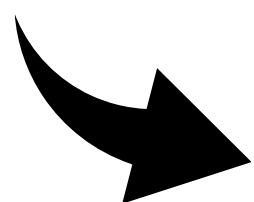


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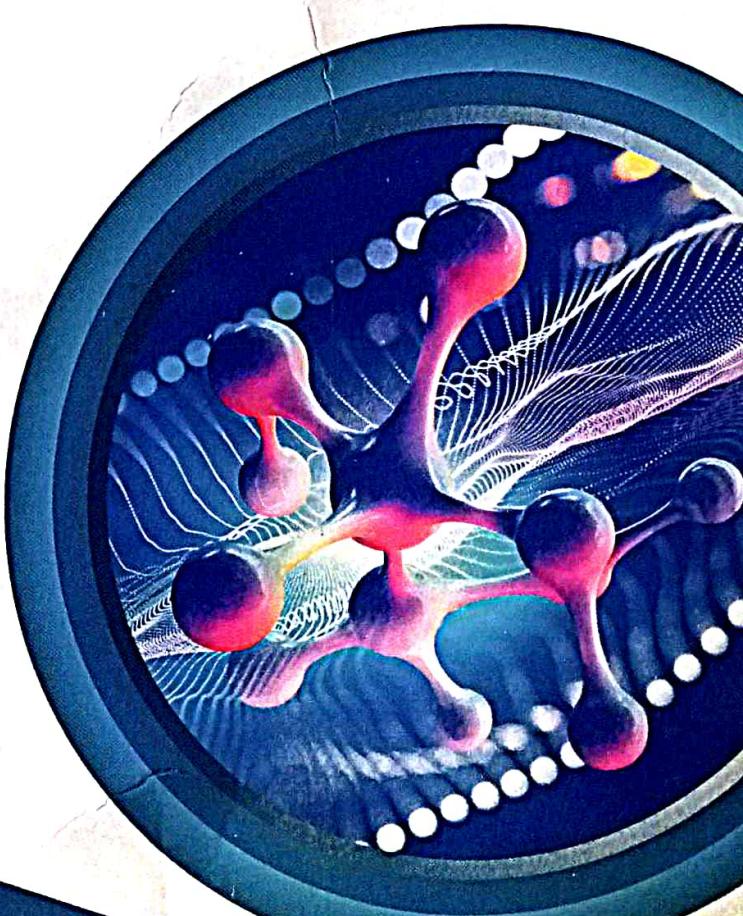
CHEMISTRY

FULL COURSE STUDY MATERIAL

Class XI

- Classification of Elements and Periodicity in Properties
- Chemical Bonding and Molecular Structure
- Hydrogen and Its Compound
- The s-Block Elements
- The p-Block Elements-I

Module-3





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CHAPTER

7

Classification of Elements and Periodicity in Properties

INTRODUCTION

The periodic table is arguably the most important concept in chemistry, both in principle and in practice. It is the everyday support for students, it suggests new avenues of research to professionals, and it provides a succinct organization of the whole of chemistry. It is a remarkable demonstration of the fact that the chemical elements are not a random cluster of entities but instead display trends and lie together in families. An awareness of the periodic table is essential to anyone who wishes to disentangle the world and see how it is built up from the fundamental building blocks of the chemistry, the chemical elements.

Glenn T. Seaborg

NEED FOR CLASSIFICATION OF ELEMENTS

With the advent of time, chemistry had come a long way of development. Till date a large number of elements had been discovered which is quite remarkable from 31 elements in 1800 to 118 till date. Out of these 94 elements are naturally occurring and rest are man-made. While efforts to synthesize new elements are still going, it becomes a difficult task to study each and every element precisely and their compounds. So an appreciable amount of attention is required to systematise and arrange in a manner according to their properties. This will not only rationalize the known chemical facts about elements but will also leave scope for the predicted elements.

HISTORICAL DEVELOPMENT OF PERIODIC TABLE

Dobereiner's Law of Triads

The German scientist, **Johann Dobereiner** in early 1800's was the first to consider the idea of trends among properties of elements. By 1829, he gave his law of triads in which a group of three elements possessing similar characteristics, the atomic mass of the central element was merely the arithmetic mean of the atomic masses of the other two elements (see table). The properties of the middle element were in between those of the other two members.

Table: Dobereiner's Triads

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

Drawback: The concept was not applicable to all known elements but only to a limited number of elements.

Newland's Law of Octaves

An English chemist, **John Alexander Newlands** in 1865 made an attempt to classify the elements known in the increasing order of their atomic masses known as law of octaves. He noticed that the every eighth element of the series has properties similar to the first element as every note resembles the first in octave of music. It means that after a difference of seven elements, the element with similar characteristics was observed.

Table: Newland's Octaves

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Na	23	K	39
Be	9	Mg	24	Ca	40
B	11	Al	27		
C	12	Si	29		
N	14	P	31		
O	16	S	32		
F	19	Cl	35.5		

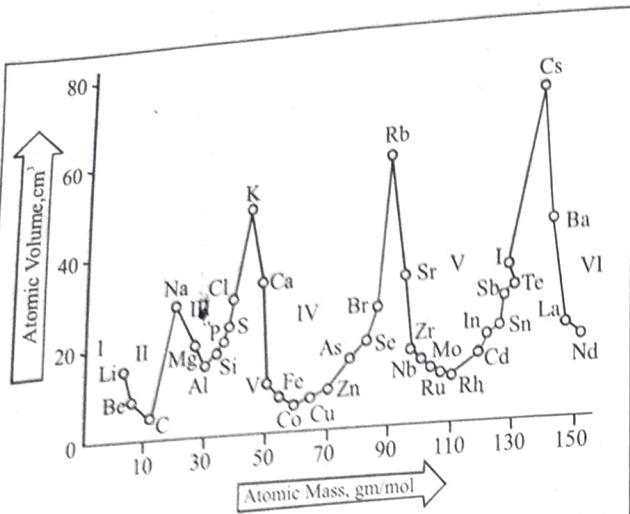
Drawback: The system worked only for lighter elements upto Calcium and failed for heavier elements.

Lothar Meyer's Curve [1869]

He plotted a curve between atomic weight and atomic volume of different elements.

Elements having similar properties occupy similar position in curve. The following observation can be made from the curve –

- Most electropositive elements i.e. alkali metals (Li, Na, K, Rb, Cs etc.) occupy the peak positions on the curve.
- Less electropositive i.e. alkaline earth metal (Be, Mg, Ca, Sr, Ba) occupy the descending position on the curve.
- Metalloids (B, Si, As, Te, At etc.) and transition metals occupy bottom part of the curve.
- Most electronegative i.e. halogens (F, Cl, Br, I) occupy the ascending position on the curve.



2. Elements which occupied position in the Lothar Mayer curve, on the peaks, were

- (a) Alkali metals
- (b) Highly electro positive elements
- (c) Elements having large atomic volume
- (d) All of these

3. Which of the following pairs of elements do not follow octave rule?

- (a) Na, K
- (b) Ca, Sr
- (c) F, Cl
- (d) O, S

Mendeleev's Periodic Table

The physical and chemical properties of elements are the periodic function of their atomic weight.

Characteristic of Mendeleev's Periodic Table

- (a) It is based on atomic weight.
- (b) 63 elements were known, noble gases were not discovered.
- (c) He was the first scientist to classify the elements in a systematic manner i.e. in horizontal rows and in vertical columns.
- (d) Horizontal rows are called periods and there were 7 periods in Mendeleev's Periodic table. (Table contains 12 series)
- (e) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.
- (f) Each group upto VII is divided into A & B subgroups.'A' sub group elements are called normal elements and 'B' sub group elements are called transition elements.
- (g) The VIII group was consists of 9 elements in three rows (Transition metals group).
- (h) The elements belonging to same group exhibit similar properties.

The primary aim of Mendeleev was to arrange elements with similar properties in the same group and predicted about some elements that were still undiscovered. He left a number of gaps for those unknown elements. For example, Gallium and Germanium were not known when Mendeleev presented his periodic table. These elements were named Eka-Aluminium and Eka-Silicon. Mendeleev not only predicted about the existence of Gallium and Germanium but their properties actually matched the properties when these elements discovered.

Table: Mendeleev's Predictions for the Elements Eka-Aluminium (Gallium) and Eka-Silicon (Germanium)

Property	Eka-aluminium (Predicted)	Gallium (Found)	Eka-silicon (Predicted)	Germanium (Found)
Atomic weight	68	70	72	72.6
Density/(g/cm³)	5.9	5.94	5.5	5.36
Melting point/(K)	Low	303K	High	1218K
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	GaCl_3	ECl_4	GeCl_4



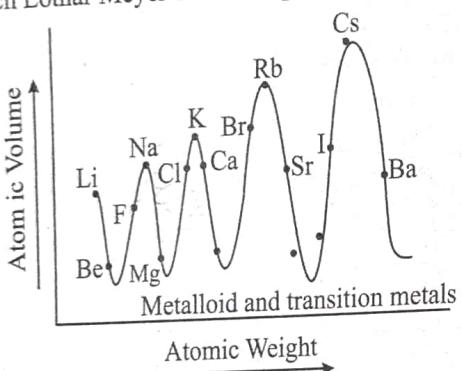
Train Your Brain

Example 1: Write any two triads present in Dobereiner Triad.

Sol. (Cl, Br, I) & (Li, Na, K), the atomic mass of the central element was merely the arithmetic mean of the atomic masses of the other two elements.

Example 2: What are the physical properties of elements in which Lothar Meyer's curve is plotted?

Sol.



Graph is plotted between atomic volume and atomic weight.

Example 3: Among the halogens F, Cl, Br and I, which does not fit in the Dobereiner's triad?

Sol. Element F does not fit in the Dobereiner's triad.



Concept Application

1. Which of the following set of elements obeys Newland's octave rule?

- (a) Na, K, Rb
- (b) F, Cl, Br
- (c) Be, Mg, Ca
- (d) B, Al, Ga

Merits or Advantages of Mendeleev's Periodic Table

(a) **Study of elements** – For the first time, all known elements were classified in groups according to their similar properties. So study of the properties of elements became easier.

(b) **Prediction of new elements** – It gave encouragement to the discovery of new elements as some gaps were left in it.

Sc (Scandium), Ga (Gallium), Ge (Germanium), Tc (Technetium) were the elements whose position and properties were well defined by Mendeleev even before their discoveries and he left the blank spaces for them in his table. e.g. - Blank space at atomic weight 72 in silicon group was called Eka silicon (means properties like silicon) and element (discovered later) was named Germanium.

Similarly other elements discovered after mendeleev periodic table were :

Eka aluminium – Gallium (Ga)

Eka Boron – Scandium (Sc)

Eka Silicon – Germanium (Ge)

Eka Manganese – Technetium (Tc)

(c) **Correction of doubtful atomic weights** – Corrections were done in atomic weight of some elements.

Atomic Weight = Valency × Equivalent weight.

Initially, it was found that equivalent weight of Be is 4.5 and it is trivalent ($V = 3$), so the weight of Be was 13.5 and there is no space in Mendeleev's table for this element. So, after correction, it was found that Be is actually divalent ($V = 2$). So, the weight of Be became $2 \times 4.5 = 9$ and there was a space between Li and B for this element in Mendeleev's table.

Corrections were done in atomic weight of elements are – U, Be, In, Au, Pt.

Demerits of Mendeleev's Periodic Table

(a) **Position of hydrogen** : Hydrogen resembles both, the alkali metals (IA) and the halogens (VIIA) in properties, so Mendeleev could not decide where to place it.

(b) **Position of isotopes** : As atomic wt. of isotopes differ, they should have placed in different position in Mendeleev's periodic table. But there were no such places for isotopes in Mendeleev's table.

(c) **Anomalous pairs of elements** : There were some pair of elements which didn't follow the increasing order of atomic weights.

Ex. Ar and Co were placed before K and Ni respectively in the periodic table, but having higher atomic weights.

(d) **Like elements were placed in different groups** :

There were some elements like Platinum (Pt) and Gold (Au) which have similar properties but were placed in different groups in Mendeleev's table.

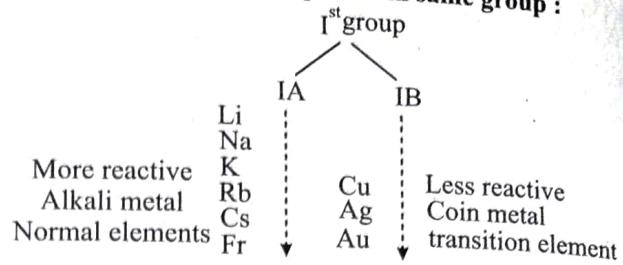
Pt

VIII

Au

IB

(e) **Unlike elements were placed in same group** :



Cu, Ag and Au placed in 1st group along with Na, K etc. While they differ in their properties (Only similar in having ns¹ electronic configuration)

(f) It was not clear that 'lanthanides' and 'actinides' are related with IIIA group or IIIB group.

(g) **Cause of periodicity:** Why physical & chemical properties repeated in a group.



Train Your Brain

Example 4: Write any two Anomalous pairs present in Mendeleev's periodic table?

Sol. (Ar, K) (Co, Ni)

Example 5: Write down the formula for the oxides and halides of following elements by use of Mendeleev's periodic table?

Eka-aluminium, Eka-silicon

Sol. Oxide of Eka-aluminium is Ga_2O_3 ,

Halide of Eka-aluminium is GaCl_3 .

Oxide of Eka-silicon is GeO_2 .

Halide of Eka-silicon is GeCl_4 .



Concept Application

4. The places that were left empty by Mendeleev were, for-

(a) Aluminium and silicon

(b) Gallium and germanium

(c) Arsenic and antimony

(d) Molybdenum and tungsten

5. Which are correct match?

(i) Eka silicon – Be

(ii) Eka aluminium – Ga

(iii) Eka manganese – Tc

(iv) Eka scandium – B

(a) (ii) & (iii)

(b) (i), (ii) & (iv)

(c) (i) & (iv)

(d) All of these

MODERN PERIODIC LAW AND THE PRESENT FORM OF THE PERIODIC TABLE

After development of atomic structure theories about subatomic particles, some spectacular achievements took into the classification of elements. In 1913, the English physicist, **Henry Moseley** observed regularities in the characteristic X-ray spectra of the elements where he found that a plot of \sqrt{v} (where v is frequency of X-rays emitted) against atomic number (Z) gave a straight line and not the plot of \sqrt{v} against atomic mass. Thus he concluded that the atomic number is more fundamental property than atomic mass. So he modified Mendeleev's periodic table and defined the modern periodic law as "**The physical and chemical properties of the elements are periodic functions of their atomic numbers**".

The periodic law revealed important characteristics among the 94 naturally occurring elements (neptunium and plutonium like actinium and protactinium are also found in pitch blende-an ore of uranium).

Modern Periodic Table

Various tables devised from time to time could not stand to the simplicity and informative modern form of periodic table known as "**long form**" of the periodic table of the elements. It was based on **Bohr-Bury concept** of electronic configuration.

Salient Features of the Modern Periodic Table

- It contains 7 horizontal rows like that of Mendeleev series called periods and 18 vertical columns called groups.
- Elements with similar valence shell configuration are arranged in the vertical columns referred to as families or groups.
- Each period corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consist of 8, 8, 18, 18, 32 and 32 elements respectively.
- Fourteen elements of both sixth and seventh periods /i.e., **lanthanoids** and **actinoids** respectively are placed in separate panels at the bottom

Periodic table of the elements

		Periodic Table of Elements																		
		Periodic Table of Elements																		
		Periodic Table of Elements																		
Period ↑	group ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	H	He																		
2	Li	Be																		
3	Na	Mg																		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn								
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd								
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Rg								
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cu								
lanthanoid series	6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu					
actinoid series	7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr					



Train Your Brain

Example 6: Explain that Cu, Ag and Au are transition elements?

Sol. These elements are transition elements because these elements have incomplete $(n-1)d$ subshell in their neutral or in any stable oxidation state.

Example 7: Why 16th group elements are known as chalcogens?

Sol. 16th group elements are known as chalcogens or the ore-forming elements because many elements can be extracted from sulphide or oxide ores.

Example 8: How many of the given element(s) belongs to oxygen family?

Cd, Ba, Mo, Te, Ra, La, Po

Sol. [2] Te, Po belongs to oxygen family.



Concept Application

NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBER > 100

New elements with very high atomic numbers are very unstable that they can be obtained in very small quantities. Discovering new elements requires a sophisticated technologies which is possessed by few countries only. Scientists are tempted to claim for its discovery which may lead to dispute between these countries due to competitive spirits.

For example, both American and Soviet scientists claimed credit for discovering element 104. The Americans named it

Rutherfordium, whereas Soviets named it Kurchatovium.

So, to avoid such problems IUPAC has given recommendation that until a new discovery is proved and its name is officially recognized, a systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1 – 9. The roots are put together in order of digits which make the atomic number and “ium” is added at the end.

Table: Notation for IUPAC Nomenclature of Elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Table: Nomenclature of Elements with Atomic Number above 100

Atomic Number	Name	Symbol	IUPAC Official Name	IUPAC symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Uun	Darmstadtium	Ds
111	Unununium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

The permanent name might reflect the country (or state of the country) in which the element was discovered, or pay tribute to a notable scientist. As of now, elements with atomic numbers up to 118 have been discovered. Official names of all elements have been announced by IUPAC.



Train Your Brain

Example 9: What would be the IUPAC name and symbol for the element with atomic number 120?

Sol. The root for 1, 2 and 0 are un, bi and nil respectively. Hence, the name becomes unbinilium and the symbol is Ubn.

Example 10: What is the atomic number of Ununhexium?

Sol. [116]

Un - 1

Un - 1

Hex - 6



Concept Application

10. In modern periodic table, the element with atomic number $Z = 118$ will be :
- Uuo ; Ununoctium ; alkaline earth metal
 - Uno ; Unniloctium ; transition metal
 - Uno ; Unniloctium; alkali metal
 - Uuo ; Ununoctium; noble gas

11. Unnilbium belongs to which block and groups of the periodic table?
- d-block, group-10
 - f-block, group-3
 - p-block, group-13
 - d-block, group-11

12. Atomic number of the recently discovered element Nihonium (Nh) is?
- 118
 - 114
 - 113
 - 104

ELECTRONIC CONFIGURATION OF ELEMENTS AND THE PERIODIC TABLE

We know that an electron in an atom is characterised by a set of four quantum numbers (n, l, m and s) where the principal quantum number (n) defines the main energy level known as the shell.

Electronic Configuration in Periods

The period indicates the value of n for the outermost or valence shell. In other words, successive period in the periodic table is associated with the filling of the next higher principal energy level like $n = 1, n = 2, n = 3$ refers to the filling of the 1st, 2nd, 3rd and higher principal energy levels.

- (a) **First period :** It corresponds to the filling of electrons in the first energy shell i.e., (K shell), $n = 1$, since this energy shell has only one orbital, i.e. 1s which can accommodate only two electrons, therefore the first period contains only two elements. Hydrogen ($1s^1$) and Helium ($1s^2$).

(b) **Second period:** It corresponds to the filling of electrons in the 2nd energy shell (L shell) i.e. $n = 2$. Since this shell has four orbitals (one 2s and three 2p) can accommodate eight electrons therefore 2nd period contains eight elements. It starts with Li ($Z = 3$) which has three electrons where two electrons are in the 1s orbital and third electron enters the 2s orbital. The next element Be ($Z = 4$) has four electrons with configuration $1s^22s^2$. From next element B ($Z = 5$) the 2p orbitals are filled with electrons and the L shell completes at Ne ($Z = 10$) with electronic configuration $1s^22s^22p^6$.

(c) **Third period:** This period corresponds to the filling of electrons in the third shell i.e., $n = 3$. This shell has nine orbitals (one 3s, three 3p and five 3d). However according to the energy level diagram of multielectron atoms, 3d-orbitals have high energy so filled after 4s-orbital. Consequently the third period contains only four orbitals (3s and 3p) accommodating only eight electrons. Thus have only eight elements. It begins at sodium ($Z = 11$) where the added electron enters the 3s orbital. Successive filling of electrons completing the 3s and 3p orbitals ends at Argon ($Z = 18$) with electronic configuration $3s^23p^6$.

(d) **Fourth period:** It corresponds to the filling of electrons in the fourth energy level i.e., $n = 4$. It starts with potassium ($Z = 19$) and the added electron first goes to 4s-orbital which completes at calcium ($Z = 20$). After filling of 4s orbital, filling of five 3d-orbital starts that can accommodate ten electrons. Before the filling of 4p-orbital, first filling of 3d orbitals take place. In the fourth period there are nine orbitals in total which can accommodate eighteen electrons i.e., eighteen elements.

(e) **Fifth period:** Fifth period corresponds to the fifth shell i.e., $n = 5$. Like fourth period it also have nine orbitals (one 5s, three 5p and five 4d) which can accommodate eighteen electrons i.e., it can have eighteen elements.

(f) **Sixth period:** It corresponds to the filling of the sixth energy level i.e., $n = 6$. Since in this period only sixteen orbitals (one 6s, seven 4f, five 5d and three 6p) are available, thereby sixth period contains thirty two elements.

(g) **Seventh period:** It corresponds to the filling of the seventh energy shell, i.e., $n = 7$. Like sixth period, it also contains thirty two elements due to the sixteen orbitals (one 7s, seven 5f, five 6d and three 7p). This includes most of the man-made radioactive elements.

METHOD TO PREDICT THE PERIOD, GROUP AND BLOCK OF A GIVEN ELEMENT

Following steps are followed to predict the group, period and block of the element:

1. Electronic configuration of the element is written by following various rules (Afbau principle, Hund's rule etc.).
2. Period of the element is represented by the highest principal quantum number of the valence shell.

- Block of the element is predicted on the basis of sub-shell which receives the last electron.
 - Group is predicted from the number of electrons in the outermost or penultimate shell as follows:
 - In case the element belongs to s-block, then the group = (number of valence electrons)
 - In case the element belongs to p-block, then the group = (10 + total number of valence electrons)
 - In case the element belongs to d-block, then the group = (number of electrons in (n - 1) d-subshell + n s-subshell).
- Maximum number of elements in period can be calculated by following way:

$$= \frac{(n+1)^2}{2}, \text{ for odd period, } n = 1, 3, 5, 7, 9, \dots$$

$$= \frac{(n+2)^2}{2}, \text{ for even period, } n = 2, 4, 6, 8, \dots$$



Train Your Brain

Example 11: Write down the general electronic configuration of inner transition elements.

Sol. General electronic configuration of inner transition element $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

Example 12: Find out the group, period & block for the N-atom.

Sol. E. C. of $_7N = 1s^2 2s^2 2p^3$

Last electron enters in p orbital, so block = p-block.

Highest value of n is 2, so period number = 2

Group for p-block = 10 + total no. of valence electron
= $10 + 5 = 15$

Example 13: Explain how Fe atom belongs to d-block (Given Z of Fe = 26).

Sol. E. C. of Fe = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

According to $(n+l)$ rule,

for 4s, n = 4, l = 0, n + l = 4

3d, n = 3, l = 2, n + l = 5

(n + l) is highest for 3d. So last electron enter into d-block.

Example 14: How would you justify the presence of 18 elements in the 5th period of the periodic table?

Sol. When n = 5, l = 0, 1, 2, 3, 4. The order of the increasing energy orbitals are 5s < 4d < 5p. The total number of orbitals available are nine. The maximum number of electrons that can accommodate is 18 and therefore 18 elements are there in the 5th period.



Concept Application

- The number of elements in 5th and 6th period of periodic table are respectively -
 - 8, 18
 - 18, 18
 - 18, 32
 - 18, 28
- 4th shell of an atom contains 4s, 4p, 4d and 4f subshell, which subshells are not filled in any 4th period element?
 - 4p, 4d, 4f
 - 4s, 4p
 - 4p, 4f
 - 4d, 4f
- Total no. of elements which should be theoretically present in 8th period of the modern long form of periodic table, is:
 - 32
 - 40
 - 50
 - 48
- Atomic number Z = 58 belongs to which period, block and group
 - 4th period, d-block and 3rd group
 - 6th period, d-block and 4th group
 - 6th period, f-block and 3rd group
 - 5th, d-block and 5th group
- Total number of orbitals in 5th shell
 - 16
 - 36
 - 9
 - 25

CLASSIFICATION OF ELEMENTS ON THE BASIS OF ELECTRONIC CONFIGURATION

On the basis of electronic configuration, the elements can be classified into the following four blocks.

i) s-block elements : Those elements in which last electron enters in s-orbital, called s-block elements. These elements contain 1 or 2 electrons in s-subshell of outermost shell. Elements of 1 and 2 group belong to this class. These elements enter into chemical reaction by losing valency electrons so as to acquire noble gas configuration in the outermost orbit.

ns^1 (group 1) ns^2 (group 2)
(Alkali metals) (Alkaline earth metals)
These elements generally form electrovalent compounds and basic oxides.

ii) p-block elements: These elements contain 1 to 6 electrons in the p-subshell of the outermost orbit ($ns^2 np^{1-6}$). The elements belonging to 13th to 18th group are p-block elements. In these last electron enters to the p-subshell. For example:

Group	Elements	At.No.	Configuration
13	Boron (B)	Z = 5	$1s^2 2s^2 2p^1$
14	Carbon (C)	Z = 6	$1s^2 2s^2 2p^2$
15	Nitrogen (N)	Z = 7	$1s^2 2s^2 2p^3$
16	Oxygen (O)	Z = 8	$1s^2 2s^2 2p^4$
17	Fluorine (F)	Z = 9	$1s^2 2s^2 2p^5$

Note: 15, 16 and 17 group elements are called pnicogens, chalcogens and halogens respectively.

The main characteristics of these elements are :

- (a) The non-metallic character increases along a period from 13 to 17.
- (b) They form covalent compounds among themselves but electrovalent (ionic) compounds with s-block elements.

(iii) **d-block elements** : Those elements in which last electron enters in d-orbital, called d-block elements. These are also called transition elements. The elements of group 3 to 12 belong to this class. Their general configuration can be represented as : $(n-1)d^{1-10} ns^{1-2}$

General characteristics of transition (d-block elements) are:

- (a) These are metals, hard, malleable, ductile and possess high tensile strength.
- (b) These are good conductors of heat and electricity.
- (c) These elements exhibit variable valency.
- (d) These generally form coloured compounds.
- (e) These metals, their alloys and compounds possess marked catalytic activity.

Note : Zn, Cd, Hg and Cn are not considered as transition elements because these have fully filled d^{10} configuration in atomic as well as oxidation state.

(iv) **f-block elements** : They are inner transition or f-block elements. These elements are arranged in the two rows at the bottom of the periodic table. In the first row, these are 14 elements from atomic number 58 to 71 known as **Lanthanides** or **rare earth elements**. The second row of elements from atomic number 90 to 103, known as **actinides**. Their general electronic configuration can be represented as

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

They show most of the properties similar to each other since outermost and penultimate orbits are similar. Their properties are similar to 'd' block elements.

CLASSIFICATION OF ELEMENTS AS METALS, NON-METALS AND METALLOIDS

Though elements are classified into s, p, d and f-blocks, it is possible to further classify them into metals, non-metals and metalloids. More than 78% of the known elements are metals. These elements are present on the left side and centre of the periodic table. Metals are the elements which are malleable and ductile, possess lustre, are good conductors of heat and electricity and have high densities.

Metals usually have high melting points and boiling points and generally are solid at room temperature. Mercury is an exception which despite of being a metal is liquid at room temperature. **Gallium** (303 K) and **Caesium** (302 K) also have very low melting points. Non-metals are much less in number than metals.

There are only about 20 non-metals. These are located at the top right hand side of the periodic table. Non-metals have low melting points and low boiling points. They usually are solids or

gases at room temperature. These non-metals are neither ductile nor malleable. They are poor conductor of heat and electricity. In a period, the non-metallic character increases from left to right. Metallic character increases down the group.

There is no sharp line dividing metals from non-metals. A zig-zag line separates the metals from non-metals. The borderline elements such as silicon, germanium, arsenic, antimony and tellurium exhibit characteristic properties of metals as well as non-metals. These elements are called **semi-metals or metalloids**.

Periodic Trends in Physical Properties: Most of the properties of the elements such as atomic volume, atomic size, ionization enthalpy, electron gain enthalpy and electronegativity are directly related to the electronic configuration of the atoms. These properties undergo periodic variation with the change in the atomic number within a period or a group. These properties indirectly control the physical properties such as melting point, boiling point, density etc.

SCREENING EFFECT (σ) AND EFFECTIVE NUCLEAR CHARGE (Z_{eff})

- (i) Valence shell e^- suffer force of attraction due to nucleus and force of repulsion due to inner shell electrons.
- (ii) The decrease in force of attraction on valence e^- is due to inner shell e^- is called screening effect or shielding effect. (i.e. total repulsive force is called shielding effect.)
- (iii) Due to screening effect, valence shell e^- experiences less force of attraction exerted by nucleus. (i.e. total attraction force experienced by valence e^- is called Z_{eff})
- (iv) There is a reduction in nuclear charge on electron due to screening effect. Reduced nuclear charge is called effective nuclear charge.
- (v) If nuclear charge is Z , then effective nuclear charge is $Z - \sigma$ [Where σ (Sigma) = Screening constant]
So, $Z_{\text{eff}} = (Z - \sigma)$

Slater's Rule is used to know Screening Constant (σ).

Slater's Rule

First write down the electronic configuration & then arrange in increasing order of shell.

$$\text{eg } {}_{30}\text{Zn} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$$

According to Slater,

$$1s^2/2s^2 2p^6/3s^2 3p^6 3d^{10}/4s^2$$

Rule-1: For s & p electrons

For remaining shell e^- , shield by a factor of 0.35 & e^- in $(n-1)$ shell shield by a factor of 0.85 and remaining e^- 's shields by a factor of 1.

screening constant for 4s electron,

$${}_{30}\text{Zn} = \frac{1s^2/2s^2 2p^6}{(\times 1)}, \frac{3s^2 3p^6}{(n-1) \times 0.85}, \frac{4s^2}{(n) \times 0.35}$$

$$\sigma = 10 \times 1 + 18 \times 0.85 + 1 \times 0.35$$

$$\sigma = 25.65$$

$$Z_{\text{eff}} = Z - \sigma = 30 - 25.65 = 4.35$$

$$\text{Potassium (Z = 19)} = \frac{2,8}{n-2}, \frac{8}{n-1}, \frac{1}{n}$$

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

$$Z_{\text{eff}} = 19 - (10 \times 1 + 8 \times 0.85) \\ = 19 - 16.8 = 2.2$$

$$\text{Sodium (Z = 11)} = \frac{2}{n-2}, \frac{8}{n-1}, \frac{1}{n}$$

$$Z_{\text{eff}} = 11 - (2 \times 1 + 8 \times 0.85) \\ = 11 - 8.8 = 2.2$$

Rule-2: For d & f orbitals

The remaining e^- in the same subshell (not shell) shield by factor of 0.35 & remaining e^- is shielded by a factor 1.

$$\sigma_{3d}(\text{Zn}) = 9 \times 0.35 + 18 \times 1 = 21.15$$

$$Z_{\text{eff}} = Z - \sigma = 30 - 21.15 = 8.85$$

ATOMIC RADII

Atom is considered to be a very small spherical entity. So, in simple terms atomic radii can be defined as the distance of the outermost shell of an atom from the centre of its nucleus. Being very small, it is usually expressed in nm

(1nm = 10 \AA = 10 3 pm = 10 $^{-9}$ m).

Atomic radius is taken as the effective size which is the distance of closest approach of one atom to the another atom in a given bonded situation.

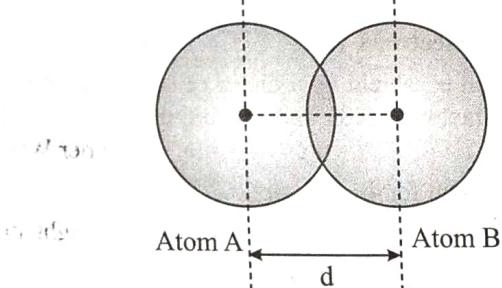
Various names had been proposed for the atomic radii depending upon their experimental determinations and nature of atom. These are:

- (i) Covalent radius
- (ii) Metallic radius
- (iii) Ionic radius
- (iv) Van der Waals radius

(i) Covalent radius : Covalent bond is normally formed between the non-metals hence this term, covalent radius is used for them. It is defined as half of the internuclear distance between two successively covalently bonded atoms in a molecule.

Atomic radii can be measured by X-ray or other spectroscopic methods. Covalent radius = $\frac{1}{2} \times d$. Covalent radius can be of

either homodiatomic molecules like that of H₂, Cl₂, Br₂ etc. or heterodiatomic molecules like that of HCl, HBr, etc.



where d is the internuclear distance between two covalently bonded atoms A and B

For example, if we consider a covalently bonded chlorine molecule (Cl₂), the bond distance in it is 198 pm. The half of

the distance (99 pm) is taken as the atomic radius of chlorine atom. The atomic radii of few elements are given below which gives an inference about two trends in the terms of nuclear charge and energy level.

Table: Atomic Radii/pm Across the period

Atom (Period II)	Li	Be	B	C	N	O	F
Atomic radius	152	111	88	77	74	66	64
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Atomic radius	186	160	143	117	110	104	99

Table: Atomic Radii/pm Down a Family

Atom (Group 1)	Atomic Radius	Atom (Group 17)	Atomic Radius
Li	152	F	64
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140

If we observe the trend in atomic radii across the period and down the group, we find that the atomic size generally decreases across the period whereas there is an increase in the size down the group. The reason which can be attributed to this variation in the nuclear charge.

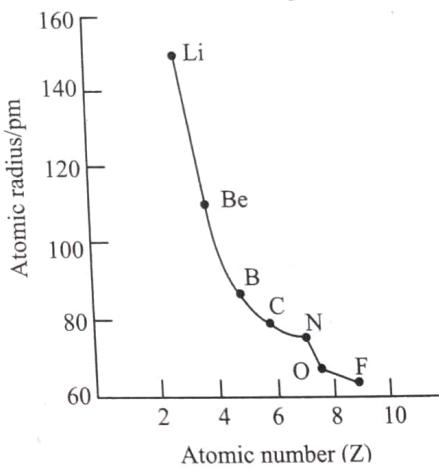


Fig. (a) Variation of atomic radius with atomic number across the second period

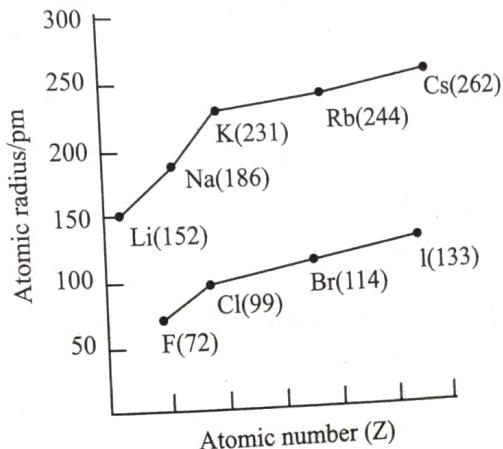


Fig. (b) Variation of atomic radius with atomic number for alkali metals and halogens

In a period as the atomic number increases, the increasing number of electrons are added to the same valence shell. This increases the effective nuclear charge, consequently the force of attraction of the electrons to the nucleus goes on increasing. Thus gradual increase in the effective nuclear charge results in the decrease of the atomic size along the period.

(ii) Metallic radius: Metallic radius is taken as half of the distance between two successive nuclei of two adjacent metal atoms.

For example, the distance between two adjacent copper atoms in solid copper is 256 pm hence, the metallic radius of copper is assigned a value of 128 pm.

(iii) Ionic radius: The removal of an electron from an atom results in the formation of a cation, whereas the gain of electron leads to the formation of an anion.

So, the ionic radius can be defined as the distance of outermost shell of an anion or cation from its nucleus. For example, the bond length (d_{A-B}) between an ionic molecule is given as

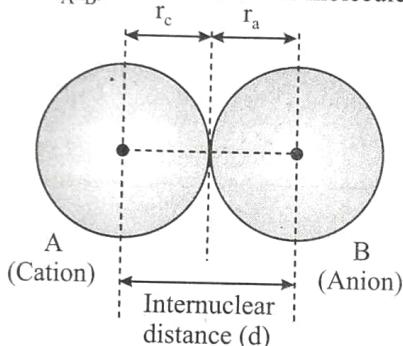
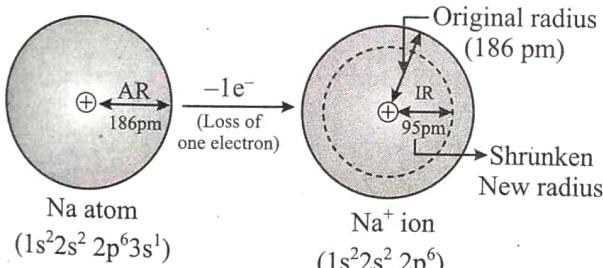


Fig. showing the bond length (d) between the cation and an anion of an ionic molecule AB.

$$d_{A-B} = r_c + r_a$$

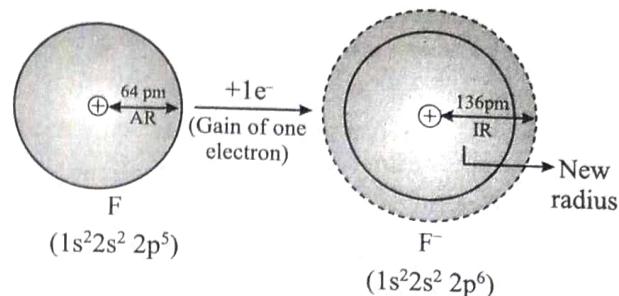
The size of a cation is always smaller than its parent atom because the cation formed after the loss of electron has fewer electrons. Though the nuclear charge remains the same, effective nuclear charge increases.

For example, the atomic radius of sodium is 186 pm whereas the ionic radius for sodium ion (Na^+) is 95 pm.



Atom	Li	Na	K	Rb	Cs
Atomic Radii (pm)	152	186	231	244	262
Ion	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic Radii (pm)	76	102	138	152	167

The size of the anion is always larger than the parent atom because addition of one or more electrons results in the increased repulsion among the electrons and a decreased effective nuclear charge. For example, the ionic radius of fluorine is 136 pm whereas the atomic radius is 64 pm.



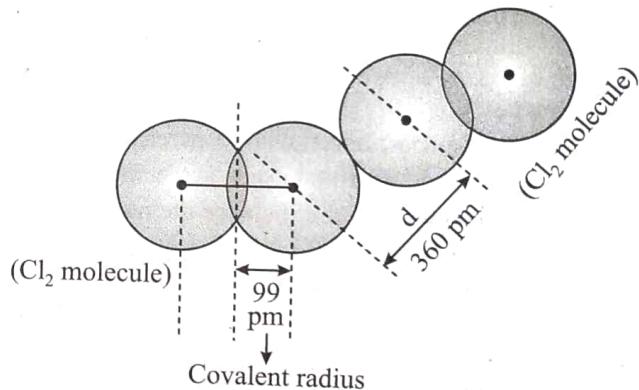
There are atoms and ions which contain the same number of electrons. These are known as **isoelectronic species**.

The cation with a greater positive charge has a smaller radius because of the greater nuclear attraction of the electrons while the anion with the greater negative charge has a larger radius.

Element	N	O	F	Na	Mg	Al
Atomic size (pm)	74	66	64	186	160	143
Ion	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
Ionic size (pm)	171	140	136	95	72	57

(iv) Van der Waals radius: It is defined as half the distance between the nuclei of two non-bonded neighbouring atoms of two adjacent molecules in solid state. This term is used for non-metals (in covalent compounds) and noble gases.

For example, the van der Waals radius of chlorine is 180 pm



van der Waals radius = $\frac{1}{2} \times d$ (Internuclear distance between two non-bonded neighbouring atoms of two covalently bonded molecules)

$$\begin{aligned} \text{van der Waals radius of chlorine} &= \frac{1}{2} \times 360 \\ &= 180 \text{ pm} \end{aligned}$$

Note : Order of radius : covalent < metallic < van der Waals
Periodic variation of atomic size :

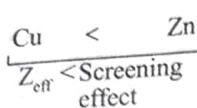
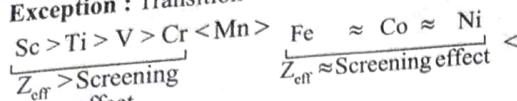
(i) Across a period : It decreases from left to right in a period as nuclear charge increases

eg. $\text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F} < \text{Ne}$

(ii) In a group: It increases from top to bottom in a group as number of shell increases

eg. $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$

Exception : Transition elements



Order of atomic radius –



Lanthanoid Contraction

- (a) Outermost electronic configuration of inner transition elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ ($n = 6$ or 7)
- (b) e^- enters in $(n-2)f$ orbitals.
- (c) Mutual screening effect of e^- is very less, because of complicated structure of f -orbital.
- (d) Nuclear charge increases by one (+1) in lanthanides and actinides so atomic size of these elements slightly decreases. It is known as lanthanoid contraction.
Here Nuclear charge > Screening effect.
- (e) In 1st, 2nd and 3rd transition series,

Radius –	$3d < 4d \approx 5d$ (except III rd B)
	IIIB IVB
size increases ↓	Sc Ti ↓ size increases
	Y Zr } Equal due to
	La Hf } lanthanide contraction

Transition Contraction : IIIA → B < Al ≈ Ga

- Note:** While atomic size should increase down the group.
- (a) At. size of Ga = At. size of Al, due to transition contraction (d-contraction).
 - (b) In transition elements nuclear charge increases by 1.
 - (c) but e^- enters in $(n-1)d$ orbital exerts screening effect.
 - (d) Screening effect of $(n-1)d$ e^- balance the nuclear charge by 85%.
 - (e) Z_{eff} increasing as on each electron = $1 - 0.85 = 0.15$
 - (f) Increase in nuclear charge is only 0.15. So atomic size remains almost constant.

Different orders of atomic and ionic radii:

- | | |
|---|---|
| 1. $\text{Na}^+ < \text{Ne} < \text{F}^-$ | 2. $\text{Ni} < \text{Cu} < \text{Zn}$ |
| 3. $\text{H}^+ < \text{H}^-$ | 4. $\text{Ti} < \text{Zr} \approx \text{Hf}$ |
| 5. $\text{Be} < \text{Li} < \text{Na}$ | 6. $\text{Cr} < \text{V} < \text{Ti} < \text{Sc}$ |
| 7. $\text{I}^+ < \text{I}^-$ | 8. $\text{Sc} < \text{Y} < \text{La}$ |
| 9. $\text{Cl}^- < \text{Na} < \text{Ar}$ | 10. $\text{Cu} < \text{Au} < \text{Ag}$ |

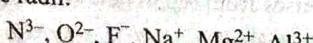


Train Your Brain

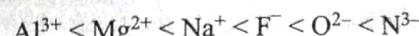
Example 15: Arrange the following in increasing order of radius Covalent radius, Metallic radius, Vander Waals radius.

Sol. Covalent < Metallic radius < Vander Waals radius.

Example 16: Arrange the following in increasing order of ionic radii.



Sol. The correct order of ionic radii is



Example 17: Which of the following species will have the largest and the smallest size?



Sol. Cations are smaller than their parent atoms due to higher effective nuclear charge. Among the isoelectronic species, the one with a greater positive charge will have smaller radius. Hence, we can say out of Mg, Mg²⁺, Al and Al³⁺ the largest size will be of Mg and smallest size is of Al³⁺.

Example 18: On the basis of their positions in the periodic table which among the following will have the largest atomic radii?



Sol. Ne, has van der Waals forces of attraction and Ne has the largest size in its period. All the elements belong to the same period. (For noble gases van der Waal radii is considered)



Concept Application

18. What will be the distance between H and Cl atom in HCl? If radius of hydrogen is 0.37 Å and the radius of chlorine is 1.67 Å - (According to the concept of covalent radius)

- | | |
|------------|------------|
| (a) 2.04 Å | (b) 1.96 Å |
| (c) 2.12 Å | (d) 1.0 Å |

19. For a molecule Br₂, total distance between two nuclei is 3.2 Å. What will be the covalent radius of Br atom?

- | | |
|-----------|-----------|
| (a) 1.6 Å | (b) 6.4 Å |
| (c) 2.4 Å | (d) 4.9 Å |

20. Which of the following orders of atomic radii are correct?

- | |
|--------------------|
| (i) Li < Be < Na |
| (ii) Ni < Cu < Zn |
| (iii) Ti < Zr ≈ Hf |
| (iv) Ti > V > Cr |

Correct code is:

- | | |
|--------------------|-------------|
| (a) i, ii, iii, iv | (b) only ii |
| (c) ii, iii, iv | (d) only iv |

21. Which of the following pair have approximately the same atomic radii?

- | | |
|------------|------------|
| (a) Cu, Zn | (b) Co, Ni |
| (c) Mg, Al | (d) Na, Ne |



IONIZATION ENTHALPY ($\Delta_i H^\circ$)

It is also known as ionization potential or ionization energy which can be defined as the minimum amount of energy required to remove an electron from the valence shell of an isolated gaseous atom in its ground state resulting in the formation of positive ion.



Since energy is always required to remove the electrons from the atom, ionization enthalpy is always positive.

The ionization enthalpy goes on increasing for each successive removal of electrons. This is due to the fact that after the removal of an electron, the number of electrons decreases while the nuclear charge remains the same. Consequently the remaining electrons are held more tightly by the nucleus and removal of each successive electron becomes more difficult. Hence, successive ionization enthalpies go on increasing. So order becomes

$$IE_1 < IE_2 < IE_3 < \dots$$

For example,



Table: Successive ionization enthalpies (kJ/mol) of some elements

Element	Electronic configuration	IE ₁ (kJ/mol)	IE ₂ (kJ/mol)	IE ₃ (kJ/mol)
Li	1s ² 2s ¹	520	7297	11810
Be	1s ² 2s ²	899	1758	14810
B	1s ² 2s ² 2p ¹	801	2428	3660
C	1s ² 2s ² 2p ²	1086	2353	4618
N	1s ² 2s ² 2p ³	1402	2855	4577
O	1s ² 2s ² 2p ⁴	1314	3388	5297
F	1s ² 2s ² 2p ⁵	1681	3375	6045
Ne	1s ² 2s ² 2p ⁶	2080	3963	6130

When the first ionization enthalpies of elements having atomic number upto 60 are plotted, a graph of striking periodicity is obtained. The maxima positions in the graph is occupied by the noble gases because of the high ionization enthalpies due to completely filled octet acquiring a stable electronic configuration. On the other hand, the alkali metals occupy the minima positions in the graph correlating the low ionization enthalpies and their high reactivity.

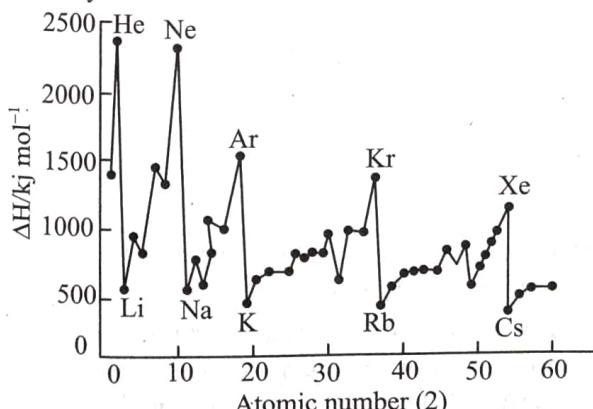


Fig. variation of first ionization enthalpies (ΔH) with atomic number for elements with $Z = 1$ to 60

Two noticeable trends are observed in respect to the first ionization enthalpies. It increases as we move across the period while it decreases down the group.

Factors Affecting Ionisation Potential

- (a) **Atomic size:** Larger the atomic size, smaller is the Ionisation Potential. It is due to that the size of atom increases the outermost electrons farther away from the nucleus and nucleus loses the attraction on that electrons and hence can be easily removed.

$$\text{Ionisation Potential} \propto \frac{1}{\text{Atomic size}}$$

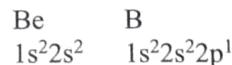
- (b) **Effective nuclear charge (Z_{eff}):** Ionisation potential increases with the increase in nuclear charge between outermost electrons and nucleus.

$$\text{Ionisation Potential} \propto \text{Effective nuclear charge}$$

- (c) **Penetration power of sub shells:**

- (i) Order of attraction of subshells towards nucleus (Penetration power) is - s > p > d > f
- (ii) As subshell is more closer to nucleus so more energy will be required to remove e^- from s-subshell in comparison to p,d & f.

Ex.

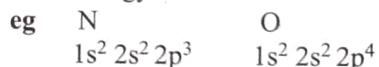


first Ionisation Potential Be > B

After losing one e^- , B attains electronic configuration of Be, so IInd ionisation potential of B is more than Be. IInd Ionisation Potential of B > Be.

- (d) **Stability of half filled and fully filled orbitals:**

- (i) Half filled orbitals p³, d⁵, f⁷ or fully filled orbitals s², p⁶, d¹⁰, f¹⁴ are more stable than others. So it requires more energy.



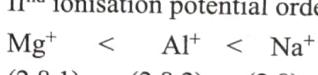
Ist Ionisation Potential order is O < N

Because of half filled p-orbitals in N, its ionisation energy (stability) is higher than O.

Ist ionisation potential order Na < Al < Mg

- (ii) Because s-orbital in Mg is completely filled and its penetration power is also higher than p-orbital (Al).

IInd ionisation potential order



- (e) **Oxidation state:**

$$\text{Ionisation Potential} \propto \text{oxidation state of an atom}$$

Ion with high oxidation state will have high ionisation potential. Ex. $\text{Fe}^{3+} > \text{Fe}^{2+} > \text{Fe}$

- (i) **In a group :** Size increase so ionisation potential decrease.

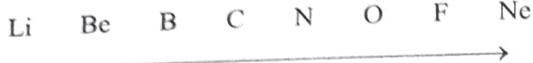


Size increases, Ionisation Potential decreases

Exception :

- Ionisation Potential Ga > Al (While Ionisation Potential decreases down the group it is due to Transition contraction)
- Ionisation Hf > Zr } (While Ionisation Potential should decrease down the group. It is due to lanthanide contraction)

(ii) In a period : In a period atomic size decreases and z_{eff} increases so removal of electron becomes difficult and ionisation potential increases.



atomic size decreases, z_{eff} increases, Ionisation Potential increases.

Order of ionisation potential

**Application of Ionisation Potential****(a) Metallic and non metallic character :**

Metallic \longrightarrow Ionisation Potential Low
(Na, K, Rb etc.)

Non metallic \longrightarrow Ionisation Potential High
(F, Cl, Br etc.)

$$\text{Ionisation Potential} \propto \frac{1}{\text{Metallic property}}$$

(b) Reactivity :

$$\text{Reactivity} \propto \frac{1}{\text{Ionisation Potential}}$$

Reactivity increases down the group as ionisation potential decreases.

(c) Reducing character :

$$\text{Reducing character} \propto \frac{1}{\text{Ionisation Potential}}$$

(i) IA group has minimum ionisation potential so they are strong reducing agents in gaseous state
(Li < Na > K > Rb > Cs)

(ii) IA group – In Aqueous state reducing character (Li > Rb > Cs > K > Na)

As the degree of hydration is more in Li due to high charge density.

(d) Stability of oxidation states :

(i) If the difference between two successive ionisation potential $\geq 16 \text{ eV}$ then lower oxidation state is stable.

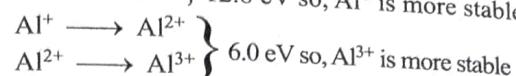
eg. $\text{Na} \longrightarrow \text{Na}^+$, Ist ionisation potential } 42.7 eV
 $\text{Na}^+ \longrightarrow \text{Na}^{2+}$, IInd ionisation potential } 10.5 eV

Difference of ionisation potential $> 16 \text{ eV}$, so Na^+ is more stable.

(ii) If the difference between two successive ionisation potential $\leq 11 \text{ eV}$ higher oxidation state is stable.

eg. $\text{Mg} \longrightarrow \text{Mg}^+$, Ist ionisation potential } 7.4 eV
 $\text{Mg}^+ \longrightarrow \text{Mg}^{2+}$, IInd ionisation potential } 11.6 eV

Difference of ionisation potential $< 11 \text{ eV}$ so Mg^{2+} is more stable.



Al^+ is stable only in gaseous state

Al^{2+} is stable in liquid and solid state.

