (At. no. 63) and Yb (At. no. 70) as the outermost electrons are favoured to participate in bonding. In these two cases, one electron from $5d$ orbital is shifted to $4f$ orbital to get half-filled and fully filled stable electronic configuration. Hence, these two elements use only two electrons in metallic bonding and atomic radii does not show the expected decrease.

The radii of lanthanoid ions with the same charge are compared in Table 12.2. The ionic radii for lanthanoid ions (Ln^{3+}) change by a small amount from one element to the next (Table 12.2) and since their charge is the same, their chemical properties are also very similar.

Table 12.2 Ionic radii of Sc^{3+} , Y^{3+} , La^{3+} and Ln^{3+} ions (pm)

Sc														
74.5														
Y														
90														
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
103.2	102	99	98.3	97	95.8	94.7	93.8	92.3	91.2	90.1	89	88	86.8	86.1

Oxidation states

The very common and stable oxidation state for lanthanoids is +3 which can also be explained easily from their electronic configurations, that is, two electrons from 6s orbital and one electron from 5d orbital are lost easily from all elements except Eu and Yb. Hence, lanthanoids placed in Group 3 in the periodic table. The stability of Eu^{2+} and Yb^{2+} can be explained based on their electronic configuration. Sometimes, +4 oxidation state is observed when this leads to

1. half-filled electronic configuration: For example, Tb^{4+} (f^7)
2. noble gas configuration: For example, Ce^{4+} (Xe)

Some higher oxidation states are also possible but not so important for discussion.

Color

1. Lanthanoid ions have unpaired electrons in f -orbitals and they exhibit color due to $f-f$ transition.
2. The exhibited color generally depends upon the number of unpaired electrons but we cannot be predict the colour shown.
3. The ions having $4f^n$ configuration and $4f^{14-n}$ configuration will have similar color (expected).
4. The ions having configuration f^0 and f^{14} are colourless as they are diamagnetic; and if any colour is present it is not due to $f-f$ transition.

Magnetic properties

1. From Ce^{3+} to Gd^{3+} , the paramagnetic behaviour increases, then decreases and finally becomes diamagnetic for Lu^{3+} .
2. Ce^{4+} , Yb^{2+} and Lu^{3+} are diamagnetic.

Some other properties of lanthanoids

1. They typically form compounds which are ionic and trivalent.
2. Ionization energies are fairly low and comparable to alkaline earth metals. Hence, they are good reducing agents.
3. Complex formation tendencies are less. However, Lu^{3+} forms several complexes due to its small size.
4. Basic nature gradually decreases from $\text{Ce}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$ due to high polarization caused by gradual decrease in size of M^{3+} ion. The hydroxides of lanthanoids, $\text{Ln}(\text{OH})_3$ are less basic than $\text{Ca}(\text{OH})_2$ and more basic than $\text{Al}(\text{OH})_3$.
5. They form carbides of MC_2 type which on hydrolysis produce C_2H_2 .
6. Other reaction of lanthanoids can be summarized as shown in Figure 12.1.

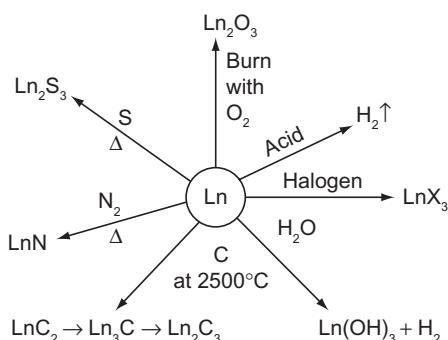


Figure 12.1 Some important reactions of lanthanoids.

Uses of lanthanoids

1. An unseparated mixture of La and the lanthanoids called Misch metal (50% Ce, 40% La, 7% Fe and 3% other metals) is added to steel to improve its strength and workability. It is pyrophoric and also used in gas lighters.
2. CeO_2 is used to polish glass. Again CeO_2 , La_2O_3 , Nd_2O_3 and Pr_2O_3 are used as decolourizing agents for glasses.
3. Cerium molybdate and cerium tungstate are used in paints and dyes.
4. CeS is used for making crucibles that can withstand temperatures up to 1950°C (as the melting point is 2000°C).

12.2 | ACTINOIDS

The elements Th (At. no. 90) to Lr (At. no. 103) are together known as actinoids. Actinium, the *d*-block element preceding *5f*-series has outer shell structure $6d^17s^2$. For the first four actinoids Th, Pa, U and Np, the difference between the energy levels of *5f* and *6d* orbitals is small. Thus in these elements (or ions) electrons may occupy either *5d* or *6f* orbitals. From Pu onwards, the energy of *5f* orbitals becomes lower and electrons fill the orbitals as in case of lanthanoids.

The electronic configurations of the elements, their M^{3+} ions and other possible oxidation states are given in the Table 12.3.

Table 12.3 The elements and their oxidation states

Element	Symbol	Atomic number	Outer electronic structure	Electronic configuration M^{3+}	Oxidation states ^a
Thorium	Th	90	$6d^2$	$7s^2$	$5f^1$
Protactinium	Pa	91	$5f^2 6d^1$	$7s^2$	$5f^2$
Uranium	U	92	$5f^3 6d^1$	$7s^2$	$5f^3$
Neptunium	Np	93	$5f^4 7s^2$	$6d^1$	$5f^4$
Plutonium	Pu	94	$5f^6 7s^2$		$5f^5$
Americium	Am	95	$5f^7 7s^2$		$5f^6$
Curium	Cm	96	$5f^7 6d^1$	$7s^2$	$5f^7$
Berkelium	Bk	97	$5f^9 7s^2$		$5f^8$
Californium	Cf	98	$5f^{10} 7s^2$		$5f^9$
Einsteinium	Es	99	$5f^{11} 7s^2$		$5f^{10}$
Fermium	Fm	100	$5f^{12} 7s^2$		$5f^{11}$
Mendelevium	Md	101	$5f^{13} 7s^2$		$5f^{12}$
Nobelium	No	102	$5f^{14} 7s^2$		$5f^{13}$
Lawrencium	Lr	103	$5f^{14} 6d^1$	$7s^2$	$5f^{14}$
Rutherfordium	Rf	104	$5f^{14} 6d^2$	$7s^2$	

^aThe most important oxidation states (generally the most abundant and stable) are shown in bold. Other well-characterized but less important states are shown in normal type.

Some important points to be noted are as follows:

1. Uranium is the heaviest naturally occurring element.
2. After uranium, 12 more elements have been artificially synthesized (having atomic number more than 92) and are sometimes called the transuranium elements.
3. All actinoids are radioactive (having the half-lives ranging from 1 day for earlier members to 3 min for Lr).
4. Due to their high radioactivity, studies of their properties become difficult.
5. The *5f* orbitals extend in space beyond *6s* and *6p* orbitals and participate in bonding.

Properties of actinoids and their ions

Atomic and ionic radii

There is no data for their atomic radii due to instability. The ionic radii for M^{3+} and M^{4+} (according to data available) gradually decrease due to actinoid contraction as the number of $5f$ electrons increase. This is because the extra charge on the nucleus is poorly shielded by the f -electrons. This decrease is shown in Table 12.4.

Table 12.4 Ionic radii of the actinoids

Element	Radius M^{3+} (pm)	Radius M^{4+} (pm)
Ac	112	–
Th	(108)	94
Pa	104	90
U	102.5	89
Np	101	87
Pu	100	86
Am	97.5	85
Cm	97	85
Bk	96	83
Cf	95	82
Es		

Oxidation states

1. The most stable oxidation state is +3.
2. Maximum oxidation state of +7 is shown by Np (At no. 93) and Pu (At no. 94).
3. Other available oxidation states are shown in Table 12.3.

Magnetic properties

Ions are paramagnetic or diamagnetic depending upon the number of unpaired 58 electrons, as can be seen from their electronic configurations.

Colour

In general, actinoid ions are coloured, unless they are diamagnetic.

Melting points and boiling points

There is no regular trend with increase in atomic number.

Physical appearance

They are silvery white metals but get tarnished when exposed to alkaline solution.

Uses of actinoids

1. Thorium is used as fuel rods in nuclear reactors and in the treatment of cancer.
2. Uranium is used as nuclear fuel. Its salts are used to impart green colour to glass and are used in medicines.

12.3 | COMPARISON BETWEEN LANTHANOIDS AND ACTINOIDS

Similarities

- Both are electropositive and strongly reducing in nature.
- Both have stable oxidation state of +3.
- Ions of both series are coloured due to $f-f$ transition.
- Both series show a gradual decrease in ionic radii.

Differences

The differences are tabulated in Table 12.5.

Table 12.5 Lanthanoids vs actinoids

Lanthanoids	Actinoids
<ol style="list-style-type: none"> Apart from +3 oxidation state, +2 and +4 are available for some of the elements. All elements are non-radioactive except Pm. Lanthanoid contraction is less than actinoid contraction. Lanthanoids have lesser tendency towards complex formation. Oxides and hydroxides are relatively less basic. Elements have less density. 	<ol style="list-style-type: none"> Apart from +3 oxidation state, +4, +5, +6 and +7 are available for some of the elements. All elements are radioactive. Actinoid contraction is more than lanthanoid contraction. Actinoids have relatively stronger tendency towards complex formation. Oxides and hydroxides are more basic. Elements have relatively more density.

SINGLE CORRECT CHOICE TYPE QUESTIONS

- Colour of La^{2+} is due to
 - $d-d$ transition.
 - $f-f$ transition.
 - charge transfer.
 - None of these.
- The colour of Nd^{3+} (At no. 60) will be similar to
 - Ho^{3+} (At. no. 67).
 - Gd^{3+} (At. no. 64).
 - Er^{3+} (At. no. 68).
 - Yb^{2+} (At. no. 70).
- Choose the correct order of ionic radius from the given options (where atomic numbers of Ce, Pr, Eu and Dy are 58, 59, 63, and 66, respectively)
 - $\text{Ce}^{3+} > \text{Pr}^{3+} > \text{Dy}^{3+} > \text{Eu}^{3+}$
 - $\text{Pr}^{3+} > \text{Dy}^{3+} > \text{Eu}^{3+} > \text{Ce}^{3+}$
 - $\text{Dy}^{3+} > \text{Eu}^{3+} > \text{Ce}^{3+} > \text{Pr}^{3+}$
 - $\text{Ce}^{3+} > \text{Pr}^{3+} > \text{Eu}^{3+} > \text{Dy}^{3+}$
- Which of following characteristics is not the point of resemblance between lanthanoids and actinoids?
 - Reducing property.
 - Oxidation state of +3.
 - Trends of ionic radii for M^{3+} ions.
 - Tendency towards complex formation.
- Which of the following properties varies between lanthanoids and actinoids?
 - Highest oxidation state.
 - Radioactive nature.
 - Basicity of hydroxides.
 - All of these.
- Which of the following elements is used in the treatment of cancer?

(A) Uranium	(B) Thorium
(C) Cerium	(D) Plutonium
- Which of the following species is not paramagnetic?
 - Yb^{2+} (At. no. 70)
 - Ce^{4+} (At. no. 58)
 - Lu^{3+} (At. no. 71)
 - All of these.
- Calculate the $Z_{\text{effective}}$ for the f -electron in Ce^{3+} .

(A) 54	(B) 5	(C) 4	(D) 3
--------	-------	-------	-------
- Tb^{4+} (At. no. 65) is stable because
 - it has noble gas configuration.
 - it has half-filled electronic configuration of f -orbitals.
 - it has fully-filled electronic configuration of d -orbitals.
 - it has fully-filled electronic configuration of f -orbitals.
- Actinoid contraction is more compared to lanthanoid contraction because

- (A) $5f$ orbitals are more diffused as compared to $4f$ -orbital from nucleus.
 (B) $4f$ -orbitals are more diffused as compared to $5f$ -orbitals.
 (C) Shielding effect of electrons present in $4f$ - and $5f$ -orbitals is equal.
 (D) The azimuthal quantum numbers of $4f$ - and $5f$ -orbitals are the same.
- 11.** Which of the following cations has the strongest tendency towards complex formation?
 (A) Sm^{3+} (B) Lu^{3+} (C) Gd^{3+} (D) Yb^{3+}
- 12.** Which of the following elements has maximum composition in Misch metal, which is used in gas lighters?
 (A) La (B) Fe (C) Ce (D) Other metals
- 13.** Which of the following Ce compound is used for making crucibles?
 (A) CeO_2 (B) CeS (C) ThO_2 (D) Nd_2O_3
- 14.** The gradual decrease in radius for lanthanoid elements is not obeyed by
 (A) Eu only (B) Yb only
 (C) Both Eu and Yb (D) None
- 15.** The gradual decrease in radius of M^{3+} ion for lanthanoids is not obeyed by
 (A) Eu only (B) Yb only
 (C) Both Eu and Yb (D) None of these
- 16.** The magnetic moment of Am^{5+} (At. no. 95) is
 (A) $\sqrt{24}$ BM (B) $\sqrt{35}$ BM
 (C) $\sqrt{15}$ BM (D) $\sqrt{3}$ BM
- 17.** Which of the following elements is not an *f*-block element?
 (A) No (B) Nd (C) Nb (D) Np
- 18.** On moving from Ce^{3+} to Lu^{3+} , the cation having maximum number of unpaired electrons is
 (A) Ce^{3+} (B) Lu^{3+} (C) Eu^{3+} (D) Gd^{3+}
- 19.** Lanthanoid from series is
 (A) La to Lu
 (B) Th to Lr
 (C) Ce to Lu
 (D) Ac to Lr
- 20.** Which of the following statements is true for *f*-block elements?
 (A) They can have electrons from f^0 to f^{14} .
 (B) Group number is 3 in the periodic table.
 (C) With the increase in number of *f*-electrons, the
 (D) All of these.

ANSWERS**Single Correct Choice Type Questions**

- | | | | |
|---------------|----------------|----------------|----------------|
| 1. (A) | 6. (B) | 11. (B) | 16. (A) |
| 2. (C) | 7. (D) | 12. (C) | 17. (C) |
| 3. (D) | 8. (C) | 13. (B) | 18. (D) |
| 4. (D) | 9. (B) | 14. (C) | 19. (C) |
| 5. (D) | 10. (A) | 15. (D) | 20. (D) |

APPENDIX

Abundance of the Elements in the Earth's Crust

A

	Name	Symbol	Abundance*		Name	Symbol	Abundance
1	Oxygen	O	455 000	40	Samarium	Sm	7.0
2	Silicon	Si	272 000	41	Gadolinium	Gd	6.1
3	Aluminium	Al	83 000	42	Dysprosium	Dy	4.5
4	Iron	Fe	62 000	43	Erbium	Er	3.5
5	Calcium	Ca	46 600	44	Ytterbium	Yb	3.1
6	Magnesium	Mg	27 640	45	Hafnium	Hf	2.8
7	Sodium	Na	22 700	46	Caesium	Cs	2.6
8	Potassium	K	18 400	47	Bromine	Br	2.5
9	Titanium	Ti	6 320	48 =	Uranium	U	2.3
10	Hydrogen	H	1 520	49 =	Tin	Sn	2.1
11	Phosphorus	P	1 120	49 =	Europium	Eu	2.1
12	Manganese	Mn	1 060	51	Beryllium	Be	2.0
13	Fluorine	F	544	52	Arsenic	As	1.8
14	Barium	Ba	390	53	Tantalum	Ta	1.7
15	Strontium	Sr	384	54	Germanium	Ge	1.5
16	Sulphur	S	340	55	Holmium	Ho	1.3
17	Carbon	C	180	56 =	Molybdenum	Mo	1.2
18	Zirconium	Zr	162	56 =	Tungsten	W	1.2
19	Vanadium	V	136	56 =	Terbium	Tb	1.2
20	Chlorine	Cl	126	59	Lutetium	Lu	0.8
21	Chromium	Cr	122	60	Thallium	Tl	0.7
22	Nickel	Ni	99	61	Thulium	Tm	0.5

(continued)

Appendix A (continued)

	Name	Symbol	Abundance*		Name	Symbol	Abundance
23	Rubidium	Rb	78	62	Iodine	I	0.46
24	Zinc	Zn	76	63	Indium	In	0.24
25	Copper	Cu	68	64	Antimony	Sb	0.20
26	Cerium	Ce	66	65	Cadmium	Cd	0.16
27	Neodymium	Nd	40	66 =	Silver	Ag	0.08
28	Lanthanum	La	35	66 =	Mercury	Hg	0.08
29	Yttrium	Y	31	68	Selenium	Se	0.05
30	Cobalt	Co	29	69	Palladium	Pd	0.015
31	Scandium	Sc	25	70	Platinum	Pt	0.01
32	Niobium	Nb	20	71	Bismuth	Bi	0.008
33	Nitrogen	N	19	72	Osmium	Os	0.005
34	Gallium	Ga	19	73	Gold	Au	0.004
35	Lithium	Li	18	74 =	Iridium	Ir	0.001
36	Lead	Pb	13	74 =	Tellurium	Te	0.001
37	Praseodymium	Pr	9.1	76	Rhenium	Re	0.0007
38	Boron	B	9.0	77 =	Ruthenium	Ru	0.0001
39	Thorium	Th	8.1	77 =	Rhodium	Rh	0.0001

* Units are ppm of the earth's crust, which is the same as g/tonne. Values mainly from *Geochemistry* by W.S. Fyfe, Oxford University press. 1974, with some newer data.

APPENDIX

B

Melting Points of the Elements

Group Period	1	2											13	14	15	16	17	18
1	H • -259																H • -259	He • -
2	Li • 181	Be • 1287											B • 2180	C • 4100	N • -210	O • -229	F • -219	Ne • -249
3	Na • 98	Mg • 649											Al • 660	Si • 1420	P • 44	S • 114	Cl • -101	Ar • -189
4	K • 63	Ca • 839	Sc • 1539	Ti • 1667	V • 1915	Cr • 1903	Mn • 1244	Fe • 1535	Co • 1495	Ni • 1453	Cu • 1083	Zn • 419	Ga • 30	Ge • 945	As • 816	Se • 221	Br • -7	Kr • -157
5	Rb • 39	Sr • 768	Y • 1523	Zr • 1857	No • 2468	Mo • 2620	Tc • 2172	Ru • 2310	Rh • 1966	Pd • 1554	Ag • 962	Cd • 321	In • 157	Sn • 232	Sb • 631	Te • 452	I • 114	Xe • -112
6	Cs • 28.5	Ba • 727	La • 920	Hf • 2227	Ta • 3000	W • 3410	Re • 3180	Os • 3045	Ir • 2410	Pt • 1772	Au • 1064	Hg • -38	Tl • 303	Pb • 327	Bi • 271	Po • 254	At • 302 ^e	Rn • -71 ^e
7	Fr • 27 ^e	Ra • (700)	Ac • 817															

Temperatures are in degrees Celsius. Large circles indicate high values and small circles low values;
e indicates estimated value. Values given in parentheses are approximate.

<0 •
1-1500 •
1501-3000 •
>3000 •

APPENDIX

C

Boiling Points of the Elements

Group Period.	1	2											13	14	15	16	17	18
1																	H	He
2	Li •	Be ●											• -253	• -269				
3	Na •	Mg ●											B ● 3650	C • -195.8	N • -183.1	O • -188	F • -246	Nc • -186
4	K •	Ca ●	Sc ●	Ti ●	V ●	Cr ●	Mn ●	Fe ●	Co ●	Ni ●	Cu ●	Zn ●	Ga ● 2403	Ge ● 2850	As • 615	Se • 685	Br • 60	Kr • -153.6
5	Rb •	Sr ●	Y ●	Zr ●	Nb ●	Mo ●	Tc ●	Ru ●	Rh ●	Pd ●	Ag ●	Cd ●	In ● 2080	Sn ● 2623	Sb ● 1587	Te • 1087	I • 185	Xe • -108.1
6	Cs •	Ba ●	La ●	Hf ●	Ta ●	W ●	Re ●	Os ●	Ir ●	Pt ●	Au ●	Hg ●	Tl ● 1457	Pb ● 1751	Bi ● 1564	Po • 962	At • -62	Rn • -62
7	Fr •	Ra ● (1700)	Ac ● 2470															

Temperatures are in degrees Celsius. Large circles indicate high values and small circles low values.

Values given in parentheses are approximate, s indicates sublimation.

<0 •
 1-1500 •
 1501-3000 ●
 >3000 ●

APPENDIX

Densities of the Solid and Liquid Elements

D

Group Period	1	2											13	14	15	16	17	18
1	H															H	He	
2	Li	Be											B	C	N	O	F	Ne
	•	•											2.35	2.26				
3	Na	Mg											Al	Si	P	S	Cl	Ar
	•	•											•	•	•	•		
	0.97	1.74	3	4	5	6	7	8	9	10	11	12	2.70	2.34	1.82	2.1		
4	K	Ca	Se	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•		
	0.86	1.55	3.0	4.50	6.11	7.14	7.43	7.87	8.90	8.91	8.95	7.14	5.90	5.32	5.77	4.19	3.19	
5	Rb	Sr	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•		
	1.53	2.63	4.5	6.51	8.57	10.28	11.5	12.41	12.39	11.99	10.49	8.65	7.31	7.27	6.70	6.25	4.94	
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•		
	1.90	3.62	6.17	13.28	16.65	19.3	21.0	22.57	22.61	21.41	19.32	13.53	11.85	11.34	9.81	9.14	—	
7	Fr	Ra	Ac															
	•	—	—															
	—	5.5	—															

Densities are given in g cm⁻³ (which equals 10⁻³ kg m⁻³). The value for carbon is the value for graphite. Large circles indicate large values and small circles small values.

APPENDIX

Electronic Structures of the Elements

E

Z	Element	Symbol	Structure
1	Hydrogen	H	$1s^1$
2	Helium	He	$1s^2$
3	Lithium	Li	$[\text{He}] 2s^1$
4	Beryllium	Be	$[\text{He}] 2s^2$
5	Boron	B	$[\text{He}] 2s^2 2p^1$
6	Carbon	C	$[\text{He}] 2s^2 2p^2$
7	Nitrogen	N	$[\text{He}] 2s^2 2p^3$
8	Oxygen	O	$[\text{He}] 2s^2 2p^4$
9	Fluorine	F	$[\text{He}] 2s^2 2p^5$
10	Neon	Ne	$[\text{He}] 2s^2 2p^6$
11	Sodium	Na	$[\text{Ne}] 3s^1$
12	Magnesium	Mg	$[\text{Ne}] 3s^2$
13	Aluminium	Al	$[\text{Ne}] 3s^2 3p^1$
14	Silicon	Si	$[\text{Ne}] 3s^2 3p^2$
15	Phosphorus	P	$[\text{Ne}] 3s^2 3p^3$
16	Sulphur	S	$[\text{Ne}] 3s^2 3p^4$
17	Chlorine	Cl	$[\text{Ne}] 3s^2 3p^5$
18	Argon	Ar	$[\text{Ne}] 3s^2 3p^6$

(continued)

Appendix E (continued)

Z	Element	Symbol	Structure
19	Potassium	K	[Ar] 4s ¹
20	Calcium	Ca	[Ar] 4s ²
21	Scandium	Sc	[Ar]3d ¹ 4s ²
22	Titanium	Ti	[Ar] 3d ² 4s ²
23	Vanadium	V	[Ar] 3d ³ 4s ²
24	Chromium	Cr	[Ar] 3d ⁵ 4s ¹
25	Manganese	Mn	[Ar] 3d ⁵ 4s ²
26	Iron	Fe	[Ar] 3d ⁶ 4s ²
27	Cobalt	Co	[Ar] 3d ⁷ 4s ²
28	Nickel	Ni	[Ar] 3d ⁸ 4s ²
29	Copper	Cu	[Ar] 3d ¹⁰ 4s ¹
30	Zinc	Zn	[Ar] 3d ¹⁰ 4s ²
31	Gallium	Ga	[Ar] 3d ¹⁰ 4s ² 4p ¹
32	Germanium	Ge	[Ar] 3d ¹⁰ 4s ² 4p ²
33	Arsenic	As	[Ar] 3d ¹⁰ 4s ² 4p ³
34	Selenium	Se	[Ar] 3d ¹⁰ 4s ² 4p ⁴
35	Bromine	Br	[Ar] 3d ¹⁰ 4s ² 4p ⁵
36	Krypton	Kr	[Ar] 3d ¹⁰ 4s ² 4p ⁶
37	Rubidium	Rb	[Kr] 5s ¹
38	Strontium	Sr	[Kr] 5s ²
39	Yttrium	Y	[Kr] 4d ¹ 5s ²
40	Zirconium	Zr	[Kr] 4d ² 5s ²
41	Niobium	Nb	[Kr] 4d ⁴ 5s ¹
42	Molybdenum	Mo	[Kr] 4d ⁵ 5s ¹
43	Technetium	{Tc}	[Kr] 4d ⁵ 5s ²
		{Tc}	[Kr] 4d ⁶ 5s ¹
44	Ruthenium	Ru	[Kr] 4d ⁷ 5s ¹
45	Rhodium	Rh	[Kr] 4d ⁸ 5s ¹
46	Palladium	Pd	[Kr] 4d ¹⁰ 5s ⁰
47	Silver	Ag	[Kr] 4d ¹⁰ 5s ¹
48	Cadmium	Cd	[Kr] 4d ¹⁰ 5s ²
49	Indium	In	[Kr] 4d ¹⁰ 5s ² 5p ¹
50	Tin	Sn	[Kr] 4d ¹⁰ 5s ² 5p ²
51	Antimony	Sb	[Kr] 4d ¹⁰ 5s ² 5p ³
52	Tellurium	Te	[Kr] 4d ¹⁰ 5s ² 5p ⁴

(continued)

Appendix E (continued)