(e) **Basic nature :** It is property of elements with loosely held electrons

$$\text{Ionisation Potential} \propto \frac{1}{\text{Basic Property}}$$

**(f) To determine the number of valence electron :**

eg. Li Ist Ionisation Potential (5.4 eV) and IInd Ionisation Potential (75 eV)

High energy difference in two successive ionisation potential shows change in energy levels i.e., valence shell has only one electron.

**Train Your Brain**

Example 19: The first ionisation enthalpy values of 3rd period elements Na, Mg and Si are respectively 496, 737 and 786 kJ/mol. Predict whether the first ionisation enthalpy value for Aluminium will be more close to 575 or 760 kJ/mol justify your answer?

Sol. It will be more close to 575 kJ mol⁻¹. The value for Al should be lower than that of Mg because of less effective shielding of 3p electrons from the nucleus as 3s-electrons.

Example 20: The first ionisation enthalpy values in kJ/mol of 13th group elements are:

B	Al	Ga	In	Tl
801	577	579	558	589

How would you explain this deviation from the general trend.

Sol. Deviation from Al to Ga is due to poor shielding of d-electrons (Transition contraction) and deviation from In to Tl is due to f-electrons (Lanthanoid contraction).

Example 21: Explain, why the first ionisation energy of nitrogen is more than that of oxygen?

Sol. The first ionisation enthalpy of nitrogen is more than that of oxygen because nitrogen is more stable due to its half filled electronic configuration.

- (i) Has high standard reduction potential.
- (ii) Has high hydration enthalpy.
- (iii) Low bond dissociation energy.



Train Your Brain

Example 22: Which of the following will have the most negative electron gain enthalpy and which has the least negative?

P, S, Cl, F.

Sol. Electron gain enthalpy generally become more negative across a period, as we move left to right. Within the group electron gain enthalpy becomes less negative as we move down the group. However electron addition in 2p orbital is lead to greater repulsion than the electron addition in 3p orbital. Hence, Chlorine has most negative EA and phosphorous has least negative EA.

Example 23: Arrange the following elements in increasing order of electron affinity.

F, Cl, O, N, B.

Sol. Cl > F > O > B > N → Nitrogen has stable electronic configuration



Concept Application

25. Relation between electron gain enthalpy and electron affinity is
 - (a) E.A. = $\Delta H_{c.g}$
 - (b) E.A. = $2\Delta H_{c.g}$
 - (c) E.A. = $-2\Delta H_{c.g}$
 - (d) E.A. = $-\Delta H_{c.g}$
26. The process requiring the absorption of energy is -
 - (a) $F \rightarrow F^-$
 - (b) $Cl \rightarrow Cl^-$
 - (c) $O \rightarrow O^{2-}$
 - (d) $H \rightarrow H^-$
27. Arrange S, O and Se in ascending order of electron affinity -
 - (a) $Se < S < O$
 - (b) $O < Se < S$
 - (c) $S < O < Se$
 - (d) $S < Se < O$
28. Elements of which group form anions most readily?
 - (a) Oxygen family
 - (b) Nitrogen group
 - (c) Halogens
 - (d) Alkali metals

ELECTRONEGATIVITY

Electronegativity of an element is the tendency of an atom to attract the shared pair of electrons towards itself. It is a qualitative measure, because unlike ionization enthalpy and electron gain enthalpy which are related to atoms in the isolated gaseous state, it is in the bonded state and hence not a measurable quantity.

Although a number of numerical scales of electronegativity such as Pauling scale, Mulliken-Jaffe scale, Allred Rochow scale have been developed. Yet the Pauling scale is most widely used.

(a) Electronegativity values (on Pauling scale) Across the periods

Atom (Period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

(b) Electronegativity values (on Pauling scale) Down a family

Atom (Group 1)	Electronegativity value	Atom (Group 17)	Electronegativity value
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

The electronegativity of any given element is not constant, it varies depending on the element to which it is bonded. Even though it is a qualitative quantity, it helps in the prediction of the type of bond which exists between two bonded atoms.

Factors Affecting Electronegativity:

(a) Atomic size

$$\text{Electronegativity} \propto \frac{1}{\text{Atomic size}}$$

(b) Effective nuclear charge (Z_{eff})

$$\text{Electronegativity} \propto Z_{eff}$$

(c) Hybridisation state of an atom

$$\text{Electronegativity} \propto \% \text{ s character in hybridised atom}$$

sp	>	sp ²	>	sp ³
s character	50%	33%	25%	
Electronegativity	3.25	2.75	2.5	

(d) Oxidation state

$$\text{Electronegativity} \propto \text{oxidation state e.g.}$$

$$(i) Mn^{2+} < Mn^{4+} < Mn^{7+}$$

$$(ii) O^{2-} < O^- < O < O^+ < O^{2+}$$

$$(iii) Fe < Fe^{2+} < Fe^{3+}$$

Periodic Table & Electronegativity

(a) Electronegativity decreases down the group.

(b) In period on moving from left to right electronegativity increases.

Exceptions : In '0' group – Electronegativity is always zero, because inert gases do not form molecule.

(c) Electronegativity of Cs and Fr are equal, it is because from ^{55}Cs to ^{87}Fr only one shell increases but nuclear charge (No. of proton) increases by +32.

So effect of nuclear charge balanced the effect of increase in number of shell.

- (d) Electronegativity of F > Cl but Electron affinity of Cl > F.
So Fluorine is called **Black sheep** element.
- (e) In group of IIB elements (Zn, Cd, Hg) value of electronegativity increases down the group, because of lanthanide contraction
- (f) In IIIA group, value of electronegativity increases down the group, because of transition contraction. Electronegativity of Ga > Al.

Application of Electronegativity

(a) Metallic and non metallic nature:

Low electronegativity → Metals
High electronegativity → Non metals
Metallic character increases down the group but decreases along a period.

(b) Bond length:

$$\Delta EN \propto \frac{1}{\text{Bond length}}$$

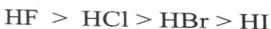
Here ΔEN = difference in electronegativities of bonded atoms

Ex. HF < HCl < HBr < HI

Note: HF has minimum bond length because of much difference in the electronegativities of H and F.

(c) **Bond energy, Strength and Thermal stability :** By increasing difference in electronegativity of bonded atoms, bond length decreases and hence bond energy increases.

$$\text{Bond energy} \propto \text{Electronegativity difference}$$



Thermal stability decreases, so acidic character increases.

(d) **Acidic strength of hydrides:** It increases with decrease in difference of electronegativity.

Order of acidic strength



(e) Nature of bonds:

According to Hanny & Smith formula

$$\text{Ionic \%} = 16(X_A - X_B) + 3.5(X_A - X_B)^2$$

Here X_A = Electronegativity of A

X_B = Electronegativity of B

Note:

If $X_A - X_B \geq 2.1$, Ionic % > 50% i.e. Ionic bond

If $X_A - X_B \leq 2.1$, Ionic % < 50% i.e. covalent bond

(f) Nature of hydroxides:

- (i) As per Gallis, In AOH, if electronegativity of A is more than 1.7 (Non metal) then it is acidic in nature.
(ii) If electronegativity of 'A' is less than 1.7 (metal) then AOH will be basic in nature.

eg.	NaOH	ClOH
X_A	0.9	3.0
Nature	Basic	Acidic

(g) Nature of oxides : Consider an oxide AO

If $X_A - X_O > 2.3$, Basic oxide

If $X_A - X_O = 2.3$, Amphoteric oxide

If $X_A - X_O < 2.3$, Acidic oxide

(i) Along a period acidic nature increases.

(ii) Down the group basic nature increases

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

$$X_A - X_O > 2.3 \quad X_A - X_O = 2.3 \quad X_A - X_O < 2.3$$

Basic Amphoteric Acidic

i.e. when in periodic table the distance between the element and oxygen increases, basic character increases.



acidic character decreases

Note: BeO, Al_2O_3 , ZnO , SnO , PbO , SnO_2 , PbO_2 , Sb_2O_3 etc. are amphoteric oxides.

CO , H_2O , NO , N_2O etc. are neutral oxides.

Acidic strength of oxide and oxyacid \propto Electronegativity

B_2O_3	CO_2	N_2O_5
EN increase, acidic nature increase.		

Order of acidic nature:

- $\text{SO}_3 > \text{SeO}_3 > \text{TeO}_3$
- $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4 > \text{H}_2\text{TeO}_4$
- $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_3 > \text{H}_2\text{TeO}_3$
- $\text{HNO}_3 > \text{H}_2\text{CO}_3 > \text{H}_3\text{BO}_3$
- $\text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{SbO}_4$
- $\text{HOF} > \text{HOCl} > \text{HOBr} > \text{HOI}$
- $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$
- $\text{N}_2\text{O}_5 > \text{P}_2\text{O}_5 > \text{As}_2\text{O}_5$
- $\text{N}_2\text{O}_3 > \text{P}_2\text{O}_3 > \text{As}_2\text{O}_3 > \text{Sb}_2\text{O}_3$

$$\text{Acidic nature} \propto \text{oxidation state}$$

Acidic properties increases with increasing oxidation state of an element

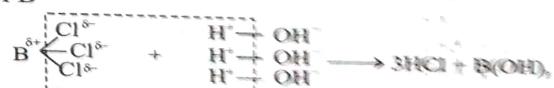
- $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$
- $\text{HNO}_3 > \text{HNO}_2$
- $\text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3$
- $\text{N}_2\text{O}_5 > \text{N}_2\text{O}_3$
- $\text{SO}_3 > \text{SO}_2$
- $\text{Sb}_2\text{O}_5 > \text{Sb}_2\text{O}_3$

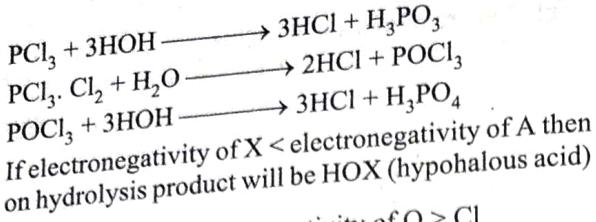
(H) Hydrolysis of AX :

Where A = Other element and X = Halogen

- (a) If electronegativity of X > Electronegativity of A then on hydrolysis product will be HX .

e.g. (BCl_3) , Electronegativity of Cl > Electronegativity of B

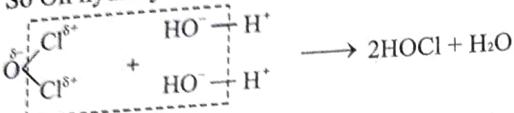




Ex. Cl_2O , Here electronegativity of O > Cl



So On hydrolysis -



(i) Nomenclature of inorganic compounds :

Prefix — less electronegative element

Suffix — More electronegative element

e.g. Cl_2O (Right), OCl_2 (Wrong)

In Dichloroxide the electronegativity of Cl is less than 'O' i.e. why Cl is in prefix position.

OF_2 - Oxygen difluoride

ICl - Iodine chloride

NH_3 -Exception (Here H is less electronegative but it is suffix)

FORMULA TO DETERMINE ELECTRONEGATIVITY

(i) Mulliken scale :

$$\text{Electronegativity} = \frac{\text{IE}_1 + \text{EA}_1}{2}$$

(ii) Pauling scale :

$$\text{Electronegativity} = \frac{\text{Mulliken scale}}{2.8}$$

(iii) Allred Roschow's Scale :

As per Roschow, electronegativity is the force by which nucleus of an atom attracts electron which are on the covalent radius.

$$(\text{X}_{\text{AR}}) \text{ Electronegativity} = \frac{0.359 Z_{\text{eff}}}{r^2}$$

r is the covalent radius in Å and Z_{eff} is the effective nuclear charge on incoming electron.

$$\text{or } X_p = X_{\text{AR}} + 0.744$$



Train Your Brain

Example 24: What is the value of Electronegativity of fluorine on the Pauling scale?

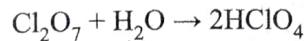
Sol. Electronegativity value of fluorine on Pauling scale is equal to 4.

Example 25: Among the all alkali metals, which element do you expect to be least electronegative?

Sol. Among the all Alkali metals Cesium (Cs) is least electronegative elements.

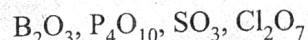
Example 26: Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

Sol. Na_2O with water forms a strong base whereas Cl_2O_7 forms strong acid.

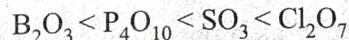


Their basic or acidic nature can be qualitatively tested with litmus paper.

Example 27: Arrange the given oxides in increasing order of acidic nature:



Sol. Acidic nature of oxide \propto non-metallic nature of element



Concept Application

29. Which of the following relation is correct ?

- (a) $2\text{IP} - \text{E.A.} - \text{EN} = 0$ (b) $2\text{EN} - \text{IP} - \text{EA} = 0$
 (c) $2\text{EA} - \text{IP} - \text{EA} = 0$ (d) $\text{EN} - \text{IP} - \text{EA} = 0$

30. Electronegativity of which of the following is high?

- (a) $-\text{CH}_3(\text{sp}^3)$ (b) $\text{H}_2\text{C} = \text{CH}_2(\text{sp}^2)$
 (c) $\text{CH} \equiv \text{CH}(\text{sp})$ (d) Equal in all

31. Which is not the correct order of electronegativity

- (a) $\text{Cl} > \text{S} > \text{P} > \text{Si}$ (b) $\text{Si} > \text{Al} > \text{Mg} > \text{Na}$
 (c) $\text{F} > \text{Cl} > \text{Br} > \text{I}$ (d) None of these

32. Which of the following acid is the strongest -

- (a) HF (b) H_2O
 (c) NH_3 (d) CH_4

PERIODIC TRENDS IN CHEMICAL PROPERTIES

The elements in the periodic table show chemical properties with striking periodicity. Here we shall discuss the periodicity of the valence state shown by elements and anomalous behaviour of the elements of the second period (from lithium to fluorine).

(a) Periodicity of Valence or Oxidation States: Valence is the most characteristic property of an element and can be understood in terms of number of electrons present in the outermost shell of the atom.

The valence electrons determine the valence or the valency of the atom. The valence of representative elements is usually equal to the number of electrons in the outermost orbitals (s and p-block elements) or equal to eight minus the number of outermost electrons as shown below.

Group	1	2	13	14	15	16	17	18
Number of Valency electron	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3,5	2,6	1,7	0,8

In contrast, transition and inner transition elements, exhibit variable valence due to involvement of not only valence electrons but d or f-electrons as well.

(ii) **Variation along a period:** Observing the number of valence electrons from left to right, it increases from 1 to 8. But the valence of element w.r.t. H or O first increases from 1 to 4 and then decreases to zero. These trends observed in the valence of element in hydrides and oxides are given below in the table.

Table: Periodic trends in valence of elements as shown by the formulas of their compounds

Group	1	2	13	14	15	16	17
Formula of hydride	LiH		B ₂ H ₆	CH ₄	NH ₃	H ₂ O	HF
NaH	CaH ₂	AlH ₃	SiH ₄	PH ₃	H ₂ S	HCl	
KH			GeH ₄	AsH ₃	H ₂ Se	HBr	
			SnH ₄	SbH ₃	H ₂ Te	HI	
Formula of oxide	Li ₂ O	MgO	B ₂ O ₃	CO ₂	N ₂ O ₅	—	
Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	P ₄ O ₆ , P ₄ O ₁₀	SO ₃	Cl ₂ O ₇	
K ₂ O	SrO	Ga ₂ O ₃	GeO ₂	As ₂ O ₃ , As ₂ O ₅	SeO ₃	—	
	BaO	In ₂ O ₃	SnO ₂	Sb ₂ O ₃ , Sb ₂ O ₅	TeO ₃	—	
			PbO ₂	Bi ₂ O ₃	—		

In the 3rd period elements from their respective oxides displaying variable valencies. The gradation observed in respect to oxygen in a regular increase upto 7. Nowadays the term oxidation state is more frequently used for valence. To clearly illustrate the concept of oxidation states, consider two oxygen-containing compounds: OF₂ and Na₂O.

The three elements (Na, O and F) involved in bonding in these compounds have the electronegativity in the decreasing order, F > O > Na. The valence shell electronic configuration of F is 1s²2s²2p⁵ and that of O is 1s²2s²2p⁴. Therefore in the formation of OF₂ molecule, each of the two F atom contributes one electron in sharing for the formation of a bond with oxygen atom while O atom shares two electrons with F atoms. F being most electronegative element, is given an oxidation state of -1 while O being less electronegative than F is given an oxidation state of +2. In Na₂O, oxygen being more electronegative accepts two electrons from Na, which has the electronic configuration 1s²2s²2p⁶3s¹, thus showing an oxidation state of -2. On the other hand, Na which loses one electron from the 3s¹ to oxygen hence, attains an oxidation state of +1.

Thus the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule.

(ii) **Variation within a group:** When we move down the group, the number of valence electrons remains the same, therefore all the elements in a group exhibit the same valency.

(b) **Anomalous Properties of Second Period Elements:** The first element of each of the groups 1 (lithium) and 2 (beryllium) and group 13-17 (boron to fluorine) differs in many respect from the other members of their respective groups. For example, lithium unlike other elements of the alkali metals and beryllium unlike other elements of the alkaline earth metals, form compounds with significantly covalent character whereas other members of their respective groups form ionic compounds.

On observation it had been found that the elements of second period have a striking similarity with the elements of the third period placed diagonally to each other, though belonging to different groups. The behaviour of lithium and beryllium is more similar to magnesium and aluminium respectively. This similarity in properties of elements placed diagonally to each other is called **diagonal relationship** in periodic properties.

For Example

Group 1 Group 2 Group 13 Group 14



The reasons attributed to the various anomalous chemical behaviour of the first member of a particular group of elements in the s and p-blocks compared to the other members of the same group are due to their (i) small size (ii) large charge/radius ratio (iii) high electronegativity of the elements.

The first member of each group has only four valence orbitals (i.e., one 2s and three 2p-orbitals) available for bonding and hence, at the maximum 8 electrons can be accommodated. Whereas the second member of these groups have nine orbitals (i.e., one 3s, three 3p, five 3d) and hence, can accommodate more than 8 electrons. As a result the maximum covalency of first member of each group is 4, e.g., boron forms [BF₄]⁻ whereas other members of the group can have maximum covalency of six, e.g., aluminium forms [AlF₆]³⁻.

Further more, the first member of p-block elements because of smaller size and higher electronegativity, displays a greater ability to form π-π multiple bonds either with itself (e.g., C = C, C ≡ C, N = N, N ≡ N) or with other elements of the second period (e.g., C = O, C = N, C ≡ N, N = O) as compared to the subsequent members of the same group.

(c) **Nature of Oxide :** The normal oxides of the elements at the extreme left of the periodic table are most basic in nature. On the other hand, the elements at the extreme right react with oxygen to form most acidic oxides. Oxides of the elements in the centre are amphoteric or neutral. For example, Na₂O is strongly basic whereas Cl₂O₇ is strongly acidic! Al₂O₃ is amphoteric while CO, NO and N₂O are neutral.

Short Notes

Periodicity

Repetition of properties after regular interval is known as periodicity and these properties are known as periodic properties.

1. Effective Atomic Number
2. Atomic Radius
3. Ionisation Potential
4. Electron Affinity
5. Electro Negativity

Atomic Radius

Distance between centre of nucleus to outermost electron.

Accurate value of atomic radius cannot be measured therefore operational definitions are used.

- (i) Covalent radius
- (ii) Metallic radius
- (iii) Vander Waals radius

Increasing order of radii: $r_{\text{cov}} < r_{\text{metallic}} < r_{\text{vw}}$

Vander wall radius mainly used for noble gases.

Factors Affecting Atomic Radius (AR)

1. AR \propto Number of shells
2. AR $\propto \frac{1}{Z_{\text{eff}}}$

Periodic Trends

1. Generally increases on moving down the group.
2. Generally decrease when we are moving left to right in the period.

Note: Atomic radius of Al > Ga : Due to poor shielding of 3d subshell electron.

Atomic radius of 4d \approx 5d series element due to the lanthanide contraction.

Lanthanide Contraction: Decrease in atomic/ionic radius with increase in atomic number of lanthanide.

Actinide Contraction: Decrease in atomic/ionic radius with increase in atomic number of actinide.

Ionic Radius



$$\begin{array}{ccc} Z_{\text{eff}} & & \\ A^+ > A > A^- & & \\ \text{Ionic radius} & A^+ < A < A^- & \end{array}$$

Factors Affecting Ionic Radius

- (+) charge $\uparrow \rightarrow$ ionic radius \downarrow
- (-) charge $\uparrow \rightarrow$ ionic radius \uparrow
- $Z_{\text{eff}} \uparrow \rightarrow$ ionic radius \downarrow
- $n \uparrow \rightarrow$ ionic radius \uparrow

\Rightarrow In isoelectronic species (+) charge \uparrow then ionic radius \downarrow
 (-) charge \uparrow then ionic radius \uparrow

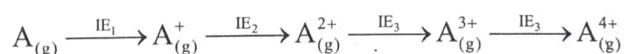
- e.g.: (i) $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$
 (ii) $K^+ > Li^+ > Mg^{2+} > Al^{3+}$

Ionization Energy (I.E.)

Energy required to remove a loosely bonded e^- from isolated gaseous atom.

Successive I.E.

I.E₁, I.E₂, combinedly termed as successive I.E.



$$IE_1 < IE_2 < IE_3 \dots$$

Factors Affecting I.E.

1. $IE \propto Z_{\text{eff}}$
2. $IE \propto \frac{1}{\text{size}}$
3. $IE \propto (+) \text{ charge}$,
4. $IE \propto \frac{1}{(-) \text{ charge}}$
5. Half filled and full filled configuration (affected upto 4th period)
6. Nature of subshell (affected upto 4th period)

Periodic Trend (s & p-Block)

1. Generally decrease on moving down the group
2. Generally increase when we are moving left to right in the period.

Note:

- ❖ upto 4th period (ionization energy)
 $ns^1 < np^1 < ns^2 < np^2 < np^4 < np^3 < np^5 < np^6$

Note:

- ❖ after 4th period (ionization Energy)
 - (a) $ns^1 < ns^2 < np^1 < np^2 < np^3 < np^4 < np^5 < np^6$
 - (b) Al < Ga (Poor shielding of 3d subshell e^-)
 - (c) Tl > In
 $Pb > Sn$ {due to lanthanide contraction}

Periodic Trend (d-block)

1. Generally increases on moving down the group
2. Generally increase when moving left to right in the period.
 $Sc > Y > La, Ag < Cu < Au, Cd < Zn < Hg$

Application of Ionization Energy

- $\text{IE} \uparrow \rightarrow$ Metallic Character \downarrow
- $\text{IE} \uparrow \rightarrow$ Electropositive Character \downarrow
- $\text{IE} \uparrow \rightarrow$ Reducing Property \downarrow

Note: Number of valence e⁻ = highest jump in successive IE

e.g.: $\text{IE}_1 < \text{IE}_2 < \text{IE}_3 < < < \text{IE}_4 < \text{IE}_5$

Highest jump between IE_3 & IE_4 therefore Valence electron is 3

Electron Affinity & Electron Gain Enthalpy

Electron affinity	Electron gain enthalpy
$\text{A}_{(g)} \xrightarrow{\text{EA}} \text{A}_{(g)}^-$	$\text{A}_{(g)}^- + \text{e}^- \longrightarrow \text{A}^-$
amount of energy released when an e ⁻ is added to isolated gaseous atom.	Change in enthalpy when an e ⁻ is added to isolated gaseous atom.
	$\Delta H_{eg} = H_p - H_R$

Successive Electron Affinity



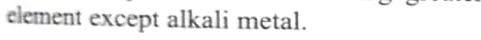
EA_1 is generally exothermic except N, Be, Mg and Noble gases.
 $\text{EA}_2, \text{EA}_3, \dots$ always endothermic

Factors Affecting

1. $\text{EA} \propto Z_{\text{eff}}$
2. $\text{EA} \propto \frac{1}{\text{size}}$
3. Nature of subshell
4. Half and full filled

Periodic Trend

1. Generally decreases on moving down the group
 2. Generally increase when moving left to right in the period.
- Note: IIIrd period element having greater EA than IInd period element except alkali metal.



Note: $|\text{IE}_A| = |\text{EA}_A|$ and $|\text{EA}_A| = |\text{IE}_A|$

Electronegativity

Tendency to attract shared pair of e⁻ towards itself in covalent bonds.

Factors Affecting

1. E.N. $\propto Z_{\text{eff}}$
2. E.N. $\propto \frac{1}{\text{size}}$
3. E.N. $\propto \frac{1}{(-) \text{ charge}}$
4. E.N. $\propto (+) \text{ charge}$,
5. E.N. $\propto \% \text{ s-characters of hybrid orbital}$

Periodic Trend

1. Generally decreases on moving down the group
2. Generally increase when moving left to right in the period.



Application of Electronegative

1. Polarity of bond
 $\Delta \text{E.N.} = 0$; non-polar bond
 $\Delta \text{E.N.} \neq 0$; polar bond
2. Bond parameter
 $\Delta \text{E.N.} \uparrow \rightarrow$ Ionic character \uparrow
 $\Delta \text{E.N.} \uparrow \rightarrow$ bond length \downarrow
 $\Delta \text{E.N.} \uparrow \rightarrow$ bond strength \uparrow
3. Nature of oxide & oxyacid
If E.N. of central atom increase, then acidic character of oxide and oxyacid increases.

Some Important Increasing Order

1. Abundance of Elements
 - (i) Elements on earth crust - Fe, Al, Si, O
 - (ii) Metals on earth crust - Ca, Fe, Al
 - (iii) Non-metals - Si, O
In atmosphere - O, N
In universe - He, Si, H
2. Atomic / Ionic Size
 - (i) $\text{Mg}^{2+}, \text{Na}^+, \text{F}^-, \text{O}^{2-}, \text{N}^{3-}$ (Hint: Isoelectronic series)
 - (ii) $\text{Ca}^{2+}, \text{Ar}, \text{Cl}^-, \text{S}^{2-}$
 - (iii) O, C, S, Se
 - (iv) B, Be, Li, Na
 - (v) F, O, F⁻, O²⁻
3. Ionization Energy
 - (i) Na, Al, Mg, Si
 - (ii) Li, B, Be, C, O, N, F, Ne, He (Ist I.P.)
 - (iii) Be, C, B, N, F, O, Ne, He, Li (IInd I.P.)
4. Electron Affinity
 - (i) I, Br, F, Cl
 - (ii) Cu, Ag, Au (EA of Au is very high = 222 kJ mol⁻¹)
 - (iii) O, S, F, Cl
 - (iv) N, P, O, S
5. Electronegativity
 - (i) As, P, S, Cl
 - (ii) I, Br, Cl, F
 - (iii) C, N, O, F
6. Hydration of Ions/Hydration Energy
 - (i) $\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Be}^{2+}$
 - (ii) $\text{Cs}^+, \text{Rb}^+, \text{K}^+, \text{Na}^+, \text{Li}^+$
 - (iii) $\text{Na}^+, \text{Mg}^{2+}, \text{Al}^{3+}$
7. Ionic Radii in water
 - (i) $\text{Cs}^+, \text{Rb}^+, \text{K}^+, \text{Na}^+, \text{Li}^+$
 - (ii) $\text{Li}^+, \text{Be}^{2+}$
 - (iii) $\text{Na}^+, \text{Mg}^{2+}, \text{Al}^{3+}$
8. Molar Conductivity in Water
 $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$

Solved Examples

1. Elements A, B, C, D and E have the following electronic configurations :

A : $1s^2 2s^2 2p^1$ B : $1s^2 2s^2 2p^6 3s^2 3p^1$
 C : $1s^2 2s^2 2p^6 3s^2 3p^3$ D : $1s^2 2s^2 2p^6 3s^2 3p^5$
 E : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Which among these will belong to the same group in the periodic table?

Sol. Out of these, elements A and B will belong to the same group of the periodic table because they have same outer electronic configuration, $ns^2 np^1$.

2. Select from each group the species which has the smallest radius stating appropriate reason.

(a) O, O^- , O^{2-} (b) P^{3+} , P^{4+} , P^{5+}

Sol. (a) O is having smallest radius. Anion is larger than its parent atom. Also the anion of the same atom with higher negative charge is bigger in size as compared to anion with smaller negative charge as proton to electron ratio decreases thus attraction between valence shell electrons and nucleus decreases. Hence electron cloud expands.

(b) The ionic radius decreases as more electrons are ionized off that is as the valency increases. So the correct order is $P^{5+} < P^{4+} < P^{3+}$.

3. Mg^{2+} is smaller than O^{2-} in size, though both have same electronic configuration. Explain?

Sol. Mg^{2+} and O^{2-} both are isoelectronic i.e., have same number of electrons. But Mg^{2+} having 12 protons in its nucleus exerts higher effective nuclear charge than O^{2-} having 8 protons and thus valence shell as well as inner shells electrons are more strongly attracted by the nucleus in Mg^{2+} resulting smaller size than O^{2-} .

4. From each set, choose the atom which has the largest ionization enthalpy and explain your answer with suitable reasons.

(a) F, O, N (b) Mg, P, Ar

Sol. (a) Fluorine (F) has the largest ionization enthalpy because in moving from left to right in a period, atomic size decreases and electrons are held more tightly. Since F has the smallest size and maximum nuclear charge. It has the largest ionization enthalpy among these elements.

(b) Argon (Ar) has the largest ionization enthalpy as argon has extra stable fully filled configuration.

5. First and second ionisation energies of magnesium are 7.646 eV and 15.035 eV respectively. The amount of energy in kJ needed to convert all the atoms of magnesium into Mg^{2+} ions present in 12 mg of magnesium vapour will be? [Given 1 eV = 96.5 kJ mol⁻¹].

- Sol.** Total energy needed to convert one Mg atom into Mg^{2+} gas ion,

$$= IE_1 + IE_{II} = 22.681 \text{ eV} = 2188.6 \text{ kJ mol}^{-1}$$

$$\Rightarrow 12 \text{ mg of Mg} = 0.5 \times 10^{-3} \text{ mole.}$$

$$\therefore \text{Total energy} = 0.5 \times 10^{-3} \times 2188.6 = 1.0943 \text{ kJ}$$

6. $M(g) \rightarrow M^+(g) + e^- ; \Delta H = 100 \text{ eV.}$

- $M(g) \rightarrow M^{2+}(g) + 2e^- ; \Delta H = 250 \text{ eV.}$

Which is/are correct statement(s)?

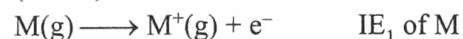
(a) IE_1 of $M(g)$ is 100 eV

(b) IE_1 of $M^+(g)$ is 150 eV.

(c) IE_2 of $M(g)$ is 250 eV.

(d) IE_2 of $M(g)$ is 150 eV.

- Sol.** (a, b, c)



7. Consider the elements N, P, O and S and arrange them in order of increasing negative electron gain enthalpy.

Sol. Order of increasing negative electron gain enthalpy is $N < P < O < S$. For detail refer text.

8. Why do halogens have high electron gain enthalpies (i.e. $-\Delta_{eg} H^\ominus$)?

Sol. The valence shell electronic configuration of halogens is $ns^2 np^5$ and thus they require one electron to acquire the stable noble gas configuration $ns^2 np^6$. Because of this they have strong tendency to accept an additional electron and hence have high electron gain enthalpies.

9. Following are the valence shell electronic configurations of some elements.

(i) $3s^2 3p^5$ (ii) $3d^{10} 4s^2$

(iii) $2s^2 3p^6 4s^1$ (iv) $1s^2 2s^2$

Find out the blocks to which they belong in the periodic table?

- Sol.** (i) p-block (ii) d-block (iii) s-block (iv) s-block

The block of the elements depend on the type of sub-shell which receive the last electron. In case of (i) it enters in 3p-subshell, (ii) it enters 3d-subshell, (iii) it enters 4s-subshell and (iv) it enters 2s-subshell.

10. Arrange the following ions in the increasing order of their size : Be^{2+} , Cl^- , S^{2-} , Na^+ , Mg^{2+} , Br^- ?

- Sol.** $Be^{2+} < Mg^{2+} < Na^+ < Cl^- < S^{2-} < Br^-$

Be^{2+} is smaller than Mg^{2+} as Be^{2+} has one shell where as Mg^{2+} has two shells.

Mg^{2+} and Na^+ are isoelectronic species: Ionic radius $\propto 1/\text{nuclear charge}$.

Cl^- and S^{2-} are isoelectronic species : Ionic radius $\propto 1/\text{nuclear charge}$.

Cl^- is smaller than Br^- as Cl^- has three shells where as Br^- has four shells.

Exercise-1 (Topicwise)

PERIODIC TABLE

- PERIODIC TABLE**

 - Three element X, Y, Z are following Doberiner's Triad rule.
If the atomic weight of X and Y are 10 and 26 respectively, then atomic weight of Z will be

(a) 34	(b) 40
(c) 42	(d) 18
 - If Aufbau rule is not followed, K ($Z = 19$) will be placed in _____ block.

(a) s	(b) p
(c) d	(d) f
 - In the general electronic configuration - $(n - 2)f^{l-1}4d^1(n - 1)d^{0-1}ns^2$, if value of n = 7 the configuration will be

(a) Lanthanoides	(b) Actinoides
(c) Transition elements	(d) None of these
 - Given atomic number 15, 33, 51 represents the following family -

(a) Carbon family	(b) Nitrogen family
(c) Oxygen family	(d) None of these
 - Which of the following elements never has an oxidation state of +1?

(a) F	(b) Cl
(c) Br	(d) I

Atomic Size, Z_{eff}

I	II	III
(a) Na^+	Be	Li^+
(b) O^{2-}	Li	H^-
(c) F^-	Na	He
(d) Na^+	Be	He

9. The ionic radii of N^{3-} , O^{2-} and F^- are respectively given by
 (a) 1.36, 1.40, 1.71 (b) 1.36, 1.71, 1.40
 (c) 1.71, 1.40, 1.36 (d) 1.71, 1.36, 1.40

10. Arrange the following element in increasing order of atomic radii:
 (a) $\text{Na} < \text{K} < \text{Mg} < \text{Rb}$ (b) $\text{K} < \text{Na} < \text{Mg} < \text{Rb}$
 (c) $\text{Mg} < \text{Na} < \text{K} < \text{Rb}$ (d) $\text{Rb} < \text{K} < \text{Mg} < \text{Na}$

11. Which of following is arranged in decreasing order of size?
 (a) $\text{Mg}^{2+} > \text{Al}^{3+} > \text{O}^{2-}$ (b) $\text{O}^{2-} > \text{Mg}^{2+} > \text{Al}^{3+}$
 (c) $\text{Al}^{3+} > \text{Mg}^{2+} > \text{O}^{2-}$ (d) $\text{Al}^{3+} > \text{O}^{2-} > \text{Mg}^{2+}$

12. In which of the following compounds, manganese show maximum radius?
 (a) MnO_2 (b) KMnO_4
 (c) MnO (d) $\text{K}_3[\text{Mn}(\text{CN})_6]$

13. The correct order of atomic size would be
 (a) $\text{Ni} < \text{Pd} = \text{Pt}$ (b) $\text{Pd} < \text{Pt} < \text{Ni}$
 (c) $\text{Pt} > \text{Ni} > \text{Pd}$ (d) $\text{Pd} > \text{Pt} > \text{Ni}$

14. Choose incorrect option regarding atomic size.
 (a) $\text{Zr} \approx \text{Hf}$ (b) $\text{Fe} \approx \text{Co} \approx \text{Ni}$
 (c) $\text{Y} \approx \text{La}$ (d) All of the above

15. If the ionic radii of K^+ and F^- are nearly the same (i.e., 1.34\AA), then the atomic radii of K and F respectively are:
 (a) $1.34\text{\AA}, 1.34\text{\AA}$ (b) $0.72\text{\AA}, 1.96\text{\AA}$
 (c) $1.96\text{\AA}, 0.72\text{\AA}$ (d) $1.96\text{\AA}, 1.34\text{\AA}$

16. In which of the following pairs, atomic size of second atom is larger than the first one?
 (a) Br, Cl (b) Na, Mg
 (c) Sr, Ca (d) N, P

17. Which of the following configuration of atom has largest radius?
 (a) $1s^2 2s^2 2p^6 3s^2$ (b) $1s^2 2s^2 2p^6 3s^2 3p^1$
 (c) $1s^2 2s^2 2p^6 3s^2 3p^3$ (d) $1s^2 2s^2 2p^6 3s^2 3p^5$

18. Which of the following sequences is correct for decreasing order of ionic radius?
 (a) $\text{Se}^{2-} > \text{I}^- > \text{Br}^- > \text{O}^{2-} > \text{F}^-$
 (b) $\text{I}^- > \text{Se}^{2-} > \text{O}^{2-} > \text{Br}^- > \text{F}^-$
 (c) $\text{Se}^{2-} > \text{I}^- > \text{Br}^- > \text{F}^- > \text{O}^{2-}$
 (d) $\text{I}^- > \text{Se}^{2-} > \text{Br}^- > \text{O}^{2-} > \text{F}^-$

19. The maximum tendency to form unipositive ion is for the element with the electronic configuration-
- $1s^2 2s^2 2p^6 3s^2$
 - $1s^2 2s^2 2p^6 3s^2 3p^1$
 - $1s^2 2s^2 2p^6 3s^2 3p^2$
 - $1s^2 2s^2 2p^6 3s^2 3p^3$
20. If internuclear distance between Cl atoms in Cl_2 is 10 Å & between H atoms in H_2 is 2 Å, then calculate internuclear distance between H & Cl (Electronegativity of H = 2.1 & Cl = 3.0).
- 5.919 Å
 - 6.9 Å
 - 7.919 Å
 - 4.91 Å
21. Which of the following is increasing order of paramagnetism?
- $Al < Mg < O < N$
 - $Mg < Al < N < O$
 - $Mg < Al < O < N$
 - $N < O < Al < Mg$
22. Lanthanide contraction can explain
- Atomic number of the series
 - Number of extra nuclear electrons
 - Density of the series
 - Ionic radius of series

Ionisation Energy (Ionisation Enthalpy)

23. Which of the following element has highest ionisation energy?
- Oxygen
 - Nitrogen
 - Fluorine
 - Helium
24. The correct order of stability of Al^+ , Al^{2+} , Al^{3+} is-
- $Al^{3+} > Al^{2+} > Al^+$
 - $Al^{2+} > Al^{3+} > Al^+$
 - $Al^{2+} < Al^+ > Al^{3+}$
 - $Al^{3+} > Al^+ > Al^{2+}$
25. IP_1 and IP_2 of Mg are 178 and 348 Kcal mol⁻¹. The enthalpy required for the reaction, $Mg \rightarrow Mg^{2+} + 2e^-$ is
- + 170 Kcal
 - + 526 Kcal
 - 170 Kcal
 - 526 Kcal
26. The order of first ionization enthalpies of the elements Li, Be, B, Na is
- $Li > Be > B > Na$
 - $Be > B > Li > Na$
 - $Na > Li > B > Be$
 - $Be > Li > B > Na$
27. Successive ionization energies of an element 'X' are given below (in KCal):
- | IP_1 | IP_2 | IP_3 | IP_4 |
|--------|--------|--------|--------|
| 165 | 195 | 556 | 595 |

Electronic configuration of the element 'X' is

- $1s^2 2s^2 2p^6 3s^2 3p^2$
- $1s^2 2s^1$
- $1s^2 2s^2 2p^2$
- $1s^2 2s^2 2p^6 3s^2$

28. Which represents alkali metals (i.e. 1st group metals) based on IE_1 and IE_2 values (in kJ/mol)?
- | | IE_1 | IE_2 |
|-------|--------|--------|
| (a) X | 500 | 1000 |
| (b) Y | 600 | 2000 |
| (c) Z | 550 | 7500 |
| (d) M | 700 | 1400 |

29. First, second and third IP values are 100eV, 150eV and 1500eV. Element can be -
- Be
 - B
 - F
 - Na
30. The correct values of ionization enthalpies (in kJ mol⁻¹) of Si, P, Cl and S respectively are -
- 786, 1012, 999, 1256
 - 1012, 786, 999, 1256
 - 786, 1012, 1256, 999
 - 786, 999, 1012, 1256
31. Consider the following changes -
 $A \rightarrow A^+ + e^- : E_1$ and $A^+ \rightarrow A^{2+} + e^- : E_2$
The energy required to pull out the two electrons are E_1 and E_2 respectively. The correct relationship between two energies would be
- $E_1 < E_2$
 - $E_1 = E_2$
 - $E_1 > E_2$
 - $E_1 \geq E_2$

Electron Affinity (Electron gain Enthalpy)

32. Which of the following conversion is exothermic?
- $Na \rightarrow Na^+$
 - $Li \rightarrow Li^-$
 - $N \rightarrow N^-$
 - $O \rightarrow O^{2-}$
33. Correct order of electron affinity is:
- $S > P$
 - $S < P$
 - $N > P$
 - $O > S$
34. Among O, O^+ , O^{2+} and O^{2-} , the species having most positive and most negative value of ΔH_{eg} are, respectively
- O^+ and O
 - O^{2+} and O^{2-}
 - O and O^{2-}
 - O^{2-} and O^{2+}
35. Of the following elements, which possess the highest electron affinity?
- As
 - O
 - S
 - Se
36. Increasing order of electron affinity for the following configuration.
- | | |
|-------------------------------|-------------------------------|
| A. $1s^2 2s^2 2p^3$ | B. $1s^2 2s^2 2p^4$ |
| C. $1s^2 2s^2 2p^6 3s^2 3p^3$ | D. $1s^2 2s^2 2p^6 3s^2 3p^4$ |
- $A < D < B < C$
 - $D < A < C < B$
 - $A < B < C < D$
 - $A < B < D < C$
37. Which of the following elements has/have electron affinity greater than S?
- O
 - Se
 - Te
 - None of these
38. Which of the following process is endothermic?
- $Cl \rightarrow Cl^-$
 - $P \rightarrow P^-$
 - $N \rightarrow N^-$
 - $C \rightarrow C^-$
39. Which of the following configuration will have least electron affinity?
- $ns^2 np^5$
 - $ns^2 np^2$
 - $ns^2 np^3$
 - $ns^2 np^4$

40. Second electron affinity of an element is

- (a) Always exothermic
- (b) Endothermic for few elements
- (c) Exothermic for few elements
- (d) Always endothermic

41. Which of the following element is expected to have highest electron gain enthalpy?

- (a) $1s^2 2s^2 2p^6 3s^2 3p^5$
- (b) $1s^2 2s^2 2p^3$
- (c) $1s^2 2s^2 2p^4$
- (d) $1s^2 2s^2 2p^5$

Electronegativity and its Application

42. Electronegativity of the following elements increases in the order -

- (a) O < N < S < P
- (b) P < S < N < O
- (c) P < N < S < O
- (d) S < P < N < O

43. Which of the following statement is incorrect?

- (a) An element which has high electronegativity always has high electron gain enthalpy.
- (b) Electron gain enthalpy is the property of an isolated atom.
- (c) Electronegativity is the property of a bonded atom.
- (d) Both electronegativity and electron gain enthalpy are usually directly related to nuclear charge and inversely related to atomic size.

44. Which of the following statement is not true?

- (a) F atom can hold additional electron more tightly than Cl atom.
- (b) Cl atom can hold additional electron more tightly than F atom.
- (c) The incoming electron encounters greater repulsion for F atom than for Cl atom.
- (d) It is easier to remove an electron from F^- than Cl^- .

45. Which of the following is most electronegative element?

- (a) Li
- (b) Mg
- (c) H
- (d) Na

46. The correct order of electronegativity on Pauling scale is:

- (a) F > Cl > O > S
- (b) Li > Na > K > Rb > Cs
- (c) Be < B < N < C
- (d) Both (a) and (b)

47. The order in which the following oxides are arranged according to decreasing basic nature is-

- (a) $Na_2O > MgO > Al_2O_3 > SiO_2$
- (b) $SiO_2 > Al_2O_3 > MgO > Na_2O$
- (c) $Al_2O_3 > SiO_2 > MgO > Na_2O$
- (d) $SiO_2 > MgO > Na_2O > Al_2O_3$

48. Which of the following is most acidic oxide?

- (a) MnO
- (b) MnO_2
- (c) Mn_2O_7
- (d) Mn_3O_4

49. Which of the following is an amphoteric oxide?

- (a) SnO
- (b) V_2O_5
- (c) Cr_2O_3
- (d) All of these



Exercise-2 (Learning Plus)

1. Which of the following is not an actinoid?

- (a) Curium ($Z = 96$)
- (b) Californium ($Z = 98$)
- (c) Uranium ($Z = 92$)
- (d) Terbium ($Z = 65$)

2. The period number in the long form of the periodic table is equal to:

- (a) Magnetic quantum number of any element of the period.
- (b) Atomic number of any element of the period.
- (c) Maximum principal quantum number of any element of the period.
- (d) Maximum azimuthal quantum number of any element of the period.

3. Which one of the following statements related to the modern periodic table is incorrect?

- (a) The p-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a p-subshell.
- (b) The d-block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a d-subshell.

(c) Each block contains a number of columns equal to the number of electrons that can occupy that subshell.

(d) The block indicates value of azimuthal quantum number (ℓ) for the last subshell that received electrons in building up the electronic configuration.

4. The elements in which electrons are progressively filled in 4f-orbital are called :

- (a) actinoids
- (b) transition elements
- (c) lanthanoids
- (d) halogens

5. Which of the following statements is not correct regarding hydrogen?

- (a) It resembles halogens in some properties.
- (b) It resembles alkali metals in some properties.
- (c) It can be placed in 17th group of modern periodic table.
- (d) It cannot be placed in 1st group of modern periodic table.

Column-I		Column-II	
A.	Mg ²⁺	p.	1.19 Å
B.	O ²⁻	q.	0.72 Å
C.	Na ⁺	r.	1.16 Å
D.	F ⁻	s.	1.26 Å

- (a) A → r; B → p; C → q; D → s
 (b) A → q; B → s; C → p; D → r
 (c) A → q; B → s; C → r; D → p
 (d) A → s; B → q; C → r; D → p

18. Arrange in the increasing order of atomic radii of the following elements: O, C, F, Cl, Br
 (a) F < O < C < Cl < Br
 (b) F < C < O < Cl < Br
 (c) F < Cl < Br < O < C
 (d) C < O < F < Cl < Br

19. Which group of atoms have nearly same atomic radius?
 (a) Na, K, Rb, Cs
 (b) Li, Be, B, C
 (c) Fe, Co, Ni
 (d) F, Cl, Br, I

20. Which of the following transitions involves maximum amount of energy?
 (a) $M^-(g) \rightarrow M(g)$ (b) $M(g) \rightarrow M^+(g)$
 (c) $M^+(g) \rightarrow M^{2+}(g)$ (d) $M^{2+}(g) \rightarrow M^{3+}(g)$

21. From the given information of element M:
 $M(g) \rightarrow M^{3+}(g) + 3e^-$, $\Delta H = x \text{ kJ/mol}$
 $IE_1(M) = y \text{ kJ/mol}$, $IE_1(M^{2+}) = z \text{ kJ/mol}$
 The value of $IE_2(M)$ will be
 (a) $(x + y + z)\text{kJ/mol}$ (b) $(x - y - z)\text{kJ/mol}$
 (c) $(x - y + z)\text{kJ/mol}$ (d) $z - (x + y)\text{kJ/mol}$

22. Match the elements with their corresponding IE_1 .

Column-I		Column-II (relative values)	
A.	N	p.	+800 kJ/mol
B.	O	q.	+900 kJ/mol
C.	Be	r.	+1300 kJ/mol
D.	B	s.	+1400 kJ/mol

- (a) $A \rightarrow q$; $B \rightarrow r$; $C \rightarrow p$; $D \rightarrow s$
 (b) $A \rightarrow p$; $B \rightarrow q$; $C \rightarrow r$; $D \rightarrow s$
 (c) $A \rightarrow s$; $B \rightarrow r$; $C \rightarrow q$; $D \rightarrow p$
 (d) $A \rightarrow p$; $B \rightarrow s$; $C \rightarrow q$; $D \rightarrow r$

23. Choose the correct order of ionization energy for the following species.

(a) $Sc > La > Y$	(b) $Sc > Y = La$
(c) $Sc > Y > La$	(d) $Sc < Y > La$

- 24. Assertion:** The first ionization energy of Be is greater than that of B.
Reason: 2p orbital is lower in energy than 2s orbital.
- Both assertion and reason are true and reason is the correct explanation of assertion.
 - Both assertion and reason are true but reason is not correct explanation of Assertion.
 - Assertion is true but reason is false.
 - Assertion is false but reason is true.
- 25.** The set representing the correct order of first ionization potential is:
- $K > Na > Li$
 - $Be > Mg > Ca$
 - $B > C > N$
 - $Ge > Si > C$
- 26.** Which of the following relation is correct with respect to first (I) and second (II) ionization enthalpies of potassium and calcium?
- $I_{Ca} > II_K$
 - $I_K > I_{Ca}$
 - $II_{Ca} > II_K$
 - $II_K > II_{Ca}$
- 27.** Which of the following is the correct order of ionisation enthalpy ?
- | | |
|-----------------|------------------|
| (I) $Be^+ > Be$ | (II) $Be > Be^+$ |
| (III) $C > Be$ | (IV) $B > Be$ |
| (a) II, III | (b) III, IV |
| (c) I, III | (d) I, IV |
- 28.** The decreasing order of the ionization potential of the following elements is -
- $Ne > Cl > P > S > Al > Mg$
 - $Ne > Cl > P > S > Mg > Al$
 - $Ne > Cl > S > P > Mg > Al$
 - $Ne > Cl > S > P > Al > Mg$
- 29.** Mg forms Mg(II) because of -
- The oxidation state of Mg is +2.
 - Difference between I.P₁ and I.P₂ is greater than 16.0 eV.
 - There are only two electrons in the outermost energy level of Mg.
 - Difference between I.P₁ and I.P₂ is less than 11 eV.
- 30.** The correct order of second I.E. of C, N, O and F are in the order:
- $F > O > N > C$
 - $C > N > O > F$
 - $O > N > F > C$
 - $O > F > N > C$
- 31.** Electronic configurations of four elements A, B, C and D are given below :
- $1s^2 2s^2 2p^6$
 - $1s^2 2s^2 2p^4$
 - $1s^2 2s^2 2p^6 3s^1$
 - $1s^2 2s^2 2p^5$
- Which of the following is the correct order of increasing tendency to gain electron:
- (i) < (iii) < (ii) < (iv)
 - (i) < (ii) < (iii) < (iv)
 - (iv) < (ii) < (iii) < (i)
 - (iv) < (i) < (ii) < (iii)
- 32.** The formation of the oxide ion $O^{2-}(g)$ requires first an exothermic and then an endothermic step as shown below:
 $O(g) + e^- \rightarrow O^-(g); \Delta H = -142 \text{ kJ mol}^{-1}$
 $O^-(g) + e^- \rightarrow O^{2-}(g); \Delta H = 884 \text{ kJ mol}^{-1}$
This is because:
- O^- ion has comparatively larger size than oxygen atom.
 - Oxygen has high electron affinity.
 - O^- ion will tend to resist the addition of another electron.
 - Oxygen is more electronegative.
- 33.** Which of the given anion is highly unstable?
- F^-
 - O^-
 - Be^-
 - Cl^-
- 34.** In which of the following processes, energy is absorbed?
- $Cl + e^- \rightarrow Cl^-$
 - $O^- + e^- \rightarrow O^{2-}$
 - $O^{2-} - e^- \rightarrow O^-$
 - $Na^+ + e^- \rightarrow Na$
- 35.** Which of the following processes is endothermic?
- $S \rightarrow S^-$
 - $S^- \rightarrow S^{2-}$
 - $Na \rightarrow Na^-$
 - $P \rightarrow P^-$
- 36.** Which of the following processes is exothermic?
- $N^- \rightarrow N$
 - $N \rightarrow N^+$
 - $N \rightarrow N^-$
 - $N^+ \rightarrow N^{2+}$
- 37.** The correct electron affinity order among the following is
- $F > Cl$
 - $Cl > F$
 - $S < P$
 - $N > O$
- 38.** Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species ?
- $Cl < F < S < O$
 - $O < S < F < Cl$
 - $S < O < Cl < F$
 - $F < Cl < O < S$
- 39.** The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be :
- 2.55 eV
 - 5.1 eV
 - 10.2 eV
 - +2.55 eV
- 40.** Which of the following statement is correct ?
- Electron gain enthalpy may be positive for some elements.
 - Second electron gain enthalpy always remains positive for all the elements.
 - $\Delta_{eg}H(K^+) = -IE(K)$
 - All of these
- 41.** Choose the correct order of the property given below:
- $N^{3-} < O^{2-}$: Ionic radius
 - $N > O$: First ionization energy
 - $N > O$: Second ionization energy
 - $N > O$: Electron affinity order

42. Which of the following is affected by the stable electronic configuration of an atom?

 - Electronegativity
 - Ionisation enthalpy
 - Electron gain enthalpy

Correct answer is:

 - Only electronegativity
 - Only ionisation enthalpy
 - Both electron gain enthalpy and ionisation enthalpy
 - All of the above

43. The correct set of decreasing order of electronegativity is -

 - Li, H, Na
 - Na, H, Li
 - H, Li, Na
 - Li, Na, H

44. Which of the following given properties is wrong?

 - $\text{Li} > \text{Na} > \text{K}$ (Ionisation energy)
 - $\text{Li} < \text{Na} < \text{K}$ (Atomic size)
 - $\text{Li}_2\text{O} < \text{Na}_2\text{O} < \text{K}_2\text{O}$ (Acidic nature)
 - All of these

45. Considering the elements B, Al, Mg and K, the correct order of their metallic character is :

 - $\text{B} > \text{Al} > \text{Mg} > \text{K}$
 - $\text{Al} > \text{Mg} > \text{B} > \text{K}$
 - $\text{Mg} > \text{Al} > \text{K} > \text{B}$
 - $\text{K} > \text{Mg} > \text{Al} > \text{B}$

46. Which of the following is different from other three oxides?

 - MgO
 - SnO
 - ZnO
 - PbO

47. Which of the following compound is most acidic?

 - Cl_2O_7
 - P_4O_{10}
 - SO_3
 - B_2O_3

48. Which of the following order is wrong?

 - $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 \Rightarrow$ Acidic character
 - $\text{Li} < \text{Be} < \text{B} < \text{C} \Rightarrow \text{IE}_1$
 - $\text{Al}_2\text{O}_3 < \text{MgO} < \text{Na}_2\text{O} < \text{K}_2\text{O} \Rightarrow$ Basic character
 - $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+ \Rightarrow$ Ionic radius

49. Choose the incorrect order for acidic strength.

 - $\text{CO}_2 > \text{CO}$
 - $\text{SO}_2 < \text{SO}_3$
 - $\text{HClO}_2 > \text{HOCl}$
 - $\text{SiO}_2 > \text{CO}_2$

Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

- Which of the following is/are correct regarding oxidation state of elements in their compounds?
 - All d-Block elements show multiple oxidation state.
 - All p-Block elements show multiple oxidation state.
 - All s-Block elements show single oxidation state.
 - Some of 18 group elements can show multiple oxidation states.
 - Which of the following compounds are found to exist (General formula obtaining)?
 - MgF
 - Cu_2Cl_2
 - NaF_2
 - K_2O
 - Which of the following show non-zero multiple oxidation state?
 - S
 - O
 - Zn
 - H
 - Which of the following elements have their lower oxidation state more stable oxidation state than higher ones?
 - O
 - Pb
 - Tl
 - Bi
 - Which of the following have greater Z_{eff} than Zn?
 - Cu^+
 - Cu^{2+}
 - Fe^{3+}
 - Zn^{2+}

6. Which of the following orders is(are) correct for size?

 - $\text{Al} \approx \text{Ga}$
 - $\text{Te}^{2-} > \text{I}^- > \text{Cs}^+ > \text{Ba}^{2+}$
 - $\text{Cr}^{3+} < \text{Cr}^{6+}$
 - $\text{Pd} \approx \text{Pt}$

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

 - H^-
 - Cl^-
 - Br^-
 - I^-

8. Which of the following statements is/are correct?

 - The second ionization enthalpy of oxygen element is greater than that of fluorine element.
 - The third ionization enthalpy of phosphorus is greater than that of aluminium.
 - The first ionization enthalpy of aluminium is slightly greater than that of gallium.
 - The second ionization enthalpy of copper is greater than that of zinc.