Z	Element	Symbol	Structure
53	Iodine	I	[Kr] $4d^{10} 5s^2 5p^5$
54	Xenon	Xe	[Kr] $4d^{10} 5s^2 5p^6$
55	Caesium	Cs	[Xe] $6s^1$
56	Barium	Ba	[Xe] $6s^2$
57	Lanthanum	La	[Xe] $5d^1 6s^2$
58	Cerium	Ce	[Xe] $4f^1 5d^1 6s^2$
59	Praseodymium	Pr	[Xe] $4f^3 5d^0 6s^2$
60	Neodymium	Nd	[Xe] $4f^4 5d^0 6s^2$
61	Promethium	Pm	[Xe] $4f^5 5d^0 6s^2$
62	Samarium	Sm	[Xe] $4f^6 5d^0 6s^2$
63	Europium	Eu	[Xe] $4f^7 5d^0 6s^2$
64	Gadolinium	Gd	[Xe] $4f^7 5d^1 6s^2$
65	Terbium	Tb	[Xe] $4f^9 5d^0 6s^2$
66	Dysprosium	Dy	[Xe] $4f^{10} 5d^0 6s^2$
67	Holmium	Ho	[Xe] $4f^{11} 5d^0 6s^2$
68	Erbium	Er	[Xe] $4f^{12} 5d^0 6s^2$
69	Thulium	Tm	[Xe] $4f^{13} 5d^0 6s^2$
70	Ytterbium	Yb	[Xe] $4f^{14} 5d^0 6s^2$
71	Lutetium	Lu	[Xe] $4f^{14} 5d^1 6s^2$
72	Hafnium	Hf	[Xe] $4f^{14} 5d^2 6s^2$
73	Tantalum	Ta	[Xe] $4f^{14} 5d^3 6s^2$
74	Tungsten	W	[Xe] $4f^{14} 5d^4 6s^2$
75	Rhenium	Re	[Xe] $4f^{14} 5d^5 6s^2$
76	Osmium	Os	[Xe] $4f^{14} 5d^6 6s^2$
77	Iridium	Ir	[Xe] $4f^{14} 5d^7 6s^2$
78	Platinum	Pt	[Xe] $4f^{14} 5d^9 6s^1$
79	Gold	Au	[Xe] $4f^{14} 5d^{10} 6s^1$
80	Mercury	Hg	[Xe] $4f^{14} 5d^{10} 6s^2$
81	Thallium	Tl	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$
82	Lead	Pb	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$
83	Bismuth	Bi	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$
84	Polonium	Po	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$
85	Astatine	At	[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$
86	Radon	Rn	[Xe] $4f^{14} 5d^{10} 6s^2 6p^6$

(continued)

Appendix E (continued)

Z	Element	Symbol	Structure
87	Francium	Fr	[Rn] 7s ¹
88	Radium	Ra	[Rn] 7s ²
89	Actinium	Ac	[Rn] 6d ¹ 7s ²
90	Thorium	Th	[Rn] 6d ² 7s ²
91	Protactinium	Pa	[Rn] 5f ² 6d ¹ 7s ²
92	Uranium	U	[Rn] 5f ³ 6d ¹ 7s ²
93	Neptunium	Np	[Rn] 5f ⁴ 6d ¹ 7s ²
94	Plutonium	Pu	[Rn] 5f ⁶ 6d ⁰ 7s ²
95	Americium	Am	[Rn] 5f ⁷ 6d ⁰ 7s ²
96	Curium	Cm	[Rn] 5f ⁷ 6d ¹ 7s ²
97	Berkelium	{ Bk	[Rn] 5f ⁹ 6d ⁰ 7s ²
			[Rn] 5f ⁸ 6d ¹ 7s ²
98	Californium	Cf	[Rn] 5f ¹⁰ 6d ⁰ 7s ²
99	Einsteinium	Es	[Rn] 5f ¹¹ 6d ⁰ 7s ²
100	Fermium	Fm	[Rn] 5f ¹² 6d ⁰ 7s ²
101	Mendelevium	Md	[Rn] 5f ¹³ 6d ⁰ 7s ²
102	Nobelium	No	[Rn] 5f ¹⁴ 6d ⁰ 7s ²
103	Lawrencium	Lr	[Rn] 5f ¹⁴ 6d ¹ 7s ²
104	Rutherfordium	Rf	[Rn] 5f ¹⁴ 6d ² 7s ²
105	Hahnium	Ha	[Rn] 5f ¹⁴ 6d ³ 7s ²

APPENDIX

Some Average Single Bond Energies and Some Double and Triple Bond Energies

F

Some average single bond energies (kJ mol⁻¹)

	I	Br	Cl	F	S	O	P	N	Si	C	H
H	297	368	431	565	339	464	318	389	293	414	435
C	238	276	330	439	259	351	263	293	289	347	
Si	213	289	360	539	226	368	213 ^c	-	176		
N	-	243	201	272	-	201	209 ^c	159			
P	213	272	330	489	230 ^c	351 ^c	213				
O	201	-	205	184	-	138					
S	-	213	251	284	213						
F	-	255	184	159							
Cl	209	217	243								
Br	180	193									
I	151										

^cIndicates value estimated using electronegativity difference.Some double and triple bond energies (kJ mol⁻¹)

C=C	611	C≡C,	836
C=N	615	C≡N	891
C=O	740	C≡O	1071
N=N	418	N≡N	945

APPENDIX

Solubilities of Main Group Compounds in Water

G

	F ⁻	Cl ⁻	Br ⁻	I ⁻	OH ⁻	NO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	HCO ₃ ⁻
NH ₄ ⁺	vs	37	75	172		192	12	75	
Li ⁺	0.27 ^c	83	177	165	12.8	70	1.33	35	
Na ⁺	4.0	36	91	179	109	87	21	19.4	9.6
K ⁺	95	34.7	67	144	112	31.6	112	11.1	22.4
Rb ⁺	131	91	110	152	177	53	450	48	
Cs ²⁺	370	186	108	79	330	23	vs	179	
Be ²⁺	vs	vs	s	dec	ss	107		39	
Mg ²⁺	0.008	54.2	102	148	0.0009	70	ss	33	
Ca ²⁺	0.0016	74.5	142	209	0.156	129	ss	0.21	
Sr ²⁺	0.012	53.8	100	178	0.80	71	ss	0.013	
Be ²⁺	0.12	36	104	205	3.9	8.7	ss	0.00024	
Al ³⁺	0.55	70 dec	dec	dec	ss	63		38	
Ga ³⁺	0.002	vs	s	dec	ss			vs	
In ³⁺	0.04	vs	vs	dec	ss				
Tl ⁺	78.6 ^b	0.33	0.05	0.0006	25.9 ^a	9.55	4.0 ^b	s	
Tl ³⁺	Dec	vs	s	s		s		4.87	
Ge ^{II}	S	dec	dec	s					
Ge ^{IV}	dec	dec	dec	dec					
Sn ^{II}	S	270 dec ^b	s	0.98	ss	dec		33 ^d	
Sn ^{IV}	vs	Dec	dec	dec					
Pb ^{II}	0.064	0.99	0.844	0.063	0.016	55	0.00011	ss	

(continued)

Appendix G (continued)

	F^-	Cl^-	Br^-	I^-	OH^-	NO_3^-	CO_3^{2-}	SO_4^{2-}	HCO_3^-
Pb^{IV}		dec							
As^{III}	dec	dec	dec	6.0 ^d					
As^{V}									
Sb^{III}	dec	dec	dec	dec		dec		ss	
Sb^{V}		dec							
Bi^{III}	ss	dec	dec	ss	0.00014	dec			dec

Solubilities in grams of solute per 100 grams of water at 20°C unless otherwise indicated, vs = very soluble; s = soluble; ss = slightly soluble; dec = decomposes. a = at 0°C; b = at 15°C; c = at 18°C; d = at 25°C.

APPENDIX

Atomic Weights Based on $^{12}\text{C} = 12.000$

H

Element	Atomic weight	Element	Atomic weight
Actinium	227	Holmium	164.93
Aluminium	26.982	Hydrogen	1.00797
Americium	(243)	Indium	114.82
Antimony	121.75	Iodine	126.904
Argon	39.948	Iridium	192.2
Arsenic	74.922	Iron	55.847
Astatine	(210)	Krypton	83.80
Barium	137.34	Lanthanum	138.91
Berkelium	(249)	Lead	207.19
Beryllium	9.102	Lithium	6.939
Bismuth	208.98	Lutetium	174.97
Boron	10.811	Magnesium	24.312
Bromine	79.909	Manganese	54.938
Cadmium	112.40	Mendelevium	(256)
Caesium	132.905	Mercury	200.59
Calcium	40.08	Molybdenum	95.94
Californium	(251)	Neodymium	144.24
Carbon	12.01115	Neon	20.183
Cerium	140.012	Neptunium	(237)
Chlorine	35.453	Nickel	58.71
Chromium	51.996	Niobium	92.91
Cobalt	58.933	Nitrogen	14.0067
Copper	63.54	Nobelium	(254)
Curium	(.247)	Osmium	190.2

(continued)

Appendix H (continued)

Element	Atomic weight	Element	Atomic weight
Dysprosium	162.50	Oxygen	15.9994
Einsteinium	(254)	Palladium	106.4
Erbium	167.26	Phosphorus	30.9738
Europium	151.96	Platinum	195.09
Fermium	(253)	Plutonium	(242)
Fluorine	18.993	Polonium	(210)
Francium	(223)	Potassium	39.102
Gadolinium	157.25	Praseodymium	140.91
Gallium	69.72	Promethium	(147)
Germanium	72.59	Protactinium	(231)
Gold	196.967	Radium	(226)
Hafnium	178.49	Radon	(222)
Helium	4.003	Rhenium	186.22
Rhodium	102.91	Terbium	153.92
Rubidium	85.47	Thallium	204.37
Ruthenium	101.07	Thorium	232.04
Samarium	150.35	Thulium	168.93
Scandium	44.96	Tin	118.69
Selenium	78.96	Titanium	47.90
Silicon	28.086	Tungsten	183.85
Silver	107.870	Uranium	238.03
Sodium	22.9898	Vanadium	50.942
Strontium	87.62	Xenon	131.30
Sulphur	32.064	Ytterbium	173.04
Tantalum	180.95	Yttrium	88.91
Technetium	(99)	Zinc	65.37
Tellurium	127.60	Zirconium	91.22

Values in parentheses are for the most stable isotope.

APPENDIX

Values of Some Fundamental Physical Constants

Planck's constant $h = 6.6262 \times 10^{-34} \text{ J s}$

Mass of electron $m = 9.1091 \times 10^{-31} \text{ kg}$

Charge on electron $e = 1.60210 \times 10^{-19} \text{ C}$

Permittivity of a vacuum $\epsilon_0 = 8.854185 \times 10^{-12} \text{ kg}^{-1} \text{ m}^{-3} \text{ A}^2$

Permeability of a vacuum $\mu_B = 4\pi \times 10^{-7} \text{ kg m s}^{-2} \text{ A}^{-2}$

Velocity of light in a vacuum $c = 2.997925 \times 10^8 \text{ m s}^{-1}$

Avogadro constant $N_0 = 6.022045 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant $k = 1.3805 \times 10^{-23} \text{ J K}^{-1}$

Bohr magneton $\mu_B = 9.2732 \times 10^{-24} \text{ A m}^2 = \text{J T}^{-1}$

Magnetic moment and dipole moment μ units are $\text{A m}^2 = \text{J T}^{-1}$

APPENDIX

Electrical Resistivity of the Elements at the Stated Temperature

J

Element	Symbol	Temp (°C)	Resistivity (μohm cm)	Element	Symbol	Temp (°C)	Resistivity (μohm cm)
Silver	Ag	20	1.59	Vanadium	V	20	25
Copper	Cu	20	1.673	Gallium*	Ga	20	27
Gold	Au	20	2.35	Ytterbium	Yb	25	29
Aluminium	Al	20	2.655	Uranium	U	20	30
Calcium	Ca	20	3.5	Arsenic α	As	20	33.3
Beryllium	Be	20	4.0	Hafnium	Hf	25	35.1
Sodium	Na	0	4.2	Zirconium	Zr	20	40
Magnesium	Mg	20	4.46	Antimony α	Sb	20	41.7
Rhodium	Rh	20	4.51	Titanium	Ti	20	42
Molybdenum	Mo	0	5.2	Barium	Ba	20	50
Iridium	Lr	20	5.3	Yttrium	Y	25	57
Tungsten	W	27	5.65	Dysprosium	Dy	25	57
Lanthanum	La	25	5.7	Scandium	Sc	22	61
Zinc	Zn	20	5.92	Neodymium	Nd	25	64
Potassium	K	0	6.15	Praseodymium	Pr	25	68
Cobalt	Co	20	6.24	Cerium	Ce	25	75
Cadmium	Cd	0	6.83	Thulium	Tm	25	79
Nickel	Ni	20	6.84	Lutetium	Lu	25	79
Ruthenium	Ru	0	7.6	Holmium	Ho	25	87

(continued)

Appendix J (continued)

Element	Symbol	Temp (°C)	Resistivity (μohm cm)	Element	Symbol	Temp (°C)	Resistivity (μohm cm)
Indium	In	20	8.37	Samarium	Sm	25	88
Lithium	Li	20	8.55	Europium	Eu	25	90
Osmium	Os	20	9.5	Mercury	Hg	20	95.8
Iron	Fe	20	9.71	Erbium	Er	25	107
Platinum	Pt	20	10.6	Bismuth	Bi	20	120
Palladium	Pd	20	10.8	Gadolinium	Gd	25	140.5
Tinβ	Sn	0	11	Plutonium	Pu	107	141.4
Tantalum	Ta	25	12.45	Manganese	Mn	23	185
Rubidium	Rb	20	12.5	Tellurium	Te	25	4.5×10^5
Niobium	Nb	0	12.5	Germanium	Ge	22	4.7×10^7
Chromium	Cr	0	12.9	Silicon	Si	20	4.8×10^7
Thorium	Th	0	13	Boron	B	20	6.7×10^{11}
Thallium	Tl	0	18	Iodine	I	20	1.3×10^{15}
Rhenium	Re	20	19.3	Selenium	Se	20	1.2×10^{16}
Caesium	Cs	20	20	Phosphorus #	P	11	1×10^{17}
Lead	Pb	20	20.648	Carbon	C	20	$\approx 1 \times 10^{20}$
Strontium	Sr	20	23	Sulphur	S	20	2×10^{24}

* Resistivity of Ga is 8.2, 17.5 or 553 μohm cm depending on direction.

White phosphorus.

APPENDIX

K

Hardness of Minerals – Mohs' Scale

Sometimes rocks are called soft because individual particles, which may be quite hard in themselves, are loosely held as an aggregate and fall apart fairly readily. The hardness of a mineral is something quite different and refers to the resistance of the whole surface to be scratched.

More than a century ago a mineralogist called Friedrich Mohs devised a scale of hardness called after him (Table K.1). He arbitrarily assigned talc (the softest known mineral) a hardness of 1, and diamond, (the hardest known mineral) a value of 10. The scale is arbitrary and does not indicate any exact hardness. Thus a mineral of hardness 6 can scratch those below it in the scale but it does not imply that it is twice as hard as a mineral of hardness 3. Two minerals of the same hardness will both scratch each other. There is a very large difference between 9 and 10 on the scale.

Table K.1 Mohs' scale of hardness

Mohs' scale	Mineral
10	Diamond
9	Corundum
8	Topaz
7	Quartz
6	Microcline
5	Apatite
4	Fluorite
3	Calcite
2	Gypsum
1	Talc

Common objects such as a fingernail, a copper coin, a knife blade or a metal file can also be used as test instruments. It may be convenient to use these to test samples for hardness quickly and easily when out in the field (Table K.2).

Table K.2 Tools for hardness testing

Mohs' scale	Tool
6.5	Steel nail file
5.5	Penknife blade or window glass
3.5	Copper coin
2.5	Fingernail

Minerals of hardness below 6.5 can be scratched by a nail-file, those under 5.5 are scratched by a penknife, those under 3.5 are scratched by a copper coin and those under 2.5 are scratched by a fingernail and will leave a mark on paper. Conversely minerals over 5.5 will scratch glass.

JEE (ADVANCED) 2018
PAPER I (CHEMISTRY)

SECTION 1

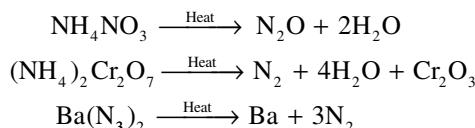
- This section contains **SIX (06)** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).

1. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300°C is (are)

(A) NH_4NO_3 (B) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (C) $\text{Ba}(\text{N}_3)_2$ (D) Mg_3N_2

Solution

(B) (C) Ammonium salts decompose quite readily on heating. If the anion is more oxidizing (e.g. NO_3^- , $\text{Cr}_2\text{O}_7^{2-}$) then NH_4^+ gets oxidized to N_2 or N_2O .



Mg_3N_2 is an ionic compound, therefore, will not decompose at 300°C .

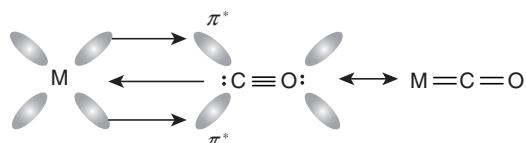
2. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers: Fe = 26, Ni = 28)
- (A) Total number of valence shell electrons at metal centre in $\text{Fe}(\text{CO})_5$ or $\text{Ni}(\text{CO})_4$ is 16.
 (B) These are predominantly low spin in nature.
 (C) Metal–carbon bond strengthens when the oxidation state of the metal is lowered.
 (D) The carbonyl C—O bond weakens when the oxidation state of the metal is increased.

Solution

(B) (C) Option (A): Incorrect. Total number of valence shell electrons in $\text{Fe}(\text{CO})_5$ [$8 + 5 \times 2 = 18$] and $\text{Ni}(\text{CO})_4$ [$10 + 4 \times 2 = 18$] is 18.

Option (B): Correct. CO being a strong field ligand cause pairing of electrons. Hence, both the complexes formed are low spin in nature.

Option (C): Correct. CO ligand not only donates the lone pair of electrons to the central atom but also accept the electron cloud from the central atom in their low-lying vacant orbitals. This kind of back donation is known as ‘synergic effect’ or ‘synergic bonding’. In case of CO, the back donation to the π^* orbital of central atom may be depicted as:



Greater the electron density on the metal atom, that is, lower the oxidation state of the metal, greater will be the back donation hence stronger will be the M—C bond.

Option (D): Incorrect. When the oxidation state of metal increases its tendency to accept the electrons from C of CO increases but tendency to donate the electrons from M to C decreases consequently M—C bond strength decreases and C—O bond strength increases.

3. Based on the compounds of group 15 elements, the correct statement(s) is (are)

- (A) Bi_2O_5 is more basic than N_2O_5 .
- (B) NF_3 is more covalent than BiF_3 .
- (C) PH_3 boils at lower temperature than NH_3 .
- (D) The N—N single bond is stronger than the P—P single bond.

Solution

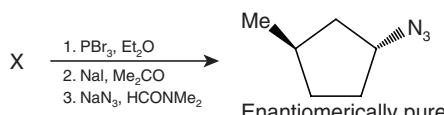
(A) (B) (C) Option (A): Correct. The basicity of oxides usually increases on descending a group. Therefore, Bi_2O_5 is more basic than N_2O_5 .

Option (B): Correct. Covalent nature of a molecule depends on the electronegativity difference between bonded atoms.

Option (C): Correct. Boiling point of NH_3 is more than that of PH_3 due to hydrogen bonding.

Option (D): Incorrect. P—P single bond is stronger than N—N single bond. This is due to the fact that N is small in size, due to smaller size of atoms lone pair of repulsion will be more.

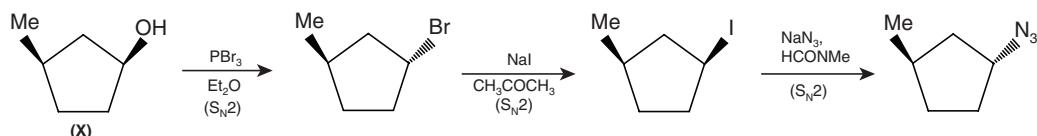
4. In the following reaction sequence, the correct structure(s) of X is (are)



- (A)
 (B)
 (C)
 (D)

Solution

(B)

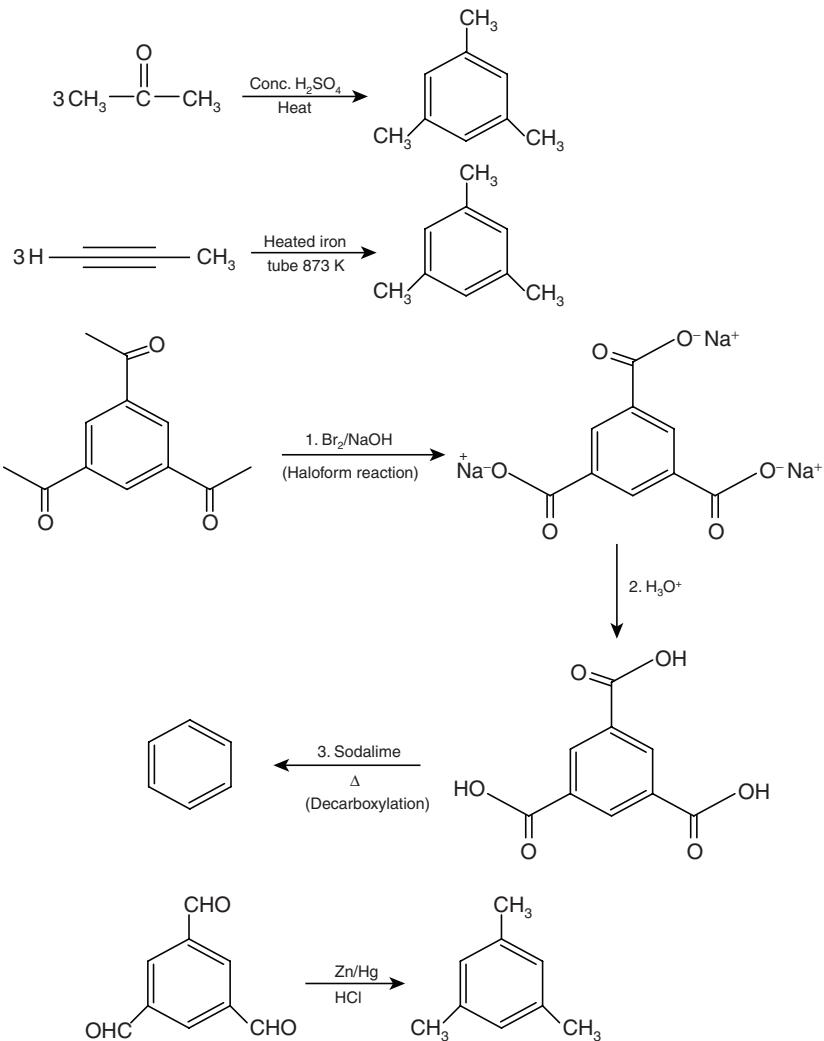


5. The reaction(s) leading to the formation of 1, 3, 5-trimethylbenzene is (are)

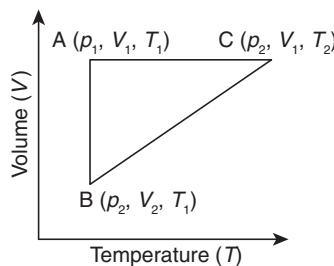
- (A)
 (B)
- (C)
- (D)

Solution

(A) (B) (D)



6. A reversible cyclic process for an ideal gas is shown below. Here p , V , and T are pressure, volume and temperature, respectively. The thermodynamic parameters q , w , H and U are heat, work, enthalpy and internal energy, respectively.



The correct option(s) is (are)

- (A) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = p_2(V_2 - V_1)$
 (B) $w_{BC} = p_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$
 (C) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$
 (D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

Solution

(B) (C) We know $\Delta U = q + w$ and $w = -p\Delta V$

In the above figure, A-C is isochoric, A-B is isothermal and B-C is isobaric process. Therefore, for an isochoric process AC, we have

$$q_{AC} = \Delta U_{AC} = nC_{V,m}(T_2 - T_1) = \Delta U_{BC}$$

For an isobaric process BC, we have

$$q_{BC} = \Delta H_{BC} = nC_{p,m}(T_2 - T_1) = \Delta H_{AC}$$

$$w_{BC} = -p_2(V_1 - V_2) = p_2(V_2 - V_1)$$

$$\Delta H_{CA} = nC_{p,m}(T_1 - T_2) \text{ and } \Delta U_{CA} = nC_{V,m}(T_1 - T_2)$$

Since, $T_2 > T_1$, therefore, ΔH_{CA} and ΔU_{CA} are negative.

$$\Delta H_{CA} = \Delta U_{CA} + V \Delta p$$

As $\Delta p < 0$, therefore, $\Delta H_{CA} < \Delta U_{CA}$.

SECTION 2

- This section contains **EIGHT (08)** questions. The answer to each question is a **NUMERICAL VALUE**.

7. Among the species given below, the total number of diamagnetic species is _____.

H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapor phase, Mn_3O_4 , $(\text{NH}_4)_2[\text{FeCl}_4]$, $(\text{NH}_4)_2[\text{NiCl}_4]$, K_2MnO_4 , K_2CrO_4

Solution

(1) The paramagnetic species are H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapor phase, Mn_3O_4 , $(\text{NH}_4)_2[\text{FeCl}_4]$, $(\text{NH}_4)_2[\text{NiCl}_4]$ and K_2MnO_4 .

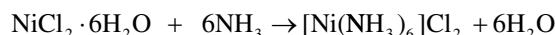
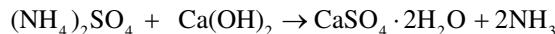
The diamagnetic species is K_2CrO_4 .

8. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ are used in the preparation, the combined weight (in grams) of gypsum and the nickel–ammonia coordination compound thus produced is _____.

(Atomic weights in g mol⁻¹: H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59)

Solution

The reactions involved are as follows:



From the above reactions we can see that

132 g of $(\text{NH}_4)_2\text{SO}_4$ will produce 172 g of gypsum

1584 g of $(\text{NH}_4)_2\text{SO}_4$ will produce $\frac{172}{132} \times 1584 = 2064$ g of gypsum

Therefore, number of moles of gypsum produced $\frac{2064}{172} = 12$ mol

238 g of $\text{NiCl}_4 \cdot 6\text{H}_2\text{O}$ will produce 314 g of Ni-complex

952 g of $\text{NiCl}_4 \cdot 6\text{H}_2\text{O}$ will produce $\frac{314}{238} \times 952 = 1256$ g of Ni-complex

Therefore, number of moles of Ni-complex produced $\frac{1256}{314} = 4$ mol

So, total mass of products is 12×172 (gypsum) + 4×232 ($[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$) = 2992 g

9. Consider an ionic solid **MX** with NaCl structure. Construct a new structure (**Z**) whose unit cell is constructed from the unit cell of **MX** following the sequential instructions given below. Neglect the charge balance.

- Remove all the anions (**X**) except the central one
- Replace all the face centered cations (**M**) by anions (**X**)
- Remove all the corner cations (**M**)
- Replace the central anion (**X**) with cation (**M**)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}} \right)$ in **Z** is _____.