9. Choose the correct statement among the following:

 - $\text{IE}_1(\text{Na}) < \text{IE}_1(\text{Mg})$
 - $\text{IE}_3(\text{Mg}) > \text{IE}_3(\text{Al})$
 - $\text{IE}_1(\text{Al}) < \text{IE}_1(\text{Mg})$
 - $\text{IE}_2(\text{N}) > \text{IE}_2(\text{O})$

10. Choose the correct ionization energy order for the given species:

 - $\text{O} > \text{S} > \text{S}^- > \text{O}^-$
 - $\text{F} > \text{F}^- > \text{Cl}^- > \text{Cl}$
 - $\text{O} > \text{O}^- > \text{S}^- > \text{S}$
 - $\text{F} > \text{Cl} > \text{Cl}^- > \text{F}^-$

- 11.** Those elements impart colour to the flame on heating in it, the atoms of which require low energy for the ionisation (i.e. absorb energy in the visible region of spectrum). The elements of which of the following groups in modern periodic table will impart colour to the flame?
- (a) 2 (b) 13
(c) 1 (d) 17
- 12.** Choose the correct statements:
- (a) In general, more the ionisation energy more will be the electronegativity.
(b) Electronegativity increase means metallic character also increases.
(c) In general, lower will be the ionisation energy, easier will be to remove outer electron.
(d) Electron affinity of S is less than that of Cl.
- 13.** Which of the following elements have electron affinity greater than O?
- (a) F (b) S
(c) Se (d) Cl
- 14.** Correct order of electron affinity is/are:
- (a) S > O (b) Al > B
(c) Mg > Na (d) P > N
- 15.** In which of the following options order of arrangement does not agree with the variation of property indicated against it?
- (a) $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$ (increasing ionic size)
(b) B < C < N < O (increasing first ionisation enthalpy)
(c) I < Br < Cl < F (increasing electron gain enthalpy)
(d) Li < Na < K < Rb (increasing metallic radius)
- 16.** Which of the following match is/are correct regarding B, Al, C and S elements?
- (a) The highest first ionisation enthalpy : C
(b) The largest atomic size : Al
(c) The most negative electron gain enthalpy : C
(d) The most metallic character : Al
- 17.** Which of the following show amphoteric behaviour?
- (a) $\text{Zn}(\text{OH})_2$ (b) $\text{Be}(\text{OH})_2$
(c) $\text{Al}(\text{OH})_3$ (d) $\text{Pb}(\text{OH})_2$

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 18 to 24): The minimum amount of energy required to remove the most loosely bound electron from an isolated atom in the gaseous state is known as ionisation energy or first ionisation energy or ionisation enthalpy (IE_1) of the element. The energy required to remove the second electron from the monovalent cation is called second ionisation enthalpy (IE_2). Similarly, we have third, fourth ionisation enthalpies. The values of ionisation energy depends on a number of factors such as (i) size of the atom (ii) screening effect (iii) nuclear charge (iv) half filled and fully filled orbitals.

In a group, the ionisation energy decreases from top to bottom. In a period, the value of ionisation energy increases from left to right which breaks where atoms have somewhat stable configurations.

- 18.** Compared to the second ionisation energy (IE_2) of an atom, the third ionisation energy (IE_3) is
- (a) The same (b) Greater
(c) Smaller (d) Half
- 19.** In a period, the ionisation energy is lowest for the -
- (a) Noble gases
(b) Halogens
(c) Alkaline earth metals
(d) Alkali metals
- 20.** The electronic configurations of some neutral elements are given below
- | | |
|--------------------|------------------------|
| (I) $1s^2, 2s^2$ | (II) $1s^2, 2s^2 2p^1$ |
| (III) $1s^2, 2s^1$ | (IV) $1s^2, 2s^2 2p^2$ |
- Which of these electronic configurations would be expected to have highest second ionisation energy (IE_2)
- (a) (I) (b) (II)
(c) (III) (d) (IV)
- 21.** The first (IE_1) and second (IE_2) ionisation energies (in kJ mol^{-1}) of a few elements are shown below
- | IE_1 | IE_2 |
|---------------|---------------|
| (A) 2372 | 5251 |
| (B) 520 | 7300 |
| (C) 900 | 1760 |
| (D) 1680 | 3380 |
- Which of the above elements is likely to be a noble gas?
- (a) (A) (b) (B)
(c) (C) (d) (D)
- 22.** Which of the order for ionisation energy is correct?
- (a) $\text{Be} > \text{B} > \text{C} > \text{N} > \text{O}$ (b) $\text{B} < \text{Be} < \text{C} < \text{O} < \text{N}$
(c) $\text{B} < \text{Be} < \text{C} < \text{N} < \text{O}$ (d) $\text{B} < \text{Be} < \text{N} < \text{C} < \text{O}$
- 23.** Which of the elements Na, Mg, Si and P would have the greatest difference between the first and second ionisation enthalpies?
- (a) Na (b) Mg
(c) Si (d) P
- 24.** The first ionisation energy of Mg, Al, P and S follows the order
- (a) $\text{Mg} < \text{Al} < \text{P} < \text{S}$ (b) $\text{Al} < \text{Mg} < \text{P} < \text{S}$
(c) $\text{Al} < \text{Mg} < \text{S} < \text{P}$ (d) $\text{Mg} < \text{Al} < \text{S} < \text{P}$

Comprehension (Q 25 to 29): Atoms of metals have only a few electrons in their valence shells while atoms of non-metals generally have more electrons in their valence shells. Metallic character is closely related to atomic radius and ionisation enthalpy. Metallic character increases from top to bottom in a group and decreases from left to right in a period. Metallic character is inversely related to electronegativity.

- 25.** Which of the following groups contains metals, non-metals and metalloids?
- (a) Group 1 (b) Group 17
(c) Group 14 (d) Group 2

26. Non-metals belong to -
 (a) s-block elements (b) p-block elements
 (c) d-block elements (d) f-block elements
27. Considering the elements B, C, N & F, the correct order of their non-metallic character is
 (a) B > C > N > F (b) C > B > N > F
 (c) F > N > C > B (d) F > B > C > N
28. The electronegativities of the following elements increase in the order
 (a) C < N < Si < P (b) N < Si < C < P
 (c) Si < P < C < N (d) P < Si < N < C
29. Considering the elements B, Al, Mg and K, the correct order of their metallic character is
 (a) B > Al > Mg > K (b) Al > K > B > Mg
 (c) Mg > Al > K > B (d) K > Mg > Al > B

MATCH THE COLUMN TYPE QUESTIONS

30. Match column-I with column-II and select the correct answer using the codes given below:

Column-I		Column-II	
	Ion		Radius (in pm)
A.	Li^+	p.	216
B.	Na^+	q.	195
C.	Br^-	r.	60
D.	I^-	s.	95

- (a) A – s, B – r, C – p, D – q
 (b) A – r, B – s, C – q, D – p
 (c) A – q, B – s, C – r, D – p
 (d) A – p, B – q, C – r, D – s

31. Match the correct atomic radius with the element :

Column-I		Column-II	
Element symbol		Atomic radius (pm)	
A.	Be	p.	74
B.	C	q.	88
C.	O	r.	111
D.	B	s.	77
E.	N	t.	66

- (a) A – t, B – r, C – s, D – q, E – p
 (b) A – t, B – q, C – p, D – r, E – s
 (c) A – r, B – s, C – t, D – q, E – p
 (d) A – p, B – q, C – r, D – s, E – t

32. Match column-I with column-II and choose the correct answer from the code given below:

Column-I		Column-II	
		(Atomic number)	
A.	57	p.	is a d-block or a p-block element
B.	17	q.	is 4 th period element

C.	19	r.	violates Aufbau's principle
D.	29	s.	is a non-metal
		t.	is s-block element

- (a) A – p, r; B – p, s; C – q, t; D – p, q, r
 (b) A – s, r, q; B – t, s; C – q, s; D – p, r
 (c) A – q, r; B – p, s; C – q, t; D – p, q
 (d) A – p, q, r; B – t, s; C – p, s; D – t, q, r

33. Match the characteristics mentioned in column-II with the process in column-I.

	Column-I		Column-II
A.	$\text{O(g)} + \text{e}^- \rightarrow \text{O}^-(\text{g})$	p.	Positive electron gain enthalpy
B.	$\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g})$	q.	Negative electron gain enthalpy
C.	$\text{Na}^-(\text{g}) \rightarrow \text{Na}(\text{g}) + \text{e}^-$	r.	Exothermic process
D.	$\text{Mg}^+(\text{g}) + \text{e}^- \rightarrow \text{Mg}(\text{g})$	s.	Endothermic process

- (a) A – p, r; B – p, s; C – s, q; D – r
 (b) A – p, r; B – p, q; C – r; D – q, s
 (c) A – q, r; B – p, s; C – s; D – q, r
 (d) A – s, r; B – p, q; C – s; D – r

34. Match column-I with column-II and choose the correct answer from the code given below:

	Column-I		Column-II
A.	Strongest reductant	p.	Aurum
B.	Half filled d-orbital	q.	Cerium
C.	Coinage metal	r.	Chromium
D.	Lanthanide	s.	Iodide ion

- (a) A – q, B – r, C – p, D – s
 (b) A – s, B – r, C – p, D – q
 (c) A – q, B – s, C – r, D – p
 (d) A – p, B – q, C – r, D – s

35. Match column-I with column-II and select the correct answer using the codes given below:

	Column-I (Element)		Column-II (Electronic configuration)
A.	Gallium	p.	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
B.	Vanadium	q.	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^10$
C.	Zinc	r.	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$
D.	Scandium	s.	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

- (a) A – s, B – r, C – p, D – q
 (b) A – s, B – q, C – p, D – r
 (c) A – q, B – s, C – r, D – p
 (d) A – r, B – s, C – q, D – p

NUMERICAL TYPE QUESTIONS

- 36.** What is the maximum number of electrons possible in Ni^+ having same spin?

37. The lattice enthalpy of solid NaCl is 772 kJ mol^{-1} and enthalpy of solution is 2 kJ mol^{-1} . If the hydration enthalpy of Na^+ & Cl^- ions are in the ratio of $3:2.5$, what is the magnitude of enthalpy of hydration (in kJ) of chloride ion?

38. If internuclear distance between A atoms in A_2 is 10\AA and between B atoms in B_2 is 6\AA , then calculate internuclear distance between A and B in \AA . [Electronegativity difference between A and B has negligible value].

39. Report atomic number of the element having largest size among the following :
Ni, Cu, Zn

40. $\text{A}^-(\text{g}) \rightarrow \text{A}^{2+}(\text{g}) \quad \Delta H = 1100 \text{ kJ/mol}$
 $\text{A}(\text{g}) \rightarrow \text{A}^{2+}(\text{g}) \quad \Delta H = 1200 \text{ kJ/mol}$
 Electron gain enthalphy of A is $P \times 10^2 \text{ kJ/mol}$. What is the value of P?

41. The electron gain enthalpy of a hypothetical element ‘A’ is -3 eV per atom. How much energy in kcal is released when 10 g of ‘A’ are completely converted to A^- ions in gaseous state?
 (Take : 1 eV per atom = 23 kcal mol^{-1} ,
 Molar mass of A = 30 g)

42. How many of the following radii order(s) is/are incorrect?
 (i) $\text{N}^{3-} > \text{P}^{3-}$ (ii) $\text{O}^{2-} > \text{F}^-$
 (iii) $\text{Ca}^{2+} > \text{Sr}^{2+}$ (iv) $\text{S}^{2-} > \text{S}$
 (v) $\text{Cl}^- > \text{S}^{2-}$

43. The number of electrons for Zn^{2+} cation that have the value of azimuthal quantum number = 0, is _____.

44. How many number of pair(s) of elements exhibit diagonal relationship?

45. What is the atomic number of the element present in second period and group 15?

46. Which of the following given oxide(s) is/are amphoteric in nature?
 SnO , CaO , PbO , Al_2O_3 , Na_2O , ZnO , MgO

47. In which of the following pair(s) size of first species is greater than second species?
(Cl, Br), (Na^+ , Li^+), (Se, S), (I^- , Br^-), (Ca, Mg), (S^{2-} , Cl^-)

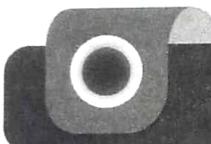
48. How many element(s) possess a positive value of electron gain enthalpy from the given element(s)?
He, Be, N, F, Cl, Li, C, Ne

49. The number of pair in which $I.E_1$ of first element is greater than second element? (N, O), (Be, B), (He, Ne), (S, P), (Mg, Na)

50. What is the value of $Z_{\text{effective}}$ on 4s electron in case of zinc (Zn)?

51. From the given element (s), how many have ionization energy less than chlorine atom?
Na, Mg, P, S, Ar, Al

52. Successive IE-values of element 'X' is IE_1 , IE_2 , IE_3 are 9.3, 18.2 and 553.8 eV respectively. Predict group number of element 'X' in modern periodic table.



Exercise-4 (Past Year Questions)

JEE MAIN

5. The electronegativity of aluminium is similar to (2019)
(a) Carbon (b) Beryllium
(c) Boron (d) Lithium

6. The correct order of atomic radii is : (2019)
(a) N > Ce > Eu > Ho (b) Ho > N > Eu > Ce
(c) Ce > Eu > Ho > N (d) Eu > Ce > Ho > N

7. The correct option with respect to the Pauling electronegativity values of the elements is: (2019)
(a) Te > Se (b) Ga < Ge
(c) Si < Al (d) P > S

8. The relative stability of + 1 oxidation state of group 13 elements follows the order: (2019)
(a) Al < Ga < Tl < In (b) Tl < In < Ga < Al
(c) Ga < Al < In < Tl (d) Al < Ga < In < Tl

9. In general, the properties that decreases and increase down a group in the periodic table respectively are (2019)
(a) Atomic radius and electronegativity
(b) Electron gain enthalpy and electronegativity.
(c) Electronegativity and atomic radius.
(d) Electronegativity and electron gain enthalpy.

10. Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to (2019)
- Inert pair effect
 - diagonal relationship
 - Lattice effect
 - Lanthanoid contraction
11. When the first electron gain enthalpy ($\Delta_{eg}H$) of oxygen is -141 kJ/mol, its second electron gain enthalpy is (2019)
- A more negative value than the first.
 - Almost the same as that of the first.
 - Negative, but less negative than the first.
 - A positive value.
12. The correct order of the atomic radii of C, Cs, Al and S is: (2019)
- $C < S < Al < Cs$
 - $S < C < Cs < Al$
 - $S < C < Al < Cs$
 - $C < S < Cs < Al$
13. The IUPAC symbol for the element with atomic number 119 would be : (2019)
- unh
 - uun
 - une
 - uee
14. In comparison to boron, beryllium has: (2019)
- Lesser nuclear charge and greater first ionisation enthalpy.
 - Lesser nuclear charge and lesser first ionisation enthalpy.
 - Greater nuclear charge and greater first ionisation enthalpy
 - Greater nuclear charge and lesser first ionisation enthalpy.
15. The group number, number of valence electrons, and valency of an element with atomic number 15, respectively, are (2019)
- 16, 5 and 2
 - 16, 6 and 3
 - 15, 5 and 3
 - 15, 6 and 2
16. The correct order of catenation is; (2019)
- $C > Si > Ge \approx Sn$
 - $C > Sn > Si \approx Ge$
 - $Ge > Sn > Si > C$
 - $Si > Sn > C > Ge$
17. The correct order of the first ionization enthalpies is: (2019)
- $Mn < Ti < Zn < Ni$
 - $Ti < Mn < Ni < Zn$
 - $Zn < Ni < Mn < Ti$
 - $Ti < Mn < Zn < Ni$
18. Within each pair of element F & Cl, S & Se, and Li & Na, respectively, the elements that release more energy upon an electron gain are: (2020)
- Cl, S and Li
 - F, S and Li
 - F, Se and Na
 - Cl, Se and Na
19. The first ionization energy (in kJ/mol) of Na, Mg, Al and Si respectively, are: (2020)
- 496, 576, 737, 786
 - 786, 737, 577, 496
 - 496, 577, 786, 737
 - 496, 737, 577, 786
20. The third ionization enthalpy is minimum for: (2020)
- Ni
 - Co
 - Mn
 - Fe
21. The increasing order of the atomic radii of following elements is: (2020)
- C
 - O
 - F
 - Cl
 - Br
- $A < B < C < D < E$
 - $C < B < A < D < E$
 - $B < C < D < A < E$
 - $D < C < B < A < E$
22. B has a smaller first ionization enthalpy than Be. Consider the following statements: (2020)
- It is easier to remove 2p electron than 2s electron.
 - 2p electron of B is more shielded from the nucleus by the inner core of electrons than the 2s electrons of Be.
 - 2s electron has more penetration power than 2p electron.
 - Atomic radius of B is more than Be (atomic number: B = 5, Be = 4).
- The correct statements are:
- (I), (III) and (IV)
 - (II), (III) and (IV)
 - (I), (II) and (IV)
 - (I), (II) and (III)
23. The first and second ionisation enthalpies of a metal are 496 and 4560 kJ mol⁻¹, respectively. How many moles of HCl and H₂SO₄, respectively, will be needed to react completely with 1 mole of the metal hydroxide? (2020)
- 1 and 0.5
 - 2 and 0.5
 - 1 and 2
 - 1 and 1
24. Three elements X, Y and Z are in the 3rd period of the periodic table. The oxides of X, Y and Z, respectively, are basic, amphoteric and acidic. The correct order of the atomic numbers of X, Y and Z is (2020)
- $X < Z < Y$
 - $Y < X < Z$
 - $Z < Y < X$
 - $X < Y < Z$
25. In general the property (magnitudes only) that show an opposite trend in comparison to other properties across a period, is (2020)
- Electron gain enthalpy
 - Electronegativity
 - Ionization enthalpy
 - Atomic radius
26. The atomic number of the element unnilennium is (2020)
- 109
 - 119
 - 102
 - 108
27. The process that is NOT endothermic in nature is (2020)
- $Ar(g) + e^- \rightarrow Ar^-(g)$
 - $H(g) + e^- \rightarrow H^-(g)$
 - $Na(g) \rightarrow Na^+(g) + e^-$
 - $O^-(g) + e^- \rightarrow O^{2-}(g)$
28. The ionic radii of O²⁻, F⁻, Na⁺ and Mg²⁺ are in the order (2020)
- $F^- > O^{2-} > Na^+ > Mg^{2+}$
 - $Mg^{2+} > Na^+ > F^- > O^{2-}$
 - $O^{2-} > F^- > Mg^{2+} > Na^+$
 - $O^{2-} > F^- > Na^+ > Mg^{2+}$

29. The elements with atomic numbers 101 and 104 belong to, respectively, (2020)

- (a) Group 6 and Actinoids
- (b) Actinoids and Group 4
- (c) Group 11 and Group 4
- (d) Actinoids and Group 6

30. The correct order of the ionic radii of O^{2-} , N^{3-} , F^- , Mg^{2+} , Na^+ and Al^{3+} is (2020)

- (a) $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$
- (b) $Al^{3+} < Na^+ < Mg^{2+} < O^{2-} < F^- < N^{3-}$
- (c) $N^{3-} < F^- < O^{2-} < Mg^{2+} < Na^+ < Al^{3+}$
- (d) $N^{3-} < O^{2-} < F^- < Na^+ < Mg^{2+} < Al^{3+}$

31. The atomic number of Unnilium is _____. (2020)

32. The set that contains atomic numbers of only transition elements, is (2020)

- (a) 21, 32, 53, 64
- (b) 9, 17, 34, 38
- (c) 37, 42, 50, 64
- (d) 21, 25, 42, 72

33. Identify the element for which electronic configuration in +3 oxidation state is [Ar] $3d^5$: (2021)

- (a) Ru
- (b) Mn
- (c) Co
- (d) Fe

34. Given below are two statements: one is labelled as **Assertion (A)** and the other is labelled as **Reason (R)**.

Assertion (A) : Metallic character decreases and non-metallic character increases on moving from left to right in a period.

Reason (R) : It is due to increase in ionisation enthalpy and decrease in electron gain enthalpy, when one moves from left to right in a period.

In the light of the above statements, choose the most appropriate answer from the options given below: (2021)

- (a) (A) is false but (R) is true.
- (b) (A) is true but (R) is false
- (c) Both (A) and (R) are correct and (R) is the correct explanation of (A)
- (d) Both (A) and (R) are correct but (R) is not the correct explanation of (A)

35. Consider the elements Mg, Al, S, P and Si, the correct increasing order of their first ionization enthalpy is (2021)

- (a) $Mg < Al < Si < S < P$
- (b) $Al < Mg < Si < S < P$
- (c) $Mg < Al < Si < P < S$
- (d) $Al < Mg < S < Si < P$

36. The major components in "Gun Metal" are: (2021)

- (a) Cu, Zn and Ni
- (b) Cu, Sn and Zn
- (c) Al, Cu, Mg and Mn
- (d) Cu, Ni and Fe

37. Match List-I with List-II

List-I		List-II	
Electronic configuration		I.E. in kJ/mol	
A.	$1s^2 2s^2$	p.	801
B.	$1s^2 2s^2 2p^4$	q.	899
C.	$1s^2 2s^2 2p^3$	r.	1314
D.	$1s^2 2s^2 2p^1$	s.	1402

Choose the most appropriate answer from the options given below:

- (a) A – q; B – r; C – s; D – p
- (b) A – p; B – r; C – q; D – s
- (c) A – p; B – r; C – s; D – q
- (d) A – s; B – p; C – q; D – r

38. The correct order of electron gain enthalpy is: (2021)

- (a) S > Se > Te > O
- (b) Te > Se > S > O
- (c) O > S > Se > Te
- (d) S > O > Se > Te

39. Which pair of oxides is acidic in nature? (2021)

- (a) B_2O_3 , CaO
- (b) B_2O_3 , SiO_2
- (c) N_2O , BaO
- (d) CaO, SiO_2

40. Identify the elements X and Y using the ionisation energy values given below: (2021)

Ionization energy (in kJ/mol)		
	1st	2nd
X	495	4563
Y	731	1450

- (a) X = Na; Y = Mg
- (b) X = Mg; Y = F
- (c) X = Mg; Y = Na
- (d) X = F; Y = Mg

41. The characteristics of elements X, Y and Z with atomic numbers, respectively, 33, 53 and 83 are: (2021)

- (a) X and Y are metalloids and Z is a metal.
- (b) X is a metalloid, Y is a non-metal and Z is a metal.
- (c) X, Y and Z are metals.
- (d) X and Z are non-metals and Y is a metalloid.

42. The absolute value of the electron gain enthalpy of halogens satisfies: (2021)

- (a) I > Br > Cl > F
- (b) Cl > Br > F > I
- (c) Cl > F > Br > I
- (d) F > Cl > Br > I

43. The set of elements that differ in mutual relationship from those of the other sets is: (2021)

- (a) Li - Mg
- (b) B - Si
- (c) Be - Al
- (d) Li - Na

44. The ionic radius of Na^+ ion is 1.02 \AA . The ionic radii (in \AA) of Mg^{2+} and Al^{3+} , respectively, are: (2021)

- (a) 1.05 and 0.99
- (b) 0.72 and 0.54
- (c) 0.85 and 0.99
- (d) 0.68 and 0.72

45. The first ionization energy of magnesium is smaller as compared to that of elements X and Y, but higher than that of Z. The elements X, Y and Z, respectively, are: (2021)
- Chlorine, lithium and sodium
 - Argon, lithium and sodium
 - Argon, chlorine and sodium
 - Neon, sodium and chlorine
46. Outermost electronic configuration of a group 13th element E is 4s²4p¹. The electronic configuration of an element of p-block, period-five placed diagonally to element E is: (2021)
- [Xe] 5d¹⁰6s²6p²
 - [Ar] 3d¹⁰4s²4p²
 - [Kr] 3d¹⁰4s²4p²
 - [Kr] 4d¹⁰5s²5p²
47. Which one of the following statements for D.I. Mendeleef, is incorrect? (2021)
- Element with atomic number 101 is named after him.
 - He authored the textbook - Principles of Chemistry.
 - He invented accurate barometer.
 - At the time, he proposed periodic table of elements structure of atom was known.
48. The ionic radii of K⁺, Na⁺, Al³⁺ and Mg²⁺ are in the order: (2021)
- Na⁺ < K⁺ < Mg²⁺ < Al³⁺
 - Al³⁺ < Mg²⁺ < Na⁺ < K⁺
 - Al³⁺ < Mg²⁺ < K⁺ < Na⁺
 - K⁺ < Al³⁺ < Mg²⁺ < Na⁺
49. The ionic radii of F⁻ and O²⁻ respectively are 1.33 Å and 1.4 Å, while the covalent radius of N is 0.74 Å.
The correct statement for the ionic radius of N³⁻ from the following is: (2021)
- It is bigger than F⁻ and N but smaller than of O²⁻.
 - It is bigger than O²⁻ and F⁻.
 - It is smaller than O²⁻ and F⁻ but bigger than of N.
 - It is smaller than F⁻ and N.
50. The correct order of first ionisation enthalpy is: (2021)
- Mg < Al < S < P
 - Mg < Al < P < S
 - Al < Mg < S < P
 - Mg < S < Al < P
51. Chalcogen group elements are: (2021)
- Se, Te and Po
 - O, Ti and Po
 - Se, Tb and Pu
 - S, Te and Pm
52. The correct order of ionic radii for the ions: P³⁻, S²⁻, Ca²⁺, K⁺, Cl⁻ is: (2021)
- K⁺ > Ca²⁺ > P³⁻ > S²⁻ > Cl⁻
 - P³⁻ > S²⁻ > Cl⁻ > K⁺ > Ca²⁺
 - Cl⁻ > S²⁻ > P³⁻ > Ca²⁺ > K⁺
 - P³⁻ > S²⁻ > Cl⁻ > Ca²⁺ > K⁺
53. Given below are the oxides: Na₂O, As₂O₃, N₂O, NO and Cl₂O₇. Number of amphoteric oxides is: (2022)
- 0
 - 1
 - 2
 - 3
54. The pair, in which ions are isoelectronic with Al³⁺ is: (2022)
- Br⁻ and Be²⁺
 - Cl⁻ and Li⁺
 - S²⁻ and K⁺
 - O²⁻ and Mg²⁺
55. The correct order of electron gain enthalpies of Cl, F, Te and Po is (2022)
- F < Cl < Te < Po
 - Po < Te < F < Cl
 - Te < Po < Cl < F
 - Cl < F < Te < Po
56. Which of the following element is considered as a metalloid? (2022)
- Sc
 - Pb
 - Bi
 - Te
57. Given below are two statements: one is labelled as Assertion (A) and the other is labelled as Reason (R)
Assertion (A): The ionic radii of O²⁻ and Mg²⁺ are same.
Reason (R): Both O²⁻ and Mg²⁺ are isoelectronic species. In the light of the above statements, choose the correct answer from the options given below. (2022)
- Both (A) and (R) are true and (R) is the correct explanation of (A).
 - Both (A) and (R) are true but (R) is not the correct explanation of (A).
 - (A) is true but (R) is false.
 - (A) is false but (R) is true.
58. The correct order of increasing ionic radii is (2022)
- Mg²⁺ < Na⁺ < F⁻ < O²⁻ < N³⁻
 - N³⁻ < O²⁻ < F⁻ < Na⁺ < Mg²⁺
 - F⁻ < Na⁺ < O²⁻ < Mg²⁺ < N³⁻
 - Na⁺ < F⁻ < Mg²⁺ < O²⁻ < N³⁻
59. Element "E" belongs to the period 4 and group 16 of periodic table. The valence shell electron configuration the element, which is just above "E" in the group. (2022)
- 3s²3p⁴
 - 3d¹⁰4s²4p⁴
 - 4d¹⁰5s²5p⁴
 - 2s²2p⁴
60. Match List-I with List-II. (2022)
- | List-I (Oxide) | List-II (Nature) |
|-----------------------------------|------------------|
| A. Cl ₂ O ₇ | p. Amphoteric |
| B. Na ₂ O | q. Basic |
| C. Al ₂ O ₃ | r. Neutral |
| D. N ₂ O | s. Acidic |
- Choose the correct answer from the options given below;
- A - s; B - r; C - p; D - q
 - A - s; B - q; C - p; D - r
 - A - q; B - s; C - r; D - p
 - A - p; B - q; C - r; D - s

61. Among the following, basic oxide is: (2022)
 (a) SO_3 (b) SiO_2 (c) CaO (d) Al_2O_3
62. Given below are two statements. One is labelled as **Assertion (A)** and the other is labelled as **Reason (R)**.
Assertion (A): The first ionization enthalpy for oxygen is lower than that of nitrogen.
Reason (R): The four electrons in 2p orbitals of oxygen experience more electron-electron repulsion.
 In the light of the above statements. Choose of correct answer from the options given below. (2022)
 (a) Both (A) and (R) are correct and (R) is the correct explanation of (A).
 (b) Both (A) and (R) are correct but (R) is NOT the correct explanation of A.
 (c) (A) is correct but (R) is not correct.
 (d) (A) is not correct but (R) is correct.
63. The IUPAC nomenclature of an element with electronic configuration $[\text{Rn}]5\text{f}^{14}6\text{d}^17\text{s}^2$ is: (2022)
 (a) Unnilbium (b) Unnilunium
 (c) Unnilquadium (d) Unniltrium
64. The first ionization enthalpies of Be, B, N and O follow the order (2022)
 (a) $\text{O} < \text{N} < \text{B} < \text{Be}$ (b) $\text{Be} < \text{B} < \text{N} < \text{O}$
 (c) $\text{B} < \text{Be} < \text{N} < \text{O}$ (d) $\text{B} < \text{Be} < \text{O} < \text{N}$
65. The total number of acidic oxides from the following list is: $\text{NO}, \text{N}_2\text{O}, \text{B}_2\text{O}_3, \text{N}_2\text{O}_5, \text{CO}, \text{SO}_3, \text{P}_4\text{O}_{10}$ (2022)
 (a) 3 (b) 4 (c) 5 (d) 6
66. Given two statements below:
Statement-I: In Cl_2 molecule the covalent radius is double of the atomic radius of chlorine.
Statement-II: Radius of anionic species is always greater than their parent atomic radius. (2022)
 Choose the most appropriate answer from options given below:
 (a) Both statement-I and statement-II are correct.
 (b) Both statement-I and statement-II are incorrect.
 (c) Statement-I is correct but statement-II is incorrect.
 (d) Statement-I is incorrect but statement-II is correct.
67. The metal that has very low melting point and its periodic position is closer to a metalloid is: (2022)
 (a) Al (b) Ga (c) Se (d) In
68. The incorrect statement is (2022)
 (a) The first ionization enthalpy of K is less than that of Na and Li.
 (b) Xe does not have the lowest first ionization enthalpy in its group.
 (c) The first ionization enthalpy of element with atomic number 37 is lower than that of the element with atomic number 38.
 (d) The first ionization enthalpy of Ga is higher than that of the d-block element with atomic number 30.

69. Outermost electronic configuration of four elements (I), (II), (III), (IV) are given below: (2022)
 (I) 3s^2 (II) $3\text{s}^2 3\text{p}^1$
 (III) $3\text{s}^2 3\text{p}^3$ (IV) $3\text{s}^2 3\text{p}^4$
 The correct order of first ionization enthalpy for them is:
 (a) (I) $<$ (II) $<$ (III) $<$ (IV) (b) (II) $<$ (I) $<$ (IV) $<$ (III)
 (c) (II) $<$ (IV) $<$ (I) $<$ (III) (d) (II) $<$ (I) $<$ (III) $<$ (IV)
70. An element A of group 1 shows similarity to an element B belonging to group 2. If A has maximum hydration enthalpy in group I, then B is: (2022)
 (a) Mg (b) Be (c) Ca (d) Sr
71. In which of the following pairs, electron gain enthalpies of constituent elements are nearly the same or identical? (2022)
 (I) Rb and Cs (II) Na and K
 (III) Ar and Kr (IV) I and At
 Choose the correct answer from the options given below:
 (a) (I) and (II) only (b) (II) and (III) only
 (c) (I) and (III) only (d) (III) and (IV) only
72. The correct decreasing order for metallic character is (2022)
 (a) $\text{Na} > \text{Mg} > \text{Be} > \text{Si} > \text{P}$
 (b) $\text{P} > \text{Si} > \text{Be} > \text{Mg} > \text{Na}$
 (c) $\text{Si} > \text{P} > \text{Be} > \text{Na} > \text{Mg}$
 (d) $\text{Be} > \text{Na} > \text{Mg} > \text{Si} > \text{P}$
73. The first ionization enthalpy of Na, Mg and Si, respectively, are: 496, 737 and 786 kJ mol^{-1} . The first ionization enthalpy (kJ mol^{-1}) of Al is (2022)
 (a) 487 (b) 768 (c) 577 (d) 856

JEE ADVANCED

74. The increasing order of atomic radii of the following group 13 elements is (2016)
 (a) Al $<$ Ga $<$ In $<$ Tl (b) Ga $<$ Al $<$ In $<$ Tl
 (c) Al $<$ In $<$ Ga $<$ Tl (d) Al $<$ Ga $<$ Tl $<$ In
75. The option(s) with only amphoteric oxides is (are) (2020)
 (a) $\text{NO}, \text{B}_2\text{O}_3, \text{PbO}, \text{SnO}_2$
 (b) $\text{Cr}_2\text{O}_3, \text{CrO}, \text{SnO}, \text{PbO}$
 (c) $\text{Cr}_2\text{O}_3, \text{BeO}, \text{SnO}, \text{SnO}_2$
 (d) $\text{ZnO}, \text{Al}_2\text{O}_3, \text{PbO}, \text{PbO}_2$
76. The 1st, 2nd and the 3rd ionization enthalpies I_1, I_2 and I_3 , of four atoms with atomic numbers n, n+1, n+2 and n+3, where n $<$ 10, are tabulated below. What is the value of n? (2020)

Atomic number	Ionization Enthalpy (kJ/mol)		
	I_1	I_2	I_3
n	1681	3374	6050
n + 1	2081	3952	6122
n + 2	496	4562	6910
n + 3	738	1451	7733

ANSWER KEY

CONCEPT APPLICATION

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

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (c) | 3. (b) | 4. (b) | 5. (a) | 6. (c) | 7. (d) | 8. (a) | 9. (c) | 10. (c) |
| 11. (b) | 12. (c) | 13. (a) | 14. (c) | 15. (c) | 16. (d) | 17. (a) | 18. (d) | 19. (b) | 20. (a) |
| 21. (c) | 22. (d) | 23. (d) | 24. (d) | 25. (b) | 26. (b) | 27. (d) | 28. (c) | 29. (a) | 30. (c) |
| 31. (a) | 32. (b) | 33. (a) | 34. (d) | 35. (c) | 36. (a) | 37. (d) | 38. (c) | 39. (c) | 40. (d) |
| 41. (a) | 42. (b) | 43. (a) | 44. (a) | 45. (c) | 46. (b) | 47. (a) | 48. (c) | 49. (d) | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (c) | 3. (b) | 4. (c) | 5. (d) | 6. (c) | 7. (b) | 8. (a) | 9. (a) | 10. (d) |
| 11. (d) | 12. (a) | 13. (c) | 14. (d) | 15. (d) | 16. (b) | 17. (c) | 18. (a) | 19. (c) | 20. (d) |
| 21. (b) | 22. (c) | 23. (c) | 24. (c) | 25. (b) | 26. (d) | 27. (c) | 28. (b) | 29. (d) | 30. (d) |
| 31. (a) | 32. (c) | 33. (c) | 34. (b) | 35. (b) | 36. (a) | 37. (b) | 38. (b) | 39. (b) | 40. (d) |
| 41. (b) | 42. (c) | 43. (c) | 44. (c) | 45. (d) | 46. (a) | 47. (a) | 48. (b) | 49. (d) | |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|-----------|-------------|---------------|--------------|--------------|-------------|---------------|------------|------------|------------|
| 1. (c,d) | 2. (b,d) | 3. (a,b,d) | 4. (a,b,c,d) | 5. (a,b,c,d) | 6. (a,b,d) | 7. (a,b,c,d) | 8. (a,b,d) | 9. (a,b,c) | 10. (a,d) |
| 11. (a,c) | 12. (a,c,d) | 13. (a,b,c,d) | 14. (a,b,d) | 15. (b,c) | 16. (a,b,d) | 17. (a,b,c,d) | 18. (b) | 19. (d) | 20. (c) |
| 21. (a) | 22. (b) | 23. (a) | 24. (c) | 25. (c) | 26. (b) | 27. (c) | 28. (c) | 29. (d) | 30. (b) |
| 31. (c) | 32. (a) | 33. (c) | 34. (b) | 35. (d) | 36. [0015] | 37. [350] | 38. [8] | 39. [30] | 40. [1] |
| 41. [23] | 42. [3] | 43. [6] | 44. [3] | 45. [7] | 46. [4] | 47. [5] | 48. [4] | 49. [4] | 50. [4.35] |
| 51. [5] | 52. [2] | | | | | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|-----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (a) | 3. (b) | 4. (c) | 5. (b) | 6. (d) | 7. (b) | 8. (d) | 9. (c) | 10. (a) |
| 11. (d) | 12. (a) | 13. (d) | 14. (a) | 15. (c) | 16. (a) | 17. (b) | 18. (a) | 19. (d) | 20. (d) |
| 21. (b) | 22. (d) | 23. (a) | 24. (d) | 25. (d) | 26. (a) | 27. (b) | 28. (d) | 29. (b) | 30. (a) |
| 31. [101] | 32. (d) | 33. (d) | 34. (b) | 35. (b) | 36. (b) | 37. (a) | 38. (a) | 39. (b) | 40. (a) |
| 41. (b) | 42. (c) | 43. (d) | 44. (b) | 45. (c) | 46. (d) | 47. (d) | 48. (b) | 49. (b) | 50. (c) |
| 51. (a) | 52. (b) | 53. (b) | 54. (d) | 55. (b) | 56. (d) | 57. (a) | 58. (a) | 59. (a) | 60. (b) |
| 61. (c) | 62. (b) | 63. (d) | 64. (d) | 65. (b) | 66. (d) | 67. (b) | 68. (d) | 69. (b) | 70. (a) |
| 71. (c) | 72. (a) | 73. (c) | | | | | | | |

JEE Advanced

74. (b) 75. (c,d) 76. [9]



CHAPTER

8

Chemical Bonding and Molecular Structure

INTRODUCTION

Atoms combine with one another in different ways to form a large number of molecules. The attractive force which holds the constituents (atoms, molecules or ions) in different chemical species, is called a **chemical bond**.

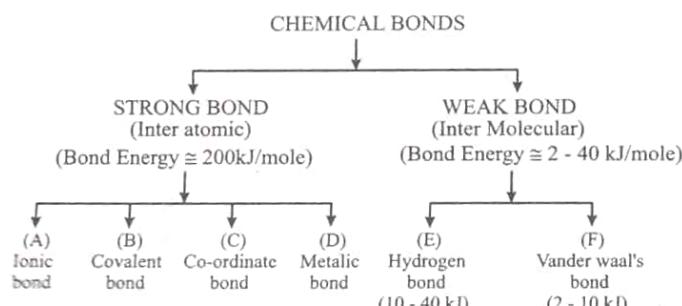
As the atomic state is regarded as a state of higher energy therefore the atoms combine with one another in a number of ways i.e., by transfer of electrons (ionic bond) or by sharing of electrons (covalent bond or coordinate bond) etc.

- ❖ It is well known fact that except for inert gases , no other element exists as independent atoms under ordinary condition.
- ❖ Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds? Such doubts will be discussed in this chapter.
- ❖ A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.

CHEMICAL BOND

- (I) A force that acts between two or more atoms to hold them together as a stable molecule.
- (II) It is union of two or more atoms involving redistribution of e^- among them.
- (III) This process accompanied by decrease in energy.
- (IV) Strength of the bond \propto Decrease in energy
- (V) Therefore molecules are more stable than atoms.

Classification of Bonds



CAUSE OF CHEMICAL COMBINATION

1. Tendency to acquire noble gas configuration

- (I) Atom combines to acquire noble gas configuration.
- (II) Outermost electron i.e., ns, np electrons participate in bond formation.
- (III) Inert gas elements do not participate, as they have stable electronic configuration and hence minimum energy. (Stable configuration $1s^2$ or ns^2np^6)

OCTET RULE

Lewis postulated that atoms achieve the stable octet (i.e. 8 electrons in their outer most shells), when they are linked by chemical bonds. This can happen (i) by the transfer of electron(s) from one atom to another and (ii) by the sharing of a pair of electrons between the atoms.



Obeyes octet rule



Doesn't obey octet rule

Limitations of the Octet Rule

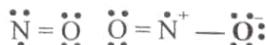
The octet rule though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

- (a) **The incomplete octet of the central atom:** In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are $LiCl$, BeH_2 and BCl_3 .



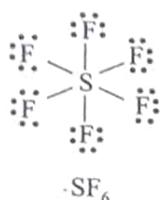
Some other such compounds are $AlCl_3$ and BF_3 .

- (b) **Odd-electron molecules:** In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide NO_2 , the octet rule is not satisfied for all the atoms.

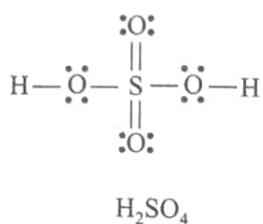


(c) The expanded octet: Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5 , SF_6 , H_2SO_4 and a number of coordination compounds.



10 electrons around the P atom 12 electrons around the S atom



12 electrons around the S atom

Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.



(d) Other drawbacks of the octet theory

- (i) It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2 , KrF_2 , XeOF_2 etc.;
- (ii) This theory does not account for the shape of molecules.
- (iii) It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

2. Tendency to acquire minimum energy: Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B . When the two atoms are at large distance from each other then there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

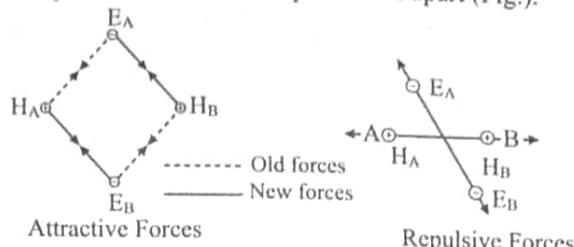
Attractive forces arise between:

- (i) nucleus of one atom and its own electron that is $N_A - e_A$ and $N_B - e_B$.
- (ii) nucleus of one atom and electron of other atom i.e., $N_A - e_B$, $N_B - e_A$.

Similarly repulsive forces arise between :

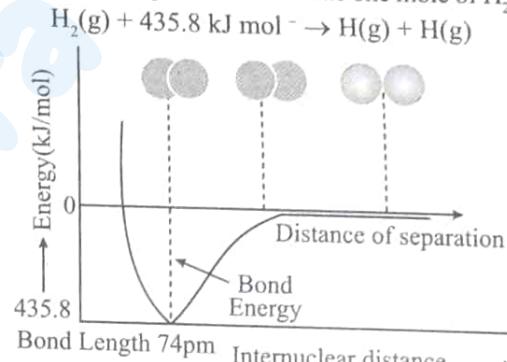
- (i) electrons of two atoms like $e_A - e_B$,
- (ii) nuclei of two atoms $N_A - N_B$.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig.).



Forces of attraction and repulsion during the formation of H_2 molecule. Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.



The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2 .



Train Your Brain

Example 1: The combination of atoms occur because they want

- (a) To decrease number of electrons in the outermost orbit
- (b) To attain an inert gas configuration or to attain stability
- (c) To increase number of electrons in the outermost orbit
- (d) To attain 18 electrons in the outermost orbit

Sol. (b) Combination of atoms occur to attain an inert gas configuration

Example 2: When two atoms combine to form a molecule

- (a) Energy is released.
- (b) Energy is absorbed.
- (c) Energy is neither released nor absorbed.
- (d) Energy may either released or absorbed.

Sol. (a) To attain stability energy is released.



Concept Application

1. To which of the following species is the octet rule applicable?
 - (a) BrF_5
 - (b) SF_6
 - (c) IF_7
 - (d) CO_2
2. Octet configuration can be achieved through :
 - (a) loss of electrons
 - (b) gain of electrons
 - (c) sharing of electrons
 - (d) All of these
3. Which of the following species does not obey octet rule:
 - (a) SiF_4
 - (b) PCl_5
 - (c) ICl
 - (d) BF_4^-

ELECTROVALENT OR IONIC BOND

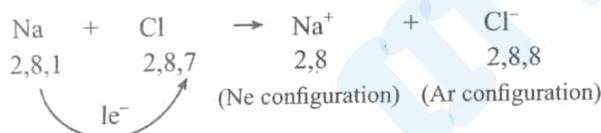
The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called **Ionic or electrovalent bond**.

- (i) Electro +ve atom loses electron (group IA to IIIA)
- (ii) Electro -ve atom gains electron (group VA to VIIA)

Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.

Nature of ionic bond \propto Electronegativity difference

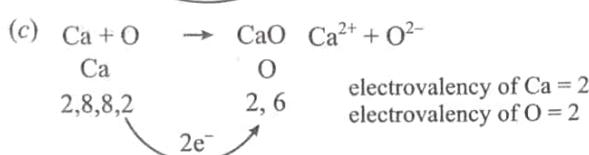
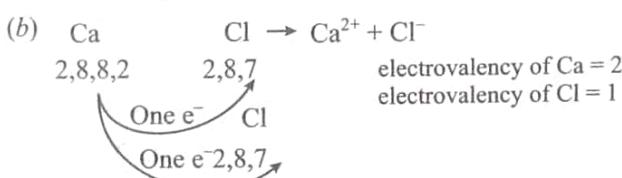
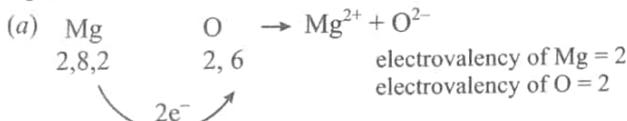
Example IA and VIIA group elements form maximum ionic compound.



More the distance between two elements in periodic table more will be ionic character of bond. Total number of electron lost or gained is called electrovalency.

Electrovalency: It is defined as number of electron lost or gained by an atom e.g. Na has electrovalency 1, Mg has 2. It is equal to their valence electrons respectively.

Example:



The force of attraction is equal in all direction so ionic bond is non-directional.

Ionic compounds do not have molecular formula. It has only empirical formula e.g. NaCl is empirical formula of sodium chloride.

CONDITIONS FOR FORMING IONIC BOND

Formation of Ionic bond depends upon these three factors

(a) Ionisation energy: Minimum amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the +ve ion or cation. (energy absorbed)

Lesser Ionisation energy \rightarrow Greater tendency to form cation.

e.g. $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$ $\left. \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+ \right\}$ ionic bond formation tendency

(b) Electron affinity: Amount of energy released when an electron is added to an isolated gaseous atoms to form -ve ion (anion). Higher electron affinity \rightarrow Greater tendency to form anion

e.g. $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ $\left. \text{F}^- > \text{O}^{2-} > \text{N}^{3-} \right\}$ tendency to form ionic bond

(c) Lattice energy: Amount of energy released when one mole of crystal lattice is formed.

Higher lattice energy \rightarrow Greater will be the stability or strength of ionic compound.

Factors affecting lattice energy (U):

(i) Magnitude of charge $\rightarrow U \propto z^+ z^-$ (Ionic charge)

Lattice energy \propto Magnitude of charge

NaF	MgF_2	AlF_3
Na^+	Mg^{2+}	Al^{3+}

– Lattice energy increases

– Size of cation decreases.

(ii) Size of Cation : – Lattice energy

LiF	NaF	KF	RbF	CsF
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– Size of cation increasing

– Size of anion is constant

– Lattice energy decreases

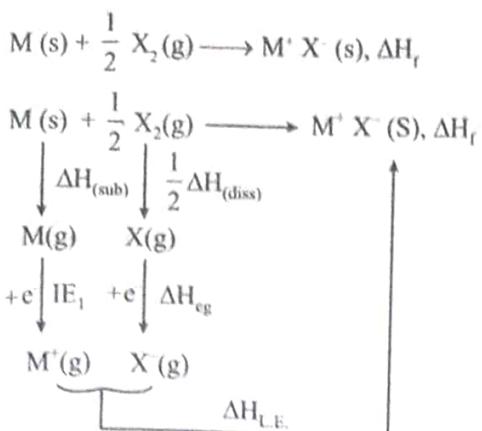
Note: This concludes that for lower value of IE and higher value of EA there is more ease of formation of the cation & anion respectively and consequently more chances of electrovalent bond formation.

DETERMINATION OF LATTICE ENERGY

Born-Haber Cycle (Indirect Method): It inter-relates the various energy terms involved during formation of an ionic compound.

It is a thermochemical cycle based on the Hess's law of constant heat summation.

Hess's Law is the net enthalpy change of a chemical reaction or of any process always remain same whether the reaction takes place in one step or many steps as given in following flow chart.



ΔH_f = heat of formation of $M^+ X^-$

$\Delta H_{(sub)}$ = heat of sublimation of M

IE_1 = ionisation energy of M

$\Delta H_{(diss)}$ = heat of dissociation of X_2

ΔH_{eg} = electron gain enthalpy of X

ΔH_{LE} = Lattice energy of $M^+ X^-$.

So according to Hess's law,

$$\Delta H_f = \Delta H_{(sub)} + IE_1 + \frac{1}{2} \Delta H_{(diss)} + \Delta H_{eg} + \Delta H_{LE}$$

Example: Calculate the lattice energy of solid KF with the help of following data :

$$\Delta H_f^0(KF) = -562.6 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{sub}}(K) = 89.6 \text{ kJ mol}^{-1}$$

$$\Delta H_{IF}(K) = 419.0 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{diss}}(F_2) = 158.2 \text{ kJ mol}^{-1}$$

$$\Delta H_{EA}(F) = -332.6 \text{ kJ mol}^{-1}$$

$$\text{Sol. } K(s) + \frac{1}{2} F_2(g) \longrightarrow KF(s); -562.6 \text{ kJ mol}^{-1}$$

$$K(s) \longrightarrow K(g); 89.6 \text{ kJ mol}^{-1}$$

$$K(g) \longrightarrow K^+(g) + e^-; 419.0 \text{ kJ mol}^{-1}$$

$$\frac{1}{2} F_2(g) \longrightarrow F(g); \frac{1}{2} (158.2) = 79.1 \text{ kJ mol}^{-1}$$

$$F(g) + e^- \longrightarrow F^-(g); -332.6 \text{ kJ mol}^{-1}$$

Let $\Delta H_{\text{lattice}}(KF)$ be U, then according to Hess's law of constant heat summation.

$$-562.6 = 89.6 + 419.0 + 79.1 - 332.6 + U$$

$$\text{So, } U = -817.7 \text{ kJ mol}^{-1}$$

Ans. Lattice energy of KF = $-817.7 \text{ kJ mol}^{-1}$

REPRESENTATION OF FORMULA OF COMPOUNDS

- (a) Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion is at the right as $A^+ B^-$
- (b) Write their electrovalencies in figure at the top of each symbol as $x \quad y$
A B

(c) Now apply criss cross rule as $\begin{array}{c} x \\ \diagup \\ A \\ \diagdown \\ y \end{array}$, i.e formula $A_y B_x$.

Examples: Calcium chloride $\begin{array}{c} 2 \\ \diagup \\ Ca \\ \diagdown \\ 1 \end{array} = CaCl_2$



Train Your Brain

Example 3: Lattice energy of $BeCO_3$ (I), $MgCO_3$ (II) and $CaCO_3$ (III) are in the order -

$$(a) I > II > III \quad (b) I < II < III$$

$$(c) I < III < II \quad (d) II < I < III$$

Sol. (a) Lattice energy $\propto \frac{1}{\text{Cation size}}$

$$BeCO_3 > MgCO_3 > CaCO_3 \text{ (L.E.)}$$

L.E. decrease from top to bottom.

Example 4: Which of the following statements is wrong regarding ionic compounds -

(a) These are generally in solid state at room temperature.

(b) The force of attraction between ions is non directional.

(c) Ionic compounds are soluble in all solvents.

(d) They conduct electricity in molten and solution state.

Sol. (c) Ionic compound rare soluble only in polar solvents.



Concept Application

4. A bond formed between two like atoms cannot be

- (a) ionic
- (b) covalent
- (c) coordinate
- (d) metallic

5. Lattice energy (LE) affects which of the following factors?

- (a) Stability of ionic compound
- (b) Melting point of ionic compound
- (c) Boiling point of ionic compound
- (d) All of the above

6. The electrovalency of the element is equal to the:

- (a) Number of electrons lost
- (b) Number of electrons gained
- (c) Number of electrons transferred
- (d) Number of electrons lost or gained by the atom of the element during the formation of ions of ionic compound

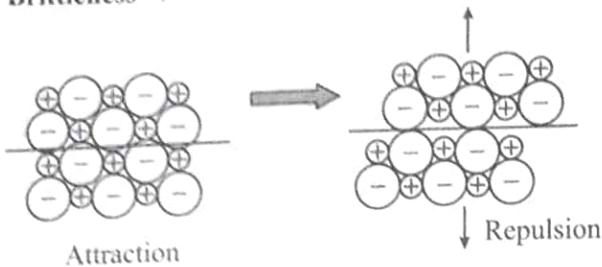
7. The compound which has the highest Lattice energy is

- (a) LiF
- (b) LiCl
- (c) NaCl
- (d) MgO

PROPERTIES OF IONIC COMPOUNDS

(a) Physical state: Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

Brittleness →



(b) Isomorphism:

- Two compounds are said to be isomorphous if they have similar number of electrons i.e. similar configuration of their cation and anion.
- They have similar crystal structure.

Example:

	Na^+	F^-	Mg^{2+}	O^{2-}
Electronic configuration	2,8,	2,8	2,8	2,8
	Ca^{+2}	2Cl^-	2K^+	S^{2-}
	2,8,8	2,8,8	2,8,8	2,8,8

(c) Boiling point and melting point: Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

(d) Conductivity: It depends on ionic mobility. In solid state - No free ions - Bad conductor of electricity.

In fused state or aqueous solution: Due to free ions - Good conductor of electricity.

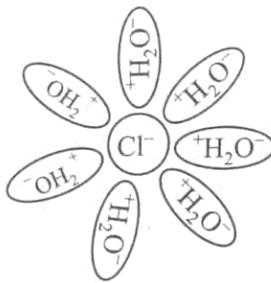
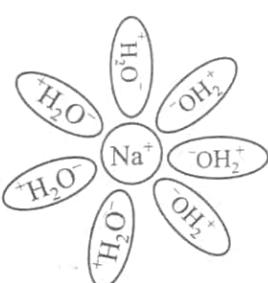
conductivity order: Solid state < Fused state < Aqueous solution

(e) Solubility: Highly soluble in water (Polar solvents)

Example : NaCl in water

(i) The Na^+ ions get associates with -vely charged 'O' of water

(ii) And Cl^- ions associates with +vely charged 'H' of water.



(iii) Thus charge on Na^+ and Cl^- decreases and electrostatics force of attraction also decreases which leads to free ion.

(iv) The energy released due to interaction between solvent and solute is called solvation energy. If water is used as solvent it is called hydration energy.

(v) For an ionic compound to be soluble in water
Hydration energy > Lattice energy

$$\text{Hydration energy (H)} \propto \frac{1}{r^+ + r^-} \quad \{r^+ \text{ & } r^- \text{ are radius of cation and anion}\}$$

(vi) Hydration energy mainly depends on the cation radius because the value $\frac{1}{r^-}$ is negligible in comparison to $\frac{1}{r^+}$.

(vii) Down the group both the lattice energy & hydration energy decreases

FACTORS AFFECTING SOLUBILITY

(I) Dielectric constant: The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant. It is represented by " ϵ "

(a) Water has maximum dielectric constant ($\epsilon = 80$)

$(\text{CH}_3\text{OH} \epsilon = 35)$, $(\text{Acetone} \epsilon = 21)$

$(\text{C}_2\text{H}_5\text{OH} \epsilon = 27)$, $(\text{Ether} \epsilon = 4.1)$

$(\text{Benzene} \epsilon = 2.3)$

$\text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3\text{COCH}_3 > \text{CH}_3\text{OCH}_3 > \text{C}_6\text{H}_6$

(b) Ionic compounds are more soluble in the solvents, having high dielectric constant.

(c) H_2SO_4 and H_2O_2 have high dielectric constant but these are not a good solvent due to their oxidising nature.

(II) Size of ion:

(a) Keeping size of cation constant, the lattice energy decreases with the increase of anionic radius.

Hence order of solubility of LiX in water is $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$

(b) In LiI covalent nature is more according to Fajan's rule but H.E. > L.E. therefore LiI is more soluble in water.

(c) Keeping size of anion constant, the hydration energy decreases with the increase of cationic radius. hence order of solubility of MSO_4 will be –

$\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$

(d) If size of cation and anion is very large, solubility decreases from top to bottom.

(III) Polarisation of anion: Polarisation capacity is maximum in pseudo inert gas configuration.

$$\text{solubility} \propto \frac{1}{\text{polarisation}}$$

$\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$

– Polarisation increases.

– Covalent character increases.

– Solubility decreases.

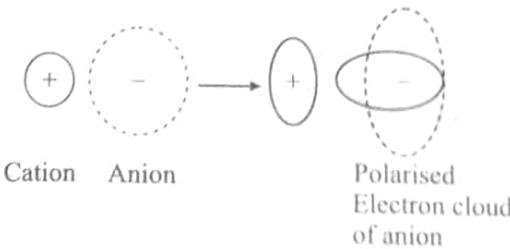
(IV) Ionic reaction:

- (a) Ionic compounds shows ionic reaction and covalent compounds shows-molecular reaction.
- (b) Ionic reactions are faster than molecular reaction because of free ions.
- e.g. When NaCl is added in AgNO₃ solution, white ppt of AgCl is formed at once.



COVALENT CHARACTER IN IONIC COMPOUNDS (FAJAN'S RULE)

When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarisation and the ability of cation to polarize a nearby anion is called as polarizing power of cation.



Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it.

More distortion of anion, more will be polarisation then covalent character increases.

Fajan's gives some rules which govern the covalent character in the ionic compounds.

- (i) **Size of cation:** Smaller is the cation more is its polarizing power and thus more will be the polarisation of anion. Hence more will be covalent character in compound.



-
- Size of cation increases
 - Polarisation decreases
 - Covalent character decreases

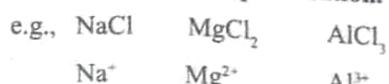
- (ii) **Size of anion:** Larger is the anion, greater is its polarisability and, therefore, more will be the polarisation. Thus more will be covalent character in compound.



-
- Size of anion increases
 - Polarisation increases
 - Covalent character increases

- (iii) **Charge on cation :** Higher is the oxidation state of cation, more will be the deformation of anion and thus, more will be covalent character in compound.

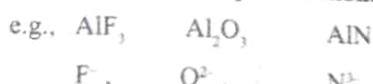
Charge on cation α polarisation.



- Charge of cation increases
- Polarisation increases
- Covalent character increases

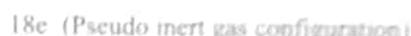
- (iv) **Charge on anion:** Higher is the charge on anion more will be the polarisation of anion and thus more will be covalent character in the compound.

Charge on anion α polarisation.



- Charge on anion increases
- Polarisation increases
- Covalent character increases

- (v) **Pseudo inert gas configuration of cation:** Cation having pseudo inert gas configuration has more polarizing power than the cation that has inert gas configuration. Thus NaCl having inert gas configuration will be more ionic whereas CuCl having pseudo inert gas configuration will be more covalent in nature.



(poor shielding of d-electrons)



(more shielding of s and p electrons)

Application & Exceptions of Fajan's Rule

- (i) Ag₂S is less soluble than Ag₂O in H₂O because Ag₂S is more covalent due to bigger S²⁻ ion.

- (ii) Fe(OH)₃ is less soluble than Fe(OH)₂ in water because Fe³⁺ is smaller than Fe²⁺ and thus charge is more.

Therefore, Fe(OH)₃ is more covalent than Fe(OH)₂.

- (iii) The colour of some compounds can be explained on the basis of polarisation of their bigger negative ions.

For example: AgCl is white AgBr, AgI, Ag₂CO₃ are yellow. Similarly, SnCl₄ is white but SnI₄ is black. PbCl₂ is white but PbI₂ is yellow. The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

- (iv) Variation of melting point [melting point of covalent compound < melting point of ionic compound]





Train Your Brain

Example 5: AgCl is colourless whereas AgI is yellow, because of:

- (a) Ag⁺ have 18 electron shell to screen the nuclear charge.
- (b) Ag⁺ shows pseudo inert gas configuration.
- (c) distortion of I⁻ is more pronounced than Cl⁻ ion.
- (d) existence of d-d transition.

Sol. (c) The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

Example 6: Compound with maximum ionic character is formed from

- | | |
|---------------|--------------|
| (a) Na and Cl | (b) Cs and F |
| (c) Cs and I | (d) Na and F |

Sol. (b) Using fajan's rule, larger cation and smaller anion will have maximum Ionic character.

Example 7: Out of following which one has least value of melting point

- | | |
|-----------------------|-----------------------|
| (a) LiCl | (b) BeCl ₂ |
| (c) MgCl ₂ | (d) CaCl ₂ |

Sol. (b) BeCl₂ has maximum covalent character due to small size of Be²⁺,

$$\text{Polarization} \propto \frac{1}{\text{Cation Size}} \propto \text{covalent character.}$$

Higher the covalent character lower will be its melting point.

Example 8: Out of following which one has maximum ionic character

- | | |
|-----------------------|-----------------------|
| (a) NaCl | (b) KCl |
| (c) CaCl ₂ | (d) MgCl ₂ |

Sol. (b) Due to larger size of Potassium it has least degree of polarization so it has maximum ionic character.

Example 9: Which of the following has highest melting point

- | | |
|----------|---------|
| (a) NaCl | (b) NaI |
| (c) NaBr | (d) NaF |

Sol. (d) Due to small size of Fluorine anion. It has least polarisation power so NaF has maximum ionic character. i.e, highest melting point.

9. Which of the following combination of ion will have highest polarisation?

- | | |
|--|--|
| (a) Fe ²⁺ , Br ⁻ | (b) Ni ⁴⁺ , Br ⁻ |
| (c) Ni ²⁺ , Br ⁻ | (d) Fe, Br ⁻ |

10. The correct order of decreasing polarizability of ion is:

- | | |
|---|---|
| (a) Cl ⁻ , Br ⁻ , I ⁻ , F ⁻ | (b) F ⁻ , I ⁻ , Br ⁻ , Cl ⁻ |
| (c) I ⁻ , Br ⁻ , Cl ⁻ , F ⁻ | (d) F ⁻ , Cl ⁻ , Br ⁻ , I ⁻ |

11. Which of the following is in order of increasing covalent character?

- | |
|--|
| (a) CCl ₄ < BeCl ₂ < BCl ₃ < LiCl |
| (b) LiCl < CCl ₄ < BeCl ₂ < BCl ₃ |
| (c) LiCl < BeCl ₂ < BCl ₃ < CCl ₄ |
| (d) LiCl < BeCl ₂ < CCl ₄ < BCl ₃ |

12. Which one of the following show correct order of covalent character?

- | | |
|---------------|-------------------|
| (a) ZnO < ZnS | (b) ZnS = ZnO |
| (c) ZnS < ZnO | (d) None of these |

COVALENT BOND

(I) A covalent bond is formed by the mutual sharing of electrons between two atoms of electronegative elements to complete their octet. (Except H which completes its duplet).



H₂ molecule O₂ molecule N₂ molecule

(II) The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.

(III) Sharing of electrons may occurs in three ways –

No. of electron shared between two atoms	Electron pair	Bond
2	1	Single bond (-)
4	2	Double bond (=)
6	3	Triple bond (≡)

e.g.: H—N—H Three single bonds (not triplet bond)
H

N≡N Triple bond. (not three single bond) O=O Double bond (Not two single bond) H—O—H (Two single bonds.)

LEWIS SYMBOLS

In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis introduced simple notations to represent valence



Concept Application

8. The hydration of ionic compounds involves :

- (a) Evolution of heat
- (b) Weakening of attractive forces
- (c) Dissociation into ions
- (d) All of these

electrons in an atom. These notations are called as Lewis symbols. For example, the Lewis symbols for the elements of second period are as follow:



Significance of Lewis Symbols

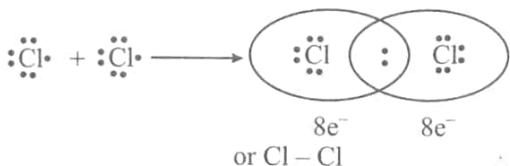
The number of dots around the symbol represents the number of valence electrons. This number of valence electrons help to calculate the common or group valence of the elements.

The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

Molecule / Ion	Lewis Representation
H ₂	H : H
O ₂	$\ddot{\text{O}}\text{:}\ddot{\text{O}}\text{:}$
O ₃	$\ddot{\text{O}}\text{:}\ddot{\text{O}}\text{:}\ddot{\text{O}}\text{:}$
NF ₃	$\ddot{\text{F}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{F}}\text{:}$
CO ₃ ²⁻	$\left[\ddot{\text{O}}\text{:}\text{C}\text{:}\ddot{\text{O}}\text{:}\right]^{2-}$
HNO ₃	$\ddot{\text{O}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}}\text{:}\text{H}$

LEWIS STRUCTURE AND COVALENT BOND

The Lewis-Langmuir theory can be understood by considering the formation of the chlorine molecule, Cl₂. The Cl atom with electronic configuration, [Ne]¹⁰ 3s² 3p⁵, is one electron short of the argon configuration. The formation of the Cl molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both



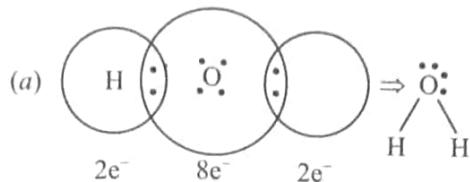
Covalent bond between two Cl atoms

Chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon). The dots represent electrons. Such structures are referred to as Lewis dot structures.

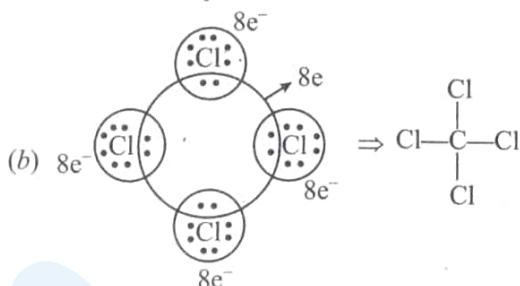
The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that:

- (i) Each bond is formed as a result of sharing of an electron pair between the atoms.

- (ii) Each combining atom contributes at least one electron to the shared pair.
- (iii) The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons. Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:

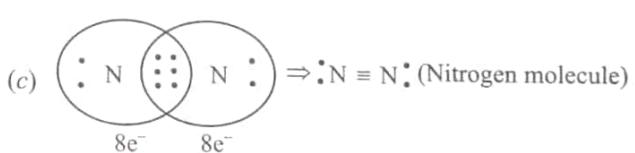
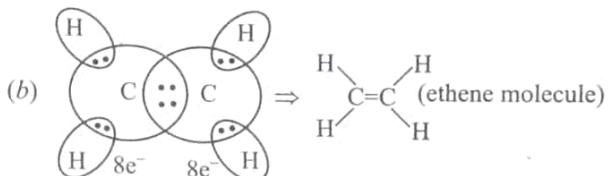
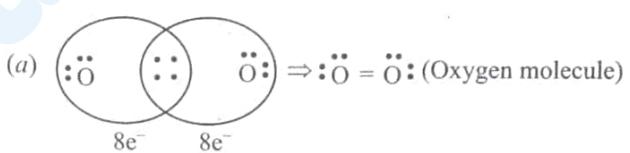


H atoms attain a duplet of electrons and O attain the octet, here O has 2 lone pairs



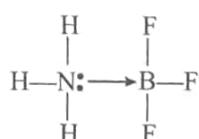
Each of the four Cl atoms along with the C atom attains octet of electrons, here each Cl atom has 3 lone pairs.

Multiple Covalent Bonds



COORDINATE OR DATIVE BOND

- ❖ In this type of combination both the electrons needed for sharing are contributed only by one atom. The atom which contributes the pair of electrons (lone pair) is known as donor and the atom which accepts these electrons is called acceptor. The coordinate bond is usually represented by an arrow pointing towards the acceptor. e.g.,
- ❖ Coordinate bond is found in the compounds like SO₂, SO₃, O₃, NH₄⁺, H₃O⁺, NH₄Cl, SO₄²⁻, H₂SO₄ and KNO₃ etc.



Characteristics of Coordinate Compounds

- These are usually insoluble in water but soluble in organic solvents. They usually do not conduct electricity. The M.P. and B.P. of these compounds are higher than covalent compounds but lesser than the ionic compounds. The coordination bond is directional so these compounds exhibit isomerism.
- Examples of the compounds in which all the three ionic, covalent and dative bonds are present are :
 CuSO_4 , NH_4X , $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

MODERN CONCEPT OF COVALENT BOND (VBT)

As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H_2 ($435.8 \text{ kJ mol}^{-1}$, 74 pm) and F_2 ($150.6 \text{ kJ mol}^{-1}$, 42 pm); although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules. Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two Important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

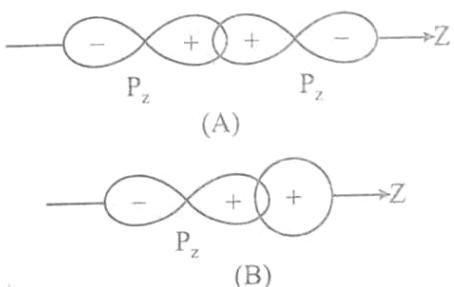
Valence Bond Theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition.

Orbital Overlap Concept: In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

Overlapping of Atomic Orbitals: When two atoms come close to each other there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of s and p orbitals resulting in positive, negative and zero overlap are depicted in the following figure.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like CH_4 , NH_3 and H_2O , the VB theory has to account for their characteristic shapes as well. We know that the shapes of CH_4 , NH_3 , and H_2O molecules are tetrahedral, pyramidal and bent respectively.

Positive overlap



Train Your Brain

Example 10: Classify the following bonds as ionic, polar or covalent and give your reasons :

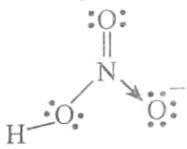
- SiSi bond in $\text{Cl}_3\text{SiSiCl}_3$
- SiCl bond in $\text{Cl}_3\text{SiSiCl}_3$
- CaF bond in CaF_2
- NH bond in NH_3

- Sol.** (a) Covalent, due to same electronegativity.
(b) Polar covalent, due to less electronegativity difference.
(c) Ionic, due to greater electronegativity difference.
(d) Polar covalent, due to different electronegativity.

Example 11: Which of the following contains a coordinate covalent bond

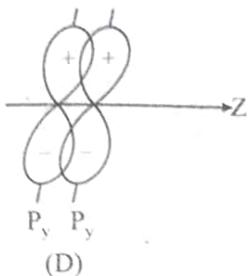
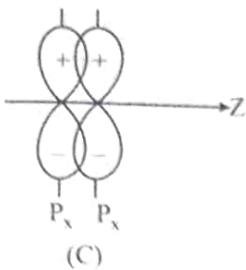
- HNO_3
- BaCl_2
- HCl
- H_2O

- Sol.** (a) HNO_3 contains 1 coordinate covalent bond

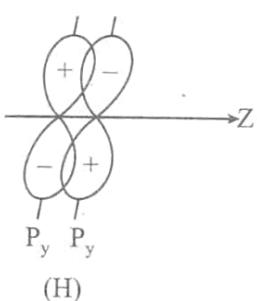
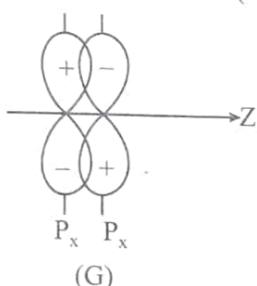
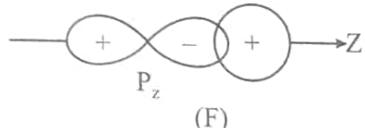
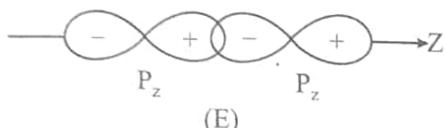


Concept Application

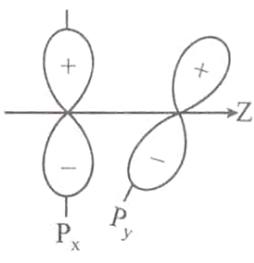
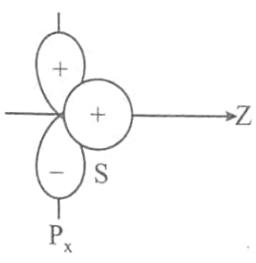
- In which of the following species the bonds are Non-directional?
 - NCl_3
 - RbCl
 - BeCl_2
 - BCl_3
- Which of the following molecules does not have coordinate bonds?
 - CH_3-NC
 - CO
 - O_3
 - CO_3^{2-}
- Which of the following compounds are covalent
 - H_2
 - CaO
 - KCl
 - Na_2S
- The number of π bonds and σ -bonds in case of lewis structure of SO_4^{2-} :
 - $4\sigma, 2\pi$
 - $4\sigma, 1\pi$
 - $4\sigma, \text{zero } \pi$
 - $4\sigma, 4\pi$



Negative overlap



Zero overlap



Positive, negative and zero overlaps of s and p atomic orbitals

Types of Overlapping and Nature of Covalent Bonds: The covalent bond may be classified into two types depending upon the types of overlapping:

(i) sigma (σ) bond, and (ii) pi (π) bond

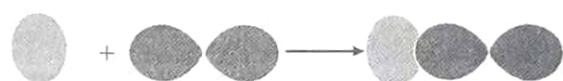
(i) **Sigma (σ) bond:** This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

❖ **s-s overlapping :** In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below:



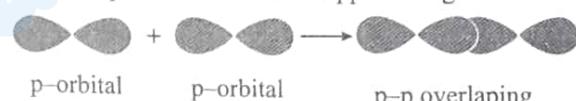
s-orbital s-orbital s-s overlapping

❖ **s-p overlapping:** This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.



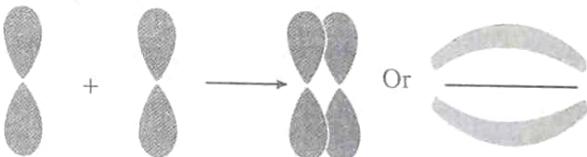
s-orbital p-orbital s-P orbital

❖ **p-p overlapping:** This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



p-orbital p-orbital p-p overlapping

(ii) **pi (π) bond:** In the formation of π bond the atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



p-orbital p-orbital p-p overlapping

Strength of Sigma and pi Bonds: Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond .

Strength of σ and π -bonds :

σ bond strength : $s - s < s - p < p - p$

π bond strength : $2\pi - 2\pi > 2\pi - 3\pi > 3\pi - 3\pi$

HYBRIDISATION

The valence bond theory (overlapping concept) explains satisfactorily the formation of various molecules but it fails to account the geometry and shapes of various molecules. It does not give the explanation why BeCl_2 is linear, BF_3 is planar, CH_4 is tetrahedral, NH_3 is pyramidal and water is V-shaped molecule.

In order to explain these cases, the valence bond theory has been supplemented by the concept of hybridization. This is a hypothetical concept and was introduced by Pauling & Slater.

According to them the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals**. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

Salient features of hybridisation: The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important Conditions for Hybridisation

- (i) The orbitals present in the valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is the orbital that undergo hybridization and not the electrons. For example, for orbitals of nitrogen atom ($2s^2 \ 2p_x^1 \ 2p_y^1 \ 2p_z^1$) belonging to valency shell when hybridize to form four hybrid orbitals , one of which has two electrons (as before) and other three have one electron each. It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Determination of Hybridisation of an Atom in a Molecule or Ion

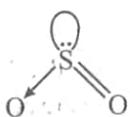
Steric number rule (given by Gillespie): Steric No. of an atom = number of atom bonded with that atom + number of lone pair(s) left on that atom.

Note: This rule is not applicable to molecules/ions which have odd e^- (ClO_2 , NO , NO_2), free radicals and compounds like B_2H_6 which involve 3 centre $2e^-$ bond (banana bond).

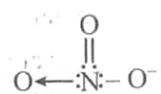
For Example :



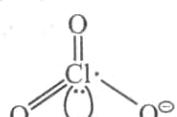
$$S.No. = 2 + 0 = 2$$



$$S.No. = 2 + 1 = 3$$



$$S.No. = 3 + 0 = 3$$



$$S.No. = 3 + 1 = 4$$

Steric number	Types of Hybridisation	Geometry
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
7	sp^3d^3	Pentagonal bipyramidal

To Predict Hybridisation Following Formula May be Used

No. of hybrid orbital = $\frac{1}{2} [\text{Total number of valence } e^- \text{ in the central atom} + \text{total number of monovalent atoms} - \text{charge on cation} + \text{charge on anion}]$

e.g. for NH_4^+ $\frac{1}{2} [5 + 4 - 1] = 4$ sp^3 hybridisation.

SF_4 $\frac{1}{2} [6 + 4] = 5$ sp^3d hybridisation.

SO_4^{2-} $\frac{1}{2} [6 + 2] = 4$ sp^3 hybridisation.

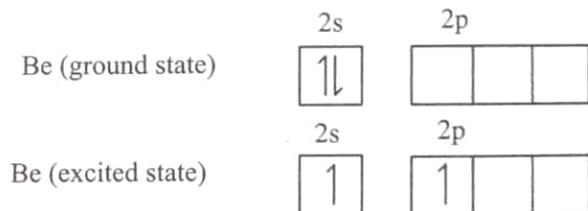
(‘O’ is divalent so add only charge on anion)

NO_3^- $\frac{1}{2} [5 + 1] = 3$ sp^2 hybridisation.

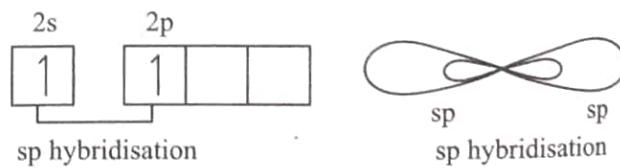
Types of Hybridisation

sp Hybridisation

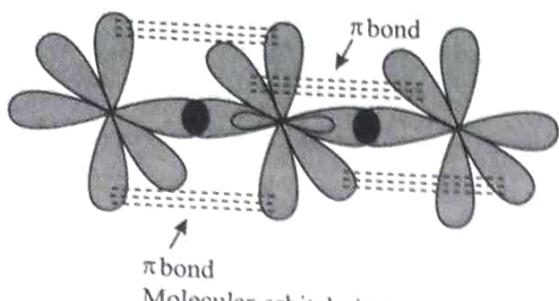
- (I) In this hybridisation one s & one p-orbital of an atom are mixed to give two new hybrid orbitals which are equivalent in shape & energy known as sp hybrid orbitals.
- (II) These two sp hybrid orbitals are arrange in straight line & at bond angle 180° .
- (III) %S - character 50%



Be atom shared two electrons from F in BeF_2 .



CO_2 Molecule ($O = C = O$): In CO_2 molecule, C has two sp hybrid orbitals & two unhybridised p orbitals.



Thus, CO_2 molecule is a linear in shape & having 180° bond angle.

sp^2 Hybridisation

- In this hybridisation one & two p orbitals are mixed to give three new sp^2 hybrid orbitals which all are in the same shape & equivalent energies.
- These three sp^2 hybrid orbitals are at angle of 120° & giving trigonal planar shape.

	2s	2p
B (ground state)	1↓	1
B (excited state)	1	1 1
	1	1 1

sp^2 hybridisation

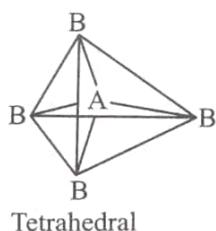
B atom accepts 3 electrons From 3 F atom in BF_3 and s-character 33.3%

sp^3 Hybridisation

- In this hybridisation one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp^3 hybrid orbitals.
- The angle between these four hybrid orbitals will be $109^\circ 28'$.

	2s	2p
C (ground state)	1↓	1 1
C (excited state)	1	1 1 1
	1	1 1 1

sp^3 hybridisation



C atom share four electrons with 4 hydrogen atoms.
The shape obtained from these hybrid orbitals would be tetrahedron.

Three following examples represent this condition.

(a) Four sigma bonds with zero lone pair of electron:

The following examples represent this condition.

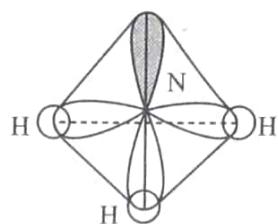


In above compounds, bond angle is $109^\circ 28'$ & tetrahedron shape.

(b) Three sigma bonds & one lone pair of electron:

(i) This condition is shown by following compounds & ions NH_3 , NF_3 , PF_3 , NCl_3 , PCl_3 , $\text{CH}_3\text{H}_3\text{O}^+$, ClO_3^-

(ii) sp^3 hybridisation, pyramidal shape & bond angle will be less than 109.5° due to the presence of the lone pair electron on nitrogen which repels bond pair electron more therefore bond angle is reduced from $109^\circ 28'$ to 107° .



Molecular pyramidal orbital or NH_3

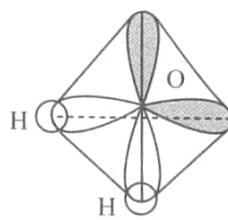
The repulsion between $\ell\text{p} - \text{b.p} > \text{bp} - \text{bp}$.

(c) Two sigma bonds & two lone pair of electrons:

(i) This condition is shown by following compounds and ions.



(ii) In all above examples, the central atom showing sp^3 hybridisation, angular shape and bond angle will be either less than $109^\circ 28'$ or more than $109^\circ 28'$.



Molecular angular orbital or H_2O

sp^3d Hybridisation

(i) In this hybridisation one s orbital and one d orbital are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as sp^3d hybrid orbitals.

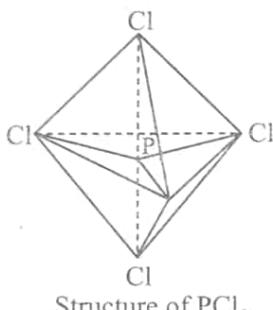
(ii) Out of these five orbitals, three hybrid orbitals are at 120° angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes is trigonal bipyramidal.

For example, PF_5 showing sp^3d hybridisation

3s	3p	3d
11	1 1 1	
P (ground state)		
3s	3p	3d
1	1 1 1	1
P* (excited state)		
3s	3p	3d
1	1 1 1	1
sp ³ d hybridisation		

P atom share electron with five electron of F

- (iii) In this hybridisation d_{z²} orbital is hybridised with s and p orbitals. In this way five sp³d hybrid orbitals form five sigma bond with five F atoms and give a molecule of PF₅, shape of this molecule is trigonal bipyramidal.



Structure of PCl₅

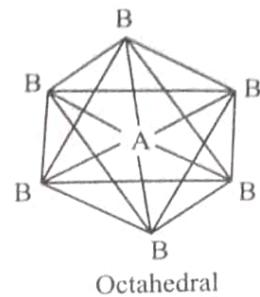
PF₅, PCl₅, PBr₅, PI₅, AsF₅, AsCl₅, SbCl₅, SbF₅ etc.

sp³d² Hybridisation

- (i) In this hybridisation, one s-orbitals, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as sp³d² hybrid orbitals.
- (ii) The shape of molecule obtained from above six hybrid orbitals will be symmetrical octahedral.
- (iii) The angle between all hybrid orbitals will be 90° or 180°.
eg.: SF₆, AlF₆³⁻, PF₆⁻, ICl₅, XeOF₄, XeOF₄⁻, ICl₄⁻,
- (iv) Two 'd' orbital participates in the hybridisation are d_{x²-y²} and d_{z²}.

SF₆ Hybridisation

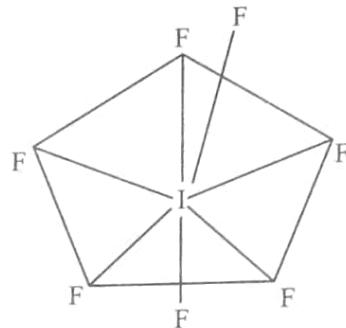
3s	3p	3d
11	1 1 1	
S (ground state)		
3s	3p	3d
1	1 1 1	1 1
S (excited state)		
3s	3p	3d
1	1 1 1	1 1
sp ³ d ² hybridisation		



Octahedral

sp³d³ Hybridisation

- (i) In this hybridisation, one s-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp³d³ hybrid orbitals.
- (ii) In this hybridisation d-orbitals used are d_{xy}, d_{z²} & d_{x²-y²} orbitals.
- (iii) These seven sp³d³ orbitals are configurated in pentagonal bipyramidal shape.
- (iv) Five bond angles are of 72° & ten bond angles of 90°.
- (v) The following examples showing sp³d³ hybridisation – IF₇ & XeF₆.



Structure of IF₇



Train Your Brain

Example 12: Which can not be explained by VBT

- (a) Overlapping
- (b) Bond formation
- (c) Paramagnetic nature of oxygen
- (d) Shapes of molecules

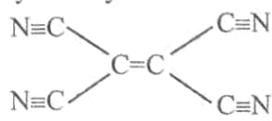
Sol. (c) Paramagnetic nature of oxygen can be explained by M.O.T

Example 13: π bond can be formed between

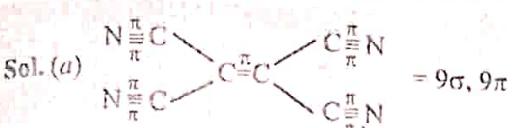
- (a) C–C
- (b) O–O
- (c) N–N
- (d) All of these

Sol. (d) π bond formed only by non hybrid orbitals.

Example 14: How many σ and π bonds are there in the molecule of tetracyanoethylene



- (a) Nine σ and nine π
- (b) Five σ and nine π
- (c) Nine σ and seven π
- (d) Five σ and eight π



Example 15: The relative overlap of orbitals decreases in the order

- (a) $sp > sp^2 > sp^3 >> p$ (b) $sp^1 > sp^2 > sp >> p$
 (c) $p > sp^1 > sp^2 > sp$ (d) $p > sp > sp^2 > sp^1$

Sol. (b) $p-p > s-p > s-s$

so p-character increases, relative overlapping of orbitals increases.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

The Main Postulates of VSEPR Theory are as follows:

- The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded] around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tends to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order :

lone pair (ℓp) - lone pair (ℓp) $>$ lone pair (ℓp) - bond pair (bp) $>$ bond pair (bp) - bond pair (bp).

Shapes of Molecules Based on Vsepr Theory

Total no. of hybrid orbitals	No. of b.p. (bond pairs)	No. of unshared pair i.e. ℓ_p	General formula	Type of hybridisation	Stereochemical formula/str.	Shape	Exam.
2	2	0	AB_2	sp		linear	$BeCl_2$
3	3	0	AB_3	sp^2		Trigonal planar	BCl_3, NO_3^- GaF_3, CO_3^{2-}
3	2	1	AB_2	sp^2		V or Bent or angular	$SnCl_2, O_3, SO_2$
4	4	0	AB_4	sp^3		Tetrahedron	CH_4, SiF_4, NH_4^+

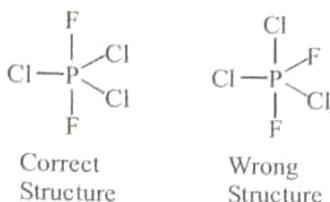
4	3	1	AB_3	sp^3		Trigonal pyramidal	NH_3 , CH_3^-
4	2	2	AB_2	sp^3		V or Bent or angular	H_2O , SF_2
4	1	3	AB	sp^3		linear	ClO^-
5	5	0	AB_5	sp^3d		Trigonal bipyramidal	PF_5 , SF_5^+ , SbBr_5 , XeO_3F_2
5	4	1	AB_4	sp^3d		Seesaw	SF_4
5	3	2	AB_3	sp^3d		T-shaped	ClF_3 , BrF_3
5	2	3	AB_2	sp^3d		Linear	ICl_2^- , XeF_2 , I_3^-
6	6	0	AB_6	sp^3d^2		Octahedral or Square bipyramidal	SF_6 , IF_6^+
6	5	1	AB_5	sp^3d^2		Square pyramidal	IF_5 , XeOF_4 , BrF_5
6	4	2	AB_4	sp^3d^2		Square planar	IF_4^- , XeF_4^- , ICl_4^-
7	7	0	AB_7	sp^3d^3		Pentagonal bipyramidal	IF_7
7	6	1	AB_6	sp^3d^3		Distorted octahedral	XeF_6 , IF_6^-
7	5	2	AB_5	sp^3d^3		Pentagonal planar	XeF_5^-

HYBRIDISATION IN IONIC SOLID SPECIES

Species	Cationic part	Anionic part
PCl ₅	PCl ₄ ⁺ (sp ³)	PCl ₆ ⁻ (sp ³ d ²)
PBr ₅	PBr ₄ ⁺ (sp ³)	Br ⁻
XeF ₆	XeF ₅ ⁺ (sp ³ d ²)	F ⁻
N ₂ O ₃	NO ₂ ⁺ (sp)	NO ₃ ⁻ (sp ²)
N ₂ O ₄ (s)	NO ⁺	NO ₂ ⁻ (sp ²)
I ₂ Cl ₆ (liquid)	ICl ₂ ⁺ (sp ³)	ICl ₄ ⁻ (sp ³ d ²)
I ₂ (liquid)	I ₃ ⁺ (sp ³)	I ₃ ⁻ (sp ³ d)
ClO ₂ ⁶	ClO ₂ ⁺ (sp ²)	ClO ₄ ⁻ (sp ³)

BENT'S RULE

- (i) A lone pair of electron prefers to occupy that hybrid orbitals which has greater percentage of s-character.
- (ii) A more electronegative atom/group prefers to occupy that hybrid orbital which has smaller percentage of s-character.
- Ex. Draw the geometry of PCl₃F₂



Because highly electronegative atom occupy axial position (axial position has smaller percentage of s-character).

DRAGO'S RULE

On the basis of experimental bond angles of certain molecules fulfilling the following three conditions,

- (i) Central atom belongs to third or lower period in periodic table
- (ii) Central atom must contain atleast one lone pair of electron.
- (iii) Electronegativity of surrounding atom is ≤ 2.5

Drago generalised that in such molecules justification of experimental bond angle can be made satisfactorily if one considers no hybridisation, i.e., overlapping of almost pure atomic orbitals from central atom.

In such molecules bond angle is approximately 90°.

Group 15 Bond angle Group 16 Bond angle

NH ₃	107°48'	H ₂ O	104°28'
PH ₃	93°36'	H ₂ S	92°
AsH ₃	91°48'	H ₂ Se	91°
SbH ₃	91°18'	H ₂ Te	90.5°

* Correct order of bond angle.

- (a) H₂O > H₂S > H₂Se > H₂Te
- (b) NH₃ > PH₃ > AsH₃ > SbH₃

MOLECULES THAT DO NOT EXIST

- (1) SF₄, SF₆ & PF₅ exist while OF₄, OF₆, NF₅ do not exist.
- (2) (a) PI₅(vap) & SCl₆ do not exist.
(b) SCl₆ does not exist while TeCl₆ exist.
(c) PI₅ (Solid) exist.
- (3) SF₆, PF₅, XeF₆, XeF₄ & XeF₂ exist while SH₆, PH₅, XeH₆, XeH₄, XeH₂ do not exist.



Train Your Brain

Example 16: The hybridization of carbon atoms in C – C single bond of H – C ≡ C – CH = CH₂ is

- (a) sp³-sp³
- (b) sp²-sp
- (c) sp²-sp²
- (d) sp³-sp

Sol. (b)

Example 17: Which of the following is not true for a hybridisation process

- (a) Electrons take part and not the orbitals
- (b) Participating orbitals have almost equal energy
- (c) Hybridised orbitals have identical shape
- (d) Hybridised orbitals have identical energies

Sol. (a) Electrons do not take part in hybridization.

Example 18: Choose the molecules in which hybridisation occurs in the ground state-

- (i) BCl₃
- (ii) NH₃
- (iii) PCl₃
- (iv) BeF₂

The correct answer is

- (a) i, ii, iv
- (b) i, ii, iii
- (c) ii, iii
- (d) iii, iv

Sol. (c) NH₃ and PCl₃ have same G.S hybridization.

Example 19: Which of the following is not applicable

- (a) CO₂ Irregular geometry
- (b) BF₃ Regular geometry
- (c) NH₃ Irregular geometry
- (d) SO₂ Irregular geometry

Sol. (a) CO₂ Linear geometry
 sp-hybridization

Example 20: The shape of sulphate ion is

- (a) hexagonal
- (b) square planar
- (c) trigonal bipyramidal
- (d) tetrahedral

Sol. (d) so structure is tetrahedral.

Example 21: Among NO₃⁻, CO₃²⁻, ClO₃⁻, SO₃²⁻, AsO₃⁻ and BO₃⁻ the non-planar species are

- (a) CO₃²⁻, SO₃²⁻, BO₃⁻
- (b) AsO₃⁻, ClO₃⁻, SO₃²⁻
- (c) NO₃⁻, CO₃²⁻, BO₃⁻
- (d) NO₃⁻, SO₃²⁻, BO₃⁻

Sol. (b) AsO₃⁻, ClO₃⁻, SO₃²⁻, are sp³ hybridised so structure are tetrahedral

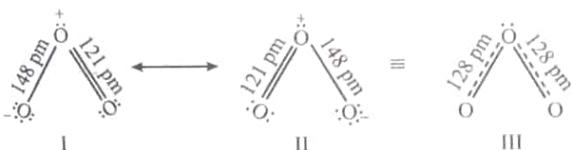


Concept Application

20. In pent-3-en-1-yne the terminal carbon-atoms have following hybridisation
 (a) sp & sp^2 (b) sp^2 & sp^3
 (c) sp^2 & sp (d) sp & sp^3
21. Specify the hybridisations of central atom in the following species respectively $\{\text{N}_3^-, \text{NOCl}, \text{N}_2\text{O}\}$
 (a) sp , sp^2 , sp (b) sp , sp , sp^3
 (c) sp^2 , sp , sp (d) sp^2 , sp^2 , sp .
22. In C-C bond in C_2H_6 undergoes heterolytic fission, the hybridisation of carbon in the resulting two species is / are
 (a) sp^2 both (b) sp^3 both
 (c) sp^2 , sp^3 (d) sp , sp^2
23. Select the CORRECT statement if internuclear axis is y-axis:
 (a) d_{xy} and d_{xy} orbital of two atoms form π -bond
 (b) p_z and p_z orbital of two atoms form s-bond
 (c) $d_{x^2-y^2}$ and $d_{x^2-y^2}$ orbital of two atoms form π -bond
 (d) p_y and d_{zx} orbital of two atoms form π -bond
24. Which of the following has a geometry different from the other three species (having the same geometry)?
 (a) BF_4^- (b) SO_4^{2-}
 (c) XeF_4 (d) PH_4^+
25. Which of the following species given below have shape similar to XeOF_4 ?
 (a) XeO_3 (b) IOF_4^+
 (c) PCl_5 (d) XeF_5^\oplus

RESONANCE

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below:



Structures I and II represent the two canonical forms while the structure III is the resonance hybrid.

In both structures we have $\text{O}-\text{O}$ single bond and $\text{O}=\text{O}$ double bond. The normal $\text{O}-\text{O}$ and $\text{O}=\text{O}$ bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate

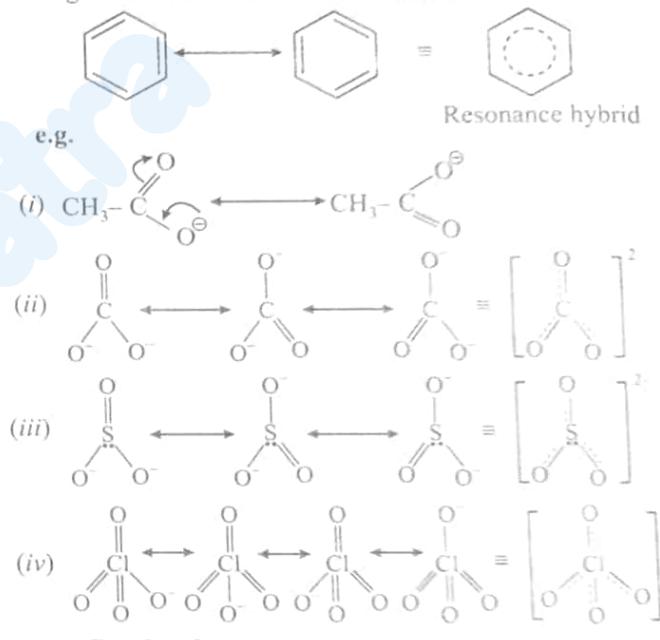
between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3 . According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid structure which describes the molecule accurately.

Thus for O_3 the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow.

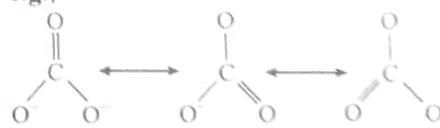
Definition: Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound. The delocalization of π e⁻ is called resonance.

Resonance Hybrid: It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.



$$\text{Bond order} = \frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}}$$

e.g.,



$$\text{Bond order} = \frac{2+1+1}{3} = 1.33$$

- ♦ Resonance energy = Actual bond energy - Energy of most stable resonating structure.
- ♦ Stability of molecule \propto resonance energy.
- ♦ More is the number of covalent bonds in molecule more will be its resonance energy.
- ♦ Resonance energy \propto number of resonating structures.

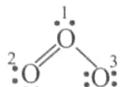
FORMAL CHARGE

Lewis dot structures, in general do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as:

Formal charge (F.C.)
On an atom in a
Lewis structure

$$\text{Total number of valence electrons in the free atom} - \left[\frac{1}{2} \left(\text{Total number of bonding electrons} \right) \right]$$

Let us consider the ozone molecule (O_3). The Lewis structure of O_3 , may be drawn as:



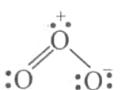
The atoms have been numbered as 1, 2 and 3. The formal charge on:

$$\text{The central } O \text{ atom marked } 1 = 6 - 2 - \frac{1}{2} (6) = +1$$

$$\text{The terminal } O \text{ atom marked } 2 = 6 - 4 - \frac{1}{2} (4) = 0$$

$$\text{The terminal } O \text{ atom marked } 3 = 6 - 6 - \frac{1}{2} (2) = -1$$

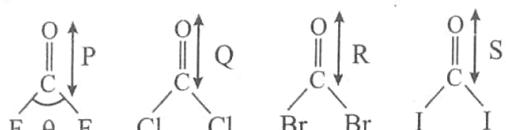
Hence, we represent O_3 along with the formal charges as follows:



Train Your Brain

Example 22: Discuss the bond angle in carbonyl halides COF_2 , $COCl_2$, $COBr_2$, COI_2

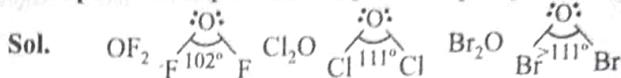
Sol.



Bond angle $\theta \Rightarrow COF_2 < COCl_2 < COBr_2 < COI_2$

Double bonds require more space than single bonds. Hence $C=O$ group compresses the molecule and bond angle decrease maximum in COF_2 as bond pairs of electrons are more closer to the fluorine atoms because of high electronegativity of fluorine. As size of halogen atoms increases and their electronegativity decreases repulsion between bond pairs increases and therefore θ increases.

Example 23: Compare bond angle of OF_2 , Cl_2O and Br_2O .



Bond pairs of electrons are more closer to the fluorine atoms (because of high electronegativity of fluorine). So the $\ell p - \ell p$ repulsion is more than $bp - bp$. Thus the $F-O-F$ bond angle decreases to 102° from 109.5° . In Cl_2O , the bond pair are more closer to the oxygen atom because of the high electronegativity of oxygen. So the $bp - bp$ repulsion is more than $\ell p - \ell p$. Thus the bond angle $Cl-O-Cl$ increases to $\approx 111^\circ$ due to $bp - bp$ repulsion and repulsion between larger Cl atoms.

Note: The steric crowding of the larger halogen atoms also contributes in the increasing bond angles.

Example 24: What is not true about resonance?