Solution

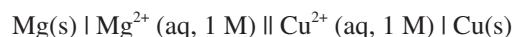
(3) Given that **MX** is an ionic solid having NaCl type structure having ccp. So, the anion X^- occupies all octahedral voids. The changes (i)-(iv) cause the following effects:

- No. of anions left = 1
- No. of anions added by replacing face centered cations $\text{M} = 3$; No. of cations left = 1
- No. of cations left = 0
- No. of cations added = 1; No. of anions left = 3

Finally, the unit cell contains 1 cation and 3 anions. So,

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}} \right)$ in **Z** is 3.

10. For the electrochemical cell,

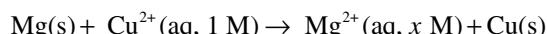


the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is _____.

(Given, $\frac{F}{R} = 11500 \text{ K V}^{-1}$, where F is the Faraday constant and R is the gas constant, $\ln(10) = 2.30$)

Solution

- (10) The cell reaction is



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - 2.303 \times \frac{RT}{2F} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$2.67 = 2.70 - 2.303 \times \frac{300}{2 \times 11500} \log(x)$$

$$0.03 = \frac{2.303 \times 3}{115 \times 2} \log x \Rightarrow \log x = 1 \Rightarrow x = 10$$

11. A closed tank has two compartments **A** and **B**, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does **NOT** allow the gas to leak across (Figure 2), the volume (in m^3) of the compartment **A** after the system attains equilibrium is _____.

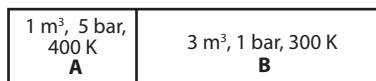


Figure 1

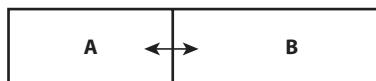


Figure 2

Solution

(2.22) Using $pV = nRT$, we have

In Figure 1,

$$n_A = \frac{p_A V_A}{RT} = \frac{5}{400R} \text{ and } n_B = \frac{p_B V_B}{RT} = \frac{1}{100R}$$

In Figure 2, after equilibrium is attained, we have

$$\begin{aligned} p_A &= p_B \text{ and } T_A = T_B = T, \text{ so} \\ \frac{n_A RT}{V_A} &= \frac{n_B RT}{V_B} \Rightarrow \frac{5}{400R \cdot V_A} = \frac{1}{100R \cdot V_B} \\ \Rightarrow 4V_A &= 5V_B \end{aligned}$$

$$\text{Now, } V_A + V_B = 4 \text{ m}^3, \text{ so } V_A + \frac{4}{5}V_A = 4 \Rightarrow V_A = \frac{20}{9} = 2.22 \text{ m}^3$$

12. Liquids **A** and **B** form ideal solution over the entire range of composition. At temperature T , equimolar binary solution of liquids **A** and **B** has vapor pressure 45 torr. At the same temperature, a new solution of **A** and **B** having mole fractions x_A and x_B , respectively, has vapor pressure of 22.5 torr. The value of x_A/x_B in the new solution is

(Given that the vapor pressure of pure liquid **A** is 20 torr at temperature T)

Solution

$$(19) \quad p_A^\circ x_A + p_B^\circ x_B = p_T = 45$$

For equimolar binary solution, $x_A = x_B = 0.5$, so

$$20 \times 0.5 + p_B \times 0.5 = 45 \Rightarrow 70 \text{ torr}$$

For the new solution,

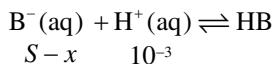
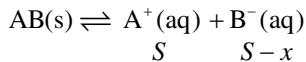
$$p_B^\circ + (p_A^\circ - p_B^\circ)x_A = 22.5 \Rightarrow 70 + (20 - 70)x_A = 22.5 \Rightarrow x_A = 47.5/50$$

$$\text{Now, } \frac{x_A}{x_B} = \frac{x_A}{1-x_A} = \frac{47.5/50}{1-(47.5/50)} = \frac{47.5}{2.5} = 19$$

13. The solubility of a salt of weak acid (AB) at pH 3 is $Y \times 10^{-3} \text{ mol L}^{-1}$. The value of Y is _____.
(Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8})

Solution

(4.47) The reactions are



Now, for HB,

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} \Rightarrow \frac{(S - x) \times 10^{-3}}{x} = 10^{-8} \\ &\Rightarrow S - x = x \times 10^{-5} \\ K_{sp} &= [\text{A}^+][\text{B}^-] = S(S - x) = 2 \times 10^{-10} \end{aligned}$$

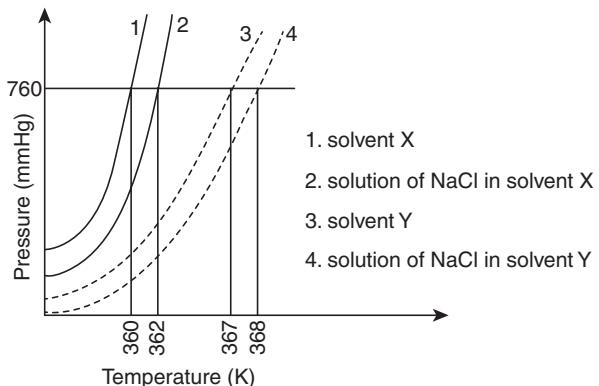
Putting $Sx = 2 \times 10^{-5}$ in $S^2 - Sx - 2 \times 10^{-10} = 0$, we get

$$S \approx \sqrt{(2 \times 10^{-5})} = 4.47 \times 10^{-3} \text{ M}$$

Alternate solution

$$S = \sqrt{K_{sp} \left(\frac{[\text{H}^+]}{K_a} + 1 \right)} = \sqrt{20 \times 10^{-10} \left(\frac{10^{-3}}{10^{-8}} + 1 \right)} \approx \sqrt{(2 \times 10^{-5})} = 4.47 \times 10^{-3} \text{ M}$$

14. The plot given below shows $p - T$ curves (where p is the pressure and T is the temperature) for two solvents **X** and **Y** and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute **S** in equal amount (in kg) of these solvents, the elevation of boiling point of solvent **X** is three times that of solvent **Y**. Solute **S** is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent **Y**, the degree of dimerization in solvent **X** is

Solution

(0.05) For solvent X,

$$\Delta T_{bX} = K_{bX} m \Rightarrow 2 = 2K_{bX} m \quad (1)$$

For solvent Y,

$$\Delta T_{bY} = K_{bY} m \Rightarrow 1 = 2K_{bY} m \quad (2)$$

Dividing Eq. (1) by Eq. (2), we get

$$\frac{K_{bX}}{K_{bY}} = 2$$

After adding solute S, molality is the same for both solutions. So, we have

For solvent X, van't Hoff factor $i = 1 - \frac{\alpha}{2}$

$$\Delta T_{bX} = iK_{bX} m = \left(1 - \frac{\alpha}{2}\right)K_{bX} m \quad (3)$$

For solvent Y, van't Hoff factor $i = 1 - \frac{0.7}{2} = \frac{1.3}{2}$

$$\Delta T_{bY} = iK_{bY} m \Rightarrow \left(\frac{1.3}{2}\right)K_{bY} m \quad (4)$$

Given that $\Delta T_{bX} = 3\Delta T_{bY}$. Dividing Eq. (3)/(4), we have

$$\frac{\Delta T_{bX}}{\Delta T_{bY}} = \frac{\left(1 - \frac{\alpha}{2}\right)K_{bX} m}{\left(\frac{1.3}{2}\right)K_{bY} m} \Rightarrow \frac{1}{3} = \frac{2(2 - \alpha)}{1.3} \Rightarrow \alpha = 0.05$$

SECTION 3

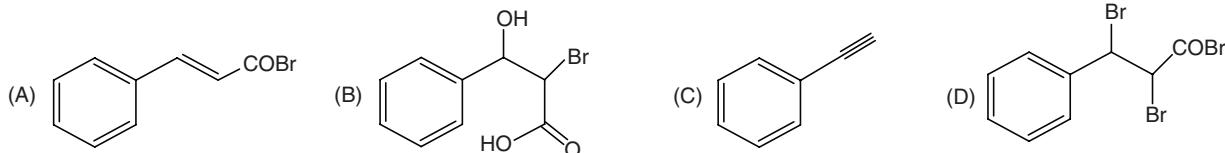
- This section contains **TWO (02)** paragraphs. Based on each paragraph, there are **TWO (02)** questions.
- Each question has **FOUR** options. **ONLY ONE** of these four options corresponds to the correct answer.

PARAGRAPH “X”

Treatment of benzene with CO/HCl in the presence of anhydrous $\text{AlCl}_3/\text{CuCl}$ followed by reaction with $\text{Ac}_2\text{O}/\text{NaOAc}$ gives compound **X** as the major product. Compound **X** upon reaction with $\text{Br}_2/\text{Na}_2\text{CO}_3$, followed by heating at 473 K with moist KOH furnishes **Y** as the major product. Reaction of **X** with $\text{H}_2/\text{Pd-C}$, followed by H_3PO_4 treatment gives **Z** as the major product.

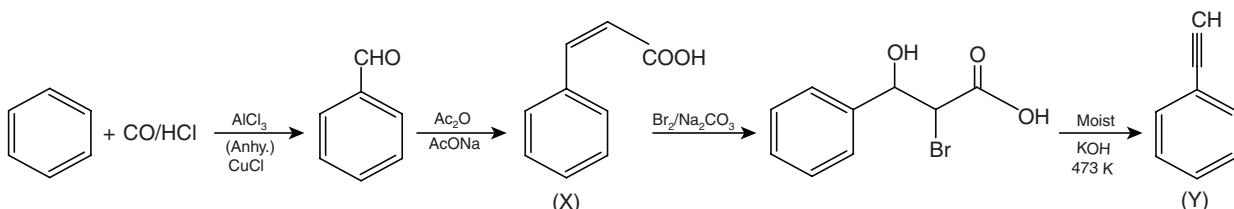
(There are two questions based on PARAGRAPH “X”, the question given below is one of them)

15. The compound **Y** is



Solution

(C)

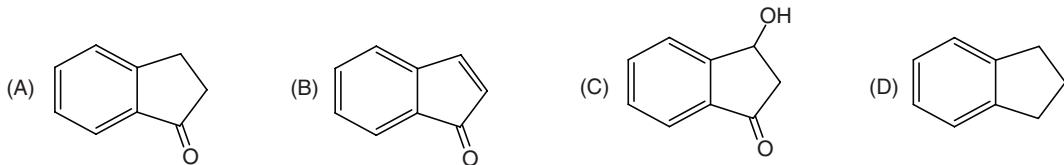


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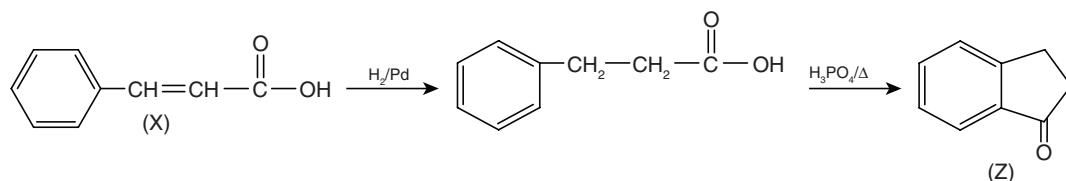
(There are two questions based on PARAGRAPH "X", the question given below is one of them)

16. The compound **Z** is



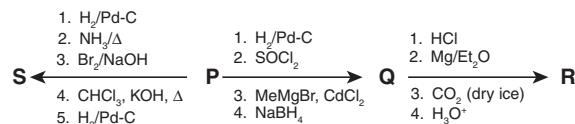
Solution

(A)



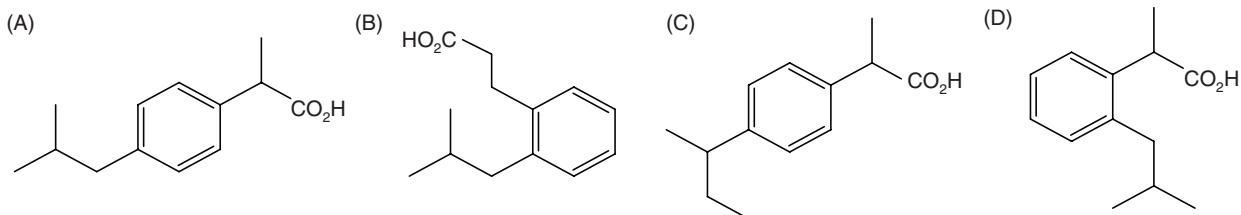
PARAGRAPH "A"

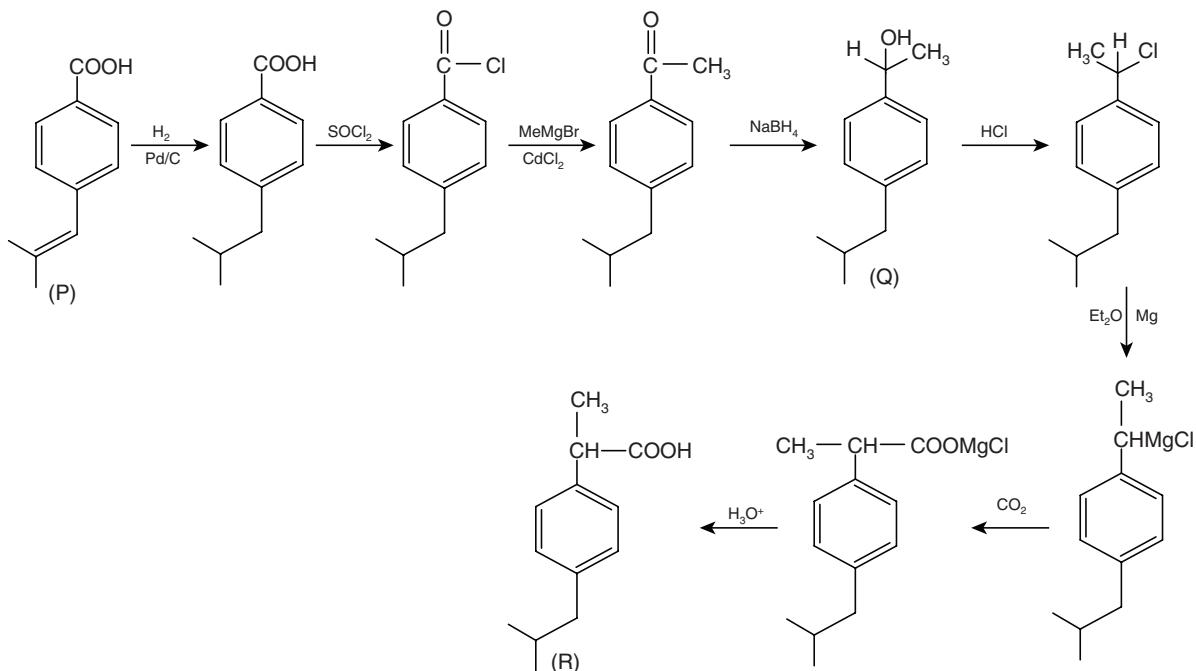
An organic acid **P** ($\text{C}_{11}\text{H}_{12}\text{O}_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** via **Q**. The compound **P** also undergoes another set of reactions to produce **S**.



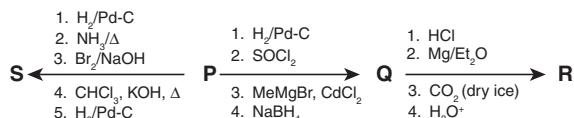
(There are two questions based on PARAGRAPH "A", the question given below is one of them)

17. The compound **R** is



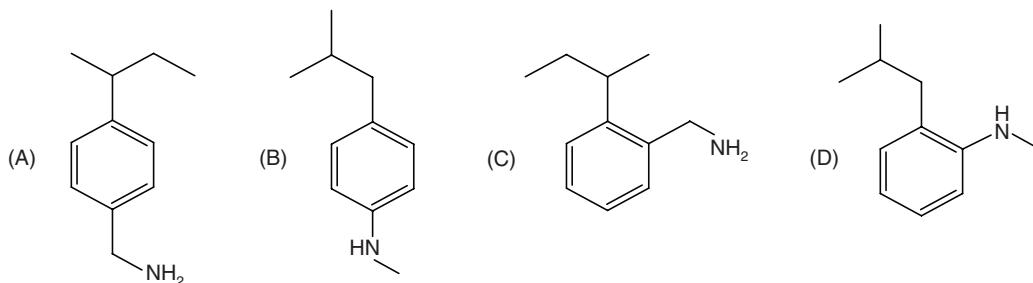
Solution**(A)****PARAGRAPH “A”**

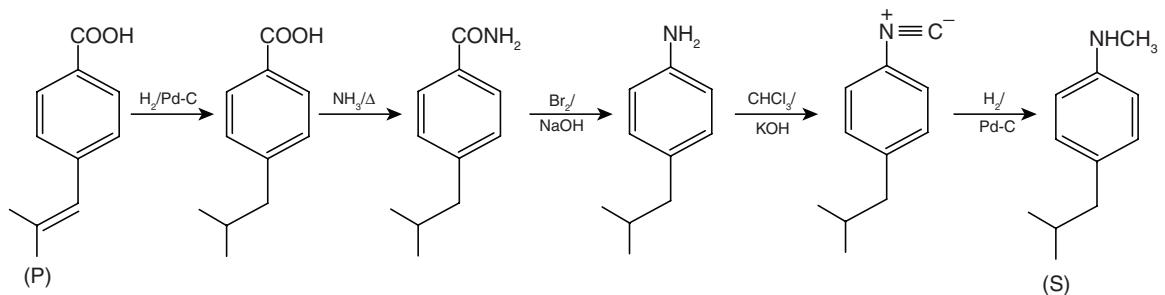
An organic acid **P** ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** via **Q**. The compound **P** also undergoes another set of reactions to produce **S**.



(There are two questions based on PARAGRAPH “A”, the question given below is one of them)

18. The compound **S** is



Solution**(B)**

JEE (ADVANCED) 2018
PAPER II (CHEMISTRY)

SECTION 1

- This section contains **SIX (06)** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).

1. The correct option(s) regarding the complex $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$

(en = $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) is (are)

(A) It has two geometrical isomers.

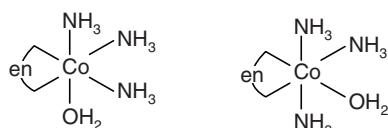
(B) It will have three geometrical isomers if bidentate ‘en’ is replaced by two cyanide ligands.

(C) It is paramagnetic.

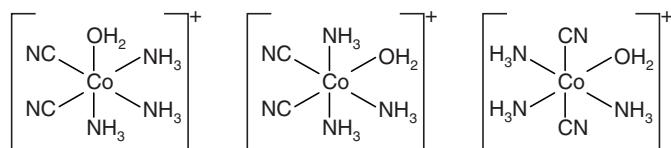
(D) It absorbs light at longer wavelength as compared to $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$.

Solution

(A) (B) (D) Option (A): Correct. The complex $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ has two following isomers:



Option (B): Correct. When bidentate ‘en’ is replaced by two cyanide ligands complex $[\text{Co}(\text{CN})_2(\text{NH}_3)_3(\text{H}_2\text{O})]^+$ will have three following isomers:



Option (C): Incorrect. In complex $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$, Co is in +3 oxidation, that is, $[\text{Ar}]d^6$. In the presence given ligands the complex will have low spin, hence, diamagnetic.

Option (D): Correct. In complex $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$ there is larger gap between t_{2g} and e_g than in complex $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$. Hence $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ will absorb light at longer wavelength as compared to $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$.

2. The correct option(s) to distinguish nitrate salts of Mn^{2+} and Cu^{2+} taken separately is (are)

(A) Mn^{2+} shows the characteristic green color in the flame test.

(B) Only Cu^{2+} shows the formation of precipitate by passing H_2S in acidic medium.

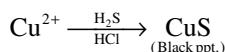
(C) Only Mn^{2+} shows the formation of precipitate by passing H_2S in faintly basic medium.

(D) Cu^{2+}/Cu has higher reduction potential than Mn^{2+}/Mn (measured under similar conditions).

Solution

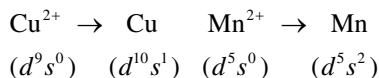
(B) (D) Option (A): Incorrect. Mn^{2+} shows purple color in the flame test.

Option (B): Correct. When H_2S gas is passed through a solution containing Cu^{2+} in the acidic medium, black ppt. is obtained.

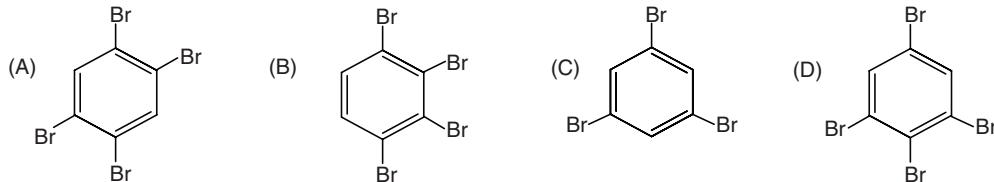
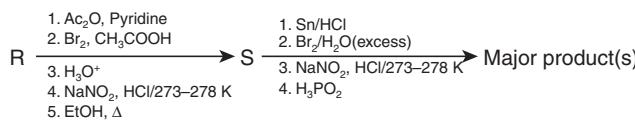


Option (C): Incorrect. Both Mn^{2+} and Cu^{2+} can form precipitate by passing H_2S in faintly basic medium.

Option (D): Correct. Higher reduction potential indicates higher tendency of Cu^{2+} to gain the electrons. Cu^{2+} ion on accepting the electrons gain stability due to fully filled d -orbital.

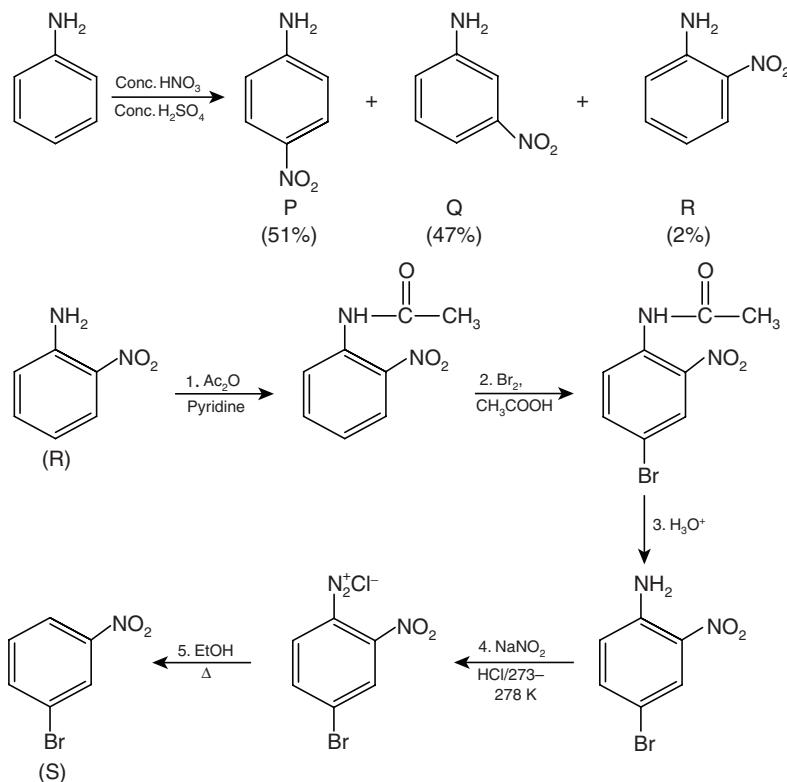


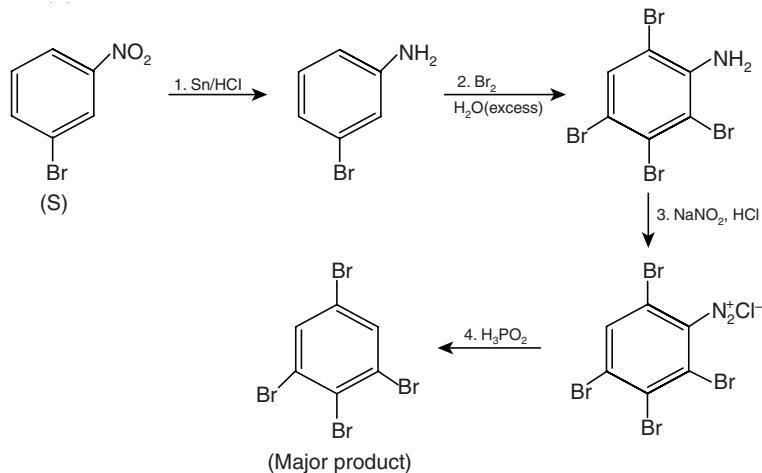
3. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give **P** (51%), **Q** (47%) and **R** (2%). The major product(s) of the following reaction sequence is (are)



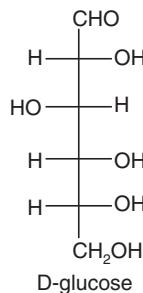
Solution

(D)

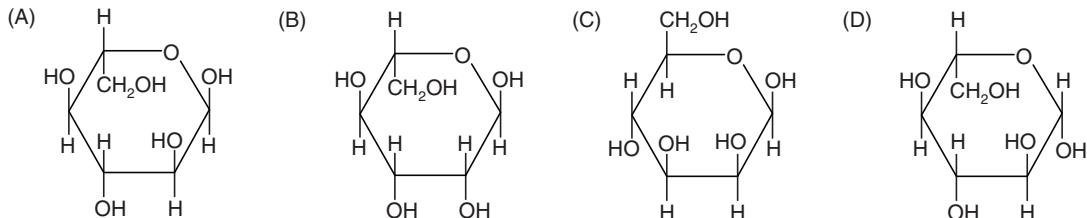




4. The Fischer presentation of D-glucose is given below.

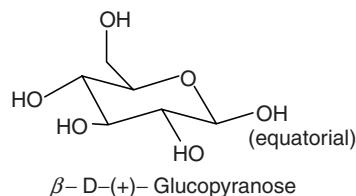


The correct structure(s) of β -L-glucopyranose is (are)

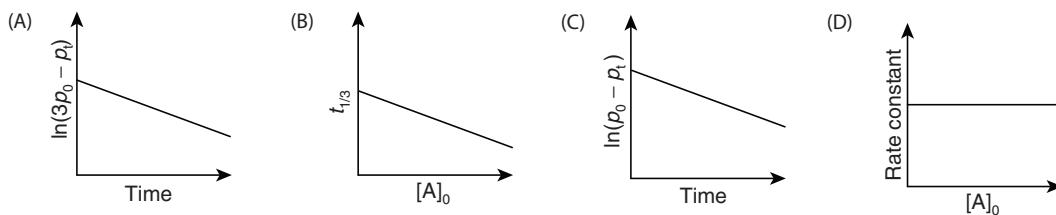


Solution

(D) The structure of β -L-glucopyranose is as follows:



5. For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning ($t = 0$) and at time t are p_0 and p_t , respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach $1/3^{\text{rd}}$ of its initial value. The correct option(s) is (are) (Assume that all these gases behave as ideal gases)

**Solution**

(A) (D) The reaction can be represented as

$A(g)$	\rightarrow	$2B(g) + C(g)$
At $t = 0$	p_0	0
At $t = t_{1/3}$	$p_0 - \frac{2p_0}{3}$	0
At $t = t$	$p_0 - x$	$2x$

$$\text{Now, } p_t = p_0 - x + 2x + x \Rightarrow x = \frac{p_t - p_0}{2}$$

Substituting in the expression $t = \frac{1}{k} \ln \left(\frac{p_0}{p_0 - x} \right)$, we get

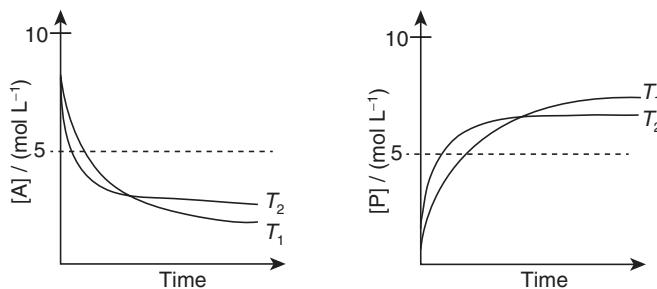
$$t = \frac{1}{k} \ln \left(\frac{p_0}{p_0 - \frac{p_t - p_0}{2}} \right) = \frac{1}{k} \ln \left(\frac{2p_0}{3p_0 - p_t} \right)$$

which can be rearranged as

$$\ln(3p_0 - p_t) = -kt + \ln 2p_0$$

Thus, the graph of $\ln(3p_0 - p_t)$ vs t is a straight line having negative slope $-k$ and intercept $\ln 2p_0$ as shown in (A). Also, as rate is independent of initial concentration, so the plot in option (D) is also correct.