- (a) The resonating structures are hypothetical
- (b) The unpaired electrons in various resonating structures are same
- (c) Hybrid structure is most energetic
- (d) Hybrid structure is least energetic

Sol. (c) In resonance hybrid structure is least energetic



Concept Application

26. Which of the following conditions is not correct for resonating structures?

- (a) The contributing structures must have the same number of unpaired electrons
- (b) The contributing structures may have different energies
- (c) The contributing structures should be so written that unlike charges reside on atoms that are far apart
- (d) The positive charge should be present on the electropositive element and the negative charge on the electronegative element

27. The compound which contains both covalent and co-ordinate bond is -

- | | |
|---------------|-------------------|
| (a) CO | (b) NaCl |
| (c) H_2SO_4 | (d) None of these |

BOND PARAMETERS

- (I) Bond Length (Bond distance)
- (II) Bond Angle
- (III) Bond Energy

(I) Bond Length: The average distance between the nucleus of two atoms is known as bond length, normally it is represented in Å. e.g. A ————— B

- It depends on electronegativities of constituent atoms

Case I: Electronegativity difference is zero then

$$\text{Bond length} = r_A + r_B \quad \text{or} \quad d_{A-B} = r_A + r_B$$

where r_A is covalent radius of A

r_B is covalent radius of B

X_A is electronegativity of A

X_B is electronegativity of B

If $r_A = r_B$ then Bond length = $2r_A$ or $2r_B$

Case II: Electronegativity difference is not equal to zero then

Bond length is given by Shomaker & Stevenson formula is

$$\text{Bond length} = r_A + r_B - 0.09 (X_A - X_B)$$

$$\text{Difference in electronegativities} = X_A - X_B$$

Factors affecting Bond Length:

(a) Electronegativity:

$$\text{Bond length} \propto \frac{1}{\Delta EN} \quad (\text{While B.E.} \propto \Delta EN)$$



(b) Bond order or number of bonds:

$$\text{Bond length} \propto \frac{1}{\text{Number of bond or bond order}}$$

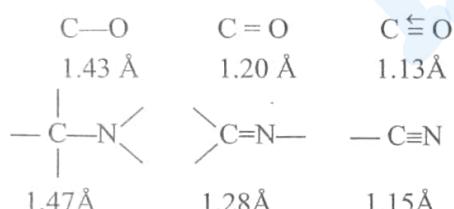


$$\text{Bond length} \quad 1.54 \text{ \AA} \quad 1.34 \text{ \AA} \quad 1.20 \text{ \AA}$$

↑
increasing

$$\text{Bond energy} \quad 80 \quad 140 \quad 180-200 \text{ K.Cal.}$$

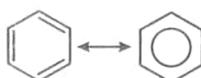
↑
increasing →



(c) Resonance: (due to resonance bond length is affected)

eg. 1. Benzene

$$\begin{aligned} \text{C-C bond length} & 1.54 \text{ \AA} \\ \text{C=C bond length} & 1.34 \text{ \AA} \end{aligned}$$



but bond length in between
single & double bond
is = 1.39 \AA

eg. 2. Bond length of C—O in CO_2 is 1.15 \AA

Resonance occurs in CO_2 as follows-



Bond length = 1.15 \AA (Between double & triple bond)

(d) Hybridisation:

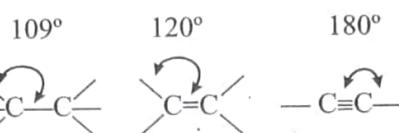
$$\text{Bond length} \propto \frac{1}{\text{s-character}}$$

Example:	Compound	Hybridisation	Bond length $\text{C}—\text{C}$
	Ethane	sp^3-sp^3	1.54 \AA
		sp^3-sp^2	1.51 \AA
		sp^3-sp	1.47 \AA
	$\text{C}=\text{C}-\text{C}=\text{C}$	sp^2-sp^2	1.46 \AA
	$\text{C}=\text{C}-\text{C}\equiv\text{C}$	sp^2-sp	1.42 \AA
	$\text{C}\equiv\text{C}-\text{C}=\text{C}$	$\text{sp}-\text{sp}$	1.37 \AA

(II) Bond Angle: The angle between any two adjacent atoms is known as bond angle. It is represented in degree ($^\circ$), min ('), and second ('')

Factors affecting the bond angle-

(a) Number of bond: Bond angle \propto Number of bonds (Bond order)



(b) Hybridisation:

Case-I: When hybridisation is same, bonded atoms are same, central atom and lone pair are different.

$$\text{Then bond angle} \propto \frac{1}{\text{No. of lonepair}}$$



$$\begin{array}{lll} \text{Hybridisation} & \text{sp}^3 & \text{sp}^3 \\ \text{Bond angle} & 109^\circ 28' > 107^\circ > 104.5^\circ & \text{sp}^3 \end{array}$$

Case-II: When hybridisation is same, bonded atoms are same lone pair is same but central atom is different.

Then bond angle \propto electronegativity of central atom

$$\begin{array}{lll} \text{Example:} & \ddot{\text{N}}\text{H}_3 & \ddot{\text{P}}\text{H}_3 & \ddot{\text{AsH}}_3 \\ \text{Bond angle} & 107^\circ & 93^\circ & 91^\circ \end{array}$$

- Electronegativity decreasing
- Bond angle will decrease

Case-III When hybridisation is same, lone pair are same, Central atom is same, bonded atoms are different.

$$\begin{array}{lll} \text{sp}^3 & \text{OF}_2 & 103-105^\circ \\ \text{sp}^3 & \text{Cl}_2\text{O} & 109-111^\circ \\ \text{sp}^3 & \text{Br}_2\text{O} & 116-118^\circ \end{array} \quad \begin{array}{l} \text{Electronegativity} \\ \text{of bonded atom is} \\ \text{decreasing} \end{array}$$

$$\text{Bond angle} \propto \frac{1}{\text{electronegativity of bonded atom}}$$

(III) Bond Energy (BE): Bond energy may be defined as-

(a) Bond formation energy: Energy released when any bond is formed is known as bond formation energy or bond energy.

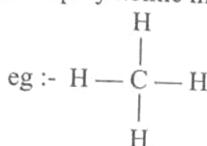
(b) **Bond dissociation energy:** Energy required to dissociate any bond is known as bond dissociation energy. Calculation of released energy is more difficult than the dissociation energy therefore dissociation energy of bond is calculated and is assumed as bond energy or bond formation energy.

Case-I: In diatomic molecule:

Bond energy = bond dissociation energy

eg :- $N_2 > O_2 > H_2 > F_2$

Case-II: For polyatomic molecule:



Bond energy = per C—H bond is 99.5 kcal/mole

Theoretical values of bond dissociation energy (d) of individual C—H bonds CH_4 are given below-

$$D(CH_3-H) = 102 \text{ kcal/mole}$$

$$D(CH_2-H) = 105 \text{ kcal/mole}$$

$$D(CH-H) = 108 \text{ kcal/mole}$$

$$D(C-H) = 83 \text{ kcal/mole}$$

Hence bond energy E per C—H bond in methane

$$E = \frac{398}{4} = 99.5 \text{ kcal/mole.}$$

❖ Bond dissociation energy (d) is related to the state of hybridisation.

Factors Affecting the Bond Energy

$$(a) \Delta \text{E.N.} \quad (b) \text{Bond order}$$

$$(c) \text{Atomic size/radius} \quad (d) \text{Bond polarity}$$

$$(e) \text{Resonance} \quad (f) \text{Hybridisation}$$

$$(g) \text{Lone pair of electron}$$

$$(a) \Delta \text{E.N. : Bond energy} \propto \Delta \text{EN}$$

eg. HF > HCl > HBr > HI

$$(b) \text{Bond order: Bond energy} \propto \text{Bond order}$$

$$\text{eg. } C-C < C=C < C \equiv C$$

$$79 \text{ kcal, } 143.3 \text{ kcal, } 199.0 \text{ kcal.}$$

$$(c) \text{Atomic size/radius: Bond energy} \propto \frac{1}{\text{Atomicsize}}$$

$$\text{eg. } C \equiv C < C \equiv N < N \equiv N$$

Exception: In case of halogen group, order of bond energy is

$$Cl-Cl > Br-Br > F-F > I-I$$

Because of higher electron density and small size of F atoms, repulsion between of two F atom, weakens the bond.

Other e.g. S-S > O-O, C-C > Si-Si > Ge-Ge

$$(d) \text{Bond Polarity: Bond energy} \propto \text{polarity}$$

$$\text{eg. } H-F > H-Cl > H-Br > H-I$$

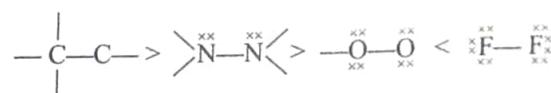
$$(e) \text{Hybridisation: Bond energy} \propto \text{s-character in hybrid orbitals.}$$

$$\text{eg. } sp-sp > sp^2-sp^2 > sp^3-sp^3$$

$$\% \text{s-character: } 50\% \quad 33.3\% \quad 25\%$$

(f) Lone pair of electrons :

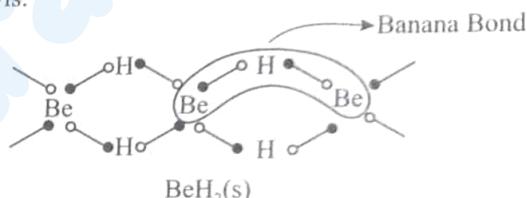
$$\text{Bond energy} \propto \frac{1}{\text{lone pair of electrons}}$$



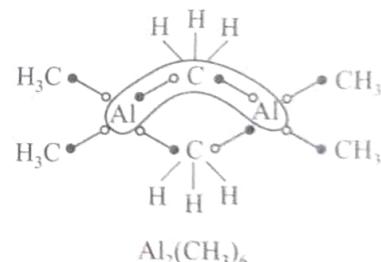
Size of F and O atoms is small so their bond energy should be high (small atomic radius) but it is actually less due to lone pair of electrons present on F and O atoms, which repels each other in F—F and —O—O— type of bonds.

BRIDGE BONDING (ELECTRON DEFICIENT BONDING)

There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds which are 2c-2e bonds(two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected such as three centre-two.electron bonds (3c-2e) present in diborane B_2H_6 , $Al_2(CH_3)_6$, $BeH_2(s)$ and bridging metal carbonyls.



Note: Special case : In B_2H_6 and BeH_2 bridge bonds are called as Banana bonds

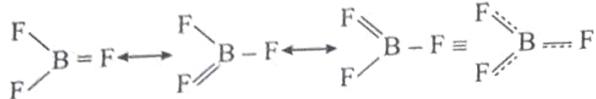
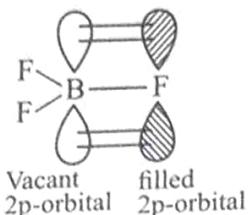


But Al_2Cl_6 have covalent bond only and there is no electron deficient bonding as depicted in the given structure.



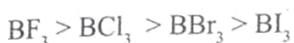
BACK BONDING

Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF_3 , the boron atom completes its octet by accepting two 2p-electrons of fluorine into 2p empty orbital.



- Decrease in B - F bond length is due to delocalised π - π bonding between filled p-orbital of F atom and vacant p-orbital of B atom.

The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example the extent of back bonding in boron trihalides is as follows :



There is π - π back bonding in boron trihalide. The extent of back bonding decreases from BF_3 to BI_3 because of increasing size of p-orbitals participating in back bonding that is from 2p(in F) to 4p(in Br).

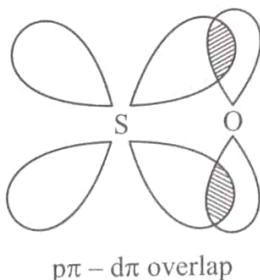
- The extent of back bonding decreases if the atom having vacant orbitals is also having some non-bonded electron pairs on it. So among the atoms of third period the extent of back bonding follows the order



The extent of π - π overlapping

$$\propto \frac{1}{\text{Lewis acid character}}$$

(c) Bond Lengths and π - $d\pi$ Bonding:

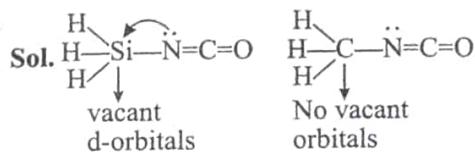


The bonds between S and O, Se and O, are much shorter than might be expected for a single bond. In some cases, they may be formulated as localized double bonds. A σ bond is formed in the usual way, In addition a π bond is formed by the sideways overlap of a 'p' orbital on the oxygen with a 'd' orbital on the sulphur giving a π - $d\pi$ interaction. This π - $d\pi$ bonding is similar to that found in the oxides and oxo-acids of phosphorus, and is in contrast to the more common π - π type of double bond found in ethene.



Train Your Brain

Example 25: Silyl isocyanate (SiH_3NCO) is linear but methyl isocyanate (CH_3NCO) is bent explain !



Lone pair on nitrogen is delocalised between N and Si through π - $d\pi$ back bonding. So silyl isocyanate is linear.

Example 26. The correct order of bond length is:

- $\text{F}-\text{F} > \text{Cl}-\text{Cl} > \text{Br}-\text{Br} > \text{I}-\text{I}$
- $\text{I}-\text{I} > \text{Br}-\text{Br} > \text{Cl}-\text{Cl} > \text{F}-\text{F}$
- $\text{Cl}-\text{Cl} > \text{Br}-\text{Br} > \text{F}-\text{F} > \text{I}-\text{I}$
- $\text{Br}-\text{Br} > \text{Cl}-\text{Cl} > \text{F}-\text{F} > \text{I}-\text{I}$

Sol. (b) I has largest atomic size. So, bond length of I-I is largest.



Concept Application

28. Select the correct statement

- C-O bond length of CO molecule is higher than the C-O bond length of CO_2
- C-O bond length of CO molecule is lower than the C-O bond length of CO_2
- N-O bond length of NO_3^- ion is same as N-O bond length of NO_2^-
- N-O bond length of NO_3^- ion is lower than the N-O bond length of NO_2^-

29. Which of the following bond angle order is incorrect.

- $\text{NH}_3 > \text{PH}_3$
- $\text{BF}_3 < \text{BH}_3$
- $\text{O}(\text{CH}_3)_2 < \text{O}(\text{C}_2\text{H}_5)_2$
- $\text{CO}_3^{2-} < \text{CO}_2$

30. Correct order of bond energy of C-O bond is

- $\text{CO}_3^{2-} > \text{CO}_2 > \text{CO}$
- $\text{CO}_2 > \text{CO} > \text{CO}_3^{2-}$
- $\text{CO} > \text{CO}_2 > \text{CO}_3^{2-}$
- None of these

31. The correct order of decreasing X-O-X bond angle is (X=F, F or Cl)

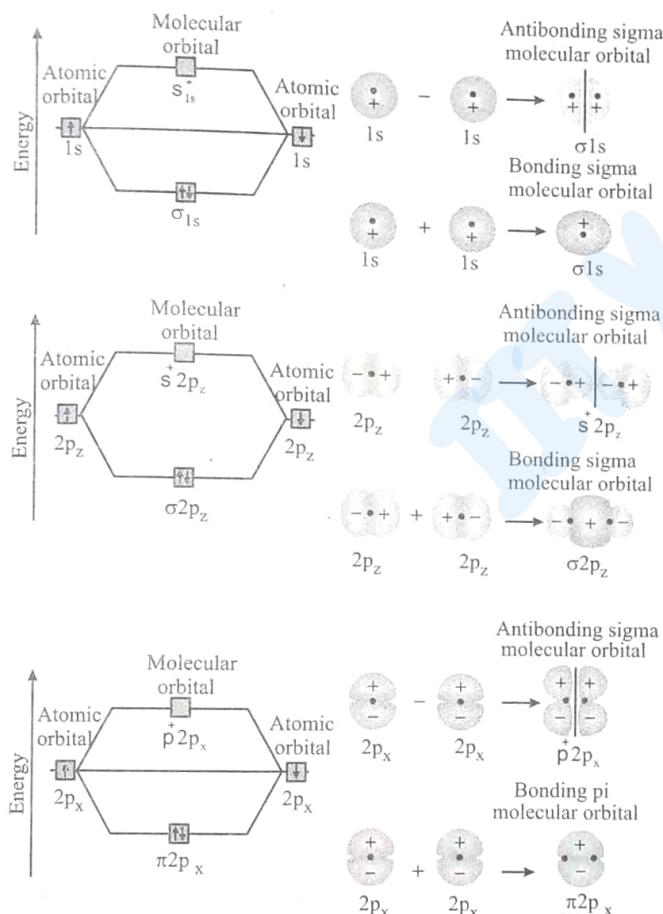
- $\text{H}_2\text{O} > \text{Cl}_2\text{O} > \text{F}_2\text{O}$
- $\text{Cl}_2\text{O} > \text{H}_2\text{O} > \text{F}_2\text{O}$
- $\text{F}_2\text{O} > \text{Cl}_2\text{O} > \text{H}_2\text{O}$
- $\text{F}_2\text{O} > \text{H}_2\text{O} > \text{Cl}_2\text{O}$



MOLECULAR ORBITAL THEORY (MOT)

Developed by Hund and Mulliken it suggests that in molecules electrons are present in new orbitals called molecular orbitals and that they are not associated with the atoms. Important postulates of the theory are as under

- ❖ Just like electrons of atoms are present in atomic orbitals, electrons of a molecule are present in molecular orbitals.
- ❖ Molecular orbitals are formed by the combination of atomic orbitals of nearly equal energies.
- ❖ The number of molecular orbitals formed is equal to the number of combining atomic orbitals. Half of these are called bonding molecular orbital (lower energy) while other half are called antibonding molecular orbital (higher energy).
- ❖ Shapes of the molecular orbital depend on the shapes of combining atomic orbitals
- ❖ Filling of electrons in various molecular orbital takes place according to Aufbau, Pauli and Hund's rules for the filling of atomic orbitals.



Linear Combination of Atomic Orbitals (LCAO)

- ❖ Molecular orbitals are formed by the linear combination of atomic orbitals i.e. the wave functions of combining atomic orbitals may either be added or may be subtracted.

$$\Psi_{(MO)} = \Psi_A \pm \Psi_B$$

$$\Psi_{(Bonding)} = \Psi_A + \Psi_B$$

$$\Psi_{(Antibonding)} = \Psi_A - \Psi_B$$

❖ A wave possesses a crest and a trough. When orbitals approach in such a way that the crest falls over the crest, a bonding molecular orbital is formed. When the crest of one wave falls over the trough of the other, an antibonding molecular orbital is formed.

❖ Probability of finding electrons in the bonding molecular orbital is always greater than that of sum of probabilities in the atomic orbitals.

$$\Psi_b^2 = (\Psi_A + \Psi_B)^2 = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B \text{ and}$$

$$\Psi_a^2 = (\Psi_A - \Psi_B)^2 = \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B$$

❖ Bonding molecular orbital are designated as σ , π while the notations for antibonding molecular orbital are σ^* , π^* . Bonding molecular orbitals are more stable while antibonding molecular orbitals are less stable.

Conditions for the Formation of Molecular Orbitals - Combination of Atomic Orbitals

- ❖ Combining atomic orbitals should have nearly equal energies.
- ❖ Combining atomic orbitals must have proper orientations.

Types of Molecular Orbitals Formed

❖ **Sigma Molecular Orbitals**: When 1s atomic orbital combines with 1s or 2s combines with 2s, two sigma molecular orbitals are formed. They are marked as bonding (σ) and antibonding (σ^*) molecular orbital.

❖ **π -Molecular Orbitals** : When $2p_x$ combines with $2p_x$ (or $2p_y$ with $2p_y$) two π -molecular orbitals are formed at z-axis namely bonding (π) and antibonding (π^*)

Electronic Configuration, Bond Order for Diatomic Molecules

❖ Before representing the molecular orbital energy level diagram we must arrange various orbitals in the order of increasing energy

$$1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi^* 2p_x = \pi^* 2p_y < \sigma 2p_z$$

❖ But the order of energy levels of $\sigma 2p_z$ and $(\pi 2p_x = \pi 2p_y)$ is reversed for molecular Carbon, Boron, Nitrogen

Bond Order (n)

❖ Bond order is defined as half of the difference between the number of electron present in the bonding and the antibonding molecular orbital.

$$\text{Bond order (n)} = 1/2 (N_b - N_a)$$

❖ Molecule is stable only when bond order is positive. If the bond order is negative or zero the molecule does not exist. It may have whole number as well as fractional values. Higher the value of bond order, greater must be the stability of molecule or molecular ion. Further, higher the bond order, shorter the bond.

To elaborate certain examples are taken as under

(a) Hydrogen

$$H_2 : \sigma(1s)^2 ; n = 1$$

$$H_2^+ : \sigma(1s)^1 ; n = 1/2$$

$$H_2^- : \sigma(1s)^2 ; \sigma^*(1s)^1 ; n = 1/2$$

This indicates that both H_2 and H_2^+ are stable and H_2 is more stable than H_2^+ . Both H_2^+ and H_2^- should be paramagnetic also as they have a half filled molecular orbital.

(b) Helium

He_2 does not exist as it is shown by configuration

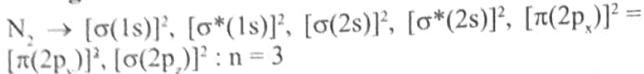


But He_2^+ may exist as its bond order will be positive



Its stability and bond length is comparable to H_2^+

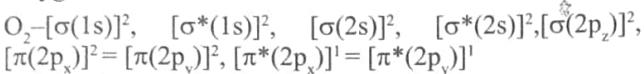
(c) Nitrogen



High value of bond order (3) implies that it should have highest bond dissociation energy as compared to all other diatomic molecules.

N_2^+ and N_2^- both exhibit bond order 2.5 and are found to be paramagnetic due to the presence of one unpaired electron. Stability of these three is in the order $\text{N}_3 > \text{N}_2^+ > \text{N}_2^-$

(d) Oxygen



Bond order, $n = 2$

O_2^+ has bond order 2.5 as one electron is removed from the antibonding molecular orbital.

O_2^- has bond order 1.5 as an additional electron is added to the antibonding molecular orbital.

O_2^{2-} has bond order 1.0 as two electrons are added to the two antibonding molecular orbital stability order (and bond dissociation energy) of the four species are as under.

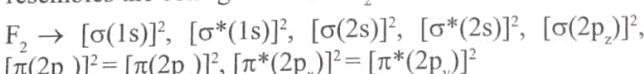


Bond distances are in the reverse order; $\text{O}_2^+ < \text{O}_2 < \text{O}_2^- < \text{O}_2^{2-}$

Out of these four species O_2 , O_2^+ and O_2^- are paramagnetic due to the presence of 2, 1, 1 unpaired electrons respectively while O_2^{2-} is diamagnetic as it has no unpaired electron.

(e) Fluorine

Total number of electrons in F_2 molecule is 18 and so it resembles the configuration of O_2^{2-}

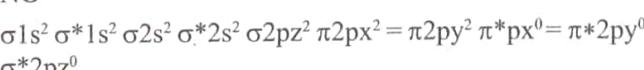


Its bond order n is 1 and it should be diamagnetic due to the presence of all orbitals as fully occupied.

(f) Neon

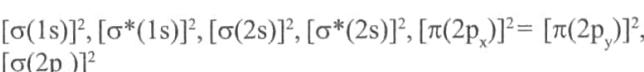
Ne_2 does not exist as its bond order comes to be zero.

(g) NO⁺



$$\text{B.O.} = \frac{10 - 4}{2} = 3$$

(h) CO

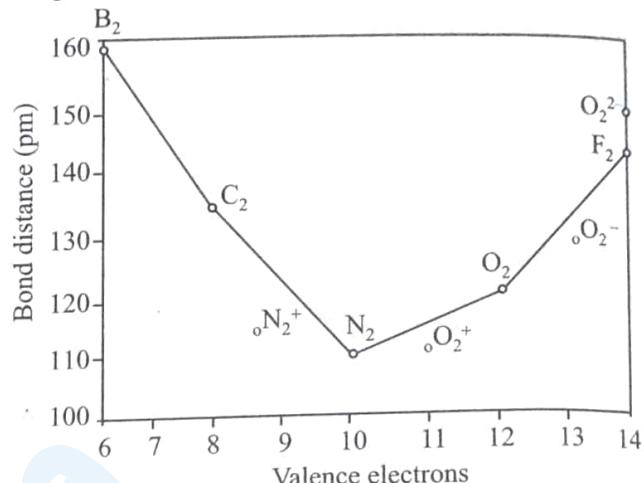


$$\text{B.O.} = 3$$

Note: HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

Bond lengths in homonuclear diatomic molecules: Figure shows the variation of bond distance with the number of valence electrons in second-period p block homonuclear diatomic molecules. As the number of electrons increases, the number in bonding orbitals also increases, the bond strength becomes greater, and the bond length becomes shorter. This continues up to 10 valence electrons in N_2 and then the trend reverses because the additional electrons occupy antibonding orbitals. The ions N_2^+ , O_2^+ , O_2^{2-} are also shown in the figure and follow a similar trend.



Train Your Brain

Example 27: Though O_2 molecule is paramagnetic yet it is a colourless gas. Why?

Sol. It is because the energy gap between HOMO and LUMO levels in O_2 molecule is so large that radiations of visible light cannot excite an e^- from HOMO to LUMO. In fact O_2 gas shows absorption in UV zone. So it is colourless.

Example 28: Correct order of bond energy is:

- (a) $\text{N}_2 > \text{N}_2^+ > \text{N}_2^- > \text{N}_2^{2-}$ (b) $\text{N}_2^+ > \text{N}_2^- > \text{N}_2^{2-} > \text{N}_2$
 (c) $\text{N}_2 > \text{N}_2^- = \text{N}_2^+ > \text{N}_2^{2-}$ (d) $\text{N}_2^- > \text{N}_2 = \text{N}_2^+ > \text{N}_2^{2-}$

Sol. (a) Bond energy is directly proportional to the bond order.

Bond order of $\text{N}_2 = 3$, $\text{N}_2^+ = 2.5$, $\text{N}_2^- = 2$

$$\text{N}_2^{2-} = 2$$

But N_2^- has more electrons in antibonding MO's and thus N_2^+ is more stable than N_2^- . So correct order of bond energy will be $\text{N}_2 > \text{N}_2^+ > \text{N}_2^- > \text{N}_2^{2-}$

Example 29: In an antibonding molecular orbital, electron density is minimum-

- (a) Around one atom of the molecule
 (b) Between the two nuclei of the molecule
 (c) At the region away from the nuclei of the molecule
 (d) at no place

Sol. (b) In an antibonding M.O., electron density is minimum between the two nuclei of the molecule.

DIPOLE MOMENT (POLARITY OF BONDS)

In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When a covalent bond is formed between two similar atoms, for example in H₂, O₂, Cl₂, N₂ or F₂ the shared pair of electrons is equally attracted by the atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

As a result of polarisation, the molecule possesses the **dipole moment** which can be defined as the product of magnitude of the partial charge (δ^+ or δ^-) developed on any of the covalently bonded atoms and the distance between two atoms.

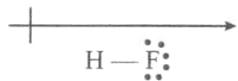
Dipole moment (μ) = Magnitude of charge (q) \times distance of separation (d)

Dipole moment is usually expressed in Debye units (d). The conversion factors are

- ❖ 1 D = 3.33564×10^{-30} Cm, where C is coulomb and m is meter.

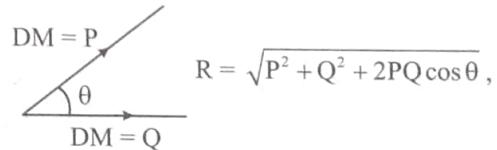
◆ 1 Debye = 1×10^{-18} e.s.u. cm.

Further dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as



The shift in electron density is represented by crossed arrow (\longrightarrow) above the Lewis structure to indicate the direction of the shift.

In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. i.e. a molecule will have a dipole moment if the summation of all of the individual moment vector is non-zero.



where R is resultant dipole moment.

For example of H_2O molecule, which has a bent structure, the two O—H bonds are oriented at an angle of 104.5° . Net dipole moment of $6.17 \times 10^{-30} \text{ Cm}$

Example 30: Which of the following are diamagnetic?

Sol. (a,b,c) Species C_2 , O_2^{-} , Li , have all the electrons paired but N_2^{+} has one unpaired electron in bonding molecular orbital so it is paramagnetic.

Example 31: Which of the following has maximum bond strength

- (a) O₂
 (c) O₂⁻ . (b) O₂⁺
 (d) O₂²⁻

Sol. (b) Bond order of O_2^+ is 2.5 which is maximum among all the species hence its bond strength will also be the maximum.

Example 32: Which have non-integral bond order

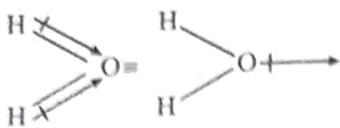
- (a) O₂⁺ (b) O₂⁻
 (c) NO (d) All of these

Sol. (d) (a) : $O_2^+ = 2.5$

- $$(c) \text{NO} = 2.5$$

Concept Application

($1D = 3.33564 \times 10^{-30} \text{ Cm}$) is the resultant of the dipole moments of two O—H bonds.



Net Dipole moment, $\mu = 1.85 \text{ D} = 1.85 \times 3.33564 \times 10^{-30} \text{ Cm} = 6.17 \times 10^{-30} \text{ Cm}$.

❖ Following compounds have zero dipole moment:

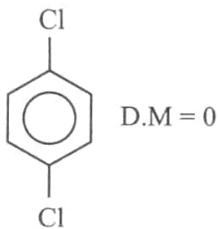
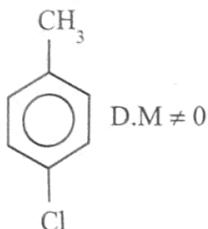
BF_3 , CO_2 , SO_3 , CF_4 , PF_5 (g), SF_6 , XeF_2 , CS_2 , CCl_4 , PCl_5 (g), XeF_4

Some important orders

$\text{HF} >$	$\text{HCl} >$	$\text{HBr} >$	HI
1.92 D	1.08	0.78	0.38
$\text{CH}_3\text{Cl} >$	$\text{CH}_2\text{Cl}_2 >$	$\text{CHCl}_3 >$	CCl_4
1.86	1.6	1.0	0

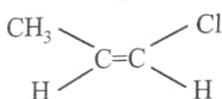
❖ Usually for disubstituted Benzene order is o > m > p

But it all depends on the substituents

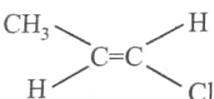


Note: For geometrical isomers usually the dipole moment of cis is more than trans but again there can be exceptions.

For example:



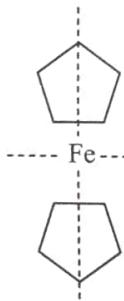
cis - form (low dipole moment)



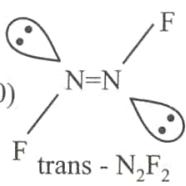
trans - form (high dipole moment)

❖ The presence of a centre of symmetry, requires that the dipole moment be zero, since any charge on one side of the molecule is canceled by an equal charge on the other side of the molecule.

Thus $[\text{CoF}_6]^{3-}$, trans- N_2F_2 and the staggered conformer of ferrocene do not have dipole moments.



----- Fe ----- C₂ staggered-ferrocene ($\mu = 0$)



Some Important Points about Dipole Moment

- ❖ A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule. e.g. B—F bonds are polar in BF_3 , but BF_3 has $\mu = 0$ due to its symmetrical geometry.
- ❖ If molecule have $\mu = 0$, then it should be linear or having symmetrical geometry.
e.g. linear – CO_2 , CS_2 , BeCl_2 (g); symmetrical geometry – BF_3 , CH_4 , PCl_5 , SF_6 , IF_7 , XeF_4 .
- ❖ If molecule has $\mu \neq 0$ then it should be angular or having unsymmetrical geometry.
 SnCl_2 , PbCl_2 , SO_2 , angular molecular geometry.
 NH_3 , H_2O , NF_3 , SF_4 , H_2S , unsymmetrical molecular geometry.
- ❖ % Ionic character =
$$\frac{\mu_{\text{Experimental}}}{\mu_{\text{Theoretical}}} \times 100$$

$$= \frac{\mu_{(\text{Observed})}}{\mu_{(100\% \text{ Ionic compound})}} \times 100$$

APPLICATION OF DIPOLE MOMENT

(I) To determine polarity and geometry of molecule:

If $\mu = 0$ compound is non polar and symmetrical
eg. CO_2 , BF_3 , CCl_4 , CH_4 , BeF_2 etc.

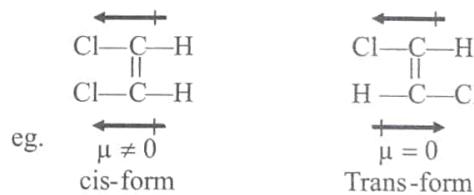
If $\mu \neq 0$ compound will be polar and unsymmetrical.
 H_2O , SO_2 , NH_3 , Cl_2O , CH_3Cl , CHCl_3 etc.

(II) To calculate % ionic character:

$$\% \text{ Ionic character} = \frac{\text{Experimental value of } \mu}{\text{Theoretical value of } \mu} \times 100$$

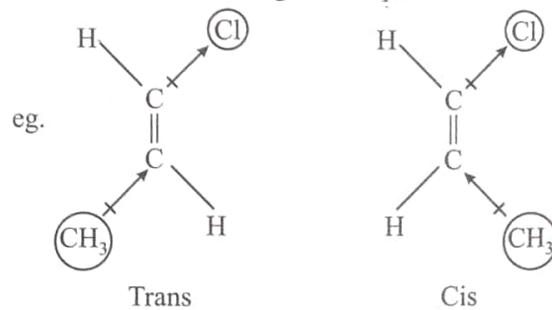
(III) To distinguish cis form or trans form:

(a) Dipole moment of cis isomers is normally higher than trans isomers.



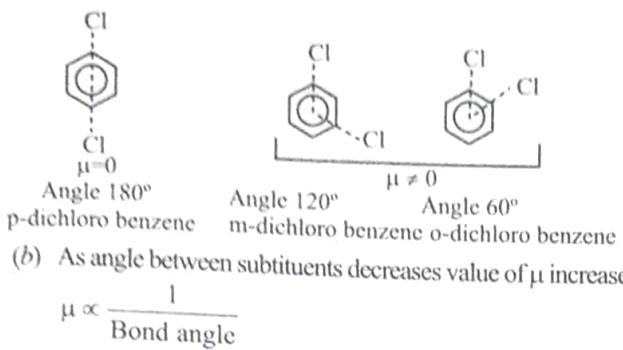
Polar ($\mu \neq 0$) Non Polar ($\mu = 0$)

(b) If two groups have opposite inductive effect then trans-isomer will have greater dipole moment :-

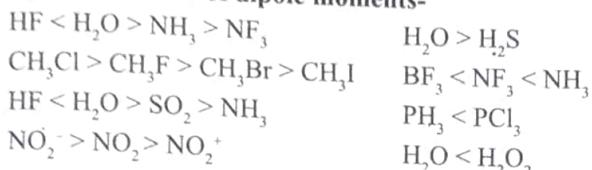


(IV) To locate position of substituents in aromatic compounds.

(a) If same substituents are present in the symmetrical position μ of benzene ring compounds will be zero

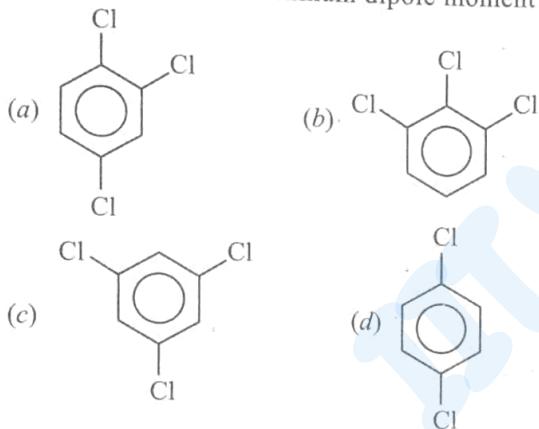


Some important orders of dipole moments-



Train Your Brain

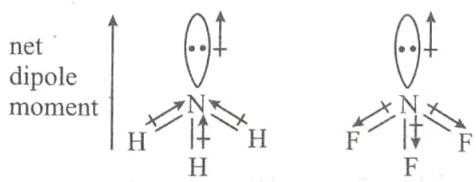
Example 33: Which has maximum dipole moment?



Sol. (b) Among these Cl has maximum dipole moment

Example 34: Why NH_3 is having more dipole moment than NF_3 .

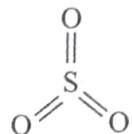
Sol. In NH_3 molecule Nitrogen is more electronegative than Hydrogen. So the net dipole moment is towards Nitrogen atom but in NF_3 molecule. Fluorine is more electronegative than nitrogen so the net dipole moment is towards fluorine atoms. In NH_3 the bond pair moments and lone pair moments are in the same direction while in NF_3 the lone pair moment and bond pair moments are in opposite direction.



Example 35: The geometry of SO_3 and its dipole moment are:

- (a) pyramidal and non-zero.
- (b) trigonal planar and non-zero.
- (c) trigonal planar and zero.
- (d) T-shaped and zero.

Sol. (c)



The steric number of sulphur = 3; so hybridisation is sp^2 . There is no lone pair on sulphur atom, therefore according to VSEPR theory, the repulsions between the bond pairs of electrons will be similar. Hence the molecule will be symmetrical (trigonal planar) with zero dipole moment

Example 36: Bond length of HCl is 1.275 \AA (Charge = 4.8×10^{-10} e.s.u.) if $\mu = 1.02 \text{ D}$, then HCl is

- (a) 100% ionic
- (b) 83% covalent
- (c) 50% covalent
- (d) 40% ionic

Sol. (b)

$$\begin{aligned} \% \text{ ionic character} &= \frac{\text{observed } \mu}{\text{theoretical } \mu} \times 100 \\ &= \frac{1.02}{1.275 \times 4.8} \times 100 = 17\% \\ &= 83\% \text{ covalent} \end{aligned}$$

Example 37: The dipole moment of the ammonia molecule is 1.48 D . The length of the dipole is

- (a) $3.08 \times 10^{-11} \text{ m}$
- (b) $5 \times 10^2 \text{ m}$
- (c) 308 m
- (d) None of these

Sol. (a) $u = 1.48 \times 3.33 \times 10^{-30} \text{ Cm} = 4.93 \times 10^{-30} \text{ Cm}$

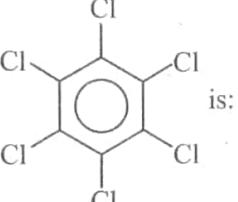
$$q = 1.6 \times 10^{-19} \text{ C}$$

$$\ell = \frac{\mu}{q} = \frac{4.93 \times 10^{-30}}{1.6 \times 10^{-19}} = 3.08 \times 10^{-11} \text{ m}$$

The NH_3 molecule can not have the shape of an equilateral triangle because in this case its dipole moment would be zero. It is actually constructed in the form of a triangular pyramid with the nitrogen atom at its vertex and the hydrogen atoms at the corners of its base.



Concept Application

37. Carbon tetrachloride has no net dipole moment because of:
- Similar electron affinity of C and Cl
 - its regular tetrahedral geometry
 - its planar geometry
 - similar sizes of C and Cl atoms
38. Which of the following has the least dipole moment?
- | | |
|---------------------|---------------------|
| (a) NF ₃ | (b) CO ₂ |
| (c) SO ₂ | (d) NH ₃ |
39. The dipole moment of  is 1.5 D. The dipole moment of  is:
- | | |
|------------|------------|
| (a) 0 D | (b) 1.5 D |
| (c) 2.86 D | (d) 2.25 D |
40. Both CO₂ and H₂O contain polar covalent bonds but CO₂ is nonpolar while H₂O is polar because :-
- H atom is smaller than C atom
 - CO₂ is a linear molecule while H₂O is an angular molecule
 - O-H bond is more polar than C-H bond
 - CO₂ contains multiple bonds while H₂O has only single bonds

HYDROGEN BOND

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are tied to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is called as hydrogen bond and is weaker than covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as given below : $\cdots \cdots \text{H}^{\delta+} - \text{F}^{\delta-} \cdots \cdots \text{H}^{\delta+} - \text{F}^{\delta-} \cdots \cdots \text{H}^{\delta+} - \text{F}^{\delta-}$

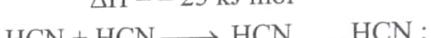
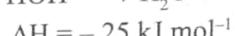
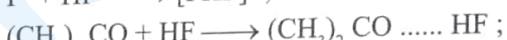
Here, hydrogen bond acts as a bridge between atoms which holds one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line ($\cdots \cdots$) while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of

one molecule with the electronegative atom (F, O or N) of another molecule.

❖ Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O is held with weak electrostatic forces by the lone pair of electrons of the electronegative atom i.e. the strongly positive H and the strongly electronegative lone pairs tend to line up and hold the molecules together. Other atoms with high electronegativity, such as Cl ; can also form hydrogen bonds in strongly polar molecules such as chloroform, CHCl₃. Conditions required for H-bond :

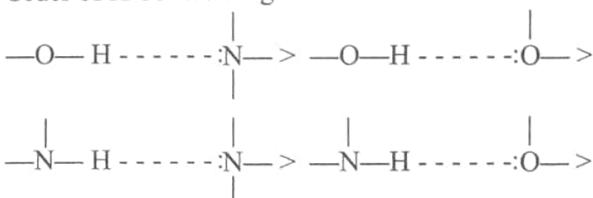
- Molecule should have more electronegative atom (F, O, N) linked to H-atom.
- Size of electronegative atom should be smaller.
- A lone pair should be present on more electronegative atom.

Strength of H-bond : The strength of H-bond is usually very low (5 - 10 kJ/mol) but in some cases this value may be as high as 50 kJ/mol. The strongest H-bonds are formed by F atoms. Deuterium is more electropositive than H, therefore it also form stronger bonds. The strength of the H-bond can be compared by the relative bond energies and the geometry of the various compounds as given below.



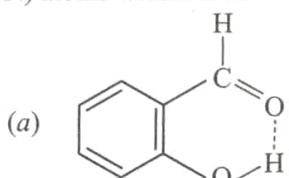
The magnitude of H-bonding depends on the physical state of the compounds. H-bonding is maximum in the solid state and minimum in the gaseous state. Thus hydrogen bonds have strong influence on the structure and properties of the compounds.

❖ Order of H-bond strength



Types of H-Bonds

(a) **Intramolecular H-Bonding:** This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule i.e., it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.

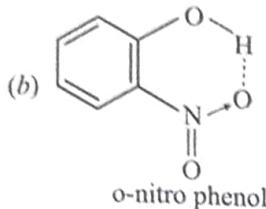


o-hydroxy benzaldehyde

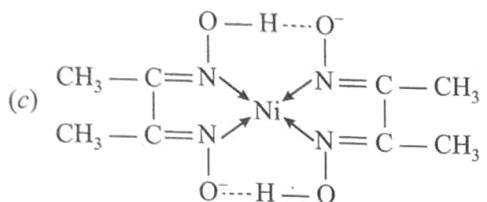
JEE (XI) Module-3



It has lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.

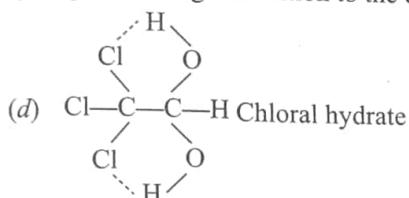


It has lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.

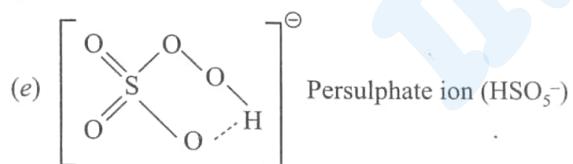


Nickel dimethyl glyoximate (a chelate)

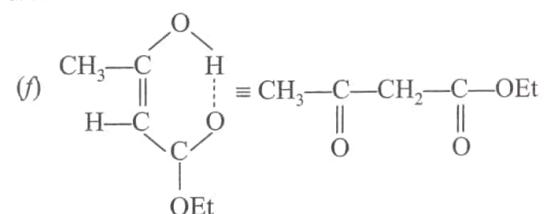
Extra stability of the complex is because of intramolecular hydrogen bonding in addition to the chelating effect.



Chloral hydrate is stable only on account of intramolecular hydrogen bonding.



K_1 of peroxomono sulphuric acid (i.e., caros acid) is greater than K_2 . After the loss of one hydrogen, the persulphate ion gets stabilised due to intramolecular hydrogen bonding and thus the removal of second hydrogen becomes difficult.



Aceto acetic ester (enolic form)

The intramolecular hydrogen bonding attributes the stability of enolic form of aceto acetic ester.

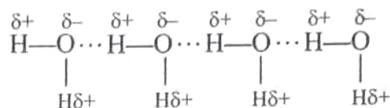
Necessary conditions for the formation of intramolecular hydrogen-bonding:

- The ring formed as a result of hydrogen bonding should be planar.

- A 5- or 6- membered ring should be formed.
- Interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

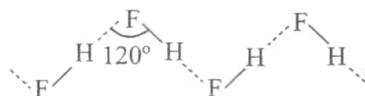
(b) **Intermolecular H-Bonding:** Exists between the negative and positive ends of different molecules of the same or different substances i.e., it is formed between two different molecules of the same or different compounds.

- In water molecules: Due to polar nature of H_2O there is association of water molecules giving a liquid state of abnormally high boiling point.



When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). The tetrahedral structure around each oxygen atom with two regular bonds to hydrogen and two hydrogen bonds to other molecules requires a very open structure with large spaces between ice molecules. Due to this volume of ice is greater than liquid water and thus ice is lighter than water. We can say that density decreases when ice is formed. Reversely when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks hence, volume increases and hence density decreases. Thus, water has maximum density at 4°C.

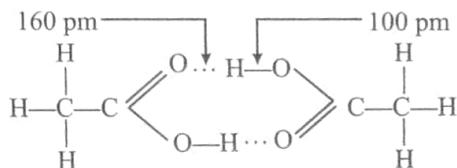
- The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a zig-zag chain $(\text{HF})_n$ in both the solid and also in the liquid.



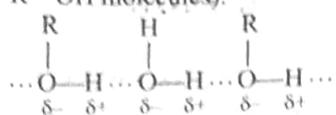
Some hydrogen-bonding also occurs in the gas, which consists of a mixture of cyclic $(\text{HF})_6$ polymers, dimeric $(\text{HF})_2$, and monomeric HF.

Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula $\text{M}[\text{HF}_2]$; in KHF_2 , for example, an X-ray diffraction study together with a neutrons diffraction study shows that there is a liner symmetrical anion having an over all, F-H-F distance of 2.26 Å, which may be compared with the H-F bond length of 0.92 Å in hydrogen fluoride monomer.

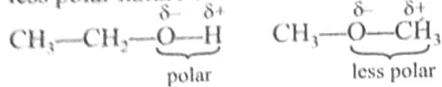
- There is also similar H-bonding in alcohol ($\text{R}-\text{OH}$) ammonia (NH_3) and phenol ($\text{C}_6\text{H}_5\text{OH}$) molecules.
- Carboxylic acid dimerises in gaseous state due to H-bonding



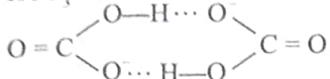
- (e) Alcohol is said to be highly soluble in water due to crossed intermolecular H-bonding (between H_2O and $\text{R}-\text{OH}$ molecules).



However isomeric ether is less soluble in water due to less polar nature of ether.



- (f) HCO_3^- ions exist as dimer in KHCO_3



In $\text{Na}^+\text{HCO}_3^-$, the HCO_3^- ions are linked in to an infinite chain through intermolecular H-bonding.

WEAK INTERMOLECULAR FORCES

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

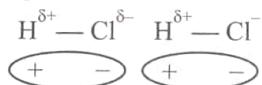
- (a) Ion-dipole attraction:
- (b) Dipole-dipole attraction:
- (c) Ion-induced dipole attraction:
- (d) Dipole-induced dipole attraction :
- (e) Instantaneous dipole- induced dipole attraction : (Dispersion force or London forces)

strength of weak forces $a > b > c > d > e$
forces (b), (d) and (e) are collectively known as Vander Waal's forces.

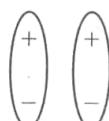
- (a) **Ion-dipole attraction :** Exists between an ion and a polar molecule. Its strength depends on (i) size of ion (ii) charge on the ion (iii) dipole moment of the polar molecule. It is thought to be directional. Ion -dipole forces are important in solutions of ionic compounds in polar solvents where solvated species such as $\text{Na}(\text{OH}_2)_x^+$ and $\text{F}(\text{H}_2\text{O})_y^-$ (for solution of NaF in H_2O) are found. Hence this force is responsible for hydration.



- (b) **Dipole-dipole attraction:** This is electrostatic attraction between the oppositely charged ends of permanent dipoles. Exists between polar molecules and due to this force gas can be liquefied.



Head to tail arrangement of dipoles



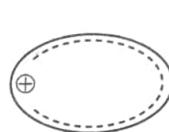
Antiparallel arrangement of dipoles

- (c) **Ion-induced dipole attraction:** Exists between ion and non-polar molecules (e.g., an atom of a noble gas such as Xenon).

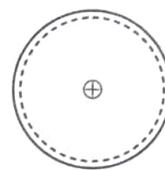
- (d) **Dipole-induced dipole attraction:** Exists between polar and non-polar molecules.



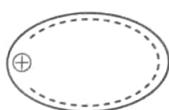
- (e) **Instantaneous dipole- induced dipole attraction:** Exists among the non-polar molecules like H_2 , O_2 , Cl_2 etc. in solid or liquid states. Even in atoms in molecules which have no permanent dipole, instantaneous dipoles will arise as a result of momentary imbalances in electron distribution. London forces are extremely short range in action and the weakest of all attractive forces. The London forces increase rapidly with molecular weight, or more properly, with the molecular volume and the number of polarizable electrons.



instantaneous dipole
due to motion of
electrons



symmetrical distribution
of electron cloud



instantaneous dipole



instantaneous induced dipole



Note: Fluorocarbons have usually low boiling points because tightly held electrons in the fluorine atoms have a small polarizability.

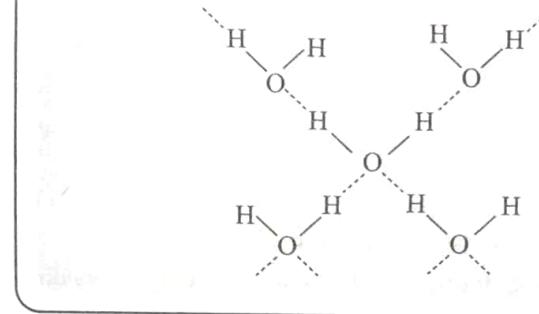


Train Your Brain

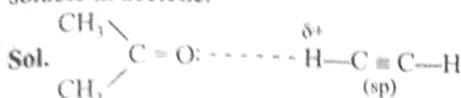
Example 38: Every H_2O molecule is surrounded by maximum how many H_2O molecule -

- (a) 2
- (b) 3
- (c) 4
- (d) 6

Sol. (c) Each H_2O molecule surrounded by four H_2O molecules



Example 39: C_2H_2 is not soluble in H_2O but it is highly soluble in acetone.



In hybridisation as %s character increases, electronegativity increases hence C_2H_2 forms H-bonds with O-atom of acetone and get dissolved. But H_2O molecules are so much associated that it is not possible for C_2H_2 molecules to break that association, hence C_2H_2 is not soluble in H_2O .

Example 40: Why $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ readily loses one molecule of water at 80°C ?

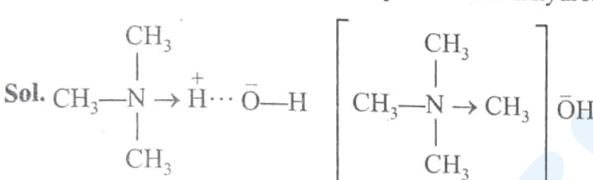
Sol. One water molecule is coordinated to lone pair of electrons on SnCl_2 and the other is hydrogen bonded to coordinated water molecules.

Example 41: Why crystalline sodium peroxide is highly hygroscopic in nature.

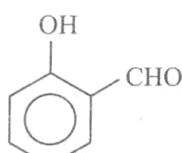
Sol. Na_2O_2 forms stable hydrates on account of H-bonding.



Example 42: Explain that tetramethyl ammonium hydroxide is a stronger base than that of trimethyl ammonium hydroxide.

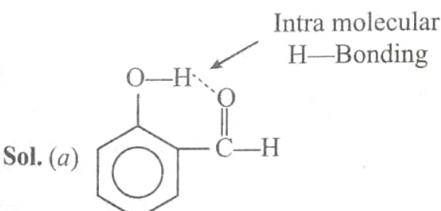


In the trimethyl compound the O-H group is hydrogen bonded to Me_3NH group and this makes it more difficult for the OH group to ionize and hence it is a weak base. In the tetramethyl compound, hydrogen bonding can not occur, so the OH⁻ group ionizes easily and thus it is a much stronger base.



Example 43: Incorrect statement about

- given compound is
- has intermolecular H-bonding
 - has intra molecular H-bonding
 - is steam-volatile
 - None of these



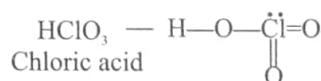
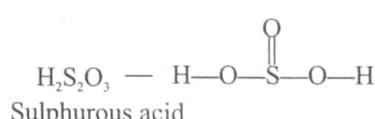
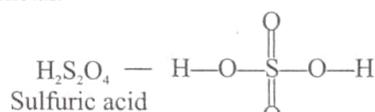
It is steam-volatile

Concept Application

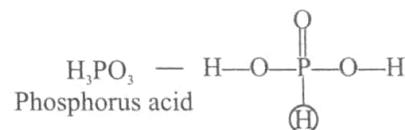
- Which one of the following does not have intermolecular H-bonding -
 - H_2O
 - α -Nitrophenol
 - HF
 - All of these
- Which of the following compounds has the highest boiling point
 - HCl
 - HBr
 - H_2SO_4
 - HNO_3
- Which of the following factor is responsible for van der Waals forces?
 - Instantaneous dipole-induced dipole interaction
 - Dipole-induced dipole interaction and ion-induced dipole interaction
 - Dipole-dipole interaction and ion-induced dipole interaction
 - All of these
- Which of the following compounds would have significant intermolecular hydrogen bonding HF, CH_2OH , N_2O_4 , CH_4 ?
 - HF, N_2O_4
 - HF, CH_4 , CH_3OH
 - HF, CH_3OH
 - CH_3OH , CH_4
- H-bonding is maximum in
 - $\text{C}_6\text{H}_5\text{OH}$
 - $\text{C}_6\text{H}_5\text{COOH}$
 - $\text{CH}_3\text{CH}_2\text{OH}$
 - CH_3COCH_3

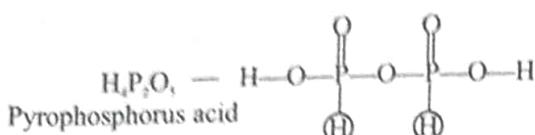
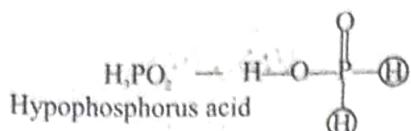
OXY-ACIDS

Those compounds which contain X-O-H bond are called oxy-acids. Where X is usually a nonmetal. But sometimes X may also be a metal.



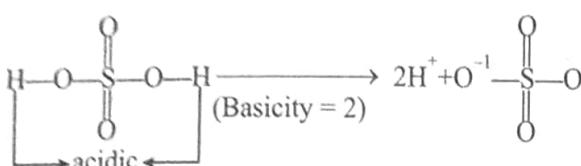
In oxy acids, all the hydrogens are attached with oxygen. Although there are a very few exceptions (as given below), in which all hydrogens are not attached with oxygen.



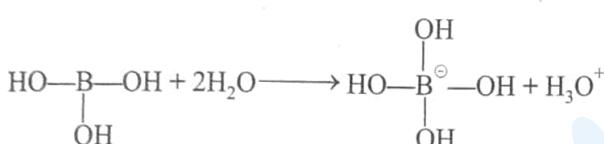


In these three oxyacids circled hydrogens are not attached with oxygen.

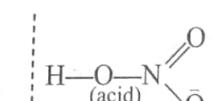
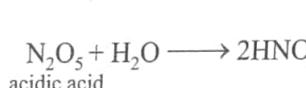
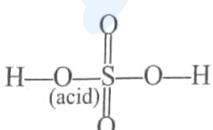
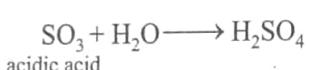
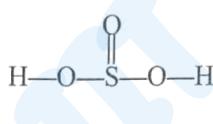
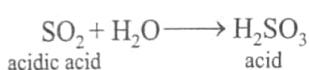
In oxyacids, those hydrogens which are attached with oxygen are acidic in nature, i.e., they ionise in solution.



No. of hydrogens attached with oxygen is known as basicity of the acid. One notable exception is H_3BO_3 in which all the three hydrogens are attached with oxygen yet, they do not ionise in solution. In fact, H_3BO_3 when dissolved in water, it behaves as a monobasic acid.



Oxyacids are actually aqueous solutions of acidic oxides.

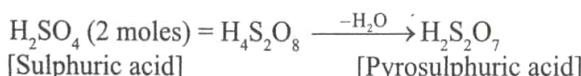
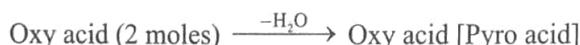


Some acids have suffix-ic acid and some has suffix-ous acid. Usually, when the central atom in oxy acid is in higher oxidation state the name of the acid ends with -ic acid and when the central atom is in lower oxidation state, its name ends with -ous acid.

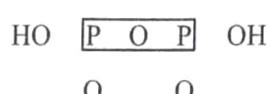
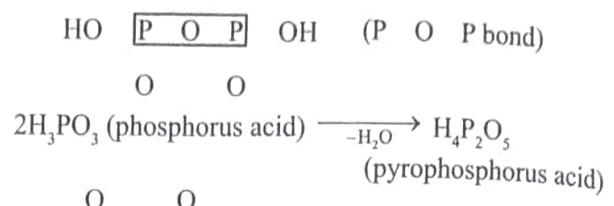
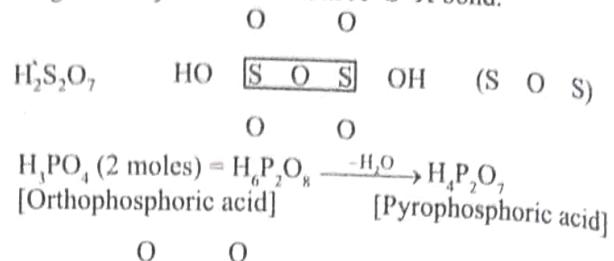
Oxyacids can be Classified as

Pyro Acids

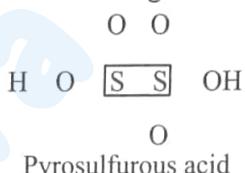
When one mole of water is removed from two moles of an oxyacid, the resultant oxy acid is known as pyro acid. In general pyro acids contain X—O—X bonds.



In general Pyro acids contain X—O—X bond.

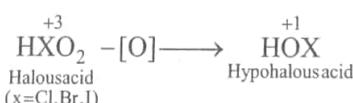
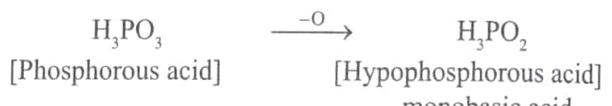


Exception: $\text{H}_2\text{S}_2\text{O}_5$ [Pyrosulfurous acid] does not contain S—O—S linkage.



Hypo Acid

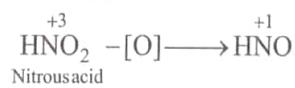
Hypo prefix is added to those oxy acids which is obtained when one oxygen atom is removed from ous form of (usually) acids.



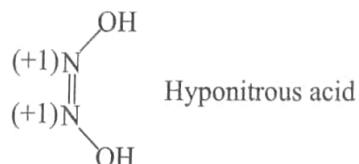
HOCl - Hypochlorous acid

HOBr - Hypobromous acid

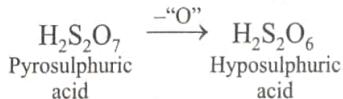
HOI - Hypiodous acid

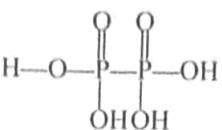
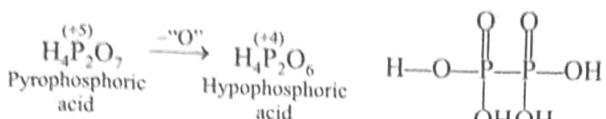


HNO exist in dimeric form i.e. as $(\text{HNO})_2 = \text{H}_2\text{N}_2\text{O}_2$

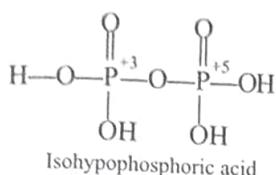


If one O is removed from pyro 'ic' acid it produce hypo 'ic' acid



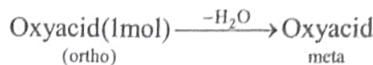


Exception: (It may exist as isohypophosphoric acid)



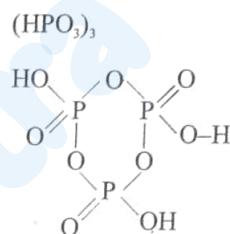
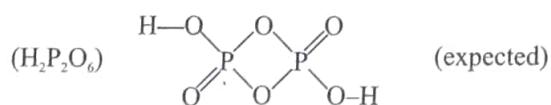
ORTHO ACIDS AND META ACIDS

When one mole of H_2O is removed from one mole of an oxy acid, the resulting compound, if an oxy acid (i.e. it contains at least one $\text{X}-\text{OH}$ bond) then the oxy acid from which H_2O is removed is named as ortho acid and the product oxyacid is known as META ACID.

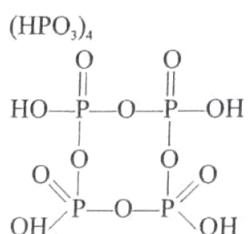


Cyclic polymetaphosphoric acids :

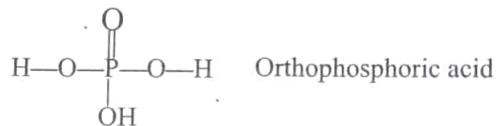
$(\text{HPO}_3)_2$ -Dimetaphosphoric acid



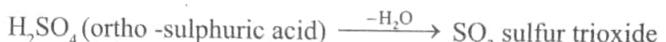
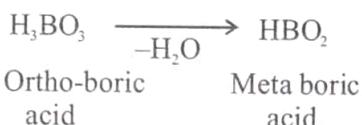
Trimetaphosphoric acid



Tetrametaphosphoric acid



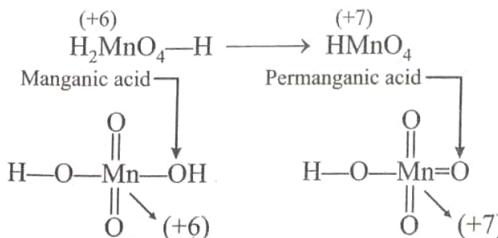
An ortho acid must contain at least three hydrogens.



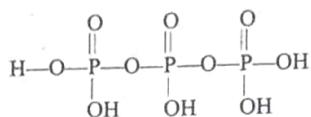
As SO_3 does not contain any hydrogen (i.e., $\text{X}-\text{OH}/\text{S}-\text{OH}$ bond), so SO_3 is not an oxy acid rather it is anhydride of sulphuric acid (H_2SO_4) so, H_2SO_4 can't be prefixed with ortho, and its name does not contain any prefix and it is named as sulphuric acid.

POLYPHOSPHORIC ACID

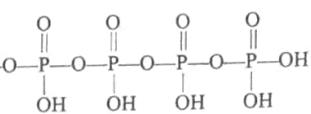
Oxy acids having general formula $\text{H}_{(n+2)}\text{P}_n\text{O}_{(3n+1)}$ are known as polyphosphoric acids. These contain $(n-1)$ $\text{P}-\text{O}-\text{P}$ bonds.



$H_5P_3O_{10}$ - Tripolyphosphoric acid



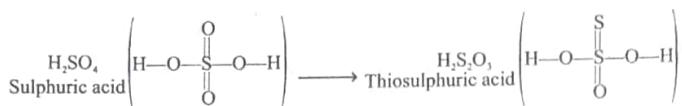
$H_8P_4O_{13}$ - Tetrapolyphosphoric acid



THIO ACID

1. Oxy acids in which one oxygen atom are replaced by sulphur are considered as thio acid.

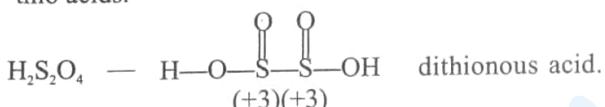
For example:



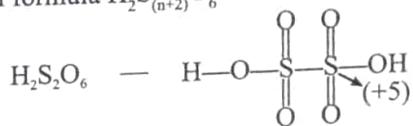
Cyanic acid

Thiocyanic acid
(Hydrothionic acid)

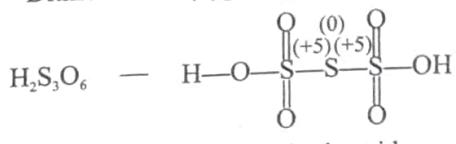
2. Oxy acids of sulphur containing S—S bonds are known as thio acids.



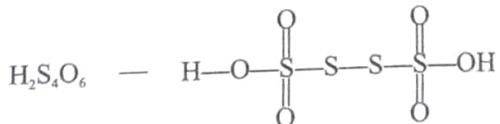
Thionic acids : Oxy acids of sulphur containing S—S bond and having general formula $H_2S_{(n+2)}O_6$ are known as thionic acids



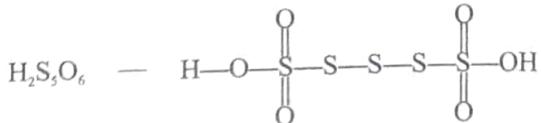
Dithionic acid(hyposulphuric acid)



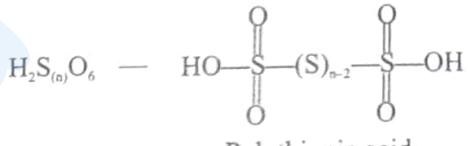
Trithionic acid



Tetrathionic acid



Pentathionic acid

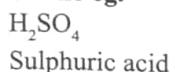


Polythionic acid

Element	-ous acid	-ic acid
P	(+3, H_3PO_3 , $H_4P_2O_5$) (+2, H_3PO_2)	(+4) $H_4P_2O_6$ (Hypophosphoric acid) +5 → $H_{n+2}P_nO_{3n+1}$ - polyphosphoric acid → H_3PO_4 , $H_4P_2O_7$, $H_4P_2O_8$ → H_3PO_5 - peroxymonophosphoric acid
S	(+4) H_2SO_3 Sulfurous acid $H-O-\overset{\text{O}}{\underset{\text{(+3)(+5)}}{\text{S}}}-S-OH$ Pyrosulfurous acid	(+6) Sulphuric acid (H_2SO_4) $H_2S_2O_7$ - Pyrosulphuric acid $H_2S_{(n+2)}O_6$ - Thionic acids e.g : $H-O-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-S-OH$ Dithionic acid
	$H_2S_2O_4$ $H-O-\overset{\text{O}}{\underset{\text{(+3)(+3)}}{\text{S}}}-S-OH$ dithionous acid	$H-O-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-S-\overset{\text{(+5)}}{\underset{\text{(0)}}{\text{S}}}-S-OH$ Tetrathionic acid (+6) H_2SO_5 - Peroxymonosulfuric acid (+6) $H_2S_2O_8$ - Peroxydisulfuric acid

X $(X=Cl, Br, I)$	<p>(+1) $H-O-X$ Hypohalous acid e.g. $H-O-Cl$ - Hypochlorous acid</p> <p>$H-O-I$ - Hypoiodous acid (+3) HXO_2; $H-O-X=O$ Halous acid $H-O-I=O$ - Iodous acid</p>	<p>(+5) Halic acid (HXO_3) $H-O-\overset{O}{\underset{(+5)}{X}}=O$</p> <p>$H-O-\overset{O}{\parallel}{Cl}=O$ [Chloric acid]</p> <p>(+7) Perhalic acid (HXO_4) $H-O-\overset{O}{\parallel\parallel}{Br}=O$ [Perbromic acid]</p>
Others		<p>(+3) H_3BO_3 Orthoboric acid (+3) HBO_2 - Metaboric acid (+4) Orthosilicic acid H_4SiO_4 H_2SiO_3 - Metasilicic acid $H_6Si_2O_7$ - Pyrosilicic acid</p>

Naming of salts of oxy acids: The name of salt ends with – “ate” if the name of the oxy acid ends with - ic acid and all prefix remain same eg.



Na_2SO_4 - Sodium sulfate
 K_2SO_4 - Potassium sulfate
 $BaSO_4$ - Barium sulfate
 $FeSO_4$ - Ferrous sulfate
 $Al_2(SO_4)_3$ - Aluminium sulfate
 Na_3PO_4 - Sodium orthophosphate
 K_3PO_4 - Potassium orthophosphate
 $Ca_3(PO_4)_2$ - Calcium Orthophosphate
 $AlPO_4$ - Aluminium orthophosphate
 $NaPO_3$ - Sodium metaphosphate
 KPO_3 - Potassium metaphosphate
 $Ca(PO_3)_2$ - Calcium metaphosphate
 $Al(PO_3)_3$ - Aluminium metaphosphate



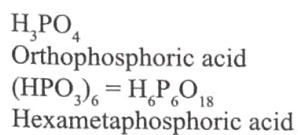
$KClO_3$ - Potassium chlorate
 $NaClO_3$ - Sodium chlorate
 $Ca(ClO_3)_2$ - Calcium chlorate
 $NaClO_4$ - Sodium perchlorate
 $KClO_4$ - Potassium perchlorate
 NH_4ClO_4 - Ammonium perchlorate
 $Ca(ClO_4)_2$ - Calcium perchlorate



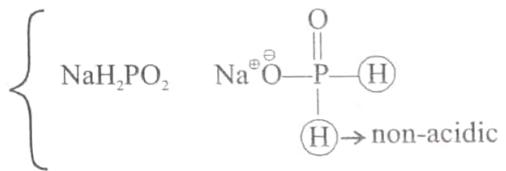
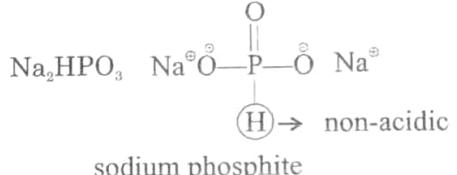
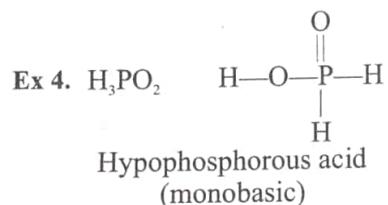
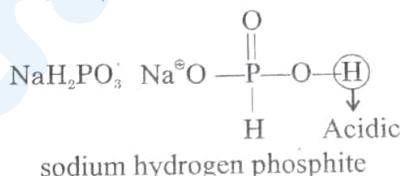
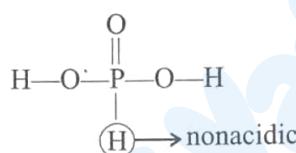
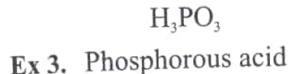
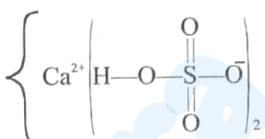
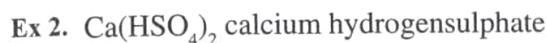
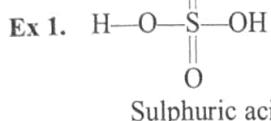
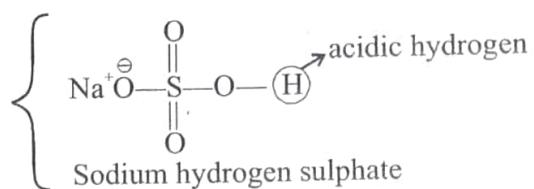
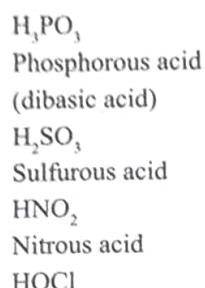
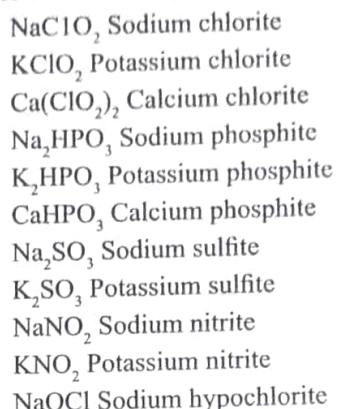
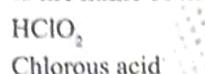
KH_2PO_4 Potassium dihydrogen orthophosphate
 $Ca(H_2PO_4)_2$ Calcium dihydrogen orthophosphate
 $Na_6P_6O_{18}$ Sodium hexametaphosphate
 $NaBO_2$ Sodium metaborate metaboric acid
 Na_2SO_5 Sodium peroxyulfate
Peroxysulphuric acid



$Na_4P_2O_7$ - Sodium Pyrophosphoric acid pyrophosphate



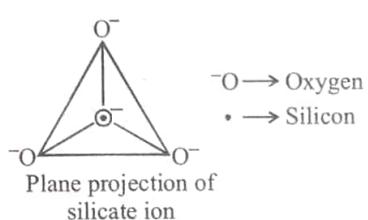
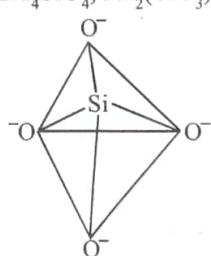
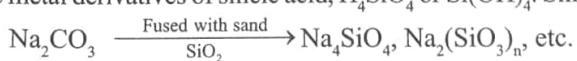
If the name of the oxy acid ends with ous acid then the name of the salt ends with "ite"



sodium hypophosphite but not sodium dihydrogen phosphite as H is not acidic.

SILICATES

Silicates are metal derivatives of silicic acid, H_4SiO_4 , or $Si(OH)_4$. Silicates are formed by heating metal oxide or metal carbonates with sand, e.g.,



Silicates have basic unit of SiO_4^{4-} , each silicon atom is bonded with four oxide ions tetrahedrally. There are following types of silicates.

Silicates	Sharing of O-atom / Basic Tetrahedral unit	Contribution of O-atom/Basic Tetrahedral unit	General formula
Ortho	$(\text{SiO}_3)_n^{2n-}$	4	SiO_4^{4-}
Pyro	1	3.5	SiO_7^{6-}
Cyclic	2	3	$(\text{SiO}_3)_n^{2n-}$
Simple chain (pyroxene)	2	3	$(\text{SiO}_3)_n^{2n-}$
Double chain (Amphibole)	$(3, 2) \text{ av} = 2.5$	$\frac{11}{4} = \left(\frac{5.5}{2}\right)$	$(\text{Si}_4\text{O}_{11})_n^{6n-}$
2D or (Sheet)	3	2.5	$(\text{Si}_2\text{O}_5)_n^{2n-}$
3D	4	2	$(\text{SiO}_2)_n$

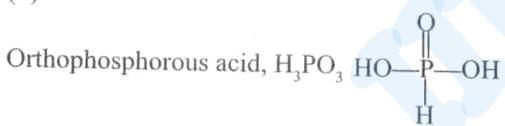


Train Your Brain

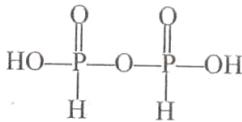
Example 44: The pair in which phosphorus atoms have a formal oxidation state of +3 is

- (a) pyrophosphorous and hypophosphoric acids
- (b) orthophosphorous and hypophosphoric acids
- (c) pyrophosphorous and pyrophosphoric acids
- (d) orthophosphorous and pyrophosphorous acids

Sol. (d)



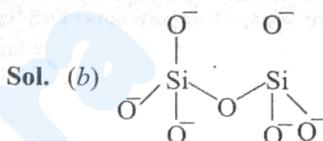
$$\text{H}_3\overset{x}{\text{P}}\text{O}_3 = 3 + x + 3(-2) = 0 \text{ or } x = +3$$



$$\text{H}_4\overset{x}{\text{P}}_2\text{O}_5 = 4 + 2x + 5(-2) = 0 \\ 4 + 2x - 10 = 0, x = +3$$

Example 45: $\text{Si}_2\text{O}_7^{6-}$ anion is obtained when

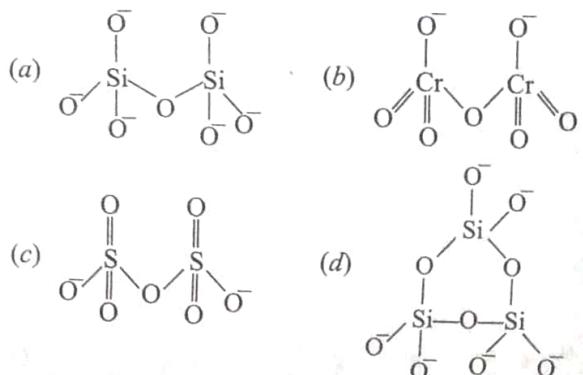
- (a) no oxygen of a SiO_4 tetrahedron is shared with another SiO_4 tetrahedron.
- (b) one oxygen of a SiO_4 tetrahedron is shared with another SiO_4 tetrahedron.
- (c) two oxygen of a SiO_4 tetrahedron are shared with another SiO_4 tetrahedron.
- (d) three or all four oxygens of a tetrahedron are shared with other SiO_4 tetrahedron.



Example 46: Which of the following specie(s) is/are having only one corner shared per tetrahedron.

- (a) $\text{Si}_2\text{O}_7^{6-}$
- (b) $\text{Cr}_2\text{O}_7^{2-}$
- (c) $\text{S}_2\text{O}_7^{2-}$
- (d) $\text{Si}_3\text{O}_9^{6-}$

Sol. (a,b,c)



Concept Application

46. Hypophosphoric acid is having _____ number of replaceable H-atom.

- (a) Four
- (b) Two
- (c) Three
- (d) Five

47. The number of P – O – P linkages in P_4O_{10} and P_4O_6 are respectively.

- (a) 6, 6
- (b) 6, 8
- (c) 8, 6
- (d) 8, 8

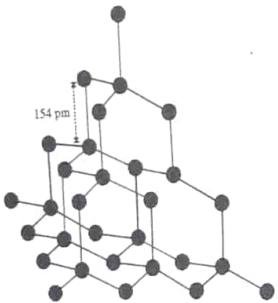
ALLOTROPIES OF CARBON FAMILY

- ⇒ Diamond (kinetically most stable allotrope of carbon, meta stable phase of carbon)

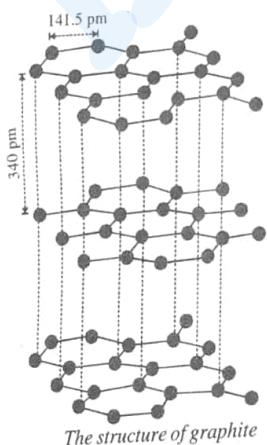
 - ❖ It has a crystalline lattice. A rigid three dimensional network of carbon atoms.
 - ❖ Each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion.
 - ❖ C – C bond length is 154 pm.
 - ❖ It is very difficult to break extended covalent bonding and therefore, diamond is a very hard substance.

Uses:

- ❖ Used as an abrasive for sharpening hard tools, in making eyeglasses and in the manufacture of tungsten filaments for electric light bulbs.
 - ❖ Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).



The structure of diamond



The structure of graphite

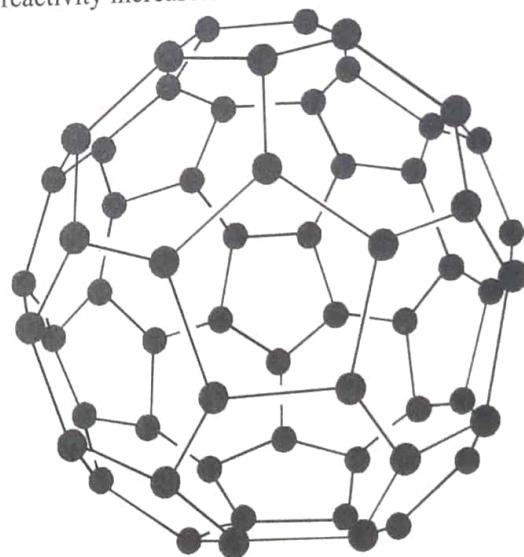
⇒ Graphite (Thermodynamically most stable allotrope of carbon)

- ❖ Layered structure. Layers are held by van der Waals forces and distance between two layers is 340 pm.
 - ❖ Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm.
 - ❖ Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a p bond. The electrons are delocalised over the whole sheet. Thus, graphite is lusturous.

- ❖ Electrons are mobile therefore, graphite conducts electricity along the sheet.
 - ❖ Graphite cleaves easily between the layers and, therefore, it is very soft and slippery.
 - ❖ Uses: Due to slippery nature graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.
 - ❖ Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.

Fullerenes

- ❖ Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon.
 - ❖ The sooty material formed by condensation of vapourised C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above.
 - ❖ Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules.
 - ❖ Fullerene C_{60} :- molecule has a shape like soccer ball and called Buckminsterfullerene. It contains 20, six-membered rings and 12, five membered rings.
 - ❖ This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C-C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky balls in short.
 - ❖ A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.
 - ❖ All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms.
 - ❖ The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. However, because of non-planar nature of fullerenes, their aromatic character gets diminished and reactivity increases.



[The structure of C₆₀, Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football)]

IMPORTANT POINTS FOR CARBON

- ❖ Thermodynamic stability order : Graphite > Diamond > Fullerene C_{60}
- ❖ It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, ΔH_f of graphite is taken as zero. ΔH_f values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol⁻¹, respectively.
- ❖ Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes.
 - ⇒ Carbon black is obtained by burning hydrocarbons in a limited supply of air.
 - ⇒ Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

Uses of Carbon

- ❖ Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes.
- ❖ Crucibles made from graphite are inert to dilute acids and alkalies.
- ❖ Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in airconditioning system to control odour.
- ❖ Carbon black is used as black pigment in black ink and as filler in automobile tyres.
- ❖ Coke is used as a fuel and largely as a reducing agent in metallurgy.

ALLOTROPES OF OXYGEN FAMILY

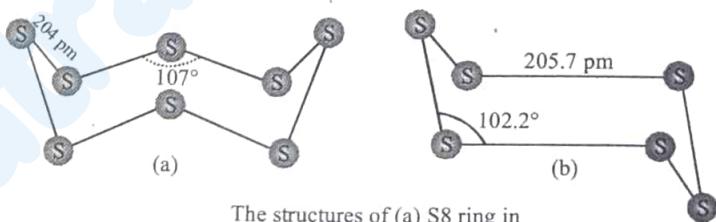
Oxygen

- ❖ Two non-metallic forms, dioxygen O_2 and ozone O_3 . Dioxygen O_2 is stable as a diatomic molecule. O_3 molecule is diamagnetic while O_2 is paramagnetic.
- ❖ Six allotropes of selenium are known.
- ❖ Tellurium has only one crystalline form, which is silvery white and semimetallic.
- ❖ This is similar to grey Se, but has stronger metallic interaction.

Sulphur Allotropic forms

- ❖ Sulphur forms numerous allotropes of which the yellow rhombic (α -sulphur) and monoclinic (β -sulphur) forms are the most important.
- ❖ The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.
 - ⇒ Rhombic sulphur (α -sulphur) (Most stable sulphur allotrope at room temperature)
 - ❖ This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2 .

- ❖ It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS_2 .
- ⇒ Monoclinic sulphur (β -sulphur)
- ❖ Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS_2 while water insoluble.
- ❖ This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β -sulphur are formed.
- ❖ It is stable above 369 K and transforms into α -sulphur below it. Conversely, α -sulphur is stable below 369 K and transforms into β -sulphur above this. At 369 K, both the forms are stable. This temperature is called transition temperature.
- ❖ Both rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in the figure.



The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

EXTRA POINTS

- ❖ Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades.
- ❖ In cyclo- S_6 , the ring adopts the chair form and the molecular dimensions are as shown in figure. At elevated temperatures (~1000 K), S_2 is the dominant species and is paramagnetic just like O_2 .
- ❖ Engel's sulphur (e -sulphur) is unstable and contains S_6 rings arranged in the chair conformation. It is made by pouring $Na_2S_2O_3$ solution into concentrated HCl and extracting the S with toluene.
- ❖ Plastic sulphur-(c) is obtained by pouring liquid sulphur into water.

Allotropes of Nitrogen Family

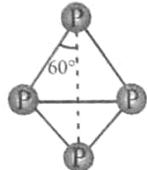
Solid As, Sb and Bi each exist in several allotropic forms. Arsenic vapour contains tetrahedral As_4 molecules. A reactive yellow form of the solid resembles white phosphorus and is thought to contain tetrahedral As_4 units. Sb also has a yellow form. All three elements have much less reactive metallic or a -forms.

PHOSPHORUS ALLOTROPIC FORMS

Phosphorus is found in many allotropic forms, the important ones being white, red and black.

⇒ White phosphorus

- ❖ Translucent, white, waxy solid.
- ❖ It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence).
- ❖ It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3 .



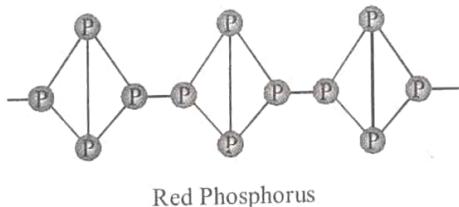
Discrete tetrahedral P_4 unit of White Phosphorus

- ❖ White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule where the angles are only 60° . It readily catches fire in air to give dense white fumes of P_4O_{10} .



⇒ Red phosphorus

- ❖ Obtained by heating white phosphorus at 573K in an inert atmosphere for several days.
- ❖ When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed.
- ❖ Red phosphorus possesses iron grey lustre. It is odourless, nonpoisonous and insoluble in water as well as in carbon disulphide.
- ❖ Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark.
- ❖ It is polymeric, consisting of chains of P_4 tetrahedral linked together in the manner as shown in Fig.

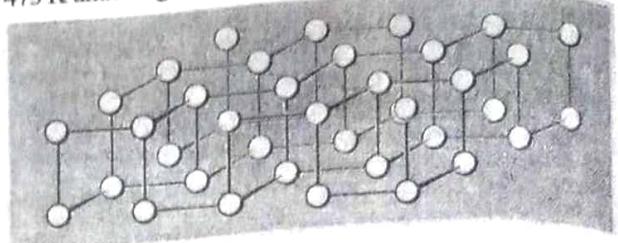


Red Phosphorus

⇒ Black phosphorus

- ❖ Two forms α -black phosphorus and β -black phosphorus.
- ❖ α -Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K . It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidise in air.

- ❖ β -Black phosphorus is prepared by heating white phosphorus at 473K under high pressure. It does not burn in air upto 673K .



Thermodynamic stability order:

Black phosphorus > Red phosphorus > White phosphorus

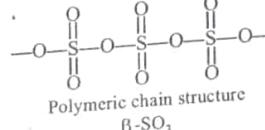
Reactivity order:

Black phosphorus < Red phosphorus < White phosphorus

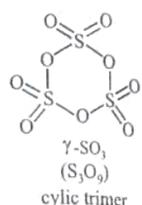
ALLOTROPIC FORM OF SO_3

SO_3 have three allotropic forms $\alpha\text{-SO}_3$, $\beta\text{-SO}_3$ and $\gamma\text{-SO}_3$

$\alpha\text{-SO}_3$
Cross linked solid

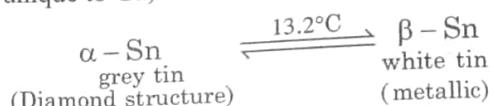


Polymeric chain structure
 $\beta\text{-SO}_3$



$\gamma\text{-SO}_3$
(S_3O_9)
cyclic trimer

Note: Si, Ge and Sn 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.



Train Your Brain

Example 47: The C–C bond length is maximum in

- | | |
|---------------------|---------------------|
| (a) Graphite | (b) C_{70} |
| (c) C_{60} | (d) diamond |

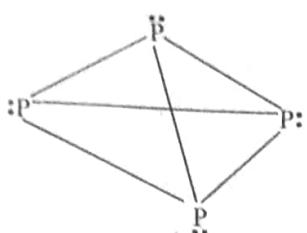
Sol. (d) In diamond, the C–C bond length is maximum (154 pm). Here, each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. It has a rigid three-dimensional network of carbon atoms. C–C bond length within the layers of graphite is 141.5 pm. In C_{60} , C–C distances between single and double bonds are 143.5 pm and 138.3 pm respectively.

Example 48: White phosphorus (P_4) has:

- | |
|----------------------------------|
| (a) six P–P single bonds |
| (b) four P–P single bonds |
| (c) four lone pairs of electrons |
| (d) P–P–P angle of 60° |

Sol. (a,c,d)

The structure of P_4 is:

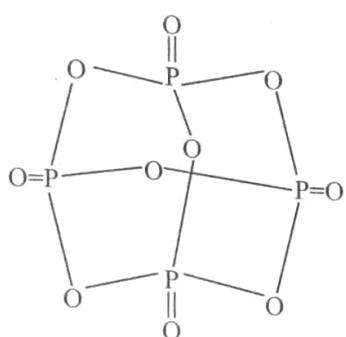


There are four lone pairs on four phosphorus. It has six P—P single bonds.

P—P—P bond angles are of 60° .

Example 49: In P_4O_{10} , the number of oxygen atoms bonded to each phosphorus atom is

Sol. (4)



Here four oxygen atoms are bonded to each phosphorus atom.



Concept Application

51. Graphite is soft while diamond is hard because

- (a) Graphite is in powder form
- (b) Graphite have sp^2 while diamond has sp Hybridized 'C' atom
- (c) Graphite is planar layered solid while diamond is 3-D giant network solid
- (d) Graphite is covalent while diamond is ionic

52. Bucky ball or buckminsterfullerene is:

- (a) An allotrope of carbon
- (b) It is referred as C-60
- (c) It has sp^2 -hybridised nature and resembles with soccer ball
- (d) All of these

53. Phosphine is not obtained, when

- (a) Red phosphorous is heated with NaOH
- (b) White phosphorous is heated with NaOH
- (c) Ca_3P_2 reacts with water
- (d) Phosphorous trioxide is boiled with water

54. Which of the following isomers of phosphorus is thermodynamically most stable?

- (a) Red
- (b) White
- (c) Black
- (d) Yellow

Short Notes

Chemical Bond

The force of attraction which hold together atom, molecule or ions with in chemical species.

Exception of Octet Rule

(a) electron deficient	(b) electron rich	(c) odd electron
Central atom: No. of electron < 8 BeH_2 BF_3 , BCl_3 , BBr_3 , Bi_3 $AlCl_3$, $AlBr_3$, AlI_3	Central atom: No. of electron > 8 PCl_5 , IF_7 SF_6 , XeF_2	species central atom: has odd electron NO , NO_2 , ClO_2 , ClO_3

Fajan's Rule

$$\text{Ionic potential of cation } (\phi) \propto \frac{\text{charge of cation}}{\text{size of cation}}$$

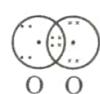
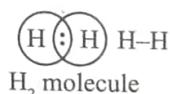
Polarisability of anion \propto size of anion \propto charge of anion

Condition of polarisation

- Smaller cation
- Large anion
- Higher charge

Covalent Bond

A covalent bond is formed by the mutual sharing of electrons between two atoms to complete their octet. (Except H which completes its duplet)



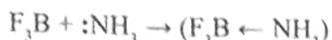
Electrovalent or Ionic bond

The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called as Ionic or electrovalent bond.



Coordinate Bond (Dative Bond)

The bond formed between two atoms in which contribution of an electron pair is made by one of them while the sharing is done by both.



Valence Shell Electron Pair Repulsion Theory

❖ Order of repulsion:

$$lp-lp > lp-bp > bp-bp$$

$$mb-mb > mb-sb > sb-sb \quad (mb = \text{multiple bond}; sb = \text{single bond})$$

Valence Bond Theory

Proposed by Heitler & London as per VBT bonding takes place for attaining stability.

$$\text{Stability} \propto \frac{1}{\text{Potential energy}}$$

❖ During this process some extent of electron cloud merge into each other; this part is known as overlapped region & this process is known as overlapping.

Hybridisation

S.No.	Type of orbital	No. of hybrid orbital	3D orientation	Example
1.	one s + one p	2; sp	Linear	BeH ₂ , BeCl ₂
2.	one s + two p	3; sp ²	Triangular	BCl ₃ , BF ₃
3.	one s + three p	4; sp ³	Tetrahedral	CH ₄ , CCl ₄
4.	one s + three p + one d	5; sp ³ d	Triangular bipyramidal	PCl ₅
5.	one s + three p + two d	6; sp ³ d ²	Octahedral	SF ₆
6.	one s + three p + three d	7; sp ³ d ³	Pentagonal bipyramidal	IF ₇

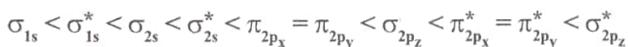
Molecular Orbital Theory (MOT)

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

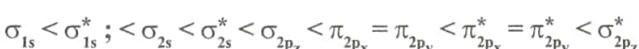
1. The combining atomic orbitals must have the same or nearly the same energy and same symmetry about the molecular axis.

Energy level diagram from MOs:

Molecular orbital energy diagram for up to N₂ (molecule having ≤ 14 electrons)



Molecular orbital energy diagram for O₂ and F₂ (molecule having > 14 electrons)



σ^*, π^* = antibonding molecular orbital

σ, π = bonding molecular orbital

$$\text{Bond order (B.O.)} = \frac{1}{2}(N_b - N_a)$$

Dipole Moment

Measurement of Polarity in a molecule

$$\bar{\mu} = q \times d \quad \text{debye} = \text{esu} \cdot \text{cm}$$

$$1 \text{ D} = 10^{-18} \text{ esu} \cdot \text{cm}$$

Diatomeric Molecule

(a) Homotomic $\Delta EN = 0 \rightarrow \bar{\mu} = 0 \rightarrow \text{Non-polar}$. H₂, F₂, Cl₂, N₂ etc.

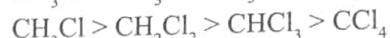
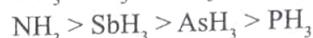
(b) Heterotomic $\Delta EN \neq 0 \rightarrow \bar{\mu}_{\text{net}} \neq 0 \rightarrow \text{polar}$. HF > HCl > HBr > HI

Polyatomic Molecule

$$\mu_R \rightarrow \text{vector sum of bond moment}$$

$$\mu_R \rightarrow \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

Important Order



Bonding Parameter

1. **Bond length:** Internuclear distance

Factor affecting Bond length

(i) Atomic size: bond length \propto size⁻¹ [No. of shell]

$$(ii) \Delta EN, \text{Bond length} \propto \frac{1}{\Delta EN}$$

$$d_{A-B} = r_A + r_B - 0.09 \times \Delta EN \text{ \AA}$$

$$(iii) \text{Bond order: Bond length} \propto \frac{1}{B.O.}$$

$$(iv) \text{Hybridisation: Bond length} \propto \frac{1}{\% \text{age of s-character}}$$

Bond Angle

(i) Bond angle \propto % age of s-character

$$(ii) \text{Bond angle} \propto \frac{1}{lp} \quad \text{Eg.: } CH_4 > \ddot{NH}_3 > H_2\ddot{O}$$

[when hybridisation is same]

Back Bonding

Condition:

(i) One atom must have lone pair.

(ii) And another atom must have vacant orbital.

Type of Back Bond:

(i) (pπ - pπ) type of back bond eg., BF₃, BCl₃, CF₂, CCl₂

(ii) (pπ - dπ) type of back bond

eg., CCl₃⁻, O(SiH₃)₂, N(SiH₃)₂, SiH₅O⁻, etc.

Hydrogen bonding

❖ It is dipole-dipole type of interaction.

❖ Electrostatic force of attraction between hydrogen (covalently bond with F/N/O) & highly electronegative atom.

❖ Hydrogen bond → Intermolecular hydrogen bond → between the molecules

❖ Hydrogen bond → Intramolecular hydrogen bond → in the molecules

Strength

Intermolecular H-bond > Intramolecular H-bond

Intramolecular H-bonding takes place in ortho derivatives only.

Solved Examples

1. The correct statement for the molecule, CsI_3 is:

- (a) It is a covalent molecule
- (b) It contains Cs^+ and I_3^- ions
- (c) It contains Cs^{3+} and I^- ions
- (d) It contains Cs^+ , I^- and lattice I_2 molecule

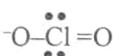
Sol. (d) $\text{I}_3^- \rightarrow \text{I}_2 + \text{I}^-$

Cs^+ is an alkali metal cation and I_3^- has linear shape.

2. The type of hybrid orbitals used by the chlorine atom in ClO_2^- is:

- (a) sp^3
- (b) sp^2
- (c) sp
- (d) None of these

Sol. (a)



Bond pair = 2, Lone Pair = 2

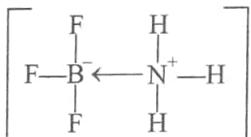
Electronic pairs = 4

Steric no. = 4, Hybridisation at Cl = sp^3

3. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3 .

- (a) N : tetrahedral, sp^3 ; B: tetrahedral, sp^3
- (b) N : pyramidal, sp^3 ; B: pyramidal, sp^3
- (c) N: pyramidal, sp^3 ; B: planar, sp^2
- (d) N: pyramidal, sp^3 ; B: tetrahedral, sp^3

Sol. (a)



Both 'B' and 'N' has sp^3 hybridisation and tetrahedral geometry.

4. In the compound $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$, the C_2-C_3 bonds is of

- (a) $\text{sp} - \text{sp}^2$
- (b) $\text{sp}^3 - \text{sp}^3$
- (c) $\text{sp} - \text{sp}^3$
- (d) $\text{sp}^2 - \text{sp}^3$

Sol. (d)



Hybridisation at $\text{C}_2 = \text{sp}^2$ and at $\text{C}_3 = \text{sp}^3$.

5. The cyanide ion CN^- and N_2 are isoelectronic, but in contrast to CN^- , N_2 is chemically inert because of

- (a) Low bond energy
- (b) Absence of bond polarity
- (c) Unsymmetrical electron distribution
- (d) Presence of more number of electron in bonding orbitals

Sol. (b) N_2 is a neutral, non-polar, inert molecule while CN^- is a highly polar, highly active ion.

6. Match each of the diatomic molecules in Column-I with its property/properties in Column-II.

Column-I

- A. B_2
- B. N_2
- C. O_2^-
- D. O_2

Column-II

- p. Paramagnetic
- q. Undergoes oxidation
- r. Undergoes reduction
- s. Bond order ≥ 2
- t. Mixing of 's' and 'p' orbitals

A	B	C	D
---	---	---	---

- | | | | |
|----------------|------------|------------|------------|
| (a) q, r, s | p, r, t, s | q, r, t | p, q, t |
| (b) p, q, r, t | q, r, s, t | p, q, r, t | p, r, s, t |
| (c) q, r, s, t | p, q, r | r, s, t | p, q, r, t |
| (d) p, q, s, t | p, q, s | p, t | q, r, t |

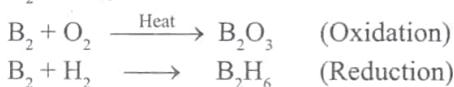
Sol. (b)

(A) $\text{B}_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, [\pi(2p_x)]^1 = [\pi(2p_y)]^1$
 $\text{Bond order} = \frac{6-4}{2} = 1$.

Paramagnetic (2 unpaired electron)

Bond is formed by mixing of s and p orbitals.

B_2 undergoes both oxidation and reduction as



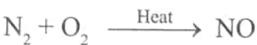
(B) $\text{N}_2 : [\sigma(1s)]^2, [\sigma^*(1s)]^2, [\sigma(2s)]^2, [\sigma^*(2s)]^2, [\pi(2p_x)]^2 = [\pi(2p_y)]^2, [\sigma(2p_z)]^2 : n = 3$

$$\text{Bond order} = \frac{10-4}{2} = 3$$

Diamagnetic (0 unpaired electron)

In N_2 , bonds are formed by mixing of s and p orbitals.

N_2 undergoes both oxidation and reduction as



(C) $\text{O}_2^- : [\sigma(1s)]^2, [\sigma^*(1s)]^2, [\sigma(2s)]^2, [\sigma^*(2s)]^2, [\sigma(2p_z)]^2, [\pi(2p_x)]^2 = [\pi(2p_y)]^1,$
 $\text{Bond order} = 1.5$

Paramagnetic (1 unpaired electron)

O_2^- undergoes both oxidation and reduction and bond involves mixing of s and p-orbitals.

(D) $\text{O}_2^- : [\sigma(1s)]^2, [\sigma^*(1s)]^2, [\sigma(2s)]^2, [\sigma^*(2s)]^2, [\sigma(2p_z)]^2, [\pi(2p_x)]^1 = [\pi(2p_y)]^1$
 $\text{Bond order} = 2$

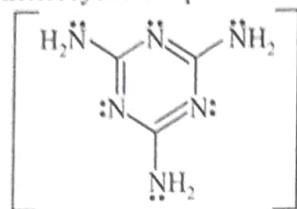
Paramagnetic (2 unpaired electron)

O_2^- undergoes reduction and bond involves mixing of s and p-orbitals.

7. The total number of lone-pair of electrons in melamine is:

Sol. [6]

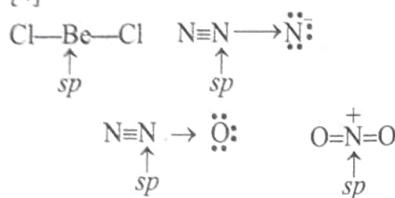
Melamine is a heterocyclic compound.



Six lone pairs are present.

8. Among the triatomic molecules/ions BeCl_2 , N_3^- , N_2O , NO_2^+ , O_3 , SCl_2 , ICl_2 , I_3^- and XeF_2 , the total number of linear molecules/ion(s) where the hybridisation of the central atom does not have contribution from the d-orbital(s) is [atomic number of S = 16, Cl = 17, I = 53 and Xe = 54].

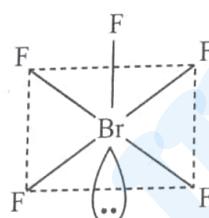
Sol. [4]



All the above mentioned molecules/ions have sp-hybridised central atom and no Lone pair at central atom, hence linear also.

9. Based on VSEPR theory, the number of 90° F—Br—F angles in BrF_5 is.

Sol. [0]



To minimize the repulsion, Lone pair would push the Br—F bond pairs in upward direction and all Br—F bond angles will contract.

10. Stability of the species Li_2 , Li_2^- and Li_2^+ increases in the order of

- (a) $\text{Li}_2 < \text{Li}_2^+ < \text{Li}_2^-$ (b) $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$
 (c) $\text{Li}_2 < \text{Li}_2^- < \text{Li}_2^+$ (d) $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$

Sol. (b)

$$\text{Li}_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$$

$$\text{Bond order} = \frac{4-2}{2} = 1$$

$$\text{Li}_2^+ = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^1$$

$$\text{Bond order} = \frac{3-2}{2} = 0.5$$

$$\text{Li}_2^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^1$$

$$\text{Bond order} = \frac{4-3}{2} = 0.5$$

Stability order is $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$

(because Li_2^- has more number of electrons in antibonding orbitals which destabilises the species).

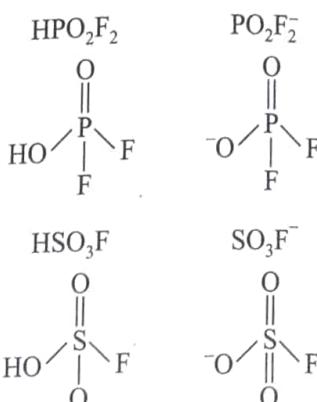
11. Consider the following molecules/anions



Identify the correct statement(s).

- (a) Both (x) and (z) have one $-\text{OH}$ group each
 (b) Hybridisation of phosphorus in (x) and (y) is same
 (c) Hybridisation of phosphorus in (y) and sulphur in (z) same
 (d) Shapes of (x) and (y) are different

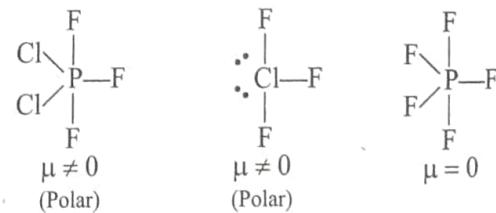
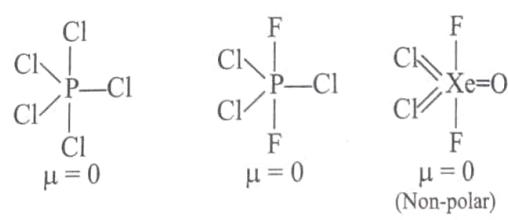
Sol. (a,b,c) Hybridisation of central atom in all 4 molecules same.



12. Which of the following set of species are non-polar and hybridisation of central atom is sp^3d^2 ?

- (a) PCl_5 , PCl_3F_2 , XeO_3F_2
 (b) PCl_5 , PCl_2F_3 , XeO_2F_2
 (c) PCl_3F_2 , SbF_5 , PF_5
 (d) ClF_3 , SF_2Cl_3 , XeO_3F_2

Sol. (a,c) For non-polar species, dipole moment is zero.



13. The total number of lone pairs of electrons in N_2O_3 is:

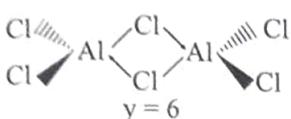
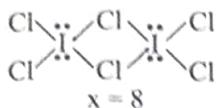
Sol. [8]



Total no. of lone pairs = 8

14. In the structure of I_2Cl_6 and Al_2Cl_6 , the maximum number of atoms lying on a plane is x and y respectively. Find the value of $x-y$.