6. For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ and $[P]$ with time at temperatures T_1 and T_2 are given below.



If $T_2 > T_1$, the correct statement(s) is (are)

(Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of $\ln K$ at T_1 to $\ln K$ at T_2 is greater than T_2/T_1 . Here H , S , G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively)

- | | |
|--|--|
| (A) $\Delta H^\theta < 0, \Delta S^\theta < 0$ | (B) $\Delta G^\theta < 0, \Delta H^\theta > 0$ |
| (C) $\Delta G^\theta < 0, \Delta S^\theta < 0$ | (D) $\Delta G^\theta < 0, \Delta S^\theta > 0$ |

Solution

(A) (C) As we increase the temperature, the concentration of the product reduces. This implies that the reaction is exothermic, and $\Delta H^\theta < 0$.

$$\frac{\ln K_{T_1}}{\ln K_{T_2}} > 1 \Rightarrow \ln K_{T_1} > \ln K_{T_2} \Rightarrow K_{T_1} > K_{T_2}$$

But

$$\frac{\ln K_{T_1}}{\ln K_{T_2}} > \frac{T_2}{T_1}$$

$$\text{As } \Delta G = -RT \ln K, \Delta G_{T_1}^\theta < \Delta G_{T_2}^\theta \Rightarrow \Delta H_{T_1}^\theta - T \Delta S_{T_1}^\theta < \Delta H_{T_2}^\theta - T \Delta S_{T_2}^\theta$$

This is only possible if $\Delta S^\theta < 0$

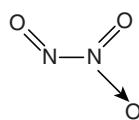
SECTION 2

This section contains **EIGHT (08)** questions. The answer to each question is a **NUMERICAL VALUE**.

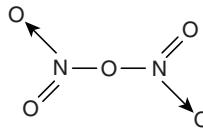
7. The total number of compounds having at least one bridging oxo group among the molecules given below is _____.
 $\text{N}_2\text{O}_3, \text{N}_2\text{O}_5, \text{P}_4\text{O}_6, \text{P}_4\text{O}_7, \text{H}_4\text{P}_2\text{O}_5, \text{H}_5\text{P}_3\text{O}_{10}, \text{H}_2\text{S}_2\text{O}_3, \text{H}_2\text{S}_2\text{O}_5$

Solution

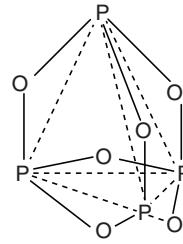
(5)



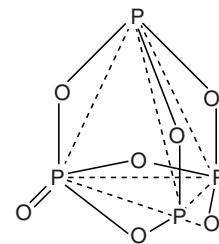
N_2O_3



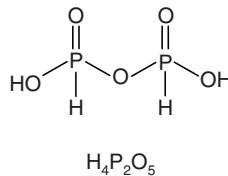
N_2O_5



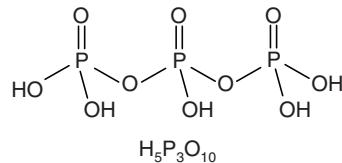
P_4O_6



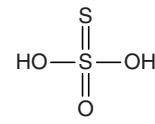
P_4O_7



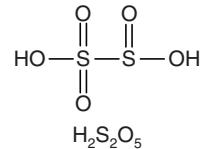
$\text{H}_4\text{P}_2\text{O}_5$



$\text{H}_5\text{P}_3\text{O}_{10}$



$\text{H}_2\text{S}_2\text{O}_3$

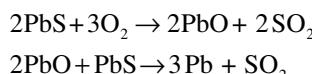


$\text{H}_2\text{S}_2\text{O}_5$

8. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of O_2 consumed is _____.
 (Atomic weights in g mol^{-1} : O = 16, S = 32, Pb = 207)

Solution

(6.47) The steps involved in the oxidation of galena (PbS) are as follows:



As per the above reactions, we can conclude that

3 mol of O_2 produces 3 mol of lead

96 kg of O_2 produces 621 kg of lead

Therefore, 1 kg of O_2 will produce $\frac{621}{96} \times 1 = 6.47 \text{ kg}$ of Pb.

9. To measure the quantity of MnCl_2 dissolved in an aqueous solution, it was completely converted to KMnO_4 using the reaction,

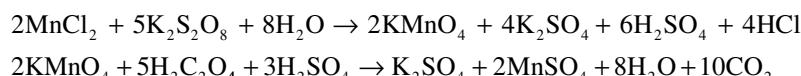


Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the color of the permanganate ion disappeared. The quantity of MnCl_2 (in mg) present in the initial solution is _____.

(Atomic weights in g mol^{-1} : Mn = 55, Cl = 35.5)

Solution

(126) The balanced equation can be written as

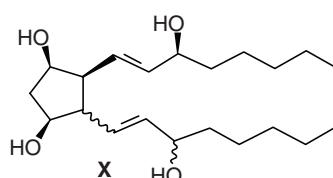


$$\text{Millimoles of KMnO}_4 = \text{Millimoles of H}_2\text{C}_2\text{O}_4$$

$$\text{Millimole MnCl}_2 \times 5 = \left(\frac{225}{90} \right) \times 2$$

So, millimole of $\text{MnCl}_2 = 1 = 126 \text{ mg}$.

10. For the given compound X, the total number of optically active stereoisomers is _____.

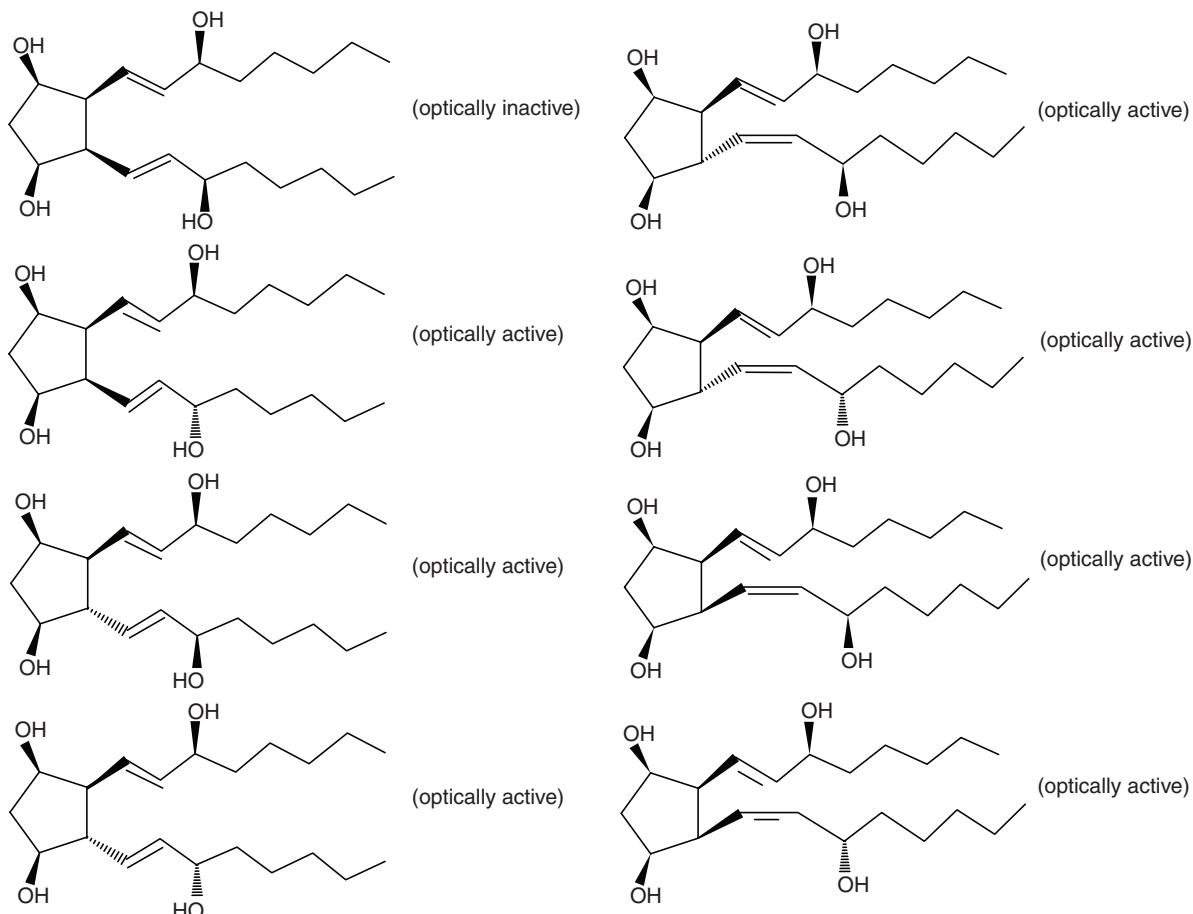


→ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed.

↔ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is not fixed.

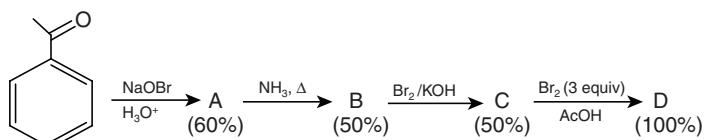
Solution

(7) There are total 7 optically active stereoisomers. Their structures are as follows:

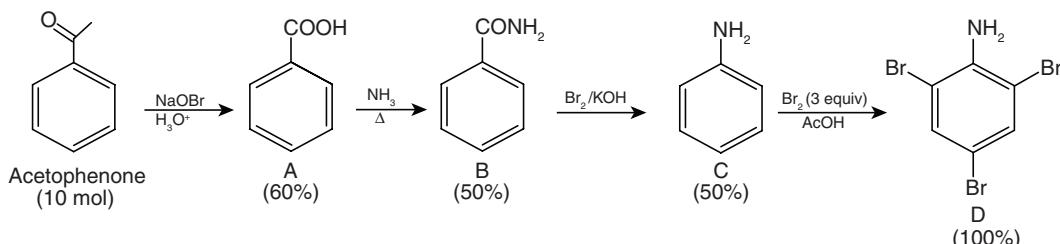


11. In the following reaction sequence, the amount of **D** (in g) formed from 10 mol of acetophenone is _____.

(Atomic weights in g mol⁻¹: H = 1, C = 12, N = 14, O = 16, Br = 80. The yield (%) corresponding to the product in each step is given in the parenthesis)

**Solution**

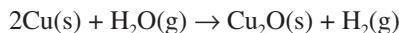
(495)



The amount of D formed in mol is $\frac{60}{100} \times \frac{50}{100} \times \frac{50}{100} \times 10 = 1.5 \text{ mol}$

Amount of D in grams is $= 1.5 \times 330 \text{ g} = 495 \text{ g}$

- 12.** The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapor as impurity. The water vapor oxidizes copper as per the reaction given below:



p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{\text{H}_2})$ is _____.

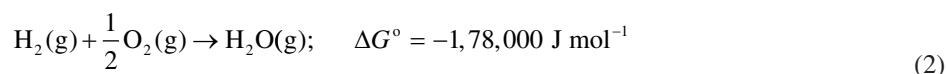
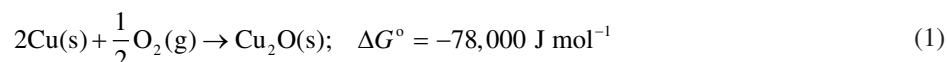
(Given: total pressure = 1 bar, R (universal gas constant) = $8 \text{ J K}^{-1} \text{ mol}^{-1}$, $\ln(10) = 2.3$. Cu(s) and $\text{Cu}_2\text{O(s)}$ are mutually immiscible.

At 1250 K: $2\text{Cu(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{Cu}_2\text{O(s)}$; $\Delta G^\circ = -78,000 \text{ J mol}^{-1}$

$\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(g)}$; $\Delta G^\circ = -1,78,000 \text{ J mol}^{-1}$; G is the Gibbs energy

Solution

(-14.6)



Subtracting Eq. (1) – Eq. (2), we get



Now,

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right)$$

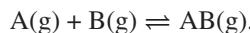
For the reaction (3) to not occur,

$$\begin{aligned} \Delta G > 0 \text{ or } \Delta G^\circ + RT \ln\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right) > 0 \\ \Rightarrow 100000 + 8 \times 1250 \ln\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right) > 0 \\ \Rightarrow 100000 + 8 \times 1250 \ln\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right) > \frac{-100000}{8 \times 1250} \\ \Rightarrow \ln\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right) > -10 \\ \ln p_{\text{H}_2} > -10 + \ln p_{\text{H}_2\text{O}} \end{aligned}$$

Now, $p_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}} \times p_{\text{T}} = 0.01 \times 1 = 10^{-2}$

So, $\ln p_{\text{H}_2} > -10 - 2 \ln 10 \Rightarrow p_{\text{H}_2} > -14.6 \text{ bar}$

13. Consider the following reversible reaction,



The activation energy of the backward reaction exceeds that of the forward reaction by $2RT$ (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^θ (in mol^{-1}) for the reaction at 300 K is _____.

(Given: $\ln(2) = 0.7$, $RT = 2500 \text{ J mol}^{-1}$ at 300 K and G is the Gibbs energy)

Solution

(-8466 J mol^{-1})

$$\Delta G^\theta = -RT \ln K$$

where

$$K = \frac{K_f}{K_b} = \frac{A_f e^{-E_{af}/RT}}{A_b e^{-E_{ab}/RT}}$$

Now, given that $A_f = 4A_b$ and $E_{ab} - E_{af} = 2RT$. Substituting, we get

$$K = \frac{K_f}{K_b} = 4e^{(E_{ab} - E_{af})/RT} = 4e^2$$

Therefore, $\Delta G^\theta = -RT \ln(4e^2) = -2500 \times [\ln(4) + 2] = -8466 \text{ J mol}^{-1}$

14. Consider an electrochemical cell: $\text{A(s)} \mid \text{A}^{n+}(\text{aq}, 2 \text{ M}) \parallel \text{B}^{2n+}(\text{aq}, 1 \text{ M}) \mid \text{B(s)}$. The value of ΔH^θ for the cell reaction is twice that of ΔG^θ at 300 K. If the emf of the cell is zero, the ΔS^θ (in $\text{J K}^{-1} \text{ mol}^{-1}$) of the cell reaction per mole of B formed at 300 K is _____.

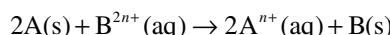
(Given: $\ln(2) = 0.7$, R (universal gas constant) = $8.3 \text{ J K}^{-1} \text{ mol}^{-1}$. H , S and G are enthalpy, entropy and Gibbs energy, respectively)

Solution

(-11.62 $\text{JK}^{-1} \text{mol}^{-1}$) The half-cell reactions are



Adding Eq. (1) and Eq. (2), we get



Given that $\Delta H^\theta = 2\Delta G^\theta$ and $E_{\text{cell}} = 0$, so

$$\begin{aligned} \Delta G^\theta &= \Delta H^\theta - T \Delta S^\theta \Rightarrow \Delta S^\theta = \frac{\Delta G^\theta}{T} = \frac{-RT \ln K}{T} \\ &\Rightarrow \Delta S^\theta = -R \ln \frac{[\text{A}^{n+}]^2}{[\text{B}^{2n+}]} = -8.3 \times \ln 4 = -11.5 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

SECTION 3

- This section contains **FOUR (04)** questions.
- Each question has **TWO (02)** matching lists: **LIST-I** and **LIST-II**.
- FOUR options are given representing matching of elements from **LIST-I** and **LIST-II**. **ONLY ONE** of these four options corresponds to a correct matching.

15. Match each set of hybrid orbitals from LIST-I with complex(es) given in LIST-II.

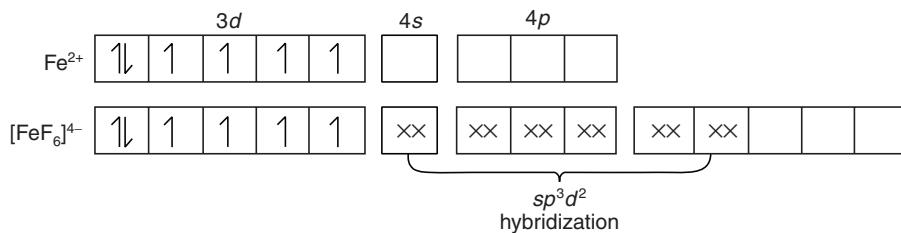
LIST-I	LIST-II
P. dsp^2	1. $[\text{FeF}_6]^{4-}$
Q. sp^3	2. $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$
R. sp^3d^2	3. $[\text{Cr}(\text{NH}_3)_6]^{3+}$
S. d^2sp^3	4. $[\text{FeCl}_4]^{2-}$
	5. $[\text{Ni}(\text{CO})]_4$
	6. $[\text{Ni}(\text{CN})_4]^{2-}$

The correct option is

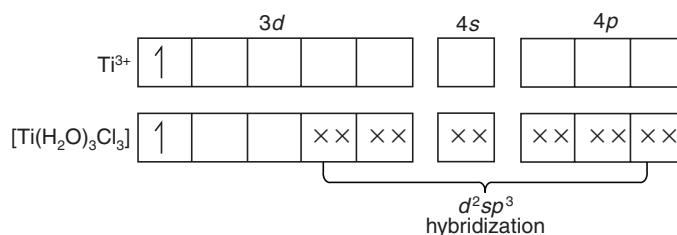
- (A) P \rightarrow 5; Q \rightarrow 4, 6; R \rightarrow 2, 3; S \rightarrow 1
 (B) P \rightarrow 5, 6; Q \rightarrow 4; R \rightarrow 3; S \rightarrow 1, 2
 (C) P \rightarrow 6; Q \rightarrow 4, 5; R \rightarrow 1; S \rightarrow 2, 3
 (D) P \rightarrow 4, 6; Q \rightarrow 5, 6; R \rightarrow 1, 2; S \rightarrow 3

Solution

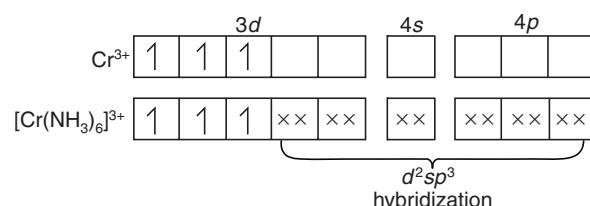
(C) $[\text{FeF}_6]^{4-}$: The arrangement of electrons in Fe^{2+} ($3d^6$) will be



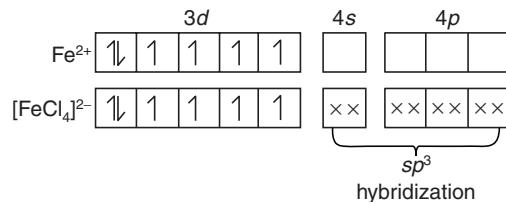
$[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$: The arrangement of electrons in Ti^{3+} ($3d^1$) will be



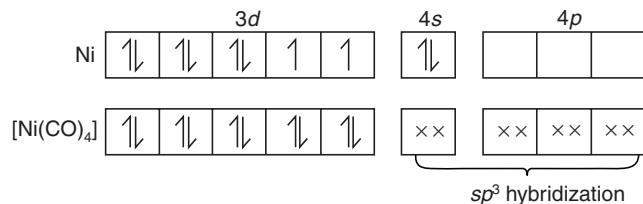
$[\text{Cr}(\text{NH}_3)_6]^{3+}$: The arrangement of electrons in Cr^{3+} ($3d^3$) will be



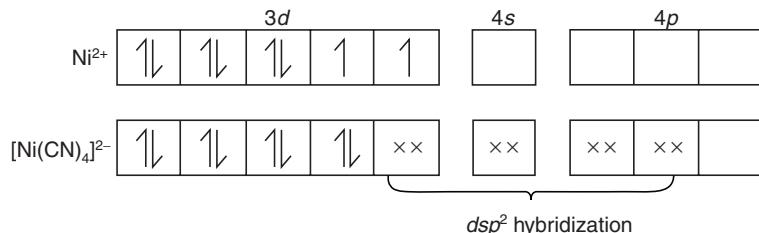
$[\text{FeCl}_4]^{2-}$: The arrangement of electrons in Fe^{2+} ($3d^6$) will be



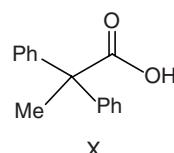
$[\text{Ni}(\text{CO})_4]$: The arrangement of electrons in Ni^0 ($3d^8 4s^2$) will be



$[\text{Ni}(\text{CN})_4]^{2-}$: The arrangement of electrons in Ni^{2+} ($3d^8$) will be



16. The desired product **X** can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II.
(Given, order of migratory aptitude: aryl > alkyl > hydrogen)



LIST-I	LIST-II
P. $\text{P} + \text{H}_2\text{SO}_4$	1. I_2, NaOH
Q. $\text{Q} + \text{HNO}_2$	2. $[\text{Ag}(\text{NH}_3)_2]\text{OH}$
R. $\text{R} + \text{H}_2\text{SO}_4$	3. Fehling solution
S. $\text{S} + \text{AgNO}_3$	4. HCHO, NaOH
	5. NaOBr

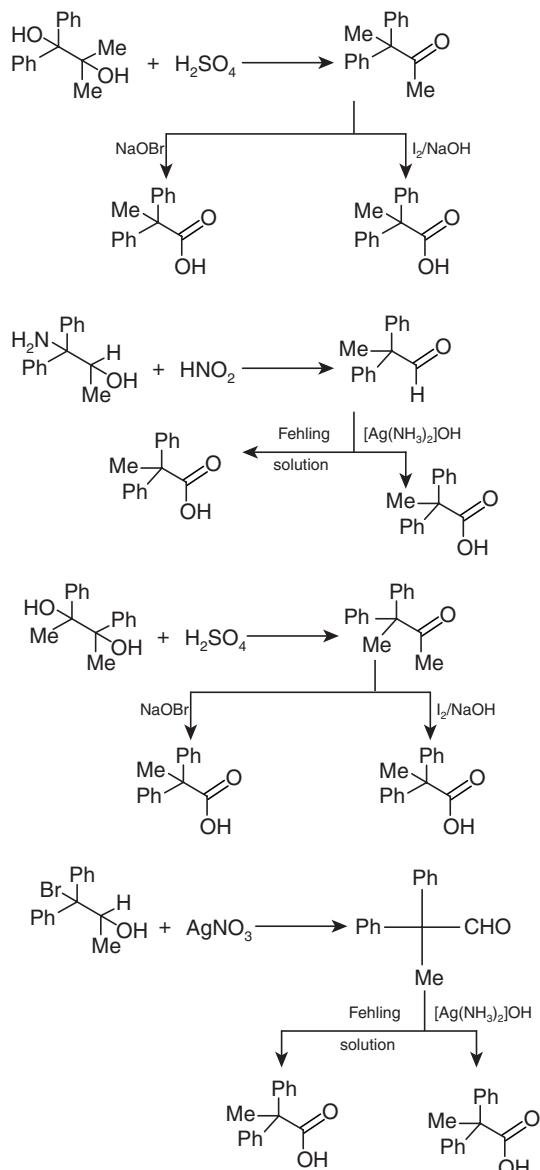
The correct option is

- (A) P \rightarrow 1; Q \rightarrow 2, 3; R \rightarrow 1, 4; S \rightarrow 2, 4
 (C) P \rightarrow 1, 5; Q \rightarrow 3, 4; R \rightarrow 5; S \rightarrow 2, 4

- (B) P \rightarrow 1, 5; Q \rightarrow 3, 4; R \rightarrow 4, 5; S \rightarrow 3
 (D) P \rightarrow 1, 5; Q \rightarrow 2, 3; R \rightarrow 1, 5; S \rightarrow 2, 3

Solution

- (D) The reactions are as follows:



17. LIST-I contains reactions and LIST-II contains major products.

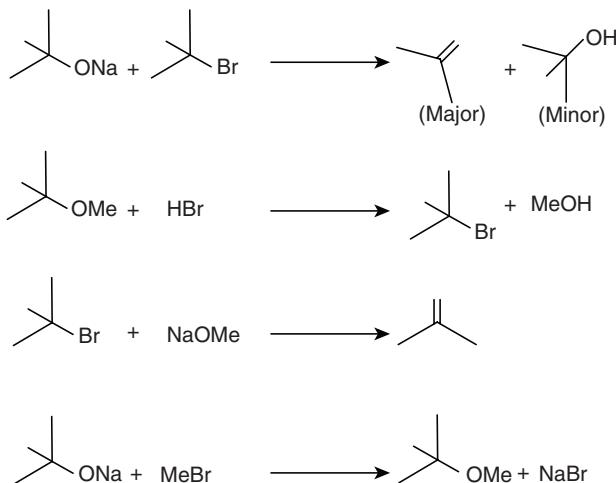
	LIST-I	LIST-II
P.		
Q.		
R.		
S.		
		1.
		2.
		3.
		4.
		5.

Match each reaction in LIST-I with one or more products in LIST-II and choose the correct option.

- (A) P → 1, 5; Q → 2; R → 3; S → 4
 (B) P → 1, 4; Q → 2; R → 4; S → 3
 (C) P → 1, 4; Q → 1, 2; R → 3, 4; S → 4
 (D) P → 4, 5; Q → 4; R → 4; S → 3, 4

Solution

(B) With *tertiary* halides, steric hindrance in the substrate is severe, thus, elimination is highly favored, especially when the reaction is carried out at higher temperatures.



18. Dilution processes of different aqueous solutions, with water, are given in LIST-I. The effects of dilution of the solutions on $[\text{H}^+]$ are given in LIST-II. (Note: Degree of dissociation (α) of weak acid and weak base is $\ll 1$; degree of hydrolysis of salt $\ll 1$; $[\text{H}^+]$ represents the concentration of H^+ ions)

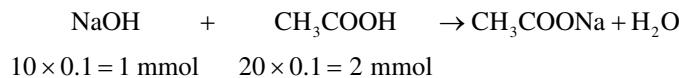
LIST-I	LIST-II
P. (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL	1. the value of $[H^+]$ does not change on dilution
Q. (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL	2. the value of $[H^+]$ changes to half of its initial value on dilution
R. (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL	3. the value of $[H^+]$ changes to two times of its initial value on dilution
S. 10 mL saturated solution of $Ni(OH)_2$ in equilibrium with excess solid $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is still present after dilution).	4. the value of $[H^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
	5. the value of $[H^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in LIST-I with one or more effect(s) in LIST-II. The correct option is

- (A) P → 4; Q → 2; R → 3; S → 1
 (B) P → 4; Q → 3; R → 2; S → 3
 (C) P → 1; Q → 4; R → 5; S → 3
 (D) P → 1; Q → 5; R → 4; S → 1

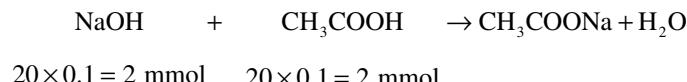
Solution

(D)



$$[\text{CH}_3\text{COO}^-] = \frac{20 \times 0.1 - 10 \times 0.1}{30} = \frac{1}{30}$$

Since it is a buffer solution, with 1 mmol of CH_3COOH and 1 mmol of CH_3COONa in solution. So, (P) → (1).



Since the solution contains 2 mmol of CH_3COONa in 40 ml solution. So, for a salt of weak acid and strong base, we have

$$[\text{H}^+]_{\text{initial}} = \sqrt{\frac{K_w K_a}{C}}$$

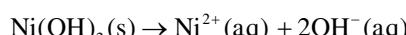
On dilution to 80 ml, C becomes $C/2$, so $[\text{H}^+]_{\text{new}} = \sqrt{\frac{K_w K_a}{C/2}} = [\text{H}^+]_{\text{initial}} \times \sqrt{2}$. So, (Q) → (5)



Since the solution contains 2 mmol of CH_3COONa in 40 mL solution. So, for a salt of strong acid and weak base, we have

$$[\text{H}^+]_{\text{initial}} = \sqrt{\frac{K_w C}{K_b}}$$

On dilution to 80 mL, C becomes $C/2$, so $[\text{H}^+]_{\text{new}} = \sqrt{\frac{K_w C}{2K_b}} = [\text{H}^+]_{\text{initial}} / \sqrt{2}$. So, (R) → (4)

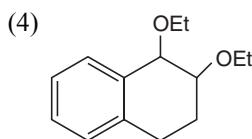


As it is a sparingly soluble salt, there is no change in $[\text{OH}^-]$ on dilution. So, (S) → (1)

JEE Main 2019 (January 9, Shift 1)

CHEMISTRY

1. Two complexes $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (A) and $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (B) are violet and yellow coloured, respectively. The incorrect statement regarding them is:
- Δ_o values of (A) and (B) are calculated from the energies of violet and yellow light, respectively.
 - both are paramagnetic with three unpaired electrons.
 - both absorb energies corresponding to their complementary colors.
 - Δ_o values for (A) is less than that of (B).
2. The correct decreasing order for acid strength is:
- $\text{NO}_2\text{CH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{CNCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$
 - $\text{FCH}_2\text{COOH} > \text{NCCH}_2\text{COOH} > \text{NO}_2\text{CH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$
 - $\text{CNCH}_2\text{COOH} > \text{O}_2\text{NCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$
 - $\text{NO}_2\text{CH}_2\text{COOH} > \text{NCCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$
3. The major product of following reaction is:
- $$\text{R}-\text{C}\equiv\text{N} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) AlH}(i-\text{Bu})_2} ?$$
- RCOOH
 - RCONH_2
 - RCHO
 - RCH_2NH_2
4. The highest value of the calculated spin-only magnetic moment (in BM) among all the transition metal complexes is:
- 5.92
 - 6.93
 - 3.87
 - 4.90
5. 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume 10 m^3 at 1000 K. Given R is the gas constant in $\text{JK}^{-1} \text{mol}^{-1}$, x is:
- $\frac{2R}{4+R}$
 - $\frac{2R}{4-R}$
6. (3) $\frac{4+R}{2R}$ (4) $\frac{4-R}{2R}$
6. The one that is extensively used as a piezoelectric material is:
- tridymite
 - amorphous silica
 - quartz
 - mica
7. Correct statements among a to d regarding silicones are:
- They are polymers with hydrophobic character.
 - They are biocompatible.
 - In general, they have high thermal stability and low dielectric strength.
 - Usually, they are resistant to oxidation and used as greases.
- (a), (b), (c) and (d)
 - (a), (b) and (c) only
 - (a) and (b) only
 - (a), (b) and (d) only
8. The major product of the following reaction is:
-



9. In general, the properties that decrease and increase down a group in the periodic table, respectively, are:
- atomic radius and electronegativity.
 - electron gain enthalpy and electronegativity.
 - electronegativity and atomic radius.
 - electronegativity and electron gain enthalpy.

10. A solution of sodium sulfate contains 92 g of Na^+ ions per kilogram of water. The molality of Na^+ ions in that solution in mol kg^{-1} is:

- 12
- 4
- 8
- 16

11. The correct match between Item-I and Item-II is:

- | Item-I (drug) | Item-II (test) |
|--|------------------------------------|
| (A)Chloroxylenol | (P) Carbylamine test |
| (B) Norethindron | (Q) Sodium hydrogen-carbonate test |
| (C) Sulphapyridine | (R) Ferric chloride test |
| (D) Penicillin | (S) Baeyer's test |
| (1) $\text{A} \rightarrow \text{R}; \text{B} \rightarrow \text{P}; \text{C} \rightarrow \text{S}; \text{D} \rightarrow \text{Q}$ | |
| (2) $\text{A} \rightarrow \text{Q}; \text{B} \rightarrow \text{S}; \text{C} \rightarrow \text{P}; \text{D} \rightarrow \text{R}$ | |
| (3) $\text{A} \rightarrow \text{R}; \text{B} \rightarrow \text{S}; \text{C} \rightarrow \text{P}; \text{D} \rightarrow \text{Q}$ | |
| (4) $\text{A} \rightarrow \text{Q}; \text{B} \rightarrow \text{P}; \text{C} \rightarrow \text{S}; \text{D} \rightarrow \text{R}$ | |

12. A water sample has ppm level concentration of the following metals: $\text{Fe} = 0.2$; $\text{Mn} = 5.0$, $\text{Cu} = 3.0$; $\text{Zn} = 5.0$. The metal that makes the water sample unsuitable for drinking is:

- Cu
- Mn
- Fe
- Zn

13. The anodic half-cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of PbSO_4 electrolyzed in g during the process is : (Molar mass of $\text{PbSO}_4 = 303 \text{ g mol}^{-1}$)

- 22.8
- 15.2
- 7.6
- 11.4

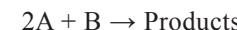
14. Which one of the following statements regarding Henry's law is not correct?

- Higher the value of K_{H} at a given pressure, higher is the solubility of the gas in the liquids.
- Different gases have different K_{H} (Henry's law constant) values at the same temperature.

- (3) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution.

- (4) The value of K_{H} increases with increase of temperature and K_{H} is function of the nature of the gas

15. The following results were obtained during kinetic studies of the reaction;

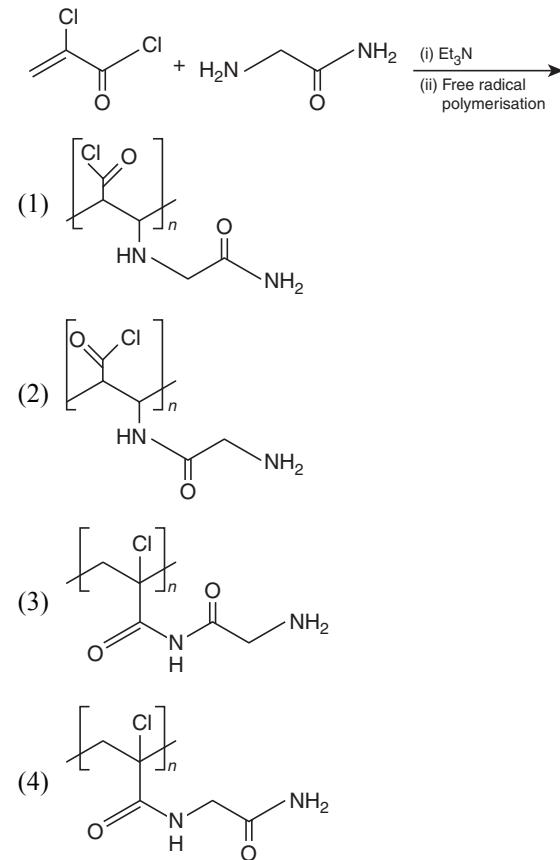


Experiment	[A] (in mol L^{-1})	[B] (in mol L^{-1})	Initial Rate of Reaction (in $\text{mol L}^{-1} \text{ min}^{-1}$)
I	0.10	0.20	6.93×10^{-3}
II	0.10	0.25	6.93×10^{-3}
III	0.20	0.30	1.386×10^{-2}

The time (in minutes) required to consume half of A is:

- 5
- 10
- 1
- 100

16. Major product of the following reaction is:



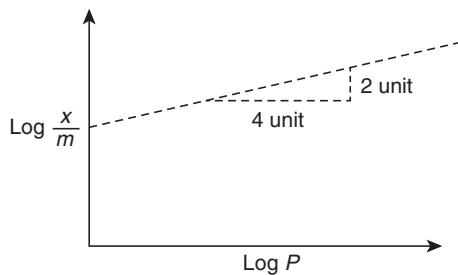
17. The alkaline earth metal nitrate that does not crystallise with water molecules, is:

- (1) $\text{Mg}(\text{NO}_3)_2$ (2) $\text{Sr}(\text{NO}_3)_2$
(3) $\text{Ca}(\text{NO}_3)_2$ (4) $\text{Ba}(\text{NO}_3)_2$

18. 20 mL of 0.1 M H_2SO_4 solution is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is : [$\text{p}K_b$ of $\text{NH}_4\text{OH} = 4.7$].

- (1) 5.2 (2) 9.0
(3) 5.0 (4) 9.4

19. Adsorption of a gas follows Freundlich adsorption isotherm. In the given plot, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p . $\frac{x}{m}$ is proportional to:



- (1) p^2 (2) $p^{1/4}$
(3) $p^{1/2}$ (4) p

20. Which amongst the following is the strongest acid?

- (1) CHBr_3 (2) CHI_3
(3) $\text{CH}(\text{CN})_3$ (4) CHCl_3

21. The ore that contains both iron and copper is:

- (1) copper pyrites (2) malachite
(3) dolomite (4) azurite

22. For emission line of atomic hydrogen from $n_i = 8$ to $n_f = n$, the plot of wave number (\bar{v}) against $\left(\frac{1}{n^2}\right)$ will be (The Rydberg constant, R_H is in wave number unit)

- (1) Linear with intercept $-R_H$
(2) Non linear
(3) Linear with slope R_H
(4) Linear with slope $-R_H$

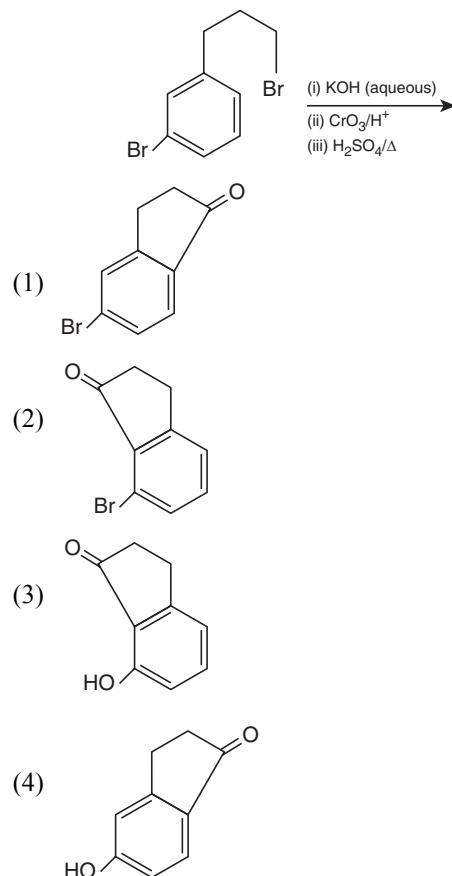
23. The isotopes of hydrogen are:

- (1) Tritium and protium only
(2) Protium and deuterium only
(3) Protium, deuterium and tritium
(4) Deuterium and tritium only

24. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^- ?

- (1) Li_2^+ is unstable and Li_2^- is stable
(2) Li_2^+ is stable and Li_2^- is unstable
(3) Both are stable
(4) Both are unstable

25. The major product of the following reaction is:



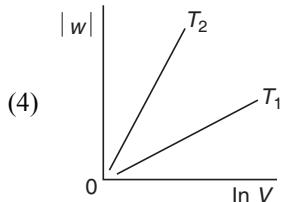
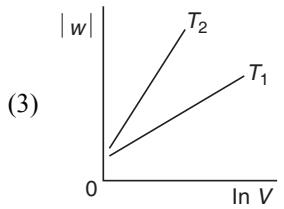
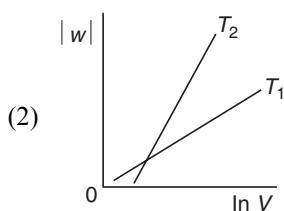
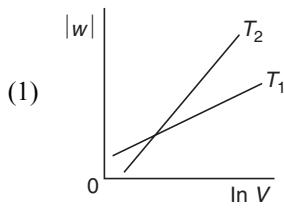
26. Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to:

- (1) inert pair effect
(2) diagonal relationship
(3) lattice effect
(4) lanthanoid contraction

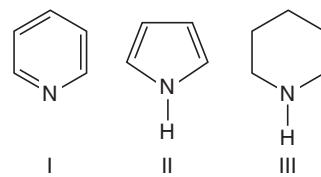
27. The increasing order of $\text{p}K_a$ of the following amino acids in aqueous solution is:

- Gly Asp Lys Arg
- (1) Asp < Gly < Arg < Lys
(2) Gly < Asp < Arg < Lys
(3) Asp < Gly < Lys < Arg
(4) Arg < Lys < Gly < Asp

28. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (w) on the final volume (V) is:

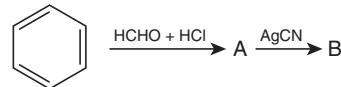


29. Arrange the following amines in the decreasing order of basicity:



- (1) I > II > III
- (2) III > I > II
- (3) III > II > I
- (4) I > III > II

30. The compounds A and B in the following reaction are, respectively:



- (1) A = Benzyl alcohol, B = Benzyl cyanide
- (2) A = Benzyl chloride, B = Benzyl cyanide
- (3) A = Benzyl alcohol, B = Benzyl isocyanide
- (4) A = Benzyl chloride, B = Benzyl isocyanide

JEE Main 2019 (January 9, Shift 2)

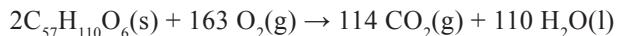
CHEMISTRY

1. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is:

(Specific heat of water liquid and water vapour are $4.2 \text{ kJ K}^{-1} \text{ kg}^{-1}$ and $2.0 \text{ kJ K}^{-1} \text{ kg}^{-1}$; heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491 kJ kg^{-1} , respectively). ($\log 273 = 2.436$, $\log 373 = 2.572$, $\log 383 = 2.583$)

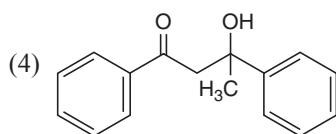
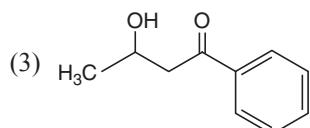
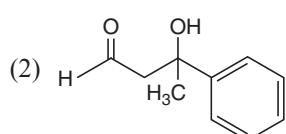
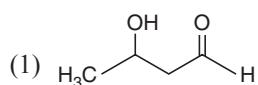
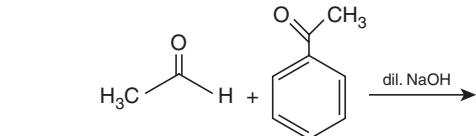
- (1) $7.90 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (2) $2.64 \text{ kJ kg}^{-1} \text{ K}^{-1}$
 (3) $8.49 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4) $9.26 \text{ kJ kg}^{-1} \text{ K}^{-1}$

2. For the following reaction, the mass of water produced from 445 g of $\text{C}_{57}\text{H}_{110}\text{O}_6$ is:



- (1) 490 g (2) 445 g
 (3) 495 g (4) 890 g

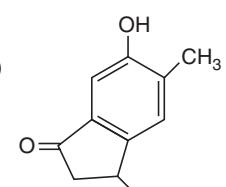
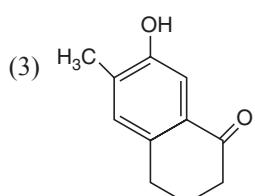
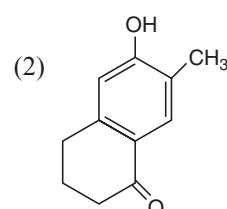
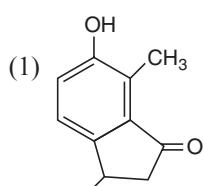
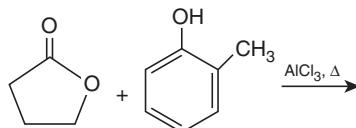
3. The major product formed in the following reaction is:



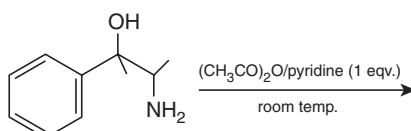
4. Which of the following conditions in drinking water causes methemoglobinemia?

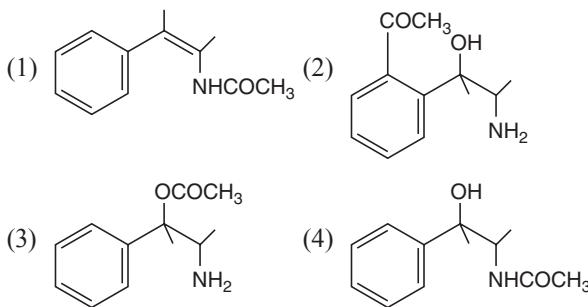
- (1) $>50 \text{ ppm}$ of lead
 (2) $>50 \text{ ppm}$ of chloride
 (3) $>50 \text{ ppm}$ of nitrate
 (4) $>100 \text{ ppm}$ of sulphate

5. The major product of the following reaction is:

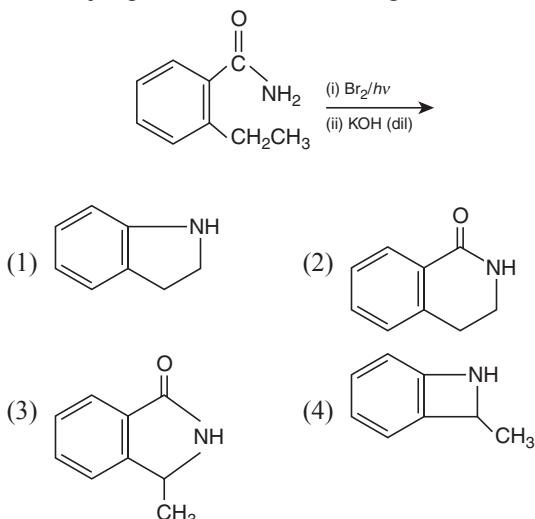


6. The major product obtained in the following reaction is:





7. The major product of the following reaction is:



8. The correct match between Item I and Item II is:

Item I	Item II
(A) Benzaldehyde	(P) Mobile phase
(B) Alumina	(Q) Adsorbent
(C) Acetonitrile	(R) Adsorbate
(1) (A) → (Q); (B) → (P); (C) → (R) (2) (A) → (R); (B) → (Q); (C) → (P) (3) (A) → (Q); (B) → (R); (C) → (P) (4) (A) → (P); (B) → (R); (C) → (Q)	

9. The metal that forms nitride by reacting directly with N_2 of air, is:

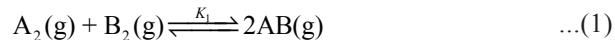
10. For coagulation of arsenious sulphide sol, which one of the following salt solution will be most effective?

11. The complex that has highest crystal field splitting energy (Δ) is:

- (1) $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ (2) $\text{K}_2[\text{CoCl}_4]$
 (3) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$ (4) $\text{K}[\text{Co}(\text{CN})_5]$

12. The pH of rain water, is approximately:

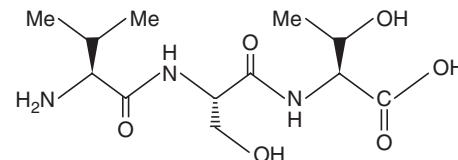
13. Consider the following reversible chemical reactions:



The relation between K_1 and K_2 is:

- (1) $K_1 K_2 = \frac{1}{3}$ (2) $K_2 = K_1^3$
 (3) $K_2 = K_1^{-3}$ (4) $K_1 K_2 = 3$

14. The correct sequence of amino acids present in the tripeptide given below is:



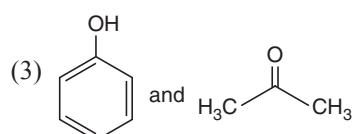
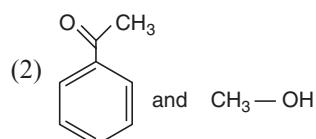
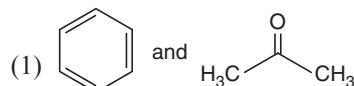
- (1) Val – Ser – Thr (2) Thr – Ser – Val
(3) Leu – Ser – Thr (4) Thr – Ser – Leu

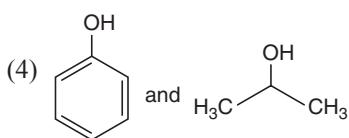
15. For the reaction, $2A + B \rightarrow$ products, when the concentrations of A and B both were doubled, the rate of the reaction increased from $0.3 \text{ mol L}^{-1} \text{ s}^{-1}$ to $2.4 \text{ mol L}^{-1} \text{ s}^{-1}$. When the concentration of A alone is doubled, the rate increased from $0.3 \text{ mol L}^{-1} \text{ s}^{-1}$ to $0.6 \text{ mol L}^{-1} \text{ s}^{-1}$.

Which one of the following statements is correct?

- (1) Total order of the reaction is 4
 - (2) Order of the reaction with respect to B is 2
 - (3) Order of the reaction with respect to B is 1
 - (4) Order of the reaction with respect to A is 2

16. The products formed in the reaction of cumene with O_2 , followed by treatment with dil. HCl are:

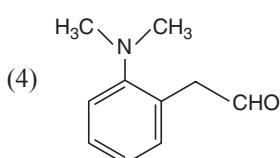
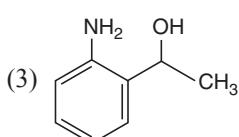
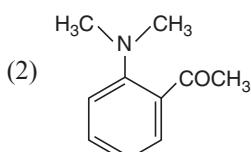
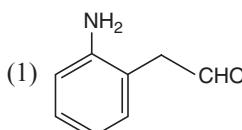




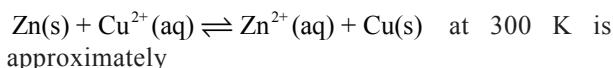
17. The tests performed on compound X and their inferences are:

Test	Inference
(a) 2, 4-DNP test	Coloured precipitate
(b) Iodoform test	Yellow precipitate
(c) Azo-dye test	No dye formation

Compound 'X' is:



18. If the standard electrode potential for a cell is 2 V at 300 K, the equilibrium constant (K) for the reaction



- (R = 8 JK⁻¹ mol⁻¹, F = 96000 C mol⁻¹)
- (1) e^{-80} (2) e^{-160}
 (3) e^{320} (4) e^{160}

19. The temporary hardness of water is due to:

- (1) Na_2SO_4 (2) NaCl
 (3) $\text{Ca}(\text{HCO}_3)_2$ (4) CaCl_2

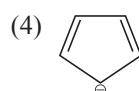
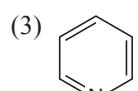
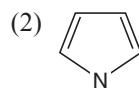
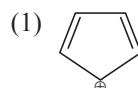
20. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic?

- (1) $\text{NO} \rightarrow \text{NO}^+$ (2) $\text{N}_2 \rightarrow \text{N}_2^+$
 (3) $\text{O}_2 \rightarrow \text{O}_2^+$ (4) $\text{O}_2 \rightarrow \text{O}_2^{2-}$

21. Which of the following combination of statements is true regarding the interpretation of the atomic orbitals?

- (a) An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.
- (b) For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.
- (c) According to wave mechanics, the ground state angular momentum is equal to $\frac{h}{2\pi}$.
- (d) The plot of ψ Vs r for various azimuthal quantum numbers, shows peak shifting towards higher r value.
- (1) (a), (d) (2) (a), (b)
 (3) (a), (c) (4) (b), (c)

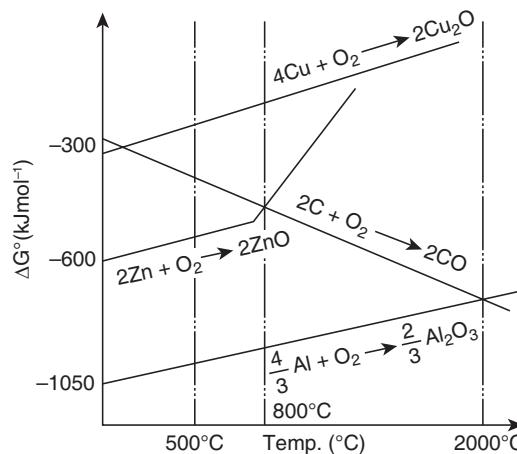
22. Which of the following compounds is not aromatic?