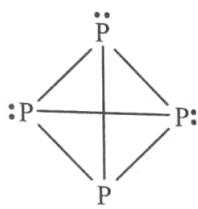
Sol. [2] I_2Cl_6 is planar



15. Which is/are correct regarding P_4 ?

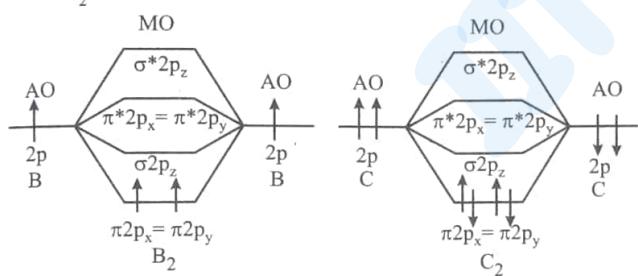
- (a) It has sp^3 hybridised P
- (b) There are 4 P – P bonds
- (c) P – P – P bond angle is 100°
- (d) There are four lone pairs per molecule

Sol. (a,d) Each P is sp^3 hybridised.



16. Which of the molecule out of B_2 and C_2 has a higher energy of dissociation into atoms? compare the magnetic properties of these molecules.

Sol. We draw energy level diagrams showing the formation of B_2 and C_2 molecules



B_2 paramagnetic and C_2 diamagnetic and C_2 has higher bond order, so C_2 has higher energy of dissociation into atoms.

17. N_2 and O_2 are converted to monocations N_2^+ and O_2^+ respectively, which is wrong statement-

- (a) In N_2^+ , the N—N bond weakens
- (b) In O_2^+ , the O—O bond order increases
- (c) In O_2^+ , the paramagnetism decreases
- (d) N_2^+ becomes diamagnetic

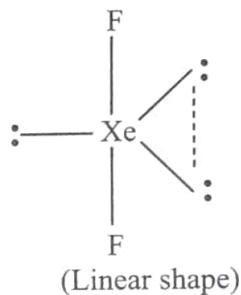
Sol. (d)

	Bond order	Unpaired	Nature
N_2	3	0	Diamagnetic
	2.5	1	Paramagnetic
O_2	2	2	Paramagnetic
O_2^+	2.5	1	Paramagnetic

18. Which does not have sp hybridized central atom

- (a) XeF_2
- (b) C_2H_2
- (c) CO_2
- (d) BeH_2

Sol. (a) $Xe F_2 = sp^3d$



(Linear shape)

19. The bond angles of NH_3 , NH_4^+ and NH_2^- are in the order -

- (a) $NH_2^- > NH_3 > NH_4^+$
- (b) $NH_4^+ > NH_3 > NH_2^-$
- (c) $NH_3 > NH_2^- > NH_4^+$
- (d) $NH_3 > NH_4^+ > NH_2^-$

Sol. (b) NH_3 , NH_4^+ and NH_2^- have sp^3 hybridization and lone pairs 1, 0 and 2 respectively so bond angle

$$NH_4^+ > NH_3 > NH_2^-$$

Exercise-1 (Topicwise)

INTRODUCTION, VALENCY

1. The octet rule is not obeyed in-
 - (a) CO_2
 - (b) BCl_3
 - (c) PCl_5
 - (d) Both (b) and (c)
2. Weakest bond is
 - (a) Ionic bond
 - (b) Covalent bond
 - (c) Coordinate bond
 - (d) Hydrogen bond
3. $\ddot{\text{N}} = \text{N} = \dot{\text{N}}$
 (I) (II) (III)
 Calculate the formal charge of each I, II and III nitrogen atom respectively
 - (a) +1, -1, 0
 - (b) -1, -1, +1
 - (c) -1, +1, -1
 - (d) 0, -1, -1
4. According to Lewis structure the number of lone pair & bond pair of electrons in SO_4^{2-} ion.
 - (a) 12, 6
 - (b) 12, 4
 - (c) 10, 8
 - (d) 8, 8
5. Which condition favours the bond formation?
 - (a) Maximum attraction and maximum potential energy
 - (b) Minimum attraction and minimum potential energy
 - (c) Minimum potential energy and maximum attraction
 - (d) None of the above
6. Which species has the maximum number of lone pair of electrons on the central atom?
 - (a) $[\text{ClO}_3]^-$
 - (b) XeF_4
 - (c) SF_4
 - (d) $[\text{I}_3]^-$

Coordinate Bond

7. A simple example of a coordinate covalent bond is exhibited by
 - (a) C_2H_2
 - (b) H_2SO_4
 - (c) NH_3
 - (d) HCl
8. Which of the following does not have a coordinate bond
 - (a) SO_2
 - (b) HNO_3
 - (c) H_2SO_3
 - (d) HNO_2
9. Which of the following compounds has coordinate (dative) bond
 - (a) CH_3NC
 - (b) CH_3OH
 - (c) CH_3Cl
 - (d) NH_3
10. The pair of compounds which can form a co-ordinate bond is:
 - (a) $(\text{C}_2\text{H}_5)_3\text{B}$ and $(\text{CH}_3)_3\text{N}$
 - (b) HCl and HBr
 - (c) BF_3 and NH_3
 - (d) Both (a) and (c)

VBT (Overlapping and Hybridization)

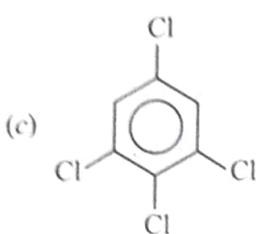
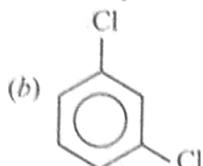
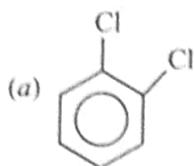
11. Correct statement regarding this reaction
 $\text{BF}_3 + \text{NH}_3 \longrightarrow [\text{F}_3\text{B} \leftarrow \text{NH}_3]$
 - (a) Hybridisation of N is changed
 - (b) Hybridisation of B is changed
 - (c) NH_3 act as a lewis base
 - (d) Both (b) & (c)
12. Which type of overlapping results the formation of a π bond?
 - (a) Axial overlapping of s – s orbitals
 - (b) Lateral overlapping of p – p orbitals
 - (c) Axial overlapping of p – p orbitals
 - (d) Axial overlapping of s – p orbitals
13. A sigma bond is formed by the overlap of atomic orbitals of atoms A and B. If the bond is formed along the x-axis, which of the following overlaps is acceptable?
 - (a) s orbital of A and p_z orbital of B
 - (b) p_x orbital of A and p_y orbital of B
 - (c) p_z orbital of A and p_x orbital of B
 - (d) p_x orbital of A and s orbital of B
14. The strength of bonds by $2s - 2s$, $2p - 2p$ and $2p - 2s$ overlapping has the order:
 - (a) $2s - 2s > 2p - 2p > 2s - 2p$
 - (b) $2s - 2s > 2p - 2s > 2p - 2p$
 - (c) $2p - 2p > 2s - 2p > 2s - 2s$
 - (d) $2p - 2p > 2s - 2s > 2p - 2s$
15. Amongst ClF_3 , BF_3 and NH_3 molecules the one with non-planar geometry is
 - (a) ClF_3
 - (b) NH_3
 - (c) BF_3
 - (d) None of these
16. Strongest bond is
 - (a) $\text{C} - \text{C}$
 - (b) $\text{C} = \text{C}$
 - (c) $\text{C} \equiv \text{C}$
 - (d) All are equally strong π
17. Which is not characteristic of π -bond?
 - (a) π -bond is formed when a sigma bond already formed
 - (b) π -bond are formed from hybrid orbitals
 - (c) π -bond may be formed by the overlapping of p-orbitals
 - (d) π - bond results from lateral overlap of atomic orbital
18. Number of σ and π bonds present in
 $\text{CH}_3 - \text{CH} = \text{CH} - \text{C} \equiv \text{CH}$ are:
 - (a) $10\sigma, 3\pi$
 - (b) $10\sigma, 2\pi$
 - (c) $9\sigma, 2\pi$
 - (d) $8\sigma, 3\pi$
19. Which molecule is not linear?
 - (a) BeF_2
 - (b) BeH_2
 - (c) CO_2
 - (d) H_2O

VSEPR, Bond Angle, Bond Length, Bond Energy

28. Which of the following is true?

 - (a) Bond order $\propto \frac{1}{\text{bond length}}$ \propto bond energy
 - (b) Bond order \propto bond length $\propto \frac{1}{\text{bond energy}}$
 - (c) Bond order $\propto \frac{1}{\text{bond length}} \propto \frac{1}{\text{bond energy}}$
 - (d) Bond order \propto bond length \propto bond energy

39. Which of the following has more dipole moment :



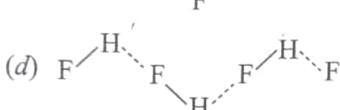
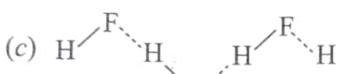
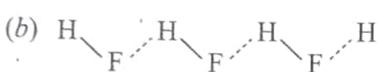
(d) All has same dipole moment

40. Zero dipole moment is present in

- (a) NH_3 (b) cis 1, 2-dichloroethene
(c) trans 1, 2-dichloroethene (d) None of these

Hydrogen Bonding

41. The H bond in solid HF can be best represented as :



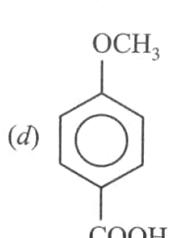
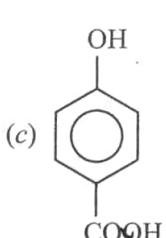
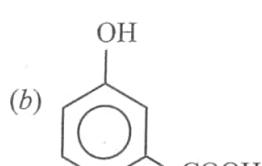
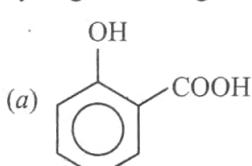
42. Contrary to other hydrogen halides, hydrogen fluoride is a liquid because

- (a) Size of F atom is small
(b) HF is a weak acid
(c) HF molecule are hydrogen bonded
(d) Fluorine is highly reactive

43. The hydrogen bond is strongest in:

- (a) $\text{O}-\text{H} \cdots \text{S}$ (b) $\text{S}-\text{H} \cdots \text{O}$
(c) $\text{F}-\text{H} \cdots \text{F}$ (d) $\text{O}-\text{H} \cdots \text{O}$

44. Which of the following has strongest intramolecular hydrogen bonding:



45. The boiling point of p-nitrophenol is higher than that of o-nitrophenol because:

- (a) NO_2 group at p-position behaves in a different way from that at o-position
(b) Intramolecular hydrogen bonding exists in p-nitrophenol
(c) There is intermolecular hydrogen bonding in p-nitrophenol
(d) p-nitrophenol has a higher molecular weight than o-nitrophenol

46. Of the following hydrides which has the lowest boiling point

- (a) NH_3 (b) PH_3
(c) SbH_3 (d) AsH_3

47. Water has high heat of vaporisation due to

- (a) Covalent bonding (b) H-bonding
(c) Ionic bonding (d) None of the above

Weak Forces

48. The nature of intermolecular forces among benzene (C_6H_6) molecules is:

- (a) Dipole-dipole attraction (b) London dispersion force
(c) Ion-dipole attraction (d) Hydrogen bonding

49. Which one of the following substances consists of small discrete molecules

- (a) NaCl (b) Graphite
(c) Copper (d) Dry ice

50. Glycerol has strong intermolecular bonding therefore it is

- (a) Sweet (b) Reactive
(c) Explosive (d) Viscous

Back Bonding, Bridge Bonding and Odd Electron Molecules

51. In BF_3 :

- (a) B-F bond has some double bond character and this bond is delocalised
(b) All the B-F bonds are single covalent in nature
(c) Bond energy and bond-length of B-F bond indicate its single bond character
(d) All of the above bonds are ionic

Molecules do not Exist

52. An element X forms compounds of formula XCl_3 , X_2O_5 and Mg_3X_2 but does not form XCl_5 then X is :

- (a) Aluminium (b) Phosphorus
(c) Nitrogen (d) Boron

53. The formation of which of the following ions is not possible -

- (a) $[\text{SiF}_6]^{2-}$ (b) $[\text{AlF}_6]^{3-}$
(c) $[\text{BF}_4]^-$ (d) $[\text{BF}_6]^{3-}$

Ionic Bond

54. Lattice energy of alkali metal chlorides follows the order

- (a) $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$
(b) $\text{CsCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{LiCl}$
(c) $\text{LiCl} > \text{CsCl} > \text{NaCl} > \text{KCl} > \text{RbCl}$
(d) $\text{NaCl} > \text{LiCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$

55. The electronic configuration of four elements L, P, Q and R are given in brackets

L($1s^2, 2s^2 2p^4$), Q($1s^2, 2s^2 2p^6, 3s^2 3p^5$)

P($1s^2, 2s^2 2p^6, 3s^1$), R ($1s^2, 2s^2 2p^6, 3s^2$)

The formulae of ionic compounds that can be formed between these elements are

- (a) L_2P , RL, PQ and R_2Q
- (b) LP, RL, PQ and RQ
- (c) P_2L , RL, PQ and RQ_2
- (d) LP, R_2L , P_2Q and RQ

56. Which among the following elements has the tendency to form covalent compounds?

- (a) Ba
- (b) Be
- (c) Mg
- (d) Ca

57. Formula of a metallic oxide is MO. The formula of its phosphate will be

- (a) $M_2(PO_4)_2$
- (b) M(PO_4)
- (c) M_2PO_4
- (d) $M_3(PO_4)_2$

58. An ionic bond A^+B^- is most likely to be formed when:

- (a) The ionization energy of A is high and the electron gain enthalpy of B is low
- (b) The ionization energy of A is low and the electron gain enthalpy of B is high
- (c) The ionization energy of A and the electron gain enthalpy of B both are high
- (d) The ionization energy of A and the electron gain enthalpy of B both are low

59. Correct order of covalent character of alkaline earth metal chloride in:

- (a) $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2$
- (b) $BeCl_2 < CaCl_2 < SrCl_2 < MgCl_2$
- (c) $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2$
- (d) $SrCl_2 > BeCl_2 > CaCl_2 > MgCl_2$

60. In the given bonds which one is most ionic

- (a) Cs – Cl
- (b) Al – Cl
- (c) C – Cl
- (d) H – Cl

61. Which of the compound is least soluble in water:

- (a) AgF
- (b) AgCl
- (c) AgBr
- (d) AgI

62. Which of the following liquids is not deflected by a non-uniform electrostatic field

- (a) Water
- (b) Chloroform
- (c) Nitrobenzene
- (d) Hexane

63. Polarization is the distortion of the shape of an anion by an adjacently placed cation. Which of the following statements is correct

- (a) Maximum polarization is brought about by a cation of high charge
- (b) Minimum polarization is brought about by a cation of low radius
- (c) A large cation is likely to bring about a large degree of polarization
- (d) A small anion is likely to undergo a large degree of polarization

MOT

64. Which of the following is the correct order of bond-orders of the given species are such that -

- (a) $O_2^- > O_2^+ > O_2^{2-} > O_2$
- (b) $O_2^+ > O_2^- > O_2^{2-} > O_2$
- (c) $O_2^+ > O_2^{2-} > O_2^- > O_2$
- (d) $O_2^{2-} > O_2^- > O_2^+ > O_2$

65. Which one is paramagnetic from the following

- (a) O_2^-
- (b) NO
- (c) Both (a) and (b)
- (d) CN^-

66. Which of the following represents correctly the order of filling of the molecular orbitals of B_2 , C_2 , N_2

- (a) $\pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi_{2p_y}^* = \pi_{2p_x}^* < \sigma_{2p_z}^*$
- (b) $\sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = < \pi_{2p_y}^* < \sigma_{2p_z}^*$
- (c) $\sigma_{2p_z} = \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = < \pi_{2p_y}^* < \sigma_{2p_z}^*$
- (d) $\pi_{2p_x} < \pi_{2p_y} < \sigma_{2p_z} > \pi_{2p_y}^* < \pi_{2p_z}^* = \sigma_{2p_z}^*$

Exercise-2 (Learning Plus)

1. The maximum covalency for representative elements is equal to (excluding 1st and 2nd period) :

- (a) The number of unpaired p-electrons
- (b) The number of paired d-electrons
- (c) The number of unpaired s and p-electrons
- (d) The actual number of s and p-electrons in the outermost shell.

2. The types of bond present in N_2O_5 are :

- (a) Only covalent
- (b) Only ionic
- (c) Ionic and covalent
- (d) Covalent & coordinate

3. Which of the following models best describes the bonding within a layer of the graphite structure?

- (a) Metallic bonding
- (b) Ionic bonding
- (c) Non-metallic covalent bonding
- (d) Vander Waals force

4. Example of super octet molecule is :

- (a) SF_6
- (b) PCl_5
- (c) IF_7
- (d) All of these

5. Which of the following species does not contain N - N covalent bond?

- (a) N_2O_3 (b) $\text{N}_2\text{O}_2^{2-}$
 (c) N_2O_5 (d) N_2O_4

6. Iron is harder than sodium because :

- (a) Iron atoms are smaller.
 (b) Iron atoms are more closely packed.
 (c) Metallic bonds are stronger in sodium.
 (d) Metallic bonds are stronger in iron.

7. Which molecule is T shaped?

- (a) BeF_2 (b) BCl_3
 (c) NH_3 (d) ClF_3

8. The correct order of hybridization of the central atom in the following species NH_3 , PtCl_4^{-2} , PCl_5 and BCl_3 is

- (a) dsp^2 , sp^3d , sp^2 and sp^3
 (b) sp^3 , dsp^2 , sp^3d , sp^2
 (c) dsp^2 , sp^2 , sp^3 , sp^3d
 (d) dsp^2 , sp^3 , sp^2 , sp^3d

9. In ICl_4^- , the shape is square planar. The number of bond pair-lone pair repulsion at 90° are :

- (a) 6 (b) 8 (c) 12 (d) 4

10. Arrange the following in order of decreasing O-N-O bond angle :

- N_2^+ , NO_2^- , NO_3^-
 (a) $\text{NO}_3^- > \text{NO}_2^- > \text{NO}_2^+$ (b) $\text{NO}_3^- > \text{NO}_2^- > \text{NO}_2^+$
 (c) $\text{NO}_2^+ > \text{NO}_3^- > \text{NO}_2^-$ (d) $\text{NO}_2^- > \text{NO}_3^- > \text{NO}_2^+$

11. Hybridization of carbon in C_3O_2 is:

- (a) sp (b) sp^2
 (c) sp^3 (d) sp^3d

12. Which of the following has been arranged in increasing order of size of the hybrid orbitals?

- (a) $\text{sp} < \text{sp}^2 < \text{sp}^3$ (b) $\text{sp}^3 < \text{sp}^2 < \text{sp}$
 (c) $\text{sp}^2 < \text{sp}^3 < \text{sp}$ (d) $\text{sp}^2 < \text{sp} < \text{sp}^3$

13. Identify the correct match.

- | | |
|--|--|
| A. XeF_2 | p. Central atom has sp^3 hybridisation and bent geometry. |
| B. N_3^- | q. Central atom has sp^3d^2 hybridisation and octahedral. |
| C. PCl_5 (s) anion | r. Central atom has sp hybridisation and linear geometry. |
| D. I_2Cl_6 (ℓ) cation | s. Central atom has sp^3d hybridisation and linear geometry. |

- (a) A \rightarrow p; B \rightarrow q; C \rightarrow r; D \rightarrow s
 (b) A \rightarrow s; B \rightarrow q; C \rightarrow s; D \rightarrow r
 (c) A \rightarrow q; B \rightarrow r; C \rightarrow p; D \rightarrow s
 (d) A \rightarrow s; B \rightarrow r; C \rightarrow q; D \rightarrow p

14. Which of the following is true statement?

- (a) All the carbon in $\text{H}_2\text{C} = \text{C} - \text{C} \equiv \text{C} = \text{CH}_2$ are in sp^2 hybridisation.
 (b) In $\text{C}_2\text{H}_2(\text{CN})_2$ there are six 'σ' bonds.
 (c) In diamond 'C' is in sp^2 hybridisation.
 (d) In C_3O_2 all the carbons are in sp hybridisation.

15. The shape of methyl radical (CH_3) is :

- (a) Linear (b) Pyramidal
 (c) Planar (d) Spherical

16. Hybridisation of Iodine atoms in ICl_3 (in its stable form, found in solid state) and $\text{I}_2\text{Cl}_4\text{Br}_2$ are :

- (a) sp^3 & sp^3d^2 (b) sp^3d^2 & sp^3d^3
 (c) Both sp^3d (d) Both sp^3d^2

17. In which of the following molecules number of lone pairs and bond pairs on central atom are not equal?

- (a) H_2O (b) I_3^-
 (c) O_2F_2 (d) SCl_2

18. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atomic no. < 21) are

- (a) pure p (b) sp hybrid
 (c) sp^2 hybrid (d) sp^3 hybrid

19. Carbon atoms in $\text{C}_2(\text{CN})_4$ are :

- (a) sp-hybridized (b) sp^2 -hybridized
 (c) sp-and sp^2 hybridized (d) sp, sp^2 and sp^3 -hybridized

20. How many bonded electrons pairs are present in IF_7 molecule

- (a) 6 (b) 7
 (c) 5 (d) 8

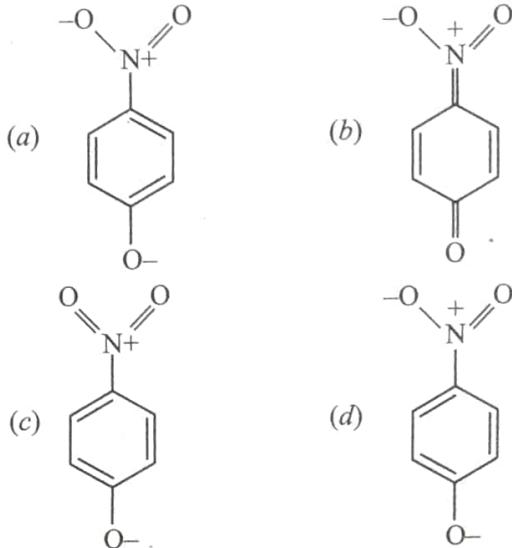
21. In the cyanide ion, the negative charge is on

- (a) C (b) N
 (c) Both C and N (d) Resonate between C and N

22. In compounds type ECl_3 , where E = B, P, As or Bi, the angles Cl - E - Cl for different E are in the order

- (a) B > P = As = Bi (b) B > P > As > Bi
 (c) B < P = As = Bi (d) B < P < As < Bi

23. The most likely representation of resonance structure of p-nitrophenoxide is :



- (a) 'A' & 'B'
(b) 'B' & 'D'
(c) only 'D'
(d) None of these
- 45.** Effective overlapping will be shown by :
(a)
(b)
(c)
(d) All the above
- 46.** A simplified application of MO theory to the hypothetical 'molecule' OF would give its bond order as
(a) 2
(b) 1.5
(c) 1.0
(d) 0.5
- 47.** Which of the following species is paramagnetic ?
(a) NO
(b) O₂²⁻
(c) CN
(d) CO

- 48.** In which of the following processes magnetic moment and Bond order, both are changed.
(a) NO → NO⁺
(b) O₂ → O₂
(c) N₂ → N₂⁻
(d) All of these
- 49.** According to Molecular orbital theory which of the following is correct?
(a) LUMO level for C₂ molecule is σ_{2p} orbital
(b) In C₂ molecules both the bonds are π bonds
(c) In C₂²⁻ ion there is one σ and two π bonds
(d) All the above are correct
- 50.** Which of the following has fractional bond order :
(a) O₂²⁺
(b) O₂⁻
(c) F₂²⁻
(d) H₂⁻

Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

1. The species/molecule is having same shape but different hybridisation.
(a) XeF₂, CO₂
(b) I₃⁻, HgCl₂
(c) OCl⁻, CO
(d) SO₂, OCl₂
2. Which of the following have planar structure ?
(a) I₃⁻
(b) ICl₃
(c) Cl₂O₆
(d) Be₂Cl₄
3. What is the state of hybridisation of Xe in cationic part of solid XeF₆?
(a) sp³d³
(b) sp³d²
(c) sp³d
(d) sp³
4. Which statement is correct about hybridization?
(a) In hybridisation orbitals take part
(b) In hybridisation electrons take part
(c) In hybridisation fully filled, half filled or empty orbitals can take part
(d) Hybridised orbitals only contains bond pair electron
5. The halogen form compounds among themselves with formula XX', XX'₃, XX'₅ and XX'₇, where X is the heavier halogen. Which of the following pairs representing their structures and being polar and non-polar are correct?
(a) XX' – Linear – polar
(b) XX'₃ – T-shaped – polar
(c) XX'₅ – square pyramidal – polar
(d) XX'₇ – Pentagonal bipyramidal – non-polar
6. Which of the following isoelectronic & isostructural species are NO₃⁻, ClO₃⁻, SO₃ & CO₃²⁻?
(a) NO₃⁻ & CO₃²⁻
(b) SO₃ & CO₃²⁻
(c) NO₃⁻ & ClO₃⁻
(d) CO₃²⁻ & ClO₃⁻

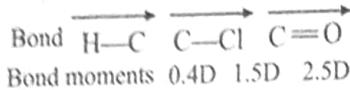
7. Which of the following statement is/are correct
(a) Hybridisation is the mixing of pure atomic orbitals having less energy difference
(b) sp³d² - hybrid orbitals are at 90° to one another
(c) sp³d - hybrid orbitals are directed towards the corners of a regular tetrahedron
(d) sp³d² - hybrid orbitals are directed towards the corners of a regular octahedron
8. A π-bond may between two p_x orbitals containing one unpaired electron each when they approach each other appropriately along :
(a) x-axis
(b) y-axis
(c) z-axis
(d) any direction
9. During the complete combustion of methane CH₄, what change in hybridisation does the carbon atom undergo?
(a) sp³ to sp
(b) sp³ to sp²
(c) sp² to sp
(d) sp² to sp³
10. Rotation around the bond (between the underlined atoms) is restricted in :
(a) C₂H₄
(b) H₂O₂
(c) C₂H₂
(d) C₂H₆
11. Correct order about bond angle is/are :
(a) H₂O > H₂S > H₂Se > H₂Te
(b) C₂H₂ > C₂H₄ > CH₄ > NH₃
(c) SF₆ < NH₃ < H₂O < OF₂
(d) ClO₂ > H₂O > H₂S > SF₆

12. N_2O has a linear, unsymmetrical structure that may be thought of as a hybrid of two resonance forms. If a resonance form must have a satisfactory Lewis structure, which two of the five structures shown below are the two resonance forms of N_2O ?
- (a) $:\ddot{\text{N}}=\text{N}=\ddot{\text{O}}:$ (b) $:\ddot{\text{N}}=\text{N}=\ddot{\text{O}}:$
 (c) $:\ddot{\text{N}}-\text{N}=\text{O}:$ (d) $:\ddot{\text{N}}=\ddot{\text{N}}-\ddot{\text{O}}:$
13. Identify the correct option(s).
- (a) $\text{NH}_4^+ > \text{NH}_3 > \text{NH}_2^-$ order of bond angle.
 (b) $(\text{CH}_3)_3\text{B}$ is a trigonal planar molecule (not considering the H-atoms on 'C').
 (c) In NH_4Cl 'N' atom is in sp^3d hybridisation.
 (d) In S_8 molecule a total of 16 electrons are left on all the 'S' atoms after bonding.
14. Which has (have) zero value of dipole moment?
- (a) I_2Cl_6 (b) CHCl_3
 (c) CO_2 (d)
15. Which of the following statement(s) is/are correct?
- (a) Ethyne gas is more soluble in acetone than in water.
 (b) CH_3F is more polar than CD_3F due to deuterium (D) being less electronegative than hydrogen (H).
 (c) Silyl isocyanate (SiH_3NCO) is linear in shape while methyl isocyanate (CH_3NCO) is bent in shape.
 (d) In $\text{CH}_2=\text{C}=\text{C}=\text{CH}_2$, the 2H-atoms on one C-atom lie in a plane perpendicular to the plane in which 2H-atoms on other C-atom lie.
16. Choose the correct statements.
- (a) CH_3NCS molecule is linear
 (b) SiH_3NCS molecule is linear
 (c) GeH_3NCS molecule is bent
 (d) $[\text{C}(\text{SiH}_3)_3]^-$ molecule is pyramidal
17. KF combines with HF to form KHF_2 . The compound contains the species:
- (a) K^+ , F^- and H^+ (b) K^+ , F^- and HF
 (c) K^+ and $[\text{HF}_2]^-$ (d) $[\text{KHF}]^+$ and F_2
18. The lattice energies of KF, KCl, KBr and KI follow the order:
- (a) $\text{KF} > \text{KCl} > \text{KBr} > \text{KI}$
 (b) $\text{KI} > \text{KBr} > \text{KCl} > \text{KF}$
 (c) $\text{KF} > \text{KCl} > \text{KI} > \text{KBr}$
 (d) $\text{KI} > \text{KBr} > \text{KF} > \text{KCl}$
19. Which of the following do not exist?
- (a) SH_6 (b) HFO_4^-
 (c) FeI_3 (d) HClO_3
20. Which of the following statements is/are true for BaO and MgO ?
- (a) BaO is more ionic than MgO
 (b) MgO is more ionic than BaO
 (c) BaO has a higher melting point than MgO
 (d) MgO has a higher melting point than BaO
21. Most ionic compounds have :
- (a) High melting points and low boiling points
 (b) High melting points and non-directional bonds
 (c) High solubilities in polar solvents and low solubilities in nonpolar solvents
 (d) Three-dimensional crystal structures, and are good conductors of electricity in the molten state
22. A, B, C are three substances. A does not conduct electricity in the solid, molten state and aqueous solution. B conducts electricity both in the fused and aqueous states, while C conducts electricity only in the aqueous state. In solid state neither B nor C conducts electricity. Which of the following statements is/are true regarding A, B and C?
- (a) A has polar covalent linkage
 (b) A has nonpolar covalent linkage
 (c) B is ionic in nature
 (d) Cation formed by C is highly polarizing
23. Which of the following have identical bond order?
- (a) O_2^{2+} (b) NO^+
 (c) CN^- (d) CN^+
24. Given the species : N_2 , CO , CN^- and NO^+ . Which of the following statements are true for these
- (a) All species are paramagnetic
 (b) The species are isoelectronic
 (c) All the species have dipole moment
 (d) All the species are linear
25. Geometry (i.e. arrangement of electron pairs around central atom) of ClOF_3 is similar to the :
- (a) XeF_4 (b) SOCl_2
 (c) I_3^- (d) ClO_4^-
26. The shape of SF_5^- can be :
- I.
 II.
 III.
 IV.
- (a) I only (b) I and II only
 (c) IV only (d) I, II, & III
27. Actual shape of the molecule BrF_5 is similar to the molecule:
- (a) PCl_5 (b) XeF_4
 (c) PCl_4^+ (d) None of these

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 28 to 30): Chemical bonding between two atoms is necessarily associated with an electrical moment arising out of the difference in electronegativity of two atoms. This means that every bond carries with it an electrical moment called the

"bond moment". The dipole moment of a molecule is really the vectorial sum of the individual bond moment present in it. To compute the dipole moment it is necessary to find out the values of various bond moment. in the following table dipole moment of different bonds are as given.



The group moments of few group as given

Group	NO_2	OH	CN	CH_3
direction of dipole	towards N	towards O	towards N	away from CH_3
Dipole moment	4D	1.6 D	3.8 D	0.4 D

28. The bond angle in H_2S is 97° and its dipole moment is 1.5D. The S – H bond distance is 0.15nm There fore approximate percentage ionic character of S – H bond is (neglect the effect of dipole moment of lone pair on sulphur atom in H_2S). (Given $[\cos 97^\circ = -0.12]$ and $\sqrt{0.88} = 0.94$)

- (a) 32 % (b) 16 %
(c) 84 % (d) 10 %

29. In CH_3CCl_3 (I), CHCl_3 (II) and CH_3Cl (III) the normal tetrahedral bond angle is maintained. Also given $\cos 70.5^\circ = \frac{1}{3}$. Therefore dipole moments of the given compounds are. (given due to – I effect of Cl, the Bond moment of H—C bond directed toward the H in CHCl_3)

- (a) I = 1.9 D, II = 1.9 D, III = 1.7 D
(b) I = 1.9 D, II = 1.7 D, III = 1.9 D
(c) I = 1.9 D, II = 1.7 D, III = 1.7 D
(d) I = 1.9 D, II = 1.1 D, III = 1.9 D

30. In the acetone molecule considering the normal planer structure, the observed dipole moment of acetone molecule is
- (a) 2.9 D (b) 2.75 D
(c) 3 D (d) None of these

Comprehension (Q. 31 to 33): Hybridisation is the mixing of atomic orbital of comparable energy and the number of hybrid orbitals formed is equal to the number of pure atomic orbitals mixed up and hybrid orbitals are occupied by σ -bond pair and lone pair.

31. Which of the following geometry is most likely to not form from sp^3d hybridisation of the central atom.
- (a) Linear (b) Tetrahedral
(c) T-Shaped (d) See-Saw

32. The orbital which is not participated in sp^3d^2 hybridisation.
- (a) p_x (b) d_{xy} (c) $\text{d}_{x^2-y^2}$ (d) p_z

33. "The hybrid orbitals are at angle of X° to one another" this statement is not valid for which of the following hybridisation.
- (a) sp^3 (b) sp^2
(c) sp^3d^2 (d) sp

MATCH THE COLUMN TYPE QUESTIONS

34. Match the species given in column-I with the type of hybridisation given in column-II.

	Column-I	Column-II
A.	IO_2F_2^-	p. sp^3d
B.	F_2SeO	q. sp^3
C.	ClOF_3	r. sp^2
D.	XeF_5^+	s. sp^3d^2

- (a) A \rightarrow s; B \rightarrow q; C \rightarrow p; D \rightarrow r
(b) A \rightarrow p; B \rightarrow q; C \rightarrow p; D \rightarrow s
(c) A \rightarrow p; B \rightarrow p; C \rightarrow q; D \rightarrow s
(d) A \rightarrow s; B \rightarrow p; C \rightarrow q; D \rightarrow r

35. Match the Column

	Column-I	Column-II
A.	I_2Cl_6	p. All atoms are sp^3 hybridised
B.	SiC	q. have non planar structure
C.	$\text{Al}_2(\text{CH}_3)_6$	r. have 3c - 4e bonds
D.	S_3O_9	s. have 3c - 2e bonds

- (a) A \rightarrow r; B \rightarrow p; C \rightarrow s; D \rightarrow q
(b) A \rightarrow q; B \rightarrow p; C \rightarrow s; D \rightarrow r
(c) A \rightarrow q; B \rightarrow s; C \rightarrow p; D \rightarrow r
(d) A \rightarrow r; B \rightarrow s; C \rightarrow p; D \rightarrow q

36. Match the species/molecules listed in column-I with their characteristics listed in column-II.

	Column-I	Column-II
A.	ClF_5 , BrF_4^+ , IF_6^-	p. All molecules/ions are polar in nature
B.	ClF_3 , BrF_2^+ , IClF_4^-	q. All molecules/ions have same number of lone pair (s) Same shape.
C.	XeF_2 , ICl_2^- , I_3^-	r. All molecules/ions have same oxidation state of central atoms.
D.	ClOF_3 , ClF_4^+ , IO_2F_2^-	s. All molecules/ions have same hybridisation of central atoms.

- (a) A \rightarrow p,q,r,s; B \rightarrow r; C \rightarrow q,s; D \rightarrow p,r
(b) A \rightarrow p,r; B \rightarrow q,s; C \rightarrow r; D \rightarrow p,q,r,s
(c) A \rightarrow p,r; B \rightarrow r; C \rightarrow q,s; D \rightarrow p,q,r,s
(d) A \rightarrow p,q,r,s; B \rightarrow q,s; C \rightarrow r; D \rightarrow p,r

37. Match the Column

Column-I		Column-II	
A.	ICl_3	p.	Hybridisation of central atom is similar in both dimer and monomer form.
B.	AlCl_3	q.	Both monomer and dimer forms are planar
C.	AlF_3	r.	In dimer form all atoms are sp^3 hybridised.
D.	NO_2	s.	Does not exist in dimer form

- (a) $\text{A} \rightarrow \text{p}; \text{B} \rightarrow \text{r}; \text{C} \rightarrow \text{s}; \text{D} \rightarrow \text{q}$
- (b) $\text{A} \rightarrow \text{q}; \text{B} \rightarrow \text{s}; \text{C} \rightarrow \text{r}; \text{D} \rightarrow \text{p}$
- (c) $\text{A} \rightarrow \text{p}; \text{B} \rightarrow \text{s}; \text{C} \rightarrow \text{r}; \text{D} \rightarrow \text{q}$
- (d) $\text{A} \rightarrow \text{q}; \text{B} \rightarrow \text{r}; \text{C} \rightarrow \text{s}; \text{D} \rightarrow \text{p}$

NUMERICAL TYPE QUESTIONS

- 38. The sum of bond order of O_2 , O_2^- and O_2^{2-} is ____.
- 39. Count the total number of X–O bonds are having equal length in HSO_4^- and $\text{S}_3\text{O}_6^{2-}$ respectively. (If the answer is 5 and 3 then represent as 53)
- 40. How many compounds among the following contains N–O–N bond?
 N_2O_3 (symmetrical), N_2O_4 , N_2O_5 , N_2O



Exercise-4 (Past Years Questions)

JEE MAIN

1. Which one of the following statements about water is FALSE? (2016)
 - (a) Water can act both as an acid and as a base.
 - (b) There is extensive intramolecular hydrogen bonding in the condensed phase.
 - (c) Ice formed by heavy water sinks in normal water.
 - (d) Water is oxidized to oxygen during photosynthesis.
2. The species in which the N atom is in a state of sp hybridization is: (2016)
 - (a) NO_2^+
 - (b) NO_2^-
 - (c) NO_3^-
 - (d) NO_2
3. Which of the following reactions is an example of a redox reaction? (2017)
 - (a) $\text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2$
 - (b) $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+ + [\text{PF}_6]^-$
 - (c) $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$
 - (d) $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$
4. Which of the following species is not paramagnetic? (2017)
 - (a) NO
 - (b) CO
 - (c) O_2
 - (d) B_2
5. The compound that does not produce nitrogen gas by the thermal decomposition is (2018)
 - (a) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
 - (b) NH_4NO_2
 - (c) $(\text{NH}_4)_2\text{SO}_4$
 - (d) $\text{Ba}(\text{N}_3)_2$
6. Total number of lone pair of electrons in I_3^- ion is: (2018)
 - (a) 6
 - (b) 9
 - (c) 12
 - (d) 3
7. According to molecular orbital theory, which of the following will not be a viable molecule? (2018)
 - (a) He_2^+
 - (b) H_2^-
 - (c) H_2^{2-}
 - (d) He_2^{2+}

8. Which of the following compounds contain(s) no covalent bond(s)? (2018)



- (a) $\text{KCl}, \text{H}_2\text{SO}_4$
- (b) KCl
- (c) $\text{KCl}, \text{B}_2\text{H}_6$
- (d) $\text{KCl}, \text{B}_2\text{H}_6, \text{PH}_3$

9. The type of hybridisation and number of lone pair(s) of electrons of Xe in XeOF_4 respectively are: (2019)

- (a) sp^3d^2 and 1
- (b) sp^3d and 2
- (c) sp^3d^2 and 2
- (d) sp^3d and 1

10. Two pi and half sigma bonds are present in (2019)

- (a) O_2^+
- (b) N_2
- (c) O_2
- (d) N_2^+

11. The element that shows greater ability to form $\text{p}\pi - \text{p}\pi$ multiple bonds, is : (2019)

- (a) Sn
- (b) C
- (c) Ge
- (d) Si

12. The number of 2-centre-2-electron and 3-centre-2-electron bonds in B_2H_6 , respectively, are: (2019)

- (a) 2 and 2
- (b) 4 and 2
- (c) 2 and 2
- (d) 2 and 4

13. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic? (2019)

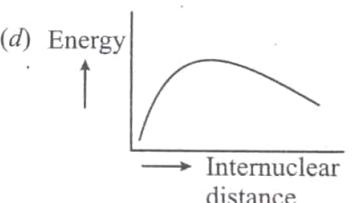
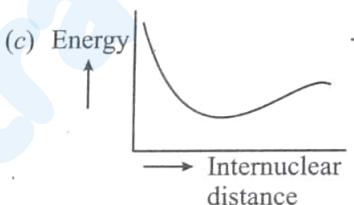
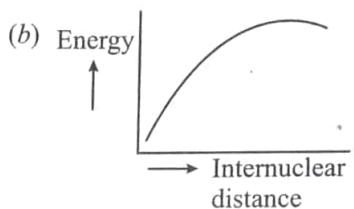
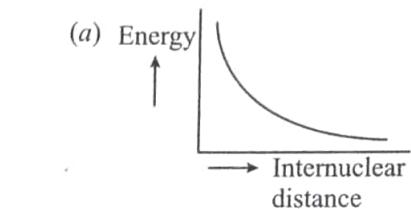
- (a) $\text{NO} \rightarrow \text{NO}^+$
- (b) $\text{N}_2 \rightarrow \text{N}_2^+$
- (c) $\text{O}_2 \rightarrow \text{O}_2^+$
- (d) $\text{O}_2 \rightarrow \text{O}_2^{2-}$

14. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^- ? (2019)

- (a) Li_2^+ is unstable and Li_2^- is stable
- (b) Li_2^+ is stable and Li_2^- is unstable
- (c) Both are stable
- (d) Both are unstable

15. Among the following, the molecule expected to be stabilized by anion formation is: (2019)
- C₂O₂, NO, F₂
 (a) NO (b) C₂ (c) F₂ (d) O₂
16. The ion that has sp³d² hybridization for the central atom, is : (2019)
- [ICl₂]⁻ [IF₆]⁻
 (c) [ICl₄]⁻ (d) [BrF₂]⁻
17. Among the following molecules / ions, C₂²⁻, N₂²⁻, O₂²⁻, O₂ which one is diamagnetic and has the shortest bond length? (2019)
- (a) C₂²⁻ (b) N₂²⁻ (c) O₂ (d) O₂²⁻
18. The correct statement about ICl₅ and ICl₄⁻ is (2019)
- (a) ICl₅ is trigonal bipyramidal and ICl₄⁻ is tetrahedral
 (b) ICl₅ is square pyramidal and ICl₄⁻ is tetrahedral
 (c) ICl₅ is square pyramidal and ICl₄⁻ is square planar.
 (d) Both are isostructural.
19. The C-C bond length is maximum in (2019)
- (a) Graphite (b) C₇₀
 (c) Diamond (d) C₆₀
20. Among the following species, the diamagnetic molecule is (2019)
- (a) O₂ (b) NO
 (c) B₂ (d) CO
21. The structures of beryllium chloride in the solid state and vapour phase respectively are: (2019)
- (a) Chain and dimeric (b) Chain and chain
 (c) Dimeric and dimeric (d) Dimeric and chain
22. HF has highest boiling point among hydrogen halides, because it has: (2019)
- (a) Lowest dissociation enthalpy
 (b) Strongest van der Waals' interactions
 (c) Strongest hydrogen bonding
 (d) Lowest ionic character
23. The correct statements among I to III are: (2019)
- (I) Valence bond theory cannot explain the color exhibited by transition metal complexes.
 (II) Valence bond theory can predict quantitatively the magnetic properties of transition metal complexes.
 (III) Valence bond theory cannot distinguish ligands as weak and strong field ones.
 (a) (I) and (II) only (b) (I), (II) and (III)
 (c) (I) and (III) only (d) (II) and (III) only
24. The correct statement among the following is (2019)
- (a) (SiH₃)₃N is pyramidal and more basic than (CH₃)₃N
 (b) (SiH₃)₃N is planar and more basic than (CH₃)₃N
 (c) (SiH₃)₃N is pyramidal and less basic than (CH₃)₃N
 (d) (SiH₃)₃N is planar and less basic than (CH₃)₃N
25. The oxoacid of sulphur that does not contain bond between sulphur atoms is : (2019)
- (a) H₂S₄O₆ (b) H₂S₂O₇
 (c) H₂S₂O₃ (d) H₂S₂O₄
26. During the change of O₂ to O₂⁻, the incoming electron goes to the orbital: (2019)
- (a) σ* 2P_z (b) π 2P_y
 (c) π* 2P_x (d) π 2P_x
27. The correct statements among (i) to (iv) are: (2019)
- (i) saline hydrides produce H₂ gas when reacted with H₂O.
 (ii) reaction of LiAlH₄ with BF₃ leads to B₂H₆.
 (iii) PH₃ and CH₄ are electron - rich and electron-precise hydrides, respectively.
 (iv) HF and CH₄ are called as molecular hydrides.
 (a) (iii) and (iv) only (b) (i), (ii) and (iii) only
 (c) (i), (ii), (iii) and (iv) (d) (i), (iii) and (iv) only
28. The relative strength of interionic/intermolecular forces in decreasing order is: (2020)
- (a) Dipole-dipole > ion-dipole > ion-ion
 (b) Ion-ion > ion-dipole > dipole-dipole
 (c) Ion-dipole > dipole-dipole > ion-ion
 (d) Ion-dipole > ion-ion > dipole-dipole
29. The dipole moments of CCl₄, CHCl₃ and CH₄ are in the order: (2020)
- (a) CH₄ < CCl₄ < CHCl₃ (b) CCl₄ < CH₄ < CHCl₃
 (c) CHCl₃ < CH₄ = CCl₄ (d) CH₄ = CCl₄ < CHCl₃
30. The bond order and the magnetic characteristics of CN⁻ are: (2020)
- (a) 2 $\frac{1}{2}$, diamagnetic (b) 3, paramagnetic
 (c) 3, diamagnetic (d) 2 $\frac{1}{2}$, paramagnetic
31. The predominant intermolecular forces present in ethyl acetate, a liquid, are: (2020)
- (a) Dipole-dipole and hydrogen bonding
 (b) London dispersion, dipole-dipole and hydrogen bonding
 (c) London dispersion and dipole-dipole
 (d) Hydrogen bonding and London dispersion
32. Arrange the following bonds according to their average bond energies in descending order: (2020)
- C – Cl, C – Br, C – F, C – I
- (a) C – Cl > C – Br > C – I > C – F
 (b) C – F > C – Cl > C – Br > C – I
 (c) C – I > C – Br > C – Cl > C – F
 (d) C – Br > C – I > C – Cl > C – F

33. If the magnetic moment of a dioxygen species is 1.73 B.M., it may be: (2020)
- O_2 or O_2^+
 - O_2 or O_2^-
 - O_2 or O_2^+
 - O_2 , O_2^- or O_2^+
34. The molecular geometry of SF_6 is octahedral. What is the geometry of SF_4 (including lone pair(s) of electrons, if any)? (2020)
- Tetrahedral
 - Trigonal bipyramidal
 - Square planar
 - Pyramidal
35. Match the type of interaction in column A with the distance dependence of their interaction energy in column B (2020)
- | A | B |
|----------------------|--------------------|
| A. Ion-ion | p. $\frac{1}{r}$ |
| B. Dipole-dipole | q. $\frac{1}{r^2}$ |
| C. London dispersion | r. $\frac{1}{r^3}$ |
| | s. $\frac{1}{r^6}$ |
- (a) A \rightarrow p; B \rightarrow q; C \rightarrow s
 (b) A \rightarrow q; B \rightarrow s; C \rightarrow r
 (c) A \rightarrow p; B \rightarrow q; C \rightarrow r
 (d) A \rightarrow p; B \rightarrow r; C \rightarrow s
36. If AB_4 molecule is a polar molecule, a possible geometry of AB_4 is (2020)
- Tetrahedral
 - Rectangular planar
 - Square pyramidal
 - Square planar
37. Of the species, NO , NO^+ , NO^{2+} and NO^- , the one with minimum bond strength is (2020)
- NO^-
 - NO^{2+}
 - NO^+
 - NO
38. The intermolecular potential energy for the molecules A, B, C and D given below suggests that: (2020)
-
- (a) A-B has the stiffest bond
 (b) A-D has the shortest bond length
 (c) A-A has the largest bond enthalpy
 (d) D is more electronegative than other atoms
39. The compound that has the largest H – M – H bond angle ($M = N, O, S, C$) is (2020)
- H_2S
 - CH_4
 - NH_3
 - H_2O
40. The potential energy curve for the H_2 molecule as a function of internuclear distance is (2020)
-



41. The spin-only magnetic moment value of B_2^+ species is $\times 10^{-2}$ BM. (Nearest integer) [Given : $\sqrt{3} = 1.73$] (2021)
42. According to molecular orbital theory, the number of unpaired electron(s) in O_2^{2-} is: (2021)
43. The number of hydrogen bonded water molecule(s) associated with stoichiometry $CuSO_4 \cdot 5H_2O$ is (2021)
44. The number of species having non-pyramidal shape among the following is (2021)
- SO_3
 - NO_3^-
 - PCl_3
 - CO_3^{2-}
45. Which of the following are isostructural pairs? (2021)
- SO_4^{2-} and CrO_4^{2-}
 - $SiCl_4$ and $TiCl_4$
 - NH_3 and NO_3^-
 - BCl_3 and $BrCl_3$
- III and IV only
 - I and II only
 - I and III only
 - II and III only

46. The correct shape and I—I—I bond angles respectively in I_3^- ion are: (2021)
- Distorted trigonal planar; 135° and 90°
 - T-shaped; 180° and 90°
 - Trigonal planar; 120°
 - Linear; 180°
47. The correct set from the following in which both pairs are in correct order of melting point is: (2021)
- $LiF > LiCl$; $MgO > NaCl$
 - $LiCl > LiF$; $NaCl > MgO$
 - $LiF > LiCl$; $NaCl > MgO$
 - $LiCl > LiF$; $MgO > NaCl$
48. According to molecular theory, the species among the following that does not exist is: (2021)
- He_2^+
 - He_2^-
 - Be_2
 - O_2^{2-}
49. The correct statement about B_2H_6 is: (2021)
- Terminal B—H bonds have less p-character when compared to bridging bonds.
 - The two B—H—B bonds are not of same length
 - All B—H—B angles are of 120°
 - Its fragment, BH_3 , behaves as a Lewis base
50. Which among the following species has unequal bond lengths? (2021)
- BF_4^-
 - XeF_4
 - SF_4
 - SiF_4
51. Given below are two statements: one is labelled as Assertion (A) and the other is labelled as Reason (R).
- Assertion (A):** Dipole-dipole interactions are the only non-covalent interactions, resulting in hydrogen bond formation.
- Reason (R):** Fluorine is the most electronegative element and hydrogen bonds in HF are symmetrical.
- In the light of the above statements, choose the most appropriate answer from the options given below. (2021)
- (A) is false but (R) is true
 - Both (A) and (R) are true and (R) is the correct explanation of (A)
 - (A) is true (R) is false
 - Both (A) and (R) are true but (R) is NOT the correct explanation of (A)
52. Match List-I with List-II. (2021)
- | List-I
(Molecule) | List-II
(Bond order) |
|----------------------|-------------------------|
| (A) Ne_2 | (i) 1 |
| (B) N_2 | (ii) 2 |
| (C) F_2 | (iii) 0 |
| (D) O_2 | (iv) 3 |
- Choose the correct answer from the options given below:
- A-(iii), B-(iv), C-(i), D-(ii)
 - A-(i), B-(ii), C-(iii), D-(iv)
 - A-(ii), B-(i), C-(iv), D-(iii)
 - A-(iv), B-(iii), C-(ii), D-(i)
53. Given below are two statements: one is labelled as Assertion (A) and the other is labelled as Reason (R):
- Assertion (A):** The H—O—H bond angle in water molecule is 104.5° .
- Reason (R):** The lone pair – lone pair repulsion of electrons is higher than the bond pair – bond pair repulsion. (2021)
- (A) is false but (R) is true
 - Both (A) and (R) are true, but (R) is not the correct explanation of (A)
 - (A) is true but (R) is false
 - Both (A) and (R) are true, and (R) is the correct explanation of (A)
54. A central atom in a molecule has two lone pairs of electrons and forms three single bonds. The shape of this molecule is: (2021)
- See-saw
 - Planar triangular
 - T-shaped
 - Trigonal pyramidal
55. The correct order of bond orders of C_2^{2-} , N_2^{2-} and O_2^{2-} , respectively. (2022)
- $C_2^{2-} < N_2^{2-} < O_2^{2-}$
 - $O_2^{2-} < N_2^{2-} < C_2^{2-}$
 - $C_2^{2-} < O_2^{2-} < N_2^{2-}$
 - $N_2^{2-} < C_2^{2-} < O_2^{2-}$
56. PCl_5 is well known, but NCl_5 is not. Because. (2022)
- Nitrogen is less reactive than phosphorous.
 - Nitrogen doesn't have d-orbitals in its valence shell.
 - Catenation tendency is weaker in nitrogen than phosphorous.
 - Size of phosphorous is larger than nitrogen.
57. Given below are two statements. (2022)
- Statement-I :** The presence of weaker π -bonds make alkenes less stable than alkanes.
- Statement-II :** The strength of the double bond is greater than that of carbon-carbon single bond.
- In the light of the above statements, choose the correct answer from the options given below.
- Both Statement-I and Statement-II are correct.
 - Both Statement-I and Statement-II are incorrect.
 - Statement-I is correct but Statement-II is incorrect.
 - Statement-I is incorrect but Statement-II is correct.
58. Amongst BeF_2 , BF_3 , H_2O , NH_3 , CCl_4 and HCl , the number of molecules with non-zero net dipole moment is _____. (2022)
59. Bonding in which of the following diatomic molecule(s) become(s) stronger, on the basis of MO Theory, by removal of an electron? (2022)
- NO
 - N_2
 - O_2
 - C_2
 - B_2
- Choose the most appropriate answer from the options given below
- (i), (ii), (iii) only
 - (ii), (iii), (v) only
 - (i), (iii) only
 - (iv) only

60. Number of electron deficient molecules among the following: (2022)

PH₃, B₂H₆, CCl₄, NH₃, LiH and BC₁ is:

 - 0
 - 1
 - 2
 - 3

61. The oxide which contains an odd electron at the nitrogen atom is: (2022)

 - N₂O
 - NO₂
 - N₂O₃
 - N₂O₅

EE ADVANCED

62. The compound(s) with Two lone pairs of electrons on the central atom is(are) (2016)

 - BrF₅
 - ClF₃
 - XeF₄
 - SF₄

63. According to Molecular Orbital Theory, (2016)

 - C₂²⁻ is expected to be diamagnetic
 - O₂²⁺ is expected to have a longer bond length than O₂
 - N₂⁺ and N₂⁻ have the same bond order
 - He₂⁺ has the same energy as two isolated He atoms

64. The order of the oxidation state of the phosphorus atom in H₃PO₂, H₃PO₃, and H₄P₂O₆ is (2017)

 - H₃PO₂ > H₃PO₂ > H₃PO₃ > H₄P₂O₆
 - H₃PO₄ > H₄P₂O₆ > H₃PO₃ > H₃PO₂
 - H₃PO₂ > H₃PO₃ > H₄P₂O₆ > H₃PO₄
 - H₃PO₃ > H₃PO₂ > H₃PO₄ > H₄P₂O₆

65. Among the following, the correct statement(s) is (are) (2017)

 - Al(CH₃)₃ has the three-centre two-electron bonds in its dimeric structure.
 - The Lewis acidity of BCl₃ is greater than that of AlCl₃
 - AlCl₃ has the three-centre two-electron bonds in its dimeric structure.
 - BH₃ has the three-centre two-electron bonds in its dimeric structure.