23. Good reducing nature of H_3PO_2 is attributed to the presence of:

- (1) Two P – OH bonds (2) One P – H bond
 (3) Two P – H bonds (4) One P – OH bond

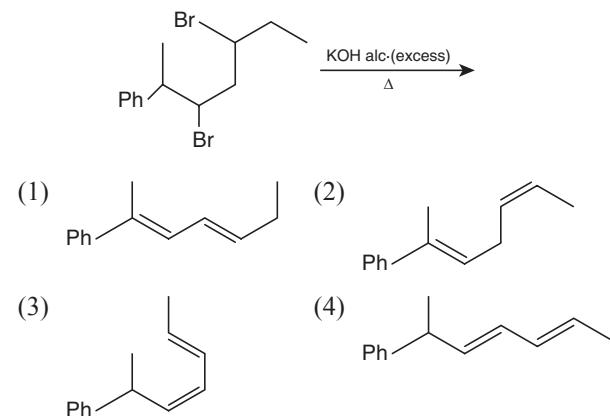
24. The correct statement regarding the given Ellingham diagram is:



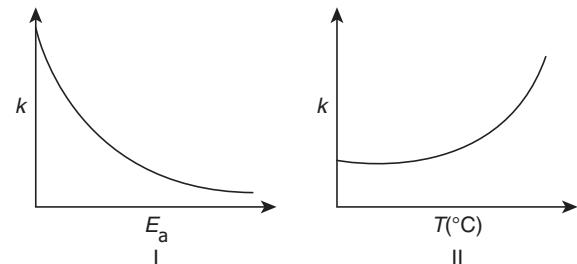
- (1) At 1400°C, Al can be used for the extraction of Zn from ZnO.
 (2) At 500°C, coke can be used for the extraction of Zn from ZnO.

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CHEMISTRY



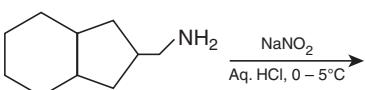
8. Consider the given plots for a reaction obeying Arrhenius equation ($0^\circ\text{C} < T < 300^\circ\text{C}$) : (k and E_a are rate constant and activation energy, respectively)



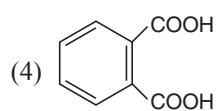
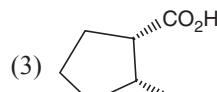
Choose the correct option:

- (1) I is right but II is wrong
 - (2) Both I and II are correct
 - (3) I is wrong but II is right
 - (4) Both I and II are wrong

9. The major product formed in the reaction given below will be:



- (1)
- (2)
- (3)
- (4)



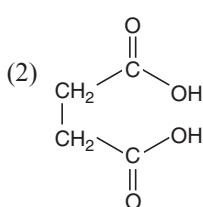
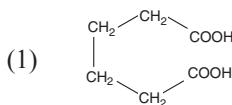
10. Wilkinson catalyst is:

- (1) $[(\text{Ph}_3\text{P})_3\text{IrCl}]$
 (2) $[(\text{Et}_3\text{P})_3\text{RhCl}]$
 (3) $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ (Et = C_2H_5)
 (4) $[(\text{Et}_3\text{P})_3\text{IrCl}]$

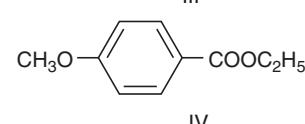
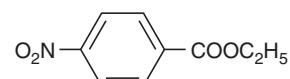
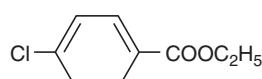
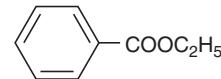
11. If dichloromethane (DCM) and water (H_2O) are used for differential extraction, which one of the following statements is correct?

- (1) DCM and H_2O would stay as lower and upper layer respectively in the S.F.
 (2) DCM and H_2O will make turbid/colloidal mixture
 (3) DCM and H_2O would stay as upper and lower layer respectively in the separating funnel (S.F.)
 (4) DCM and H_2O will be miscible clearly

12. Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride?

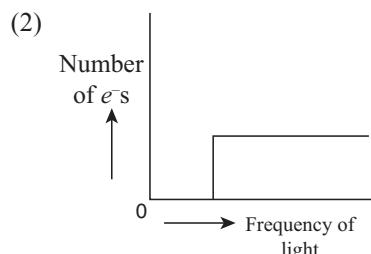
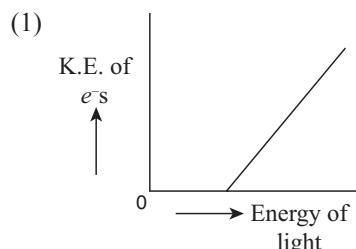


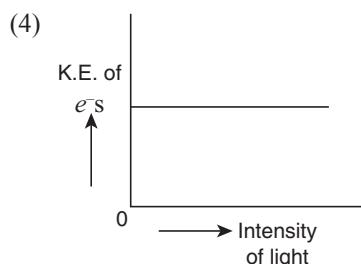
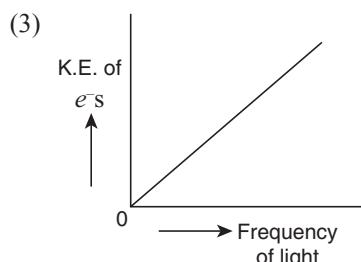
13. The decreasing order of ease of alkaline hydrolysis for the following esters is



- (1) III > II > IV > I (2) III > II > I > IV
 (3) IV > II > III > I (4) II > III > I > IV

14. Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface?





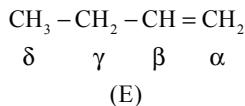
15. Which of the following is not an example of heterogeneous catalytic reaction?

- Ostwald's process
- Combustion of coal
- Hydrogenation of vegetable oils
- Haber's process

16. The effect of lanthanoid contraction in the lanthanoid series of elements by and large means:

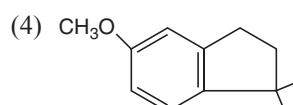
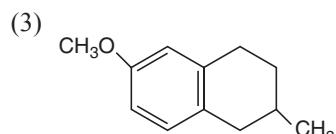
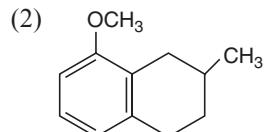
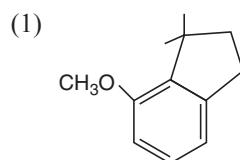
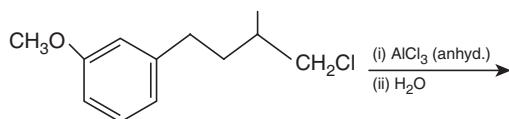
- increase in both atomic and ionic radii
- decrease in atomic radii and increase in ionic radii
- decrease in both atomic and ionic radii
- increase in atomic radii and decrease in ionic radii

17. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light?

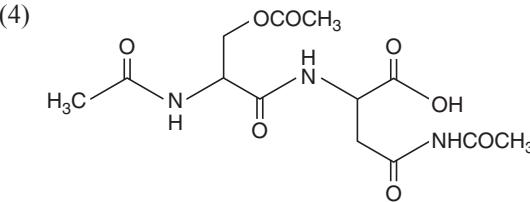
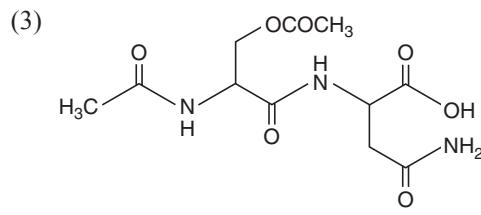
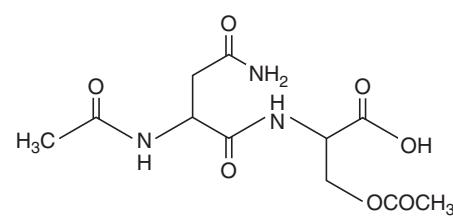
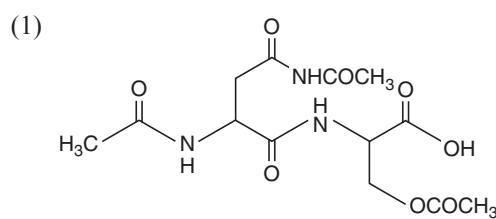


- α -hydrogen
- γ -hydrogen
- δ -hydrogen
- β -hydrogen

18. The major product of the following reaction is:



19. The correct structure of product 'P' in the following reaction is:



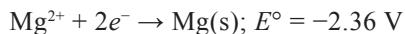
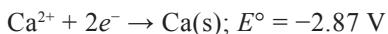
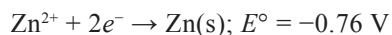
20. The type of hybridisation and number of lone pair(s) of electrons of Xe in XeOF_4 , respectively, are:

- (1) sp^3d^2 and 1 (2) sp^3d and 2
 (3) sp^3d^2 and 2 (4) sp^3d and 1

21. The electronegativity of aluminium is similar to:

- (1) carbon (2) beryllium
 (3) boron (4) lithium

22. Consider the following reduction processes:



The reducing power of the metals increases in the order:

- (1) $\text{Ca} < \text{Zn} < \text{Mg} < \text{Ni}$
 (2) $\text{Ni} < \text{Zn} < \text{Mg} < \text{Ca}$
 (3) $\text{Zn} < \text{Mg} < \text{Ni} < \text{Ca}$
 (4) $\text{Ca} < \text{Mg} < \text{Zn} < \text{Ni}$

23. The chemical nature of hydrogen peroxide is:

- (1) Oxidising agent in acidic medium, but not in basic medium.
 (2) Reducing agent in basic medium, but not in acidic medium.
 (3) Oxidising and reducing agent in acidic medium, but not in basic medium.
 (4) Oxidising and reducing agent in both acidic and basic medium.

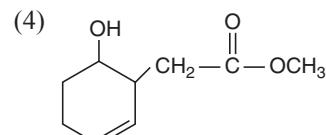
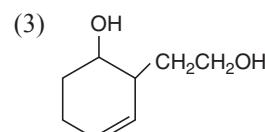
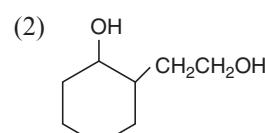
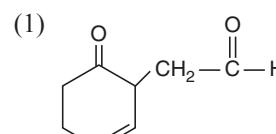
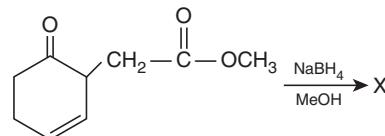
24. A mixture of 100 m mol of $\text{Ca}(\text{OH})_2$ and 2 g of sodium sulphate was dissolved in water and the volume was made up to 100 mL. The mass of calcium sulphate formed and the concentration of OH^- in resulting solution, respectively, are: (Molar mass of $\text{Ca}(\text{OH})_2$, Na_2SO_4 and CaSO_4 are 74, 143 and 136 g mol^{-1} , respectively; K_{sp} of $\text{Ca}(\text{OH})_2$ is 5.5×10^{-6})

- (1) 1.9 g, 0.28 mol L^{-1} (2) 13.6 g, 0.28 mol L^{-1}
 (3) 1.9 g, 0.14 mol L^{-1} (4) 13.6 g, 0.14 mol L^{-1}

25. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapor pressures of pure A and B are $7 \times 10^3 \text{ Pa}$ and $12 \times 10^3 \text{ Pa}$, respectively. The composition of the vapor in equilibrium with a solution containing 40 mol percent of A at this temperature is:

- (1) $x_A = 0.37; x_B = 0.63$
 (2) $x_A = 0.28; x_B = 0.72$
 (3) $x_A = 0.4; x_B = 0.6$
 (4) $x_A = 0.76; x_B = 0.24$

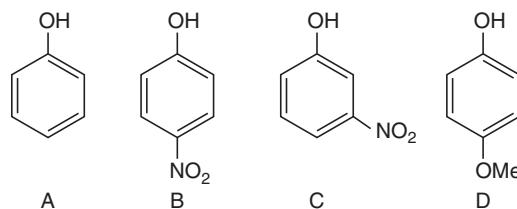
26. The major product 'X' formed in the following reaction is:



27. The metal used for making X-ray tube window is:

- (1) Mg (2) Na
 (3) Be (4) Ca

28. The increasing order of the $\text{p}K_a$ values of the following compounds is:



- (1) C < B < A < D (2) B < C < D < A
 (3) D < A < C < B (4) B < C < A < D

29. Hall-Heroult's process is given by:

- (1) $\text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Cu(s)} + 2\text{H}^+(\text{aq})$
 (2) $\text{Cr}_2\text{O}_3 + 2 \text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2 \text{Cr}$
 (3) $2 \text{Al}_2\text{O}_3 + 3 \text{C} \rightarrow 4 \text{Al} + 3 \text{CO}_2$
 (4) $\text{ZnO} + \text{C} \xrightarrow{\text{Coke, } 1673 \text{ K}} \text{Zn} + \text{CO}$

30. Two π and half σ bonds are present in:

- (1) O_2^+ (2) N_2
 (3) O_2 (4) N_2^+

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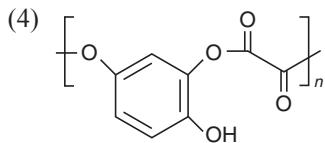
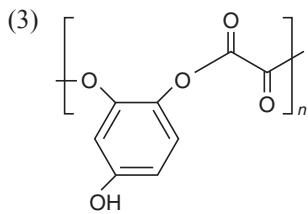
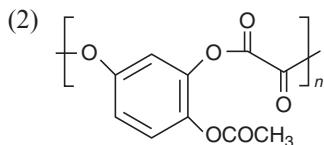
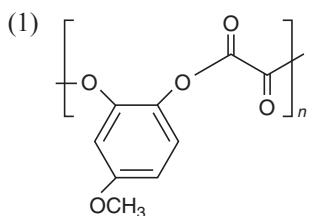
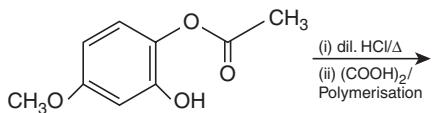
CHEMISTRY

1. The ground state energy of hydrogen atom is -13.6 eV. The energy of second excited state of He^+ ion in eV is:

- (1) -54.4 (2) -3.4
 (3) -6.04 (4) -27.2

2. Haemoglobin and gold sol are examples of:
 (1) positively and negatively charged sols, respectively
 (2) positively charged sols
 (3) negatively charged sols
 (4) negatively and positively charged sols, respectively

3. The major product of the following reaction is:



4. The amount of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) required to prepare 2 L of its 0.1 M aqueous solution is:

- (1) 136.8 g (2) 17.1 g
 (3) 68.4 g (4) 34.2 g

5. Among the following reactions of hydrogen with halogens, the one that requires a catalyst is:
 (1) $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$ (2) $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$
 (3) $\text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr}$ (4) $\text{H}_2 + \text{F}_2 \rightarrow 2 \text{HF}$

6. 5.1 g of NH_4SH is introduced in 3.0 L evacuated flask at 327°C . 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327°C is ($R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$, Molar mass of S = 32 g mol^{-1} , molar mass of N = 14 g mol^{-1})
 (1) $0.242 \times 10^{-4} \text{ atm}^2$ (2) $1 \times 10^{-4} \text{ atm}^2$
 (3) $4.9 \times 10^{-3} \text{ atm}^2$ (4) 0.242 atm^2

7. The reaction that is **NOT** involved in the ozone layer depletion mechanism in the stratosphere is:

- (1) $\text{CF}_2\text{Cl}_2(\text{g}) \xrightarrow{\text{UV}} \dot{\text{Cl}}(\text{g}) + \dot{\text{CF}}_2\text{Cl}(\text{g})$
 (2) $\dot{\text{ClO}}(\text{g}) + \text{O}(\text{g}) \rightarrow \dot{\text{Cl}}(\text{g}) + \text{O}_2(\text{g})$
 (3) $\text{CH}_4 + 2 \text{O}_3 \rightarrow 3 \text{CH}_2 = \text{O} + 3 \text{H}_2\text{O}$
 (4) $\text{HOCl}(\text{g}) \xrightarrow{\text{h}\nu} \dot{\text{O}}\text{H}(\text{g}) + \dot{\text{Cl}}(\text{g})$

8. In the cell $\text{Pt}(\text{s})|\text{H}_2(\text{g}, 1\text{bar})|\text{HCl}(\text{aq})|\text{AgCl}(\text{s})|\text{Ag}(\text{s})|\text{Pt}(\text{s})$ the cell potential is 0.92 V when a 10^{-6} molal HCl solution is used. The standard electrode potential of $(\text{AgCl}/\text{Ag}, \text{Cl}^-)$ electrode is:

$$\left\{ \text{Given, } \frac{2.303RT}{F} = 0.06 \text{ V at } 298 \text{ K} \right\}$$

10. The correct match between item 'I' and item 'II' is

Item 'I'	Item 'II'
(compound)	(reagent)
(A) Lysine	(P) 1-naphthol
(B) Furfural	(Q) ninhydrin
(C) Benzyl alcohol	(R) KMnO_4
(D) Styrene	(S) Ceric ammonium nitrate
(1) (A) \rightarrow (Q); (B) \rightarrow (P); (C) \rightarrow (S); (D) \rightarrow (R)	
(2) (A) \rightarrow (Q); (B) \rightarrow (P); (C) \rightarrow (R); (D) \rightarrow (S)	
(3) (A) \rightarrow (R); (B) \rightarrow (P); (C) \rightarrow (Q); (D) \rightarrow (S)	
(4) (A) \rightarrow (Q); (B) \rightarrow (R); (C) \rightarrow (S); (D) \rightarrow (P)	

11. An aromatic compound 'A' having molecular formula $C_7H_6O_2$ on treating with aqueous ammonia and heating forms compound 'B'. The compound 'B' on reaction with molecular bromine and potassium hydroxide provides compound 'C' having molecular formula C_6H_7N . The structure of 'A' is:

- (1)  COOH

(2)  CH=CH

(3)  CHO
OH

(4)  OHC
OH

12. The process with negative entropy change is:

 - (1) Dissociation of $\text{CaSO}_4(\text{s})$ to $\text{CaO}(\text{s})$ and $\text{SO}_3(\text{g})$
 - (2) Sublimation of dry ice
 - (3) Dissolution of iodine in water
 - (4) Synthesis of ammonia from N_2 and H_2

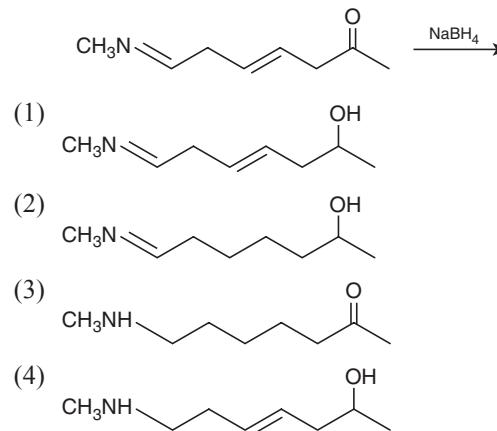
13. An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 N m^{-2} . Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is $24 \text{ J mol}^{-1} \text{ K}^{-1}$, the temperature of Al increases by:

- (1) $\frac{3}{2}$ K (2) 2 K
 (3) $\frac{2}{3}$ K (4) 1 K

14. Elevation in the boiling point for 1 molal solution of glucose is 2 K. The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is:

- (1) $K_b = 1.5 K_f$ (2) $K_b = K_f$
 (3) $K_b = 0.5 K_f$ (4) $K_b = 2 K_f$

15. The major product of the following reaction is:



16. Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of:

- (1) sodium-ammonia complex
 - (2) sodamide
 - (3) sodium ion-ammonia complex
 - (4) ammoniated electrons

17. For an elementary chemical reaction, $A_2 \rightleftharpoons \frac{k_1}{k_{-1}} 2A$,

the expression for $\frac{d[A]}{dt}$ is:

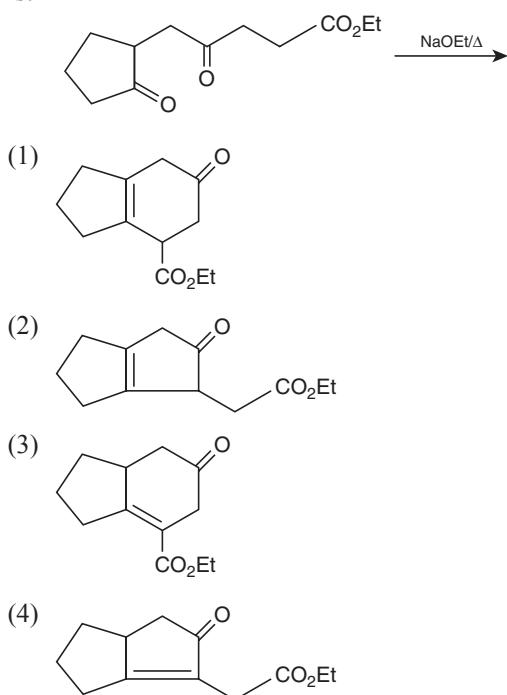
- (1) $k_1[A_2] - k_{-1}[A]^2$ (2) $2k_1[A_2] - k_{-1}[A]^2$
 (3) $k_1[A_2] + k_{-1}[A]^2$ (4) $2k_1[A_2] - 2k_{-1}[A]^2$

18. Which of the following tests cannot be used for identifying amino acids?

19. The difference in the number of unpaired electrons of a metal ion in its high-spin and low-spin octahedral complexes is two. The metal ion is:

- (1) Ni^{2+} (2) Fe^{2+}
(3) Co^{2+} (4) Mn^{2+}

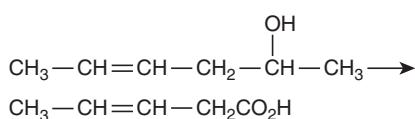
20. The major product obtained in the following reaction is:



21. The pair that contains two P – H bonds in each of the oxoacids is:

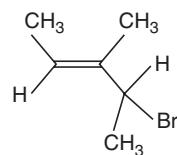
- (1) $\text{H}_4\text{P}_2\text{O}_5$ and $\text{H}_4\text{P}_2\text{O}_6$ (2) H_3PO_2 and $\text{H}_4\text{P}_2\text{O}_5$
(3) H_3PO_3 and H_3PO_2 (4) $\text{H}_4\text{P}_2\text{O}_5$ and H_3PO_3

22. Which is the most suitable reagent for the following transformation?



- (1) Tollens' reagent (2) I_2/NaOH
(3) $\text{CrO}_2\text{Cl}_2/\text{CS}_2$ (4) alkaline KMnO_4

23. What is the IUPAC name of the following compound?



- (1) 3-Bromo-1,2-dimethylbut-1-ene
(2) 3-Bromo-3-methyl-1,2-dimethylprop-1-ene
(3) 2-Bromo-3-methylpent-3-ene
(4) 4-Bromo-3-methylpent-2-ene

24. The number of 2-centre-2-electron and 3-centre-2-electron bonds in B_2H_6 , respectively, are:

- (1) 2 and 1 (2) 4 and 2
(3) 2 and 2 (4) 2 and 4

25. In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is:

- (1) 1 (2) 10
(3) 2 (4) 5

26. A reaction of cobalt(III) chloride and ethylenediamine in a 1 : 2 mole ratio generates two isomeric products A (violet coloured) and B (green coloured). A can show optical activity, but, B is optically inactive. What type of isomers does A and B represent?

- (1) Geometrical isomers (2) Coordination isomers
(3) Linkage isomers (4) Ionisation isomers

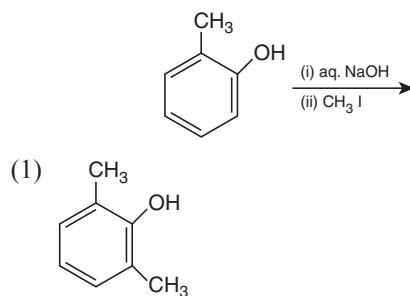
27. The electrolytes usually used in the electroplating of gold and silver, respectively, are:

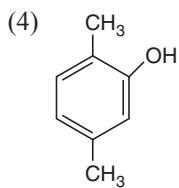
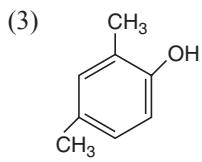
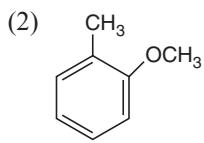
- (1) $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$
(2) $[\text{Au}(\text{CN})_2]^-$ and $[\text{AgCl}_2]^-$
(3) $[\text{Au}(\text{OH})_4]^-$ and $[\text{Ag}(\text{OH})_2]^-$
(4) $[\text{Au}(\text{NH}_3)_2]^+$ and $[\text{Ag}(\text{CN})_2]^-$

28. A compound of formula A_2B_3 has the hcp lattice. Which atom forms the hcp lattice and what fraction of tetrahedral voids is occupied by the other atoms:

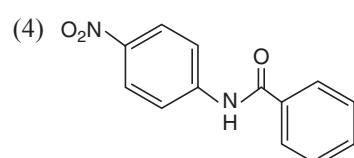
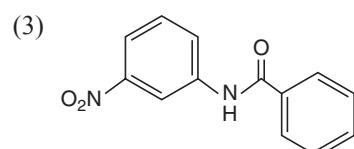
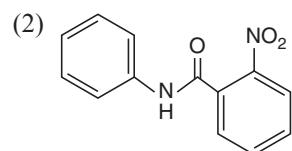
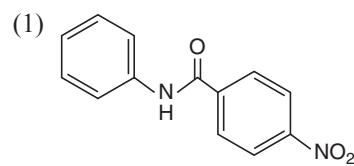
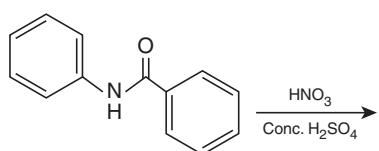
- (1) hcp lattice – A, $\frac{2}{3}$ tetrahedral voids – B
(2) hcp lattice – A, $\frac{1}{3}$ tetrahedral voids – B
(3) hcp lattice – B, $\frac{2}{3}$ tetrahedral voids – A
(4) hcp lattice – B, $\frac{1}{3}$ tetrahedral voids – A

29. The major product of the following reaction is:





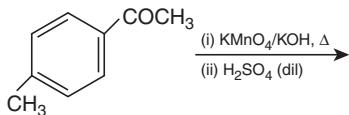
30. What will be the major product in the following mononitration reaction?



JEE Main 2019 (January 11, Shift 1)

CHEMISTRY

1. The major product of the following reaction is



- (1)
- (2)
- (3)
- (4)
2. The **correct** statements among (a) to (d) regarding H₂ as a fuel are:
- (a) It produces less pollutants than petrol.
- (b) A cylinder of compressed dihydrogen weighs ~30 times more than a petrol tank producing the same amount of energy.
- (c) Dihydrogen is stored in tanks of metal alloys like NaNi₅.
- (d) On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively.
- (1) (a) and (c) only (2) (b) and (d) only
 (3) (b), (c) and (d) only (4) (a), (b) and (c) only
3. An organic compound is estimated through Dumus method and was found to evolve 6 moles of

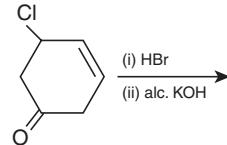
CO₂, 4 moles of H₂O and 1 mole of nitrogen gas. The formula of the compound is:

- (1) C₁₂H₈N₂ (2) C₁₂H₈N
 (3) C₆H₈N₂ (4) C₆H₈N

4. An example of solid sol is:

- (1) butter (2) paint
 (3) hair cream (4) gem stones

5. The major product of the following reaction is:

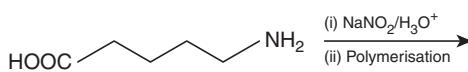


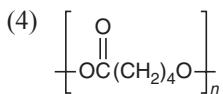
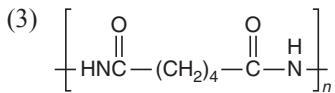
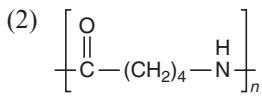
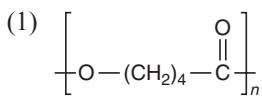
- (1)
- (2)
- (3)
- (4)

6. Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H-atom is suitable for this purpose?

- [R_H = 1 × 10⁵ cm⁻¹, h = 6.6 × 10⁻³⁴ Js, c = 3 × 10⁸ ms⁻¹]
 (1) Balmer, ∞ → 2 (2) Paschen, 5 → 3
 (3) Lyman, ∞ → 1 (4) Paschen, ∞ → 3

7. The polymer obtained from the following reactions is:

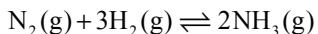




8. NaH is an example of:

- (1) saline hydride
- (2) metallic hydride
- (3) molecular hydride
- (4) electron-rich hydride

9. Consider the reaction



The equilibrium constant of the above reaction is K_p . If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $p_{NH_3} \ll p_{\text{total}}$ at equilibrium)

(1) $\frac{3^{3/2} K_p^{1/2} p^2}{4}$

(2) $\frac{3^{3/2} K_p^{1/2} p^2}{16}$

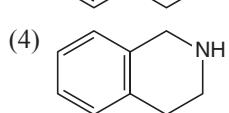
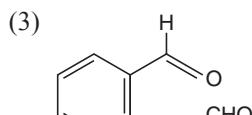
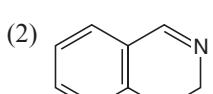
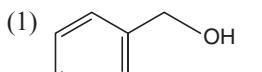
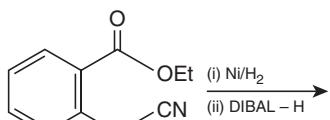
(3) $\frac{K_p^{1/2} p^2}{4}$

(4) $\frac{K_p^{1/2} p^2}{16}$

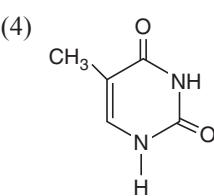
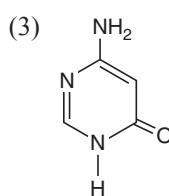
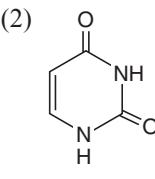
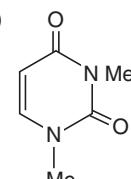
10. The chloride that CANNOT get hydrolysed is:

- (1) CCl_4
- (2) $PbCl_4$
- (3) $SnCl_4$
- (4) $SiCl_4$

11. The major product of the following reaction is:



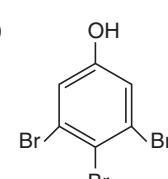
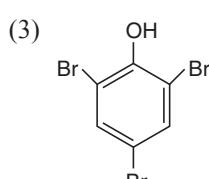
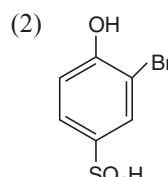
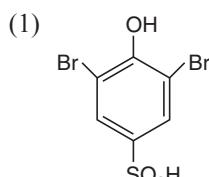
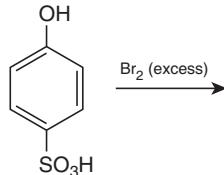
12. Among the following compounds, which one is found in RNA?



13. Peroxyacetyl nitrate (PAN), an eye irritant is produced by:

- (1) photochemical smog
- (2) organic waste
- (3) acid rain
- (4) classical smog

14. The major product of the following reaction is:



15. If a reaction follows the Arrhenius equation, the plot $\ln k$ vs $1/(RT)$ gives straight line with a gradient ($-y$) unit. The energy required to activate the reactant is:

16. The correct match between item (I) and item (II) is:

Item - I	Item - II
(A) Norethindrone	(P) Anti-biotic
(B) Ofloxacin	(Q) Anti-fertility
(C) Equanil	(R) Hypertension
	(S) Analgesics
(1) (A) \rightarrow (R); (B) \rightarrow (P); (C) \rightarrow (S)	
(2) (A) \rightarrow (Q); (B) \rightarrow (P); (C) \rightarrow (R)	
(3) (A) \rightarrow (Q); (B) \rightarrow (R); (C) \rightarrow (S)	
(4) (A) \rightarrow (R); (B) \rightarrow (P); (C) \rightarrow (R)	

17. For the chemical reaction $X \rightleftharpoons{T} Y$, the standard reaction Gibbs energy depends on temperature T (in K) as

$$\Delta_r G^\circ \text{ (in kJ mol}^{-1}\text{)} = 120 - \frac{3}{8}T.$$

The major component of the reaction mixture at T is:

(1) Y if $T = 300 \text{ K}$ (2) Y if $T = 280 \text{ K}$
 (3) X if $T = 315 \text{ K}$ (4) X if $T = 350 \text{ K}$

18. The element that usually does NOT show variable oxidation states is:

(1) Sc (2) V
 (3) Ti (4) Cu

19. Match the ores (List I) with the metals (List II):

(List I)	(List II)
Ores	Metals
(A) Siderite	(P) Zinc
(B) Kaolinite	(Q) Copper
(C) Malachite	(R) Iron
(D) Calamine	(S) Aluminium
(1) (A) \rightarrow (R); (B) \rightarrow (S); (C) \rightarrow (P); (D) \rightarrow (Q)	
(2) (A) \rightarrow (P); (B) \rightarrow (Q); (C) \rightarrow (R); (D) \rightarrow (S)	
(3) (A) \rightarrow (Q); (B) \rightarrow (R); (C) \rightarrow (S); (D) \rightarrow (P)	
(4) (A) \rightarrow (R); (B) \rightarrow (S); (C) \rightarrow (Q); (D) \rightarrow (P)	

20. The correct match between items I and II is:

Item - I	Item - II
(Mixture)	(Separation method)
(A) H_2O : Sugar	(P) Sublimation
(B) H_2O : Aniline	(Q) Recrystallization
(C) H_2O : Toluene	(R) Steam distillation
	(S) Differential extraction
(1) (A) \rightarrow (R); (B) \rightarrow (P); (C) \rightarrow (S)	
(2) (A) \rightarrow (Q); (B) \rightarrow (R); (C) \rightarrow (P)	
(3) (A) \rightarrow (S); (B) \rightarrow (R); (C) \rightarrow (P)	
(4) (A) \rightarrow (Q); (B) \rightarrow (R); (C) \rightarrow (P)	

21. The freezing point of a diluted milk sample is found to be -0.2°C , while it should have been -0.5°C for pure milk. How much water has been added to pure milk to make the diluted sample?

(1) 1 cup of water to 2 cups of pure milk
 (2) 2 cups of water to 3 cups of pure milk
 (3) 3 cups of water to 2 cups of pure milk
 (4) 1 cup of water to 3 cups of pure milk

22. For the cell $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})||\text{M}^{x+}(\text{aq})|\text{M(s)}$, different half cells and their standard electrode potentials are given below:

$\text{M}^{x+}(\text{aq})/\text{M(s)}$	$\text{Au}^{3+}(\text{aq})/\text{Au(s)}$	$\text{Ag}^+(\text{aq})/\text{Ag(s)}$	$\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$	$\text{Fe}^{2+}(\text{aq})/\text{Fe(s)}$
$E^\circ_{\text{M}^{x+}/\text{M}}/(\text{V})$	1.40	0.80	0.77	-0.44

If $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, which cathode will give a maximum value of E°_{cell} per electron transferred?

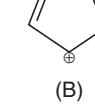
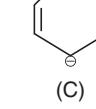
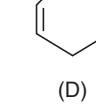
(1) Ag^+/Ag (2) Au^{3+}/Au
 (3) $\text{Fe}^{3+}/\text{Fe}^{2+}$ (4) Fe^{2+}/Fe

23. A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 mL of CO_2 at $T = 298.15 \text{ K}$ and $p = 1 \text{ bar}$. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet?

[Molar mass of $\text{NaHCO}_3 = 84 \text{ g mol}^{-1}$]

(1) 33.6 (2) 8.4
 (3) 16.8 (4) 0.84

24. Which compound (s) out of the following is/are not aromatic?

(A)  (B)  (C)  (D) 

(1) (A) and (C) (2) (B), (C) and (D)
 (3) (C) and (D) (4) (B)

25. The correct order of the atomic radii of C, Cs, Al, and S is:

(1) $\text{C} < \text{S} < \text{Cs} < \text{Al}$
 (2) $\text{S} < \text{C} < \text{Al} < \text{Cs}$
 (3) $\text{C} < \text{S} < \text{Al} < \text{Cs}$
 (4) $\text{S} < \text{C} < \text{Cs} < \text{Al}$

26. Match the metals (List I) with the coordination compound(s)/enzyme(s) (List II):

(List I)	(List II)
Metals	Coordination
	Compound(s)/Enzyme(s)
(A) Co	(P) Wilkinson catalyst
(B) Zn	(Q) Chlorophyll
(C) Rh	(R) Vitamin B ₁₂
(D) Mg	(S) Carbonic anhydrase

(1) (A) → (R); (B) → (S); (C) → (P); (D) → (Q)
 (2) (A) → (Q); (B) → (P); (C) → (S); (D) → (R)
 (3) (A) → (P); (B) → (Q); (C) → (R); (D) → (S)
 (4) (A) → (S); (B) → (R); (C) → (P); (D) → (Q)

27. Two blocks of the same metal having same mass and at temperature T_1 and T_2 , respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS , for this process is:

$$(1) 2C_p \ln \left[\frac{(T_1 + T_2)^{\frac{1}{2}}}{T_1 T_2} \right] \quad (2) C_p \ln \left[\frac{(T_1 + T_2)^2}{4T_1 T_2} \right]$$

$$(3) 2C_p \ln \left[\frac{T_1 + T_2}{2T_1 T_2} \right] \quad (4) 2C_p \ln \left[\frac{T_1 + T_2}{4T_1 T_2} \right]$$

28. The amphoteric hydroxide is:

- (1) Sr(OH)₂ (2) Mg(OH)₂
 (3) Ca(OH)₂ (4) Be(OH)₂

29. A solid having density of 9×10^3 kg m⁻³ forms face centred cubic crystals of edge length $200\sqrt{2}$ pm. What is the molar mass of the solid?

[Avogadro constant $\cong 6 \times 10^{23}$ mol⁻¹, $\pi = 3$]
 (1) 0.0432 kg mol⁻¹ (2) 0.0305 kg mol⁻¹
 (3) 0.0216 kg mol⁻¹ (4) 0.4320 kg mol⁻¹

30. The concentration of dissolved oxygen (DO) in cold water can go upto:

- (1) 10 ppm (2) 8 ppm
 (3) 14 ppm (4) 16 ppm

JEE Main 2019 (January 11, Shift 2)

CHEMISTRY

1. The reaction, $\text{MgO(s)} + \text{C(s)} \rightarrow \text{Mg(s)} + \text{CO(g)}$, for which $\Delta_f H^\circ = +491.1 \text{ kJ mol}^{-1}$ and $\Delta_f S^\circ = 198.0 \text{ JK}^{-1} \text{ mol}^{-1}$, is not feasible at 298 K. Temperature above which reaction will be feasible is:

- (1) 2040.5 K (2) 1890.0 K
 (3) 2480.3 K (4) 2380.5 K

2. The correct match between Item I and Item II is:

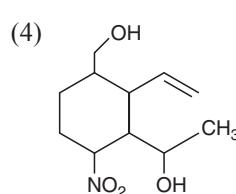
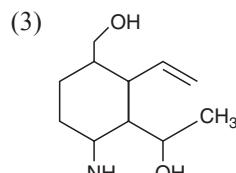
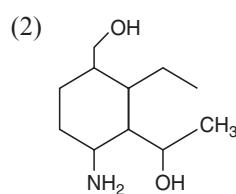
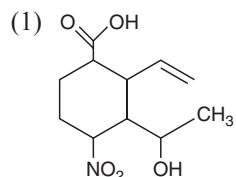
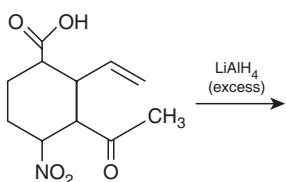
Item I	Item II
(A) Allosteric effect	(P) Molecule binding to the active site of enzyme
(B) Competitive inhibitor	(Q) Molecule crucial for communication in the body
(C) Receptor	(R) Molecule binding to a site other than the active site of enzyme
(D) Poison	(S) Molecule binding to the enzyme covalently

- (1) (A) \rightarrow (R); (B) \rightarrow (P); (C) \rightarrow (Q); (D) \rightarrow (S)
 (2) (A) \rightarrow (P); (B) \rightarrow (R); (C) \rightarrow (Q); (D) \rightarrow (S)
 (3) (A) \rightarrow (R); (B) \rightarrow (P); (C) \rightarrow (S); (D) \rightarrow (Q)
 (4) (A) \rightarrow (P); (B) \rightarrow (R); (C) \rightarrow (S); (D) \rightarrow (Q)

3. The coordination number of Th in $\text{K}_4[\text{Th}(\text{C}_2\text{O}_4)_4(\text{OH}_2)_2]$ is: ($\text{C}_2\text{O}_4^{2-}$ = Oxalato)

- (1) 14 (2) 6
 (3) 8 (4) 10

4. The major product obtained in the following reaction is:



5. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by $\Delta_f G^\circ = A - BT$

Where A and B are non-zero constants. Which of the following is TRUE about this reaction?

- (1) Endothermic if $A > 0$
 (2) Exothermic if $A > 0$ and $B < 0$
 (3) Endothermic if $A < 0$ and $B > 0$
 (4) Exothermic if $B < 0$

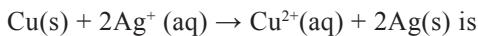
6. The radius of the largest sphere which fits properly at the centre of the edge of a body centred cubic unit cell is: (Edge length is represented by 'a')

- (1) $0.027 a$ (2) $0.047 a$
 (3) $0.134 a$ (4) $0.067 a$

7. The hydride that is NOT electron deficient is:

- (1) SiH_4 (2) B_2H_6
(3) GaH_3 (4) AlH_3

8. Given the equilibrium constant: K_c of the reaction:



10×10^{15} , calculate the E_{cell}° of this reaction at 298 K

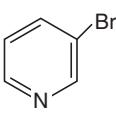
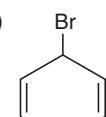
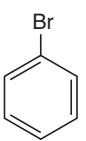
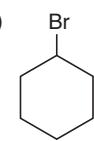
$$\left[2.303 \frac{RT}{F} \text{ at 298 K} = 0.059 \text{ V} \right]$$

- (1) 0.04736 mV (2) 0.4736 mV
(3) 0.4736 V (4) 0.04736 V

9. The correct option with respect to the Pauling electronegativity values of the elements is:

- (1) $\text{Te} > \text{Se}$ (2) $\text{Ga} < \text{Ge}$
(3) $\text{Si} < \text{Al}$ (4) $\text{P} > \text{S}$

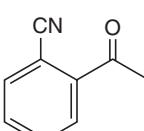
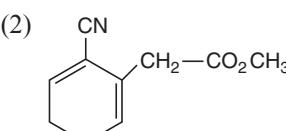
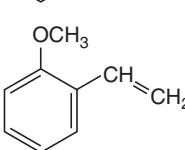
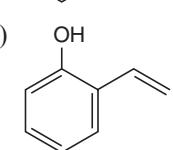
10. Which of the following compounds will produce a precipitate with AgNO_3 ?

- (1) 
(2) 
(3) 
(4) 

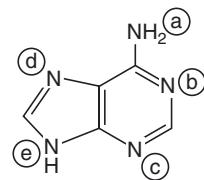
11. The de Broglie wavelength (λ) associated with a photoelectron varies with the frequency (ν) of the incident radiation as, [ν_0 is threshold frequency]:

- (1) $\lambda \propto \frac{1}{(\nu - \nu_0)}$ (2) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{4}}}$
(3) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{3}{2}}}$ (4) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{2}}}$

12. Which of the following compounds reacts with ethylmagnesium bromide and also decolourizes bromine water solution:

- (1) 
(2) 
(3) 
(4) 

13. In the following compound,



the favourable site/s for protonation is/are:

- (1) (a) and (e) (2) (b), (c) and (d)
(3) (a) and (d) (4) (a)

14. Taj Mahal is being slowly disfigured and discoloured. This is primarily due to:

- (1) global warming (2) acid rain
(3) water pollution (4) soil pollution

15. The relative stability of + 1 oxidation state of Group 13 elements follows the order:

- (1) $\text{Al} < \text{Ga} < \text{Tl} < \text{In}$ (2) $\text{Tl} < \text{In} < \text{Ga} < \text{Al}$
(3) $\text{Ga} < \text{Al} < \text{In} < \text{Tl}$ (4) $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$

16. For the equilibrium, $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$, the value of ΔG° at 298 K is approximately:

- (1) 100 kJ mol⁻¹ (2) -80 kJ mol⁻¹
(3) 80 kJ mol⁻¹ (4) -100 kJ mol⁻¹

17. The reaction that does NOT define calcination is:

- (1) $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O} \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{XH}_2\text{O}$
(2) $2\text{Cu}_2\text{S} + 3\text{O}_2 \xrightarrow{\Delta} 2\text{Cu}_2\text{O} + 2\text{SO}_2$
(3) $\text{ZnCO}_3 \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2$
(4) $\text{CaCO}_3 \cdot \text{MgCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{MgO} + 2\text{CO}_2$

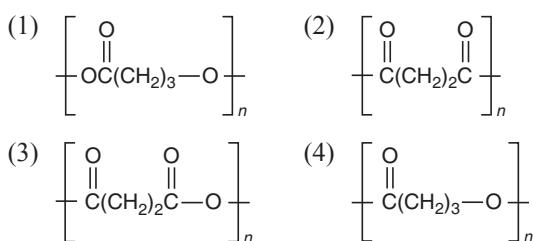
18. A compound 'X' on treatment with Br_2/NaOH , provided $\text{C}_3\text{H}_9\text{N}$, which gives positive carbylamine test. Compound 'X' is:

- (1) $\text{CH}_3\text{COCH}_2\text{NHCH}_3$ (2) $\text{CH}_3\text{CH}_2\text{COCH}_2\text{NH}_2$
(3) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$ (4) $\text{CH}_3\text{CON}(\text{CH}_3)_2$

19. Among the colloids cheese (C), milk (M) and smoke (S), the correct combination of the dispersed phase and dispersion medium, respectively is:

- (1) C: liquid in solid; M: liquid in solid; S: solid in gas
(2) C: liquid in solid; M: liquid in liquid; S: solid in gas
(3) C: solid in liquid; M: liquid in liquid; S: gas in solid
(4) C: solid in liquid; M: solid in liquid; S: solid in gas

20. The homopolymer formed from 4-hydroxy-butanoic acid is:



21. K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is:

- (1) 1.6 (2) 1.8
(3) 2.0 (4) 2.2

22. 25 mL of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution?

- (1) 25 mL (2) 75 mL
(3) 50 mL (4) 12.5 mL

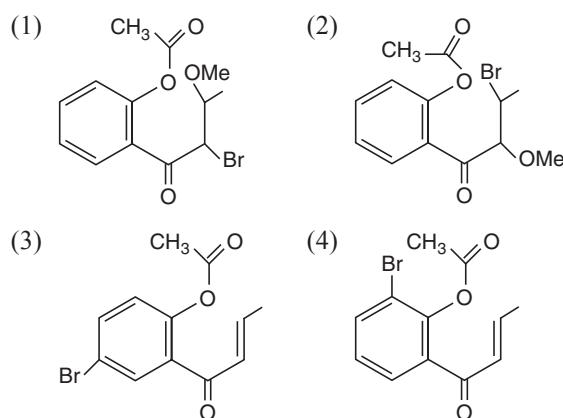
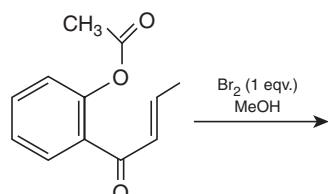
23. The reaction $2X \rightarrow B$ is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be:

- (1) 9.0 h (2) 12.0 h
(3) 18.0 h (4) 7.2 h

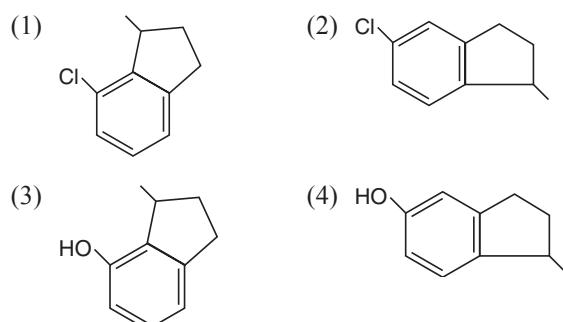
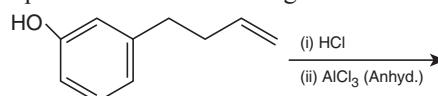
24. Match the following items in List I with the corresponding items in List II.

- | List I | List II |
|------------------------------|--------------------------------|
| (A) $Na_2CO_3 \cdot 10 H_2O$ | (P) Portland cement ingredient |
| (B) $Mg(HCO_3)_2$ | (Q) Castner-Kellner process |
| (C) $NaOH$ | (R) Solvay process |
| (D) $Ca_3Al_2O_6$ | (S) Temporary hardness |
- (1) (A) \rightarrow (Q); (B) \rightarrow (R); (C) \rightarrow (P); (D) \rightarrow (S)
(2) (A) \rightarrow (R); (B) \rightarrow (Q); (C) \rightarrow (S); (D) \rightarrow (P)
(3) (A) \rightarrow (S); (B) \rightarrow (P); (C) \rightarrow (Q); (D) \rightarrow (R)
(4) (A) \rightarrow (R); (B) \rightarrow (S); (C) \rightarrow (Q); (D) \rightarrow (P)

25. The major product obtained in the following conversion is:



26. Major product of the following reaction is:



27. The higher concentration of which gas in air can cause stiffness of flower buds?

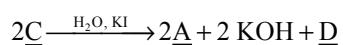
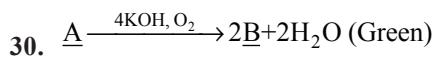
- (1) NO_2 (2) CO_2
(3) SO_2 (4) CO

28. The correct match between Item I and Item II is:

- | Item I | Item II |
|------------------------|---------|
| (A) Ester test | (P) Tyr |
| (B) Carbylamine test | (Q) Asp |
| (C) Phthalein dye test | (R) Ser |
| | (S) Lys |
- (1) (A) \rightarrow (Q); (B) \rightarrow (S); (C) \rightarrow (P)
(2) (A) \rightarrow (R); (B) \rightarrow (Q); (C) \rightarrow (P)
(3) (A) \rightarrow (R); (B) \rightarrow (S); (C) \rightarrow (Q)
(4) (A) \rightarrow (Q); (B) \rightarrow (S); (C) \rightarrow (R)

29. The number of bridging CO ligand(s) and Co-Co bond(s) in $Co_2(CO)_8$, respectively are:

- (1) 2 and 1 (2) 2 and 0
(3) 0 and 2 (4) 4 and 0



In the above sequence of reactions, A and D, respectively, are:

- (1) KI and KMnO_4 (2) MnO_2 and KIO_3
(3) KIO_3 and MnO_2 (4) KI and K_2MnO_4

JEE Main 2019 (January 12, Shift 1)

CHEMISTRY

1. In the Hall-Heroult process, aluminium is formed at the cathode. The cathode is made out of:

- (1) Pure aluminium (2) Carbon
 (3) Copper (4) Platinum

2. The correct order for acid strength of compounds

$\text{CH} \equiv \text{CH}$, $\text{CH}_3 - \text{C} \equiv \text{CH}$ and $\text{CH}_2 = \text{CH}_2$ is as follows:

- (1) $\text{CH} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{C} \equiv \text{CH}$
 (2) $\text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2$
 (3) $\text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{HC} \equiv \text{CH}$
 (4) $\text{HC} \equiv \text{CH} > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2$

3. In a chemical reaction, $\text{A} + 2\text{B} \xrightleftharpoons{K} 2\text{C} + \text{D}$, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is:

- (1) 4 (2) 16
 (3) $\frac{1}{4}$ (4) 1

4. Given

Gas	H_2	CH_4	CO_2	SO_2
Critical Temperature/K	33	190	304	630

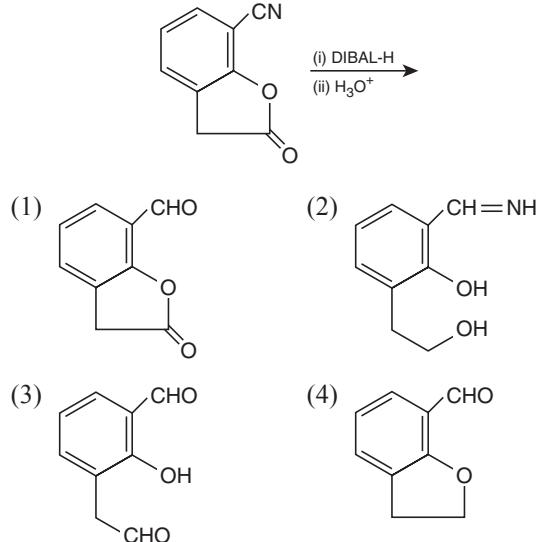
On the basis of data given above, predict which of the following gases shows least adsorption on a definite amount of charcoal?

- (1) SO_2 (2) CH_4
 (3) CO_2 (4) H_2

5. $\text{Mn}_2(\text{CO})_{10}$ is an organometallic compound due to the presence of:

- (1) Mn – C bond (2) Mn – Mn bond
 (3) Mn – O bond (4) C – O bond

6. The major product of the following reaction is:



7. A metal on combustion in excess air forms X. X upon hydrolysis with water yields H_2O_2 and O_2 along with another product. The metal is:

- (1) Na (2) Rb
 (3) Mg (4) Li

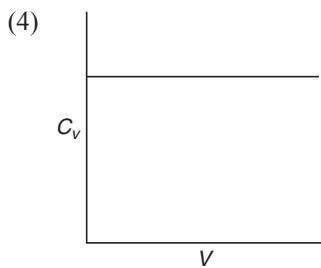
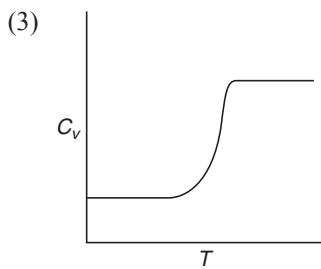
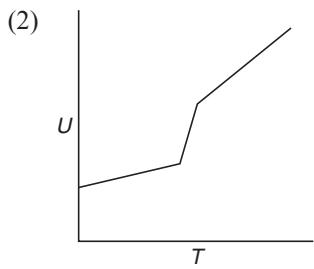
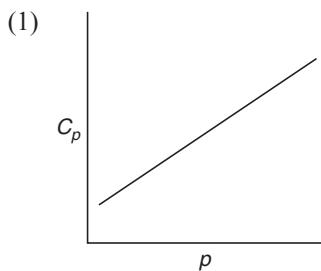
8. The molecule that has minimum/no role in the formation of photochemical smog, is:

- (1) N_2 (2) $\text{CH}_2 = \text{O}$
 (3) O_3 (4) NO

9. The pair of metal ions that can give a spin-only magnetic moment of 3.9 BM for the complex $[\text{M}(\text{H}_2\text{O})_6]\text{Cl}_2$, is:

- (1) V^{2+} and Co^{2+} (2) V^{2+} and Fe^{2+}
 (3) Co^{2+} and Fe^{2+} (4) Cr^{2+} and Mn^{2+}

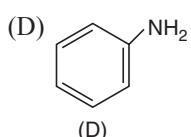
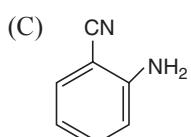
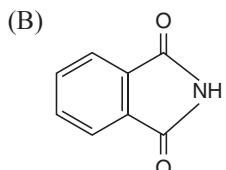
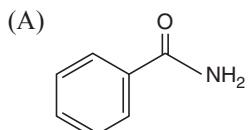
10. For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?



11. Among the following compounds most basic amino acid is

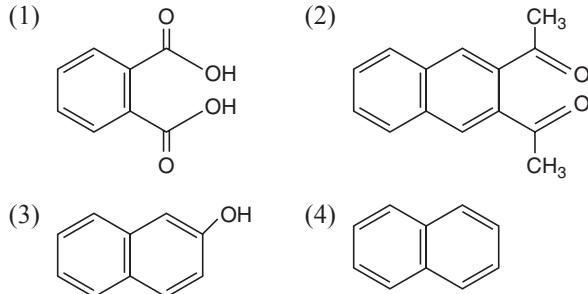
- (1) asparagine. (2) lysine.
(3) serine. (4) histidine.

12. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is:



- (1) (B) < (A) < (C) < (D)
(2) (A) < (B) < (C) < (D)
(3) (B) < (A) < (D) < (C)
(4) (A) < (C) < (D) < (B)

13. Among the following four aromatic compounds, which one will have the lowest melting point?



14. 50 mL of 0.5 M oxalic acid is needed to neutralize 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is:

- (1) 40 g (2) 10 g
(3) 20 g (4) 80 g

15. The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are:

- (1) $3p_A = 2p_B$ (2) $2p_A = 3p_B$
(3) $p_A = 3p_B$ (4) $p_A = 2p_B$

16. The hardness of a water sample (in terms of equivalents of CaCO_3) containing 10^{-3}M CaSO_4 is:

(Molar mass of $\text{CaSO}_4 = 136 \text{ g mol}^{-1}$)

- (1) 10 ppm (2) 50 ppm
(3) 90 ppm (4) 100 ppm

17. $\text{CH}_3\text{CH}_2-\overset{\text{OH}}{\underset{\text{Ph}}{\text{C}}}-\text{CH}_3$ cannot be prepared

- (1) $\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{PhMgX}$
(2) $\text{PhCOCH}_2\text{CH}_3 + \text{CH}_3\text{MgX}$
(3) $\text{PhCOCH}_3 + \text{CH}_3\text{CH}_2\text{MgX}$
(4) $\text{HCHO} + \text{PhCH}(\text{CH}_3)\text{CH}_2\text{MgX}$

18. Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous motion of Y. If molecular weight of X is A then molecular weight of Y is:

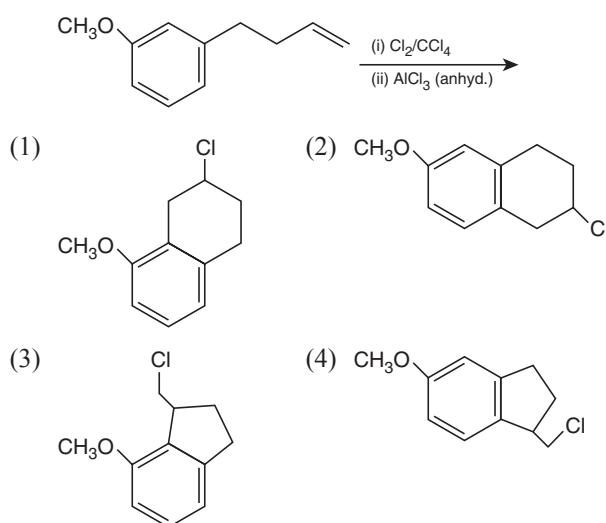
19. The metal *d*-orbitals that are directly facing the ligands in $K_4[Co(CN)_6]$ are:

- (1) d_{xy} and $d_{x^2-y^2}$ (2) $d_{x^2-y^2}$ and d_{z^2}
 (3) d_{xz} , d_{yz} and d_{z^2} (4) d_{yz} , d_{zx} and d_{xy}

20. Decomposition of X exhibits a rate constant of $0.05 \text{ } \mu\text{g/year}$. How many years are required for the decomposition of $5 \text{ } \mu\text{g}$ of X into $2.5 \text{ } \mu\text{g}$?

21. The standard electrode potential E° and its temperature coefficient $\left(\frac{dE^\circ}{dT}\right)$ for a cell are 2 V and $-5 \times 10^{-4} \text{ VK}^{-1}$ at 300 K respectively. The cell reaction is $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$. The standard reaction enthalpy ($\Delta_r H^\circ$) at 300 K in kJ mol⁻¹ is,

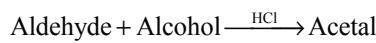
22. The major product of the following reaction is:



23. The element with $Z = 120$ (not yet discovered) will be an/a:

- (1) inner-transition metal
 - (2) alkaline earth metal
 - (3) alkali metal
 - (4) transition metal

24. In the following reaction

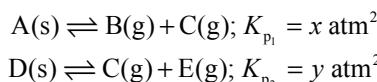


- | | |
|---------------------|-------------------|
| Aldehyde | Alcohol |
| HCHO | ^t BuOH |
| CH ₃ CHO | MeOH |

The best combination is:

- (1) CH_3CHO and $^3\text{BuOH}$
 - (2) HCHO and MeOH
 - (3) CH_3CHO and MeOH
 - (4) HCHO and $^3\text{BuOH}$

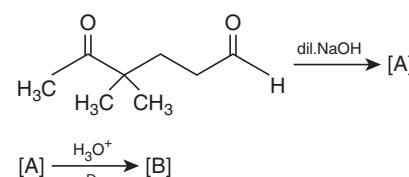
25. Two solids dissociate as follows



The total pressure when both the solids dissociate simultaneously is:

- (1) $\sqrt{x+y}$ atm (2) $2(\sqrt{x+y})$ atm
 (3) $(x+y)$ atm (4) $x^2 + y^2$ atm

26. In the following reactions, products A and B are:



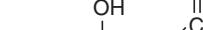
- (1)  ; 

- (2) 

A = ; B = 

- (3)

$A =$ 

; $B =$ 

- (4) 

A =  ; B = 

27. What is the work function of the metal if the light of wavelength 4000 Å generates photoelectrons of velocity $6 \times 10^5 \text{ ms}^{-1}$ from it?

(Mass of electron = 9×10^{-31} kg)

Velocity of light = $3 \times 10^8 \text{ ms}^{-1}$

Planck's constant = $6.626 \times 10^{-34} \text{ Js}$

Charge of electron = $1.6 \times 10^{-19} \text{ eV}^{-1}$

- (1) 0.9 eV (2) 3.1 eV
(3) 2.1 eV (4) 4.0 eV

28. Iodine reacts with concentrated HNO_3 to yield Y along with other products. The oxidation state of iodine in Y, is:

- (1) 5 (2) 7
(3) 3 (4) 1

29. Poly- β -hydroxybutyrate-co- β -hydroxyvalerate(PHBV) is a copolymer of _____.

- (1) 3-hydroxybutanoic acid and 4-hydroxypentanoic acid
(2) 2-hydroxybutanoic acid and 3-hydroxypentanoic acid

(3) 3-hydroxybutanoic acid and 2-hydroxypentanoic acid

(4) 3-hydroxybutanoic acid and 3-hydroxypentanoic acid

30. Water samples with BOD values of 4 ppm and 18 ppm, respectively, are:

- (1) Clean and clean
(2) Highly polluted and clean
(3) Clean and highly polluted
(4) Highly polluted and highly polluted

JEE Main 2019 (January 12, Shift 2)

CHEMISTRY

1. 8 g of NaOH is dissolved in 18 g of H₂O. Mole fraction of NaOH in solution and molality (in mol kg⁻¹) of the solution respectively are:

- (1) 0.2, 22.20 (2) 0.2, 11.11
 (3) 0.167, 11.11 (4) 0.167, 22.20

2. The magnetic moment of an octahedral homoleptic Mn(II) complex is 5.9 BM. The suitable ligand for this complex is:

- (1) ethylenediamine (2) CN⁻
 (3) NCS⁻ (4) CO

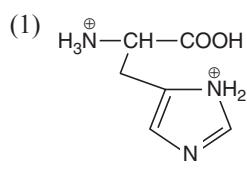
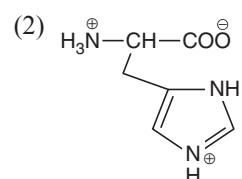
3. The element that does NOT show catenation is:

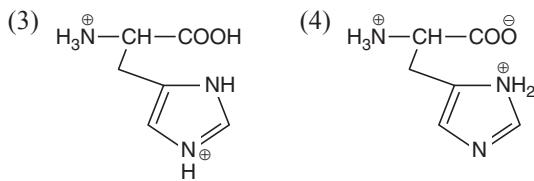
- (1) Ge (2) Si
 (3) Sn (4) Pb

4. Among the following, the false statement is:

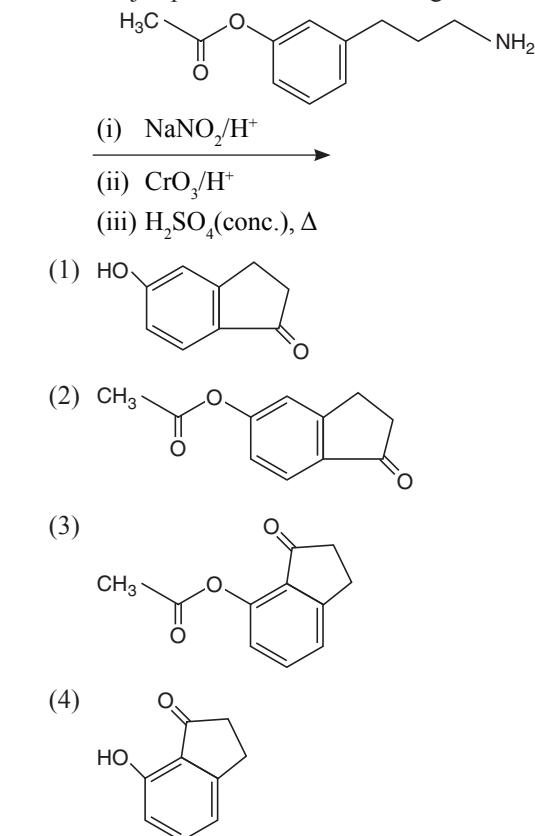
- (1) It is possible to cause artificial rain by throwing electrified sand carrying charge opposite to the one on clouds from an aeroplane.
 (2) Tyndall effect can be used to distinguish between a colloidal solution and a true solution.
 (3) Lyophilic sol can be coagulated by adding an electrolyte.
 (4) Latex is a colloidal solution of rubber particles which are positively charged

5. The correct structure of histidine in a strongly acidic solution (pH = 2) is:

- (1)  (2) 



6. The major product of the following reaction is:



7. Λ_m° for NaCl, HCl and NaA are 126.4, 425.9 and 100.5 S cm²mol⁻¹, respectively. If the conductivity of 0.001 M HA is 5×10^{-5} S cm⁻¹, degree of dissociation of HA is:

- (1) 0.50 (2) 0.25
 (3) 0.125 (4) 0.75

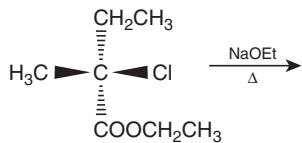
8. Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K. If the percentage association of the acid to form dimer in the solution is 80, then w is:

(Given that $K_f = 5 \text{ K kg mol}^{-1}$, Molar mass of benzoic acid = 122 g mol^{-1})

9. Chlorine on reaction with hot and concentrated sodium hydroxide gives:

- (1) Cl^- and ClO_3^-
 - (2) Cl^- and ClO^-
 - (3) ClO_3^- and ClO_2^-
 - (4) Cl^- and ClO_2^-

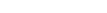
10. The major product of the following reaction is:



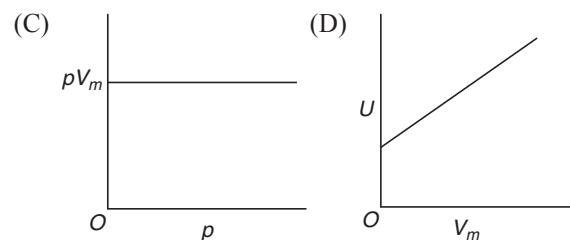
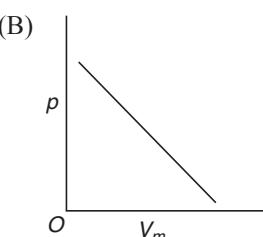
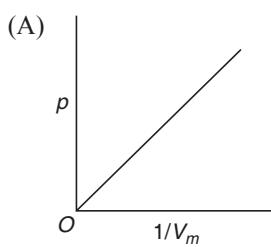
- $$(1) \text{CH}_3\text{CH}_2\underset{\text{CO}_2\text{CH}_2\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}_2$$

- (2) $\begin{array}{c} \text{CO}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3\text{C}=\text{CHCH}_3 \end{array}$

- (3)  CH₂CH₃
 H₃C — C — OCH₂CH₃
 COOCH₂CH₃

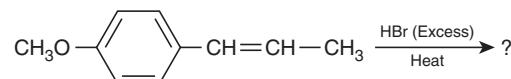
- (4) 

11. The combination of plots which does not represent isothermal expansion of an ideal gas is:



- (1) (B) and (D) (2) (A) and (C)
(3) (B) and (C) (4) (A) and (D)

12. The major product in the following conversion is:



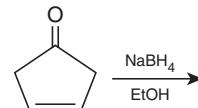
- (1) 

- $$(2) \text{ HO}-\text{C}_6\text{H}_4-\text{CH}(\text{Br})-\text{CH}_2-\text{CH}_3$$

- (3) 

- (4) 

13. The major product of the following reaction is:



- $$(1) \quad \begin{array}{c} \text{OH} \\ | \\ \text{Cyclopentyl group} \\ | \\ \text{OEt} \end{array}$$

- (3)

- $$\text{C}_5\text{H}_8\text{O}$$

-)

14. The correct order of atomic radii is:

- (1) N > Ce > Eu > Ho (2) Ho > N > Eu > Ce
 (3) Ce > Eu > Ho > N (4) Eu > Ce > Ho > N

15. The element that shows greater ability to form $p\pi - p\pi$ multiple bonds, is:

16. The two monomers for the synthesis of nylon 6, 6 are:

 - $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$
 - $\text{HOOC}(\text{CH}_2)_6\text{COOH}$, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$
 - $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$
 - $\text{HOOC}(\text{CH}_2)_6\text{COOH}$, $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$

17. The aldehydes which will not form Grignard product with one equivalent Grignard reagents are:

 -
 -
 -
 -

(1) (B), (D) (2) (B), (C)
(3) (B), (C), (D) (4) (C), (D)

18. Given:

 - $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$; $\Delta_rH^\circ = x \text{ kJ mol}^{-1}$
 - $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$; $\Delta_rH^\circ = y \text{ kJ mol}^{-1}$
 - $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$; $\Delta_rH^\circ = z \text{ kJ mol}^{-1}$

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct?

(1) $x = y + z$ (2) $z = x + y$
(3) $y = 2z - x$ (4) $x = y - z$

19. The volume strength of 1 M H_2O_2 is: (Molar mass of $\text{H}_2\text{O}_2 = 34 \text{ g mol}^{-1}$)

(1) 5.6 (2) 16.8
(3) 11.35 (4) 22.4

20. The correct statement(s) among I to III with respect to potassium ions that are abundant within the cell fluids is/are:

(A) They activate many enzymes.
(B) They participate in the oxidation of glucose to produce ATP.
(C) Along with sodium ions, they are responsible for the transmission of nerve signals.

21. The compound that is NOT a common component of photochemical smog is:

 - O_3
 - $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{OONO}_2$
 - $\text{CH}_2=\text{CHCHO}$
 - CF_2Cl_2

22. For a reaction, consider the plot of $\ln k$ versus $1/T$ given in the figure. If the rate constant of this reaction at 400 K is 10^{-5} s^{-1} , then the rate constant at 500 K is:

(1) 10^{-6} s^{-1} (2) $2 \times 10^{-4} \text{ s}^{-1}$
(3) 10^{-4} s^{-1} (4) $4 \times 10^{-4} \text{ s}^{-1}$

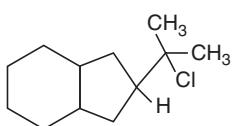
23. An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is:

(1) 500 $^\circ\text{C}$ (2) 500 K
(3) 750 $^\circ\text{C}$ (4) 750 K

24. The major product of the following reaction is:

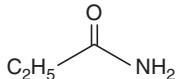
(1)
(2)
(3)

(4)

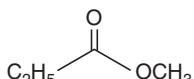


25. The increasing order of the reactivity of the following with LiAlH_4 is:

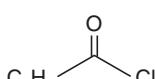
(A)



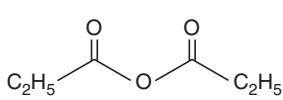
(B)



(C)



(D)

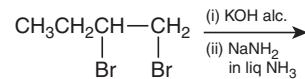


- (1) (B) < (A) < (C) < (D)
 (2) (B) < (A) < (D) < (C)
 (3) (A) < (B) < (D) < (C)
 (4) (A) < (B) < (C) < (D)

26. The pair that does NOT require calcination is:

- (1) ZnO and MgO
 (2) ZnO and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
 (3) ZnCO_3 and CaO
 (4) Fe_2O_3 and $\text{CaCO}_3 \cdot \text{MgCO}_3$

27. The major product of the following reaction is:



- (1) $\text{CH}_3\text{CH}=\text{C}=\text{CH}_2$
 (2) $\text{CH}_3\text{CH}_2\text{CH}-\text{CH}_2$
 $\qquad \qquad \qquad \text{NH}_2 \qquad \text{NH}_2$
 (3) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{NH}_2$
 (4) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$

28. If K_{sp} of Ag_2CO_3 is 8×10^{-12} , the molar solubility of Ag_2CO_3 in 0.1 M AgNO_3 is:

- (1) 8×10^{-12} M (2) 8×10^{-11} M
 (3) 8×10^{-10} M (4) 8×10^{-13} M

29. The upper stratosphere consisting of the ozone layer protects us from the Sun's radiation that falls in the wavelength region of:

- (1) 200 – 315 nm (2) 400 – 550 nm
 (3) 0.8 – 1.5 nm (4) 600 – 750 nm

30. If the de Broglie wavelength of the electron in n^{th} Bohr orbit in a hydrogenic atom is equal to $1.5 \pi a_0$ (a_0 is Bohr radius), then the value of n/Z is:

- (1) 0.40 (2) 1.50
 (3) 1.0 (4) 0.75

*CHEMISTRY - JEE Main 2019 (January)- Answer Key

JANUARY 9, SHIFT 1

1. (1)	2. (4)	3. (3)	4. (1)	5. (4)	6. (3)	7. (4)	8. (1)	9. (3)	10. (2)
11. (3)	12. (2)	13. (3)	14. (1)	15. (1)	16. (4)	17. (4)	18. (2)	19. (3)	20. (3)
21. (1)	22. (4)	23. (3)	24. (3)	25. (1)	26. (1)	27. (3)	28. (2)	29. (2)	30. (4)

JANUARY 9, SHIFT 2

1. (4)	2. (3)	3. (3)	4. (3)	5. (3)	6. (4)	7. (3)	8. (2)	9. (2)	10. (2)
11. (4)	12. (1)	13. (3)	14. (1)	15. (2)	16. (3)	17. (2)	18. (4)	19. (3)	20. (1)
21. (3)	22. (1)	23. (3)	24. (1)	25. (4)	26. (2)	27. (4)	28. (4)	29. (3)	30. (1)

JANUARY 10, SHIFT 1

1. (4)	2. (3)	3. (2)	4. (1)	5. (1)	6. (1)	7. (1)	8. (2)	9. (N*)	10. (3)
11. (1)	12. (1)	13. (2)	14. (3)	15. (2)	16. (3)	17. (2)	18. (4)	19. (2)	20. (1)
21. (2)	22. (2)	23. (4)	24. (1)	25. (2)	26. (4)	27. (3)	28. (4)	29. (3)	30. (4)

JANUARY 10, SHIFT 2

1. (3)	2. (1)	3. (1)	4. (3)	5. (1)	6. (4)	7. (3)	8. (4)	9. (3)	10. (1)
11. (1)	12. (4)	13. (3)	14. (4)	15. (4)	16. (4)	17. (4)	18. (2)	19. (3)	20. (4)
21. (2)	22. (2)	23. (4)	24. (2)	25. (1)	26. (1)	27. (1)	28. (4)	29. (2)	30. (4)

JANUARY 11, SHIFT 1

1. (4)	2. (4)	3. (3)	4. (4)	5. (2)	6. (4)	7. (1)	8. (1)	9. (2)	10. (1)
11. (2)	12. (2)	13. (1)	14. (3)	15. (1)	16. (2)	17. (3)	18. (1)	19. (4)	20. (2)
21. (3)	22. (1)	23. (2)	24. (2)	25. (3)	26. (1)	27. (2)	28. (4)	29. (2)	30. (1)

JANUARY 11, SHIFT 2

1. (3)	2. (1)	3. (4)	4. (3)	5. (1)	6. (4)	7. (1)	8. (3)	9. (2)	10. (2)
11. (4)	12. (4)	13. (2)	14. (2)	15. (4)	16. (3)	17. (2)	18. (3)	19. (2)	20. (4)
21. (2)	22. (1)	23. (3)	24. (4)	25. (1)	26. (4)	27. (3)	28. (1)	29. (1)	30. (2)

JANUARY 12, SHIFT 1

1. (2)	2. (4)	3. (1)	4. (4)	5. (1)	6. (3)	7. (2)	8. (1)	9. (1)	10. (1)
11. (2)	12. (1)	13. (4)	14. (N*)	15. (2)	16. (4)	17. (4)	18. (1)	19. (2)	20. (1)
21. (1)	22. (4)	23. (2)	24. (2)	25. (2)	26. (1)	27. (3)	28. (1)	29. (4)	30. (3)

JANUARY 12, SHIFT 2

1. (3)	2. (3)	3. (4)	4. (4)	5. (3)	6. (1)	7. (3)	8. (1)	9. (1)	10. (2)
11. (1)	12. (2)	13. (2)	14. (4)	15. (2)	16. (1)	17. (1)	18. (1)	19. (3)	20. (3)
21. (4)	22. (3)	23. (2)	24. (4)	25. (3)	26. (1)	27. (4)	28. (3)	29. (1)	30. (4)

* For complete solution visit <https://www.wileyindia.com/current-year-solved-paper>

Note:

- (N*) indicates question dropped. Candidate awarded full marks.

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FOR JEE (MAIN & ADVANCED)

Highlights of the Book

- **Chapter opener** with an opening vignette related to the topics, and contents of the chapter listed for an overview.
- **Reorganization of chapters** as per JEE syllabus flow –Chemical Bonding combined to cover ionic, covalent and metallic bonding together. Chapters on *s*-, *p*-, *d*- and *f*- block elements combined to form single chapter each, covering just the required topics.
- **Additional chapters** on Hydrolysis, Metallurgy and Qualitative Salt Analysis for complete coverage of JEE syllabus.
- **Deletion of chapters** not required as per syllabus – Atomic Nucleus and Spectra
- **Assessment as per JEE** comprising all question types – Single correct choice, Multiple correct choice, Comprehension type, Assertion-reasoning type, Integer answer type and Matrix-match type.
- **Useful appendices** with data on abundance of elements, their melting and boiling points, densities, electronic structure, bond energies, solubilities, atomic weight and electrical resistivity.
- **Includes** solved JEE Advanced 2018 Chemistry paper

About the Book

The book is an adaptation of the classic book Concise Inorganic Chemistry by J.D. LEE (fifth edition), which is widely used by students preparing for JEE. This adapted version provides a more concise and relevant treatment of Inorganic Chemistry as per JEE syllabus requirements. The concepts are explained in a simple and straightforward manner. Yet the book provides a thorough grounding of the subject, helping students approach the examination with confidence.

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- **Chapter 9:** On *s*-Block Elements is now more precise and relevant.
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