66. The correct statement(s) about the oxoacids, HClO₄ and HClO, is (are) (2017)

 - The central atom in both HClO₄ and HClO is sp³ hybridized
 - HClO₄ is formed in the reaction between Cl₂ and H₂O
 - The conjugate base of HClO₄ is weaker base than H₂O
 - HClO₄ is more acidic than HClO because of the resonance stabilization of its anion

67. The Colour of the X₂ molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to (2017)

 - Decrease in $\pi^* - \sigma^*$ gap down the group
 - Decrease in ionization energy down the group
 - The physical state of X₂ at room temperature changes from gas to solid down the group
 - Decrease in HOMO-LUMO gap down the group

68. The sum of the number of lone pairs of electrons on each central atom in the following species is (2017)

[TeBr₆]²⁻, [BrF₂]⁺, SNF₃, and [XeF₃]⁻
(Atomic numbers : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54)

69. Among H₂, He₂⁺, Li₂, Be₂, B₂, C₂, N₂, O₂ and F₂, the number of diamagnetic species is (2017)
(Atomic numbers : H = 1, He = 2, Li = 3, Be = 4B = 5, C = 6, N = 7, O = 8, F = 9)

70. A tin chloride Q undergoes the following reactions (not balanced) (2019)

$$Q + Cl^- \rightarrow X$$

$$Q + Me_3N \rightarrow Y$$

$$Q + CuCl_2 \rightarrow Z + CuCl$$

X is a monoanion having pyramidal geometry. Both Y and Z are neutral compounds.
Choose the correct option(s).

 - The central atoms in X is sp³ hybridized
 - The oxidation state of the central atom in Z is +2
 - The central atom in Z has one lone pair of electrons
 - There is a coordinate bond in Y

71. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature. (2019)

 - BeCl₂, CO₂, BCl₃, CHCl₃
 - SO₂, C₆H₅Cl, H₂Se, BrF₅
 - BF₃, O₃, SF₆, XeF₆
 - NO₂, NH₃, POCl₃, CH₃Cl

72. Among B₂H₆, B₃N₃H₆, N₂O, N₂O₄, H₂S₂O₃ and H₂S₂O₈, and total number of molecules containing covalent bond between two atoms of the same kind is _____. (2019)

73. At 143 K. the reaction of XeF₄ with O₂F₂, produces a xenon compound Y. The total number of lone pair(s) of electrons present on the whole molecule of Y is _____. (2019)

74. Consider the following compounds in the liquid form : O₂, HF, H₂O, NH₃, H₂O₂, CCl₄, CHCl₃, C₆H₆, C₆H₅Cl. When a charged comb is brought near their flowing stream, how many of them show deflection as per the following figure? (2019)

75. For diatomic molecules, the correct statement(s) about the molecular orbitals formed by the overlap of two 2p_z orbitals is(are)

 - σ orbital has a total of two nodal planes.
 - σ^* orbital has one node in the xz-plane containing the molecular axis.
 - π orbital has one node in the plane which is perpendicular to the molecular axis and goes through the center of the molecule.
 - π^* orbital has one node in the xy-plane containing the molecular axis.

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (d) | 3. (b) | 4. (a) | 5. (d) | 6. (d) | 7. (d) | 8. (d) | 9. (b) | 10. (c) |
| 11. (c) | 12. (a) | 13. (b) | 14. (d) | 15. (a) | 16. (a) | 17. (b) | 18. (b) | 19. (c) | 20. (d) |
| 21. (a) | 22. (c) | 23. (c) | 24. (c) | 25. (d) | 26. (c) | 27. (a) | 28. (b) | 29. (b) | 30. (c) |
| 31. (b) | 32. (c) | 33. (b) | 34. (b) | 35. (a) | 36. (d) | 37. (b) | 38. (b) | 39. (a) | 40. (b) |
| 41. (b) | 42. (c) | 43. (d) | 44. (c) | 45. (b) | 46. (a) | 47. (a) | 48. (d) | 49. (c) | 50. (b) |
| 51. (c) | 52. (d) | 53. (a) | 54. (c) | | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (d) | 3. (c) | 4. (b) | 5. (c) | 6. (d) | 7. (b) | 8. (d) | 9. (a) | 10. (d) |
| 11. (d) | 12. (b) | 13. (d) | 14. (c) | 15. (b) | 16. (c) | 17. (b) | 18. (a) | 19. (d) | 20. (a) |
| 21. (b) | 22. (c) | 23. (b) | 24. (d) | 25. (d) | 26. (d) | 27. (c) | 28. (a) | 29. (d) | 30. (a) |
| 31. (b) | 32. (b) | 33. (c) | 34. (c) | 35. (c) | 36. (a) | 37. (a) | 38. (a) | 39. (a) | 40. (c) |
| 41. (c) | 42. (c) | 43. (c) | 44. (a) | 45. (c) | 46. (b) | 47. (b) | 48. (b) | 49. (d) | 50. (d) |
| 51. (a) | 52. (c) | 53. (d) | 54. (a) | 55. (c) | 56. (b) | 57. (d) | 58. (b) | 59. (c) | 60. (a) |
| 61. (d) | 62. (d) | 63. (a) | 64. (b) | 65. (c) | 66. (a) | | | | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (d) | 3. (c) | 4. (d) | 5. (c) | 6. (d) | 7. (d) | 8. (b) | 9. (b) | 10. (c) |
| 11. (a) | 12. (a) | 13. (d) | 14. (d) | 15. (c) | 16. (d) | 17. (b) | 18. (c) | 19. (c) | 20. (b) |
| 21. (a) | 22. (b) | 23. (a) | 24. (d) | 25. (a) | 26. (a) | 27. (a) | 28. (a) | 29. (c) | 30. (b) |
| 31. (b) | 32. (c) | 33. (c) | 34. (a) | 35. (b) | 36. (c) | 37. (c) | 38. (b) | 39. (d) | 40. (a) |
| 41. (b) | 42. (d) | 43. (a) | 44. (c) | 45. (c) | 46. (b) | 47. (a) | 48. (c) | 49. (d) | 50. (d) |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|--------------|-------------|-------------|-------------|--------------|-------------|-------------|----------|---------|-------------|
| 1. (a,b,c,d) | 2. (a,b,d) | 3. (b) | 4. (a,c) | 5. (a,b,c,d) | 6. (a) | 7. (a,b,d) | 8. (b,c) | 9. (a) | |
| 10. (a,c) | 11. (a,b,d) | 12. (b,d) | 13. (a,b) | 14. (a,c,d) | 15. (a,c,d) | 16. (b,c,d) | 17. (c) | 18. (a) | 19. (a,b,c) |
| 20. (a,d) | 21. (b,c,d) | 22. (b,c,d) | 23. (a,b,c) | 24. (b,d) | 25. (c) | 26. (d) | 27. (d) | 28. (b) | 29. (d) |
| 30. (a) | 31. (b) | 32. (b) | 33. (c) | 34. (b) | 35. (a) | | | | |
| 36. (c) | 37. (d) | 38. [4.5] | 39. [36] | 40. [2] | | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|-----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (a) | 3. (a) | 4. (b) | 5. (c) | 6. (b) | 7. (c) | 8. (b) | 9. (a) | 10. (d) |
| 11. (b) | 12. (b) | 13. (a) | 14. (b) | 15. (b) | 16. (c) | 17. (a) | 18. (c) | 19. (c) | 20. (d) |
| 21. (a) | 22. (c) | 23. (c) | 24. (d) | 25. (b) | 26. (c) | 27. (c) | 28. (b) | 29. (d) | 30. (c) |
| 31. (c) | 32. (b) | 33. (a) | 34. (b) | 35. (d) | 36. (c) | 37. (a) | 38. (a) | 39. (b) | 40. (c) |
| 41. (173) | 42. (0) | 43. (1) | 44. (3) | 45. (b) | 46. (d) | 47. (a) | 48. (c) | 49. (a) | 50. (c) |
| 51. (a) | 52. (a) | 53. (d) | 54. (c) | 55. (b) | 56. (b) | 57. (a) | 58. [3] | 59. (c) | 60. (c) |
| 61. (b) | | | | | | | | | |

JEE Advanced

- | | | | | | | | |
|-----------|-----------|------------|-------------|-------------|-----------|---------|--|
| 62. (b,c) | 63. (a,c) | 64. (b) | 65. (a,b,d) | 66. (a,c,d) | 67. (a,d) | 68. [6] | 69. [6] (H ₂ , Cl ₂ , Be ₂ , C ₂ , N ₂ , F ₂) |
| 70. (a,d) | 71. (b,d) | 72. [4.00] | 73. [19.00] | 74. [6] | 75. (a,d) | | |

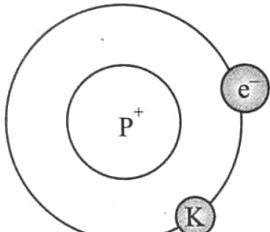
CHAPTER

9

Hydrogen and Its Compounds

INTRODUCTION

Hydrogen is the lightest gas and lightest element of periodic table and it contains 1 electron, 1 proton and zero neutron.



Structure of H-atom

Lightest metal – Li

Lightest non metal – H

Electronic Configuration – $1s^1$

For this configuration required

- (i) One shell $\rightarrow n = 1$ or K
- (ii) One subshell $\rightarrow s$
- (iii) One orbital $\rightarrow s$

Discovery of H-atom: Discovered by "Henry Cavendish" called "Inflammable" air

POSITION OF HYDROGEN IN THE PERIODIC TABLE

It's position in the periodic table is not certain and unsatisfactory. Hydrogen exhibit's properties similar to both alkali metals (Group 1) and halogens (Group 17).

Resemblance with Alkali Metals

1. Like alkali metals, hydrogen has only one electron in it's outer shell.
2. Alkali metals have a strong tendency to lose one electron from their outermost shell to form unipositive ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and attain nearest noble gas configuration. Similarly, hydrogen also loses electron to form H^+ ion.
3. Alkali metals form stable oxides, halides and sulphides, for example sodium forms Na_2O , $NaCl$ and Na_2S . Similarly, hydrogen also forms stable oxide (H_2O), halides (HF) and sulphide (H_2S).

DIFFERENCES FROM ALKALI METALS

1. The ionisation energy of hydrogen is very high in comparison to alkali metals. Example: I.E. of Li is 520 kJ mol^{-1} and that of hydrogen is 1312 kJ mol^{-1} . This is because the 1s electron of hydrogen is tightly held by the nucleus due to it's small size.
2. The size of H^+ ion is very small ($1.5 \times 10^{-3}\text{ pm}$) as compared to that of alkali metal ions. Therefore, H^+ does not exist freely and is always associated with other atoms or molecules.

RESEMBLANCE WITH HALOGENS

1. Halogens with general outer electronic configuration $(ns^2 np^5)$ have a tendency to gain one electron and attain nearest noble gas configuration. Similarly, hydrogen ($1s^1$) gains one electron to form H^- ion and attain nearest noble gas (helium gas) configuration.
2. The ionization energy of hydrogen (1312 kJ mol^{-1}) is of nearly same order as that of the halogens (I.E. of F is 1680 kJ mol^{-1}).
3. Hydrogen molecule is diatomic (H_2) and so are the molecules of halogens (say F_2).
4. Hydrogen forms hydrides with carbon (e.g., CH_4), just like halogens form halides with carbon (CCl_4).

DIFFERENCES FROM HALOGENS

1. Hydrogen is less reactive as compared to halogens.
 2. The electron affinity of hydrogen is less than those of halogens.
- Note:** So, seeing the unique behaviour of hydrogen, it is best placed separately in the periodic table.

ISOTOPES OF HYDROGEN

1. **Protium or ordinary hydrogen (${}_1^1H$):** The predominant form of hydrogen is ordinary hydrogen, protium. It has one proton and no neutron in the nucleus and one electron revolves around the nucleus.
2. **Deuterium (${}_1^2H$ or D):** It is also known as heavy hydrogen. It has one proton and one neutron in the nucleus around which one electron revolves. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD.

3. **Tritium (${}^3\text{H}$ or T):** This isotope of hydrogen is radioactive and emits low energy β^- particles having half life period of 12.33 years. It has one proton and two neutrons in the nucleus. The concentration of Tritium is very low. It is just about one atom per 10^{18} atoms of Protium.

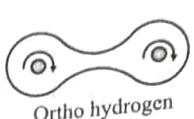
Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass (g mol^{-1})	1.008	2.014	3.016
Melting point/K	13.96	18.73	20.62
Boiling point/K	20.39	23.67	25.0
Density/g L^{-1}	0.09	0.18	0.27
Enthalpy of fusion/ kJ mol^{-1}	0.117	0.197	—
Enthalpy of vaporization/ kJ mol^{-1}	0.904	1.226	—
Enthalpy of bond dissociation/ kJ mol^{-1} at 298.2K	435.88	443.35	—
Internuclear distance/pm	74.14	74.14	—
Ionization enthalpy/ kJ mol^{-1}	1312	—	—
Electron gain enthalpy/ kJ mol^{-1}	-73	—	—
Covalent radius/pm	37	—	—
Ionic radius(H^-)/pm	208	—	—

DIHYDROGEN (H_2)

Occurrence: Dihydrogen is the most abundant element in the universe. It constitutes about 70% of the total mass of the universe. But its abundance in earth's atmosphere is very less. This is because the earth's gravitational field is too small to hold so light an element. So, it is just 0.15% by mass in the earth's atmosphere. In free state hydrogen is present in volcanic gases and in the combined form it constitutes 15.4% of the earth's crust and the oceans. However, it is also present in the plant and animal tissues, carbohydrates, proteins etc. Even hydrogen is present in mineral resources like coal and petroleum.

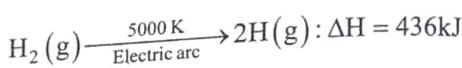
Hydrogen is the principal element in the solar atmosphere. It is present in the outer atmosphere of Sun and other stars of the universe like Jupiter and Saturn.

Ortho and Para Hydrogen: The nuclei of a molecule also have spins like electrons. If the spins of the nuclei of two H-atoms of H_2 molecule are in the same direction, the dihydrogen is called ortho hydrogen. But if the spins of the nuclei of two atoms are in the opposite directions, it is called para hydrogen.



Ordinary dihydrogen contains 75% ortho and 25% para hydrogen. While at low temperature (20 K) ortho and para hydrogens are 0.18% and 99.82% respectively. Pure para form can be obtained at very low temperature but pure ortho form cannot be obtained. The physical properties are same for both nuclear spin isomer except thermal conductivity. Thermal conductivity of para hydrogen is 50% greater and melting point is 0.15 K less than ortho hydrogen, ortho and para hydrogen also called as **allotrope**.

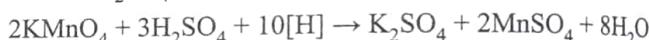
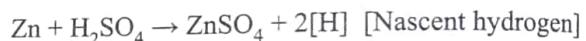
Atomic Hydrogen: It is formed by passing H_2 gas through electric arc struck between two tungsten filaments as



The life period of atomic hydrogen is 0.3 second. Hence it converts to molecular hydrogen readily liberating large amount of energy, which is used for welding purposes (in Atomic Hydrogen Torch).

Atomic hydrogen is very reactive and can reduce oxides chlorides, sulphides and sulphates of metals.

Nascent Hydrogen: It is the newly born hydrogen formed during chemical reactions in aqueous solutions. It is also a better reducing agent than molecular hydrogen. For example the addition of Zn and dil. H_2SO_4 to KMnO_4 decolourises it due to its oxidation but $\text{H}_2(\text{g})$ cannot do so.

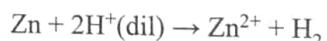


In general the reactivity order of these hydrogens is $\text{H}_2 < \text{Nascent hydrogen} < \text{Atomic hydrogen}$

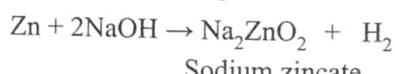
Preparation of Dihydrogen: Dihydrogen can be prepared by the following methods

1. Laboratory Preparation of Dihydrogen:

(i) In laboratory dihydrogen is prepared by the reaction of granulated zinc with dilute hydrochloric acid or dilute sulphuric acid.



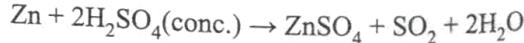
(ii) Zinc reacts with aqueous alkali to give dihydrogen



Note: During the laboratory preparation of dihydrogen, following few points should be remembered.

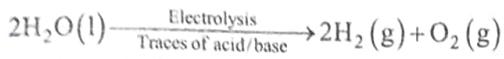
(i) Pure zinc is not used in the preparation of dihydrogen because it reacts very slowly with sulphuric acid. Therefore, the addition of some impurities enhances the rate of reaction.

(ii) During the reaction zinc is reacted with dilute sulphuric acid only because it reacts with concentrated sulphuric acid to form SO_2 gas instead of dihydrogen



2. Commercial Production of Dihydrogen:

- (i) **By the electrolysis of water:** Electrolysis of acidified water using platinum electrodes is used for the bulk preparation of hydrogen.

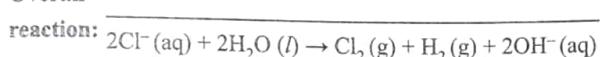
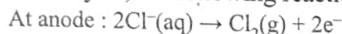


(ii) **Electrolysis of aqueous barium hydroxide solution:**

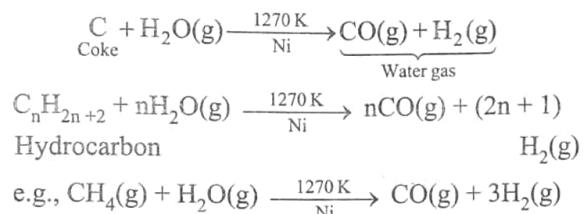
Hydrogen of high purity (> 99.95%) is obtained by electrolysing warm aqueous barium hydroxide between nickel electrodes.

- (iii) **Electrolysis of brine:** It is also produced as a by-product during the manufacture of Cl_2 and NaOH by the electrolysis of brine (aq. NaCl).

During electrolysis, the following reactions takes place

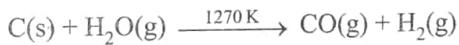


- (iv) **By the action of steam on coke:** Dihydrogen is prepared by passing steam over coke or hydrocarbons at high temperature (1270K) in the presence of Nickel catalyst.

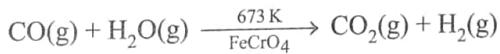


The mixture of CO(g) and H₂(g) is called as **water gas**. It is also known as **synthesis gas** or simply '**syn gas**' because it is used in the synthesis of methanol and many other hydrocarbons.

Nowadays '**syn gas**' is produced from sewage, saw-dust, scrap wood and newspapers also. When '**syn gas**' is produced from coal, then this process is known as '**coal gasification**'.

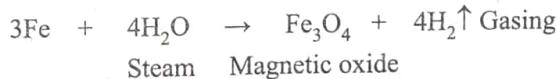


It is difficult to obtain dihydrogen from a mixture of CO and H₂ (i.e., water gas). Therefore, the production of dihydrogen is increased by reacting carbon monoxide of syn gas mixtures with steam in the presence of iron chromate as catalyst

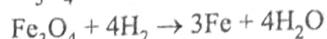


The above reaction is called **water-gas shift reaction**. The CO₂ formed in the above reaction is removed by scrubbing with sodium arsenite solution.

- (v) **Lane's process:** In this process, steam is passed over the hot iron. Iron decomposes steam with the formation of magnetic oxide (Fe_3O_4) and hydrogen. The temperature of iron is maintained between 550 to 800°C. This reaction is termed gassing reaction and time allotted for this reaction is about 10 minutes.



Iron is regenerated by reducing magnetic oxide with water gas ($\text{CO} + \text{H}_2$). This reaction is called **vivification** and time allotted for this reaction is about 20 minutes.



This iron is again used for decomposition of steam. In order to make the process continuous, the above two reactions are carried out alternatively using two or more furnaces.

- (vi) **Bosch's process:** The maximum quantity of commercial hydrogen is obtained by the use of this method. Water gas is produced first by passing steam over hot coke at 1000°C. The temperature is not allowed to fall below 1000°C.



PROPERTIES OF DIHYDROGEN

Physical Properties

1. It is a colourless, odourless, tasteless gas.
2. It is insoluble in water.
3. It is highly combustible.
4. Its critical temperature is very low (-236.9°C) so difficult to liquefy.
5. It is adsorbed by certain metals like Fe, Au, Pt & Pd. Palladium in the powdered state can occupy nearly 1000 times its own volume of hydrogen. This property is used for the purification of hydrogen because only pure hydrogen is adsorbed by these metals and is given out when they are heated in vacuum.

Adsorption: It is a process of soaking up only on the surface while absorption is a process of soaking up through the entire mass.



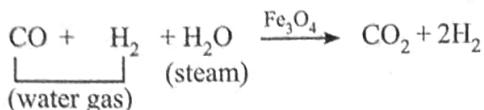
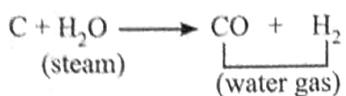
Train Your Brain

Example 1: Hydrogen

- Resembles in I A since it forms mono valent cation H⁺.
- Resembles in VII A (halogen family) since it forms monovalent anion H⁻.
- Resembles in IV A (carbon family) since both have a half filled shell of electron.
- All are correct.

Sol. (d) HCl → H has +1 oxidation state so it resembles I A group property.
NaH → H has -1 oxidation state so it resembles VII A group property.
H (1s¹) due to half filled shell of electron it resembles IV A group property.

Example 2: The incorrect option regarding the chemical reaction is



- (a) Process is called as Lane's process.
- (b) Water gas act reducing agent for Fe_3O_4 .
- (c) Fe_3O_4 shows magnetic property.
- (d) Fe_3O_4 can't be concentrate by magnetic separation method.

Sol. (d) Fe_3O_4 is magnetic oxide of iron and it has a non magnetic impurities so it is concentrate by magnetic separation method.

Example 3: Nascent hydrogen consists of

- (a) Hydrogen ions in excited state.
- (b) Hydrogen ions with excess energy.
- (c) Solvated protons.
- (d) Hydrogen atoms with excess energy.

Sol. (d) Nascent hydrogen consists of Hydrogen atoms with excess energy

Example 4: Orthohydrogen and parahydrogen have

- (a) Same electronic spin, physical and chemical properties.
- (b) Parallel electronic, and nuclear spin with identical physical and chemical properties.
- (c) Different electronic spin with differences in physical and chemical properties.
- (d) Opposite electronic spin, different nuclear spin and with different physical properties.

Sol. (d)

2. Which one of the following properties shows that hydrogen resembles alkali metals?
 - (a) It shows metallic character like alkali metals.
 - (b) It is diatomic like alkali metals.
 - (c) Its ionization energy is of the same order as that of alkali metals.
 - (d) When hydrogen halides and alkali metal halides are electrolysed, hydrogen and alkali metals are liberated at the cathode.

3. Which one is not an isotope of hydrogen?
 - (a) Tritium
 - (b) Deuterium
 - (c) Ortho hydrogen
 - (d) None of the above
4. Hydrogen from HCl can be prepared by:
 - (a) Cu
 - (b) P
 - (c) Mg
 - (d) Hg

Chemical Properties

The chemical behaviour of a molecule is determined mainly by its bond dissociation enthalpy. Dihydrogen is quite stable and dissociates into hydrogen atoms only when heated at 5000K.



Due to its high bond dissociation enthalpy, it is inert at room temperature.

However, hydrogen reacts with many elements because of its electronic configuration which is $1s^1$. Therefore, it accomplishes the reactions in the following three ways :

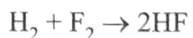
- (i) Loss of the only one electron to form H^+ .
- (ii) Gain of an electron to form H^- .
- (iii) Sharing of electron to form single covalent bond.

Hydrogen undergoes a number of reactions, out of which few are mentioned below:

1. **Reaction with halogens:** Hydrogen reacts with halogens to give hydrogen halides with general formula HX .



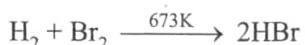
In case of Fluorine, reaction occurs even in dark.



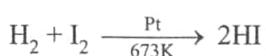
With Chlorine, it occurs in presence of sunlight.



Bromine reacts only upon heating.



With Iodine, it requires catalyst for the reaction.



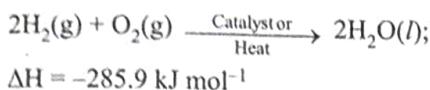
This shows that F_2 is more reactive than Cl_2 which is further more reactive than Br_2 and least reactive amongst halogens is I_2 which requires a catalyst for the reaction.



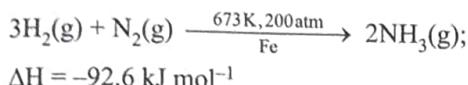
Concept Application

1. Which of the following is a method of preparation of H_2 ?
 - (a) Reaction of granulated Zn with dil. HCl
 - (b) Reaction of Zn with aqueous alkali
 - (c) By electrolysis of brine solution
 - (d) All of the above

2. Reaction with dioxygen: It reacts with oxygen to form water. This reaction is accompanied with release of heat, so it is exothermic in nature.



3. Reaction with dinitrogen: Dihydrogen is employed in Haber's process for the formation of ammonia.

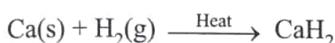
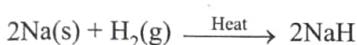


4. Reactions with metals: Dihydrogen reacts with metals to yield hydrides at high temperature.

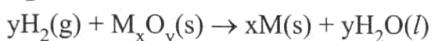
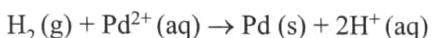


where M is an alkali metal.

For example:



5. Reactions with metal ions and metal oxides: Dihydrogen is a strong reducing agent, so it reduces metal ions and metal oxides (less active than iron) into their corresponding metals.

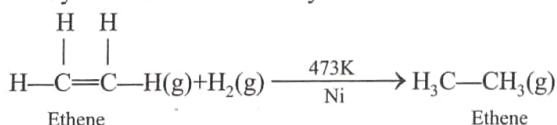


For example:



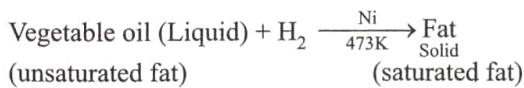
Dihydrogen reacts with many unsaturated hydrocarbons with atleast one multiple bond in them. Such reactions are even employed for the formation of products of commercial importance.

(i) With unsaturated hydrocarbons: Vapours of dihydrogen are passed through unsaturated hydrocarbons with C = C or C≡C, in the presence of catalyst to form saturated hydrocarbons.



The above reaction is called catalytic hydrogenation.

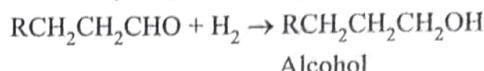
(ii) Hydrogenation of vegetable oils: Edible oils (unsaturated) like cotton seed oil, groundnut oil are converted into solid fat (saturated) also called vegetable ghee by passing hydrogen through it in the presence of Ni at 473 K.



(iii) Hydroformylation of olefins to aldehydes: Olefins react with carbon monoxide and dihydrogen in presence of catalyst to give aldehydes.



The above reaction is called hydroformylation of olefins. The aldehyde then further gets reduced to alcohol



Train Your Brain

Example 5: Which of the following pair will not produce dihydrogen gas

- (a) Cu + HCl(dil.)
- (b) Fe + H₂SO₄
- (c) Mg + steam
- (d) Na + alcohol

Sol. (a) Cu + HCl → No. reaction

The less active metals which lie below hydrogen in electrochemical series can't displaced hydrogen gas from dilute mineral acid.

Example 6: Hydrogen gas will not reduce

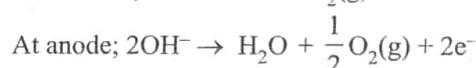
- (a) heated cupric oxide
- (b) heated ferric oxide
- (c) heated stannic oxide
- (d) heated aluminium oxide

Sol. (d) Hydrogen gas will not reduce heated aluminium oxide because ΔG for this reaction is positive.

Example 7: When dil. H₂SO₄ is electrolysed by using platinum electrodes the gas evolved at cathode is

- (a) O₂
- (b) SO₂
- (c) SO₃
- (d) H₂

Sol. (d) At cathode; 2H⁺ + 2e⁻ → H₂(g)



Hydrogen gas is evolved at cathode.



Concept Application

5. Hydrogen readily combines with metlas and thus shows it's:

- (a) Electropositive character
- (b) Electronegative character
- (c) Both (a) and (b)
- (d) None of the above

6. $\text{H}_2 + \text{CO} + \text{R}-\text{CH}=\text{CH}_2 \longrightarrow \text{R}-\text{CH}_2-\text{CH}_2-\text{CHO}$

This reaction is known as

- (a) Hydrogenation
- (b) Hydroformylation
- (c) Carbonation
- (d) decarbonylation

7. During hydrogenation of oil the catalyst commonly used is:

- (a) Pd on CuCl₂
- (b) Fe
- (c) Ni
- (d) Cl₂O

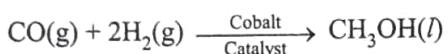
Uses of Dihydrogen

(i) **Synthesis of ammonia:** Dihydrogen is used in Haber's process in the synthesis of ammonia. A mixture of N₂ and H₂ in ratio of 1 : 3 is taken for the production of ammonia. Ammonia is further used in the manufacture of nitric acid and nitrogenous fertilizers.

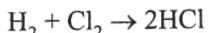


(ii) **Hydrogenation of oils:** Oils are poly-unsaturated hydrocarbons. Dihydrogen is added to oils like soyabean oil, cotton seed oil for manufacturing vanaspati fat which are saturated hydrocarbons.

(iii) **Manufacture of methyl alcohol:** Water gas enriched with hydrogen gas in the presence of cobalt catalyst gives methanol.



(vi) **Manufacture of hydrogen chloride:** It is used in the manufacturing of hydrogen chloride which is a very important chemical.



(v) **Manufacture of metal hydrides:** It is used in the manufacture of many metal hydrides.

(vi) **Metallurgical processes:** Since, dihydrogen is used to reduce heavy metal oxides to metals, as it is a reducing agent. Therefore, it finds its use in metallurgical processes.

(vii) **For cutting and welding purposes:** It is used in the atomic hydrogen torch and oxyhydrogen torches for cutting and welding purposes. Dihydrogen gets dissociated into atomic hydrogen by an electric arc and so the hydrogen atoms which are produced are allowed to combine on the surface to be welded to generate the temperature of 4000K.

(viii) **Rocket fuel:** It is used as a rocket fuel for space research in the form of liquid hydrogen and liquid oxygen.

(ix) **Fuel cells:** Dihydrogen is used in fuel cells for the generation of electrical energy. It does not pollute and produces greater energy per unit mass of fuel, therefore, it is advantageous over conventional fuels like gasoline.

HYDRIDES

The compounds of hydrogen with different elements are called hydrides. These are of three types:

1. **Ionic/Salt like/Saline hydrides:** Compounds of hydrogen with s-block elements except beryllium & magnesium are called ionic hydrides.

LiH, NaH, KH, RbH, CsH, CaH₂, SrH₂, BaH₂
BeH₂, MgH₂ are covalent polymeric hydride.

- + Structure of these hydrides are similar to rock salt, so they are also called salt like/saline hydrides.
- + Down the group size ↑ Lattice energy ↓ stability ↓ Melting point ↓ Boiling point ↓

- + On electrolysis of these hydrides, hydrogen is liberated at anode.
 - + On reaction with water these hydrides will form hydrogen
 $\text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$
 - + These hydrides forms complex hydrides which are very good reducing agents.
- $4\text{LiH} + \text{AlCl}_3 \rightarrow \text{LiAlH}_4 + 3\text{LiCl}$
 $2\text{LiH} + \text{B}_2\text{H}_6 \rightarrow 2\text{LiBH}_4$
 $\text{LiBH}_4 \rightarrow \text{Lithium borohydride}$
 $\text{NaBH}_4 \rightarrow \text{Sodium borohydride}$
 $\text{LiAlH}_4 \rightarrow \text{Lithium aluminium hydride.}$

2. **Metallic/Interstitial hydrides:** They are the compounds of d & f-block elements.

In these hydrides, hydrogen occupies interstitial sites present in metallic lattice, so they are called interstitial hydrides.

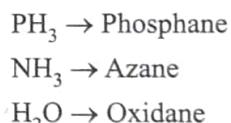
- + Properties of these hydrides are similar to parent metals, so they are also known as metallic hydrides.
 - + These hydrides are non-stoichiometric in nature (i.e. having variable composition)
- ZrH_x ($x = 1.3 - 1.75$)
 TiH_x ($x = 1.8 - 2$)

+ Metals of group 7, 8, 9 do not form any hydrides so this particular part of periodic table is known as hydride gap.

3. **Covalent / Molecules hydrides:** They are the compounds of hydrogen with p-block elements CH₄, NH₃, H₂O, HF, etc.

These hydrides exist as molecules, so they are also known as molecular hydrides. These hydrides are non-conductor of electricity.

Nomenclature – element + Suffix (ane)



These hydrides are again divides into 3 categories.

(a) **Electron deficient hydrides:** They are the hydrides of group 13 elements.

BH₃, AlH₃, GaH₃ – In these hydrides central element does not have complete octet. i.e. why they are called electron deficient compounds.

(b) **Electron precise hydrides:** They are the hydrides of group 14 element. Ex. CH₄, SiH₄, GeH₄

In these type of hydrides central elements has 8e⁻ in their outer most shell.

(c) **Electron rich hydrides:** These are the hydrides of group 15, 16 and 17

Ex. $\ddot{\text{N}}\text{H}_3$, $\text{H}_2\ddot{\text{O}}$, HF^{\ddagger} etc.

In these hydrides lone pair are present on central atom which can be given to others. So they are called electron rich hydrides.



Train Your Brain

Example 8: Which is not correct statement

- s-block elements, except Be and Mg, form ionic hydride
- Interstitial hydrides are non-stoichiometric in nature.
- p-block elements form covalent hydrides
- d and f-block elements form ionic hydrides

Sol. (d) Hydrogen atoms occupy the interstitial spaces of d & f-block elements & they form interstitial hydrides.

Example 9: Which of the following easily reacts with water producing hydrogen?

- PH_3
- B_2H_6
- CH_4
- H_2S

Sol. (b) $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \rightarrow 2\text{B(OH)}_3 + 6\text{H}_2$

Example 10: Which of the following are correct?

- $\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$
- $\text{NaH} + \text{CO}_2 \rightarrow \text{H}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\overset{\oplus}{\text{O}}-\overset{\oplus}{\text{Na}}$
- $3\text{LiH} + \text{NH}_3 \rightarrow \text{LiN} + 3\text{H}_2$
- $\text{NaH} + \text{NH}_3 \rightarrow \text{NaNH}_2 + \text{H}_2$

Sol. (a, b, d)

Example 11: Which of the following are correct?

- $\text{BCl}_3 + \text{NaH} \rightarrow \text{NaBH}_4$
- $\text{SiCl}_4 + \text{LiAlH}_4 \rightarrow \text{SiH}_4 + \text{NaCl} + \text{AlCl}_3$
- $\text{LiH} + \text{AlCl}_3 \rightarrow \text{LiAlH}_4$
- All of these

Sol. (d)

Concept Application

- Which of the following groups represents the saline hydrides?
- (a) NaH , KaH , CaH_2 (b) NaH , SiH_4 , CaH_2
 (c) NH_3 , BH_3 , AlH_3 (d) None of these
- In which of the following compounds does hydrogen have an oxidation state of -1?
- (a) PH_3 (b) NH_3
 (c) HCl (d) CaH_2
- Hydrogen acts as an oxidising agent in the reaction with:
- (a) Bromine (b) Calcium
 (c) Nitrogen (d) Sulphur
- Which of the following represents a pair of covalent hydrides?
- (a) C_5H_8 , AlH_3 (b) K_4 , NaH
 (c) H_2S , HF (d) $\text{VH}_{0.56}$, NH_3

WATER (H_2O)

Water is one of the most readily available chemicals. Water is an oxide of hydrogen. It is an important component of all living organisms. Water constitutes about 65% of human body and 95% of plants. It is therefore essential for life. The ability of water to dissolve so many other substances makes it a compound of great importance. Almost three-fourth of the earth's surface is covered with the water. The estimated world water supply is given in the following table:

Estimated World Water Supply

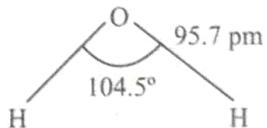
Source	% of Total
Oceans	97.33
Saline lakes and inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.0001

PHYSICAL PROPERTIES OF WATER

- Pure water is colourless, odourless and tasteless.
- Water is present in the liquid state at room temperature.
- Water boils at 100°C and changes into the gaseous state whereas it freezes at 0°C to form ice.
- Water molecules undergo extensive hydrogen bonding i.e. one H_2O molecule forms four H-bonding.
- The existence of hydrogen bonding is responsible for high freezing point, high boiling point, high value of specific heat, high latent heat of fusion and high latent heat of vaporisation of water, in comparison to those of H_2S and H_2Se .
- The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of the living beings.
- Being an excellent solvent it is essential for the transportation of metabolites in plants.
- Alcohols, ammonia and carbohydrates dissolve in water due to the formation of hydrogen bonding.

Structure of Water: The structure of water is studied in its three phases.

Gas Phase: In gas phase, water exists as discrete molecule. Due to the presence of two lone pairs, the geometry of the water gets distorted and acquires a bent geometry with a bond angle of 104.5° and O-H bond length of 95.7 pm. In water, each O-H bond is polar because of high electronegativity of oxygen in comparison to that of hydrogen.



Liquid Phase: In the liquid phase, the large number of water molecules are associated together by hydrogen bonds.

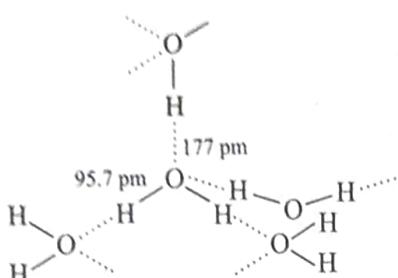


Fig.: Structure of water in liquid state

Solid Phase: The solid or crystalline form of water is ice. At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form.

Structure of Ice: In ice, each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm. Moreover each oxygen atom is attached to four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. Due to extensive hydrogen bonding the resulting structure of ice is **open cage-like structure** having a number of vacant spaces. Thus, ice has a highly ordered three-dimensional hydrogen bonded structure.

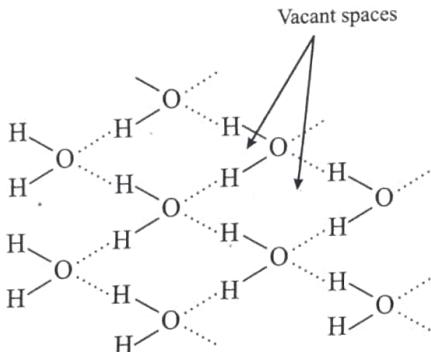


Fig.: Tetrahedral arrangement of oxygen atoms in ice

Ice is less denser than water: As ice has an open cage-like structure with vacant spaces, therefore less number of molecules are packed per mL. Melting of ice results in breaking of hydrogen bonds. In this way the molecules come closer to each other in the liquid state than they were in the solid state. Thus, ice has lower density than water. This fact is of great ecological significance as ice formed on the surface of lakes is less denser, so it does not sink to the bottom and provides thermal insulation for the water below it which ensures the survival of the aquatic life.

Density of water is maximum at 4°C: The density of water is maximum at 4°C. The density of water is affected by two factors.

- The breaking of hydrogen bonds resulting into closer packed structure.
- The thermal expansion:** With the rise in temperature, ice melts, the hydrogen bonds breaks and molecules comes closer, decreasing the volume and increasing the density until 4°C. With further increase in temperature the kinetic energy of the molecules increases progressively and they start moving away from each other increasing the volume and thus decreasing the density.

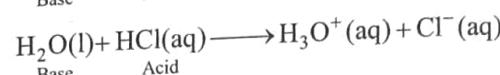
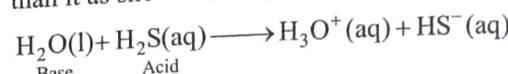
Thus, at 4°C, the two effects thermal expansion and breaking of hydrogen bonds balance each other and water is at maximum density.

Chemical Properties: Water has a unique property of reacting with a large number of substances. It can act both as a base as well as an acid. Moreover, it can be easily oxidised and reduced and further acts as ligand to metals.

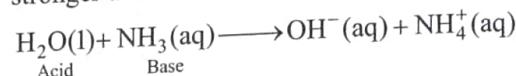
1. Amphoteric nature: Water can act both as an acid as well as a base and is thus said to be an amphoteric in nature.

According to Lowry Bronsted concept, it can act as an acid by losing a proton and as a base by accepting a proton.

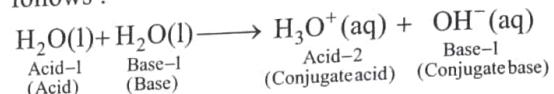
Water as base: Water acts as a base towards acids stronger than it as shown below,



Water as an acid: Water acts as an acid towards bases stronger than it

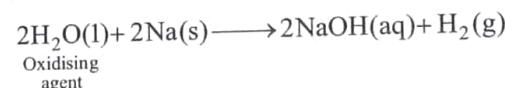


The auto-protolysis (self-ionisation) of water takes place as follows :



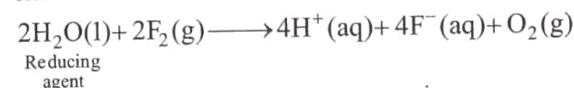
However, water is neutral towards litmus paper and its pH is 7 at 25°C.

2. Redox reactions involving water: Water can act both as oxidising as well as reducing agent. Oxidising agent : Water acts as an oxidising agent when it gets reduced.

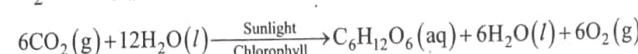


In the above reaction, H₂O gets reduced to dihydrogen by highly electropositive metal.

Reducing agent: Water acts as a reducing agent when it gets oxidised.

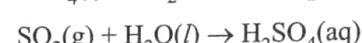


In the above reaction of fluorine with water, it acts as a reducing agent as it gets oxidised to O₂. Water is oxidised to O₂ during photosynthesis



3. Hydrolysis reaction: Water is an excellent solvent due to its high dielectric constant (78.39). In addition, water can easily hydrolyse many ionic and covalent compounds.

- Water hydrolyses oxides and halides of non-metals forming their respective acids.



- Water hydrolyses the carbides, hydrides, nitrides and phosphides of some metals with the liberation of acetylene, hydrogen, ammonia, phosphine respectively.



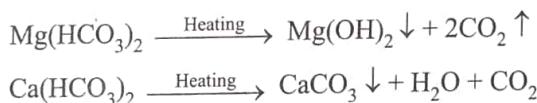
Concept Application

12. Percentage of water present in oceans.
- 2.04
 - 6.2
 - 94.8
 - 97.3
13. In ice each oxygen is surrounded by four oxygen atom in _____ manner
- Square planar
 - Tetrahedral
 - Trigonal planar
 - Angular
14. $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$. In this reaction water acts as:
- Bronsted acid
 - Bronsted base
 - Amphoteric oxide
- I only
 - I, II only
 - II, III only
 - I, II, III only
15. (i) $\text{CuCO}_4 + 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
(ii) $\text{PCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
- The processed I and II are respectively
- Hydration and dehydration
 - Hydration and hydrolysis
 - Hydrolysis and hydrolysis
 - Hydration and hydration

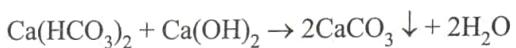
Softening of Water: The process of removal of hardness from water is called softening of water.

1. Removal of temporary hardness: Temporary hardness can be removed by the following methods:

(a) **Boiling:** The temporary hardness of water can be easily removed by boiling the water in large boilers. During boiling the soluble $\text{Mg}(\text{HCO}_3)_2$ is converted into Mg(OH)_2 instead of MgCO_3 because Mg(OH)_2 is precipitated easily, whereas $\text{Ca}(\text{HCO}_3)_2$ is changed to insoluble CaCO_3 and gets precipitated. These precipitates can be removed by filtration process. So, the filtrate obtained will be soft water.

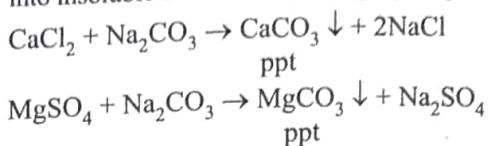


(b) **Clark's method:** In this process the calculated amount of slaked lime is added to hard water containing bicarbonates of calcium and magnesium. It precipitates out calcium carbonate and magnesium hydroxide which are then filtered to obtain soft water.



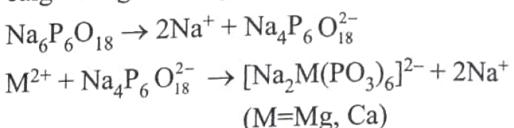
2. Removal of Permanent hardness: It cannot be removed by simple boiling. So, the following methods are employed for removing permanent hardness:

(a) **Treatment with washing soda:** When calculated amount of Na_2CO_3 (washing soda) is added to hard water containing soluble sulphates and chlorides of calcium and magnesium, then these soluble salts get converted into insoluble carbonates which get precipitated.



Thus, water free from metal ion is soft water.

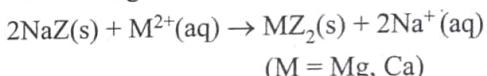
(b) **Calgon's method:** Calgon is the commercial name of sodium hexametaphosphate ($\text{Na}_6\text{P}_6\text{O}_{18}$). Calcium and magnesium salts present in hard water react with calgon to give complex salts.



The complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution.

(c) **Ion-exchange method:** Ion-exchange method of softening the water works on the principle of exchanging the ions responsible for the hardness of water with the less damaging ions present in some compounds.

This process employs the use of zeolite or permuntit which is hydrated sodium aluminium silicate (NaAlSiO_4), therefore, it is also known as zeolite/permuntit process. For the sake of simplicity sodium aluminium silicate is written as NaZ. When zeolite is added to hard water, the cations present in hard water are exchanged for sodium ions.



Regeneration of Permutit: As the reaction progresses, the zeolite gets exhausted because the whole of sodium zeolite gets converted to calcium or magnesium zeolite. It is regenerated for further use by treating with an aqueous sodium chloride solution.

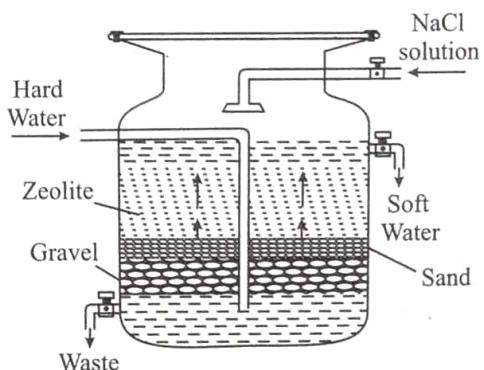
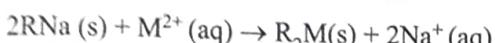


Fig.: Permutit Process for water softening

(d) **Synthetic resins method:** This method of softening of water is prevalent nowadays. The method is superior to zeolite method because they remove all types of unwanted cations as well as anions present in water.

Synthetic resins are insoluble polymeric solids having giant hydrocarbon network containing reactive acidic or basic groups. Synthetic resins are of two types:

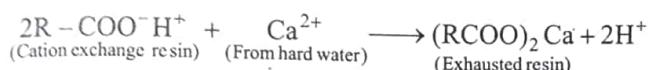
Cation exchange resins: Cation exchange resins contain large organic molecule with $-SO_3H$ group and are water insoluble. The hard water is first passed through a bed of cation exchanger. First ion exchange resin (RSO_3H) gets changed to RNa after treating it with $NaCl$. Now, RNa resin exchanges Na^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water to make water soft.



In order to obtain pure de-mineralised water free from all soluble mineral salts, the cation exchange (in the H^+ form) is used.

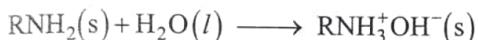


For Example:

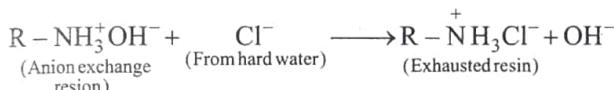


In the above process as proton is released, it makes the water acidic. This water is then passed through another bed containing anion exchanger.

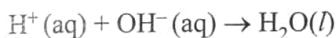
Anion exchange resin: These resins contain giant hydrocarbon framework attached to basic groups such as $-NH_2$ group or OH^- group.



For example:



In the above reaction OH^- ion exchanges for the anions in the water. OH^- ions are liberated which neutralise H^+ ions set free in the cation exchange resin.



Regeneration of resin: The cation exchanger is regenerated by the action of dilute acid and the anion exchanger is regenerated by treating it with dilute alkali.

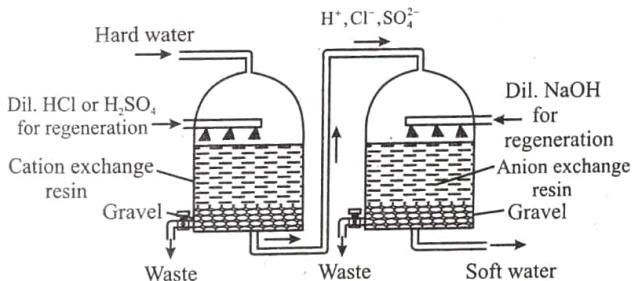


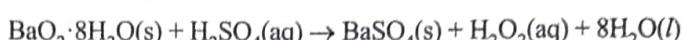
Fig.: Ion exchange process for water softening using organic resins.

HYDROGEN PEROXIDE (H_2O_2)

Hydrogen peroxide was discovered by a French chemist L.J. Thenard. It is an important chemical used in pollution control treatment of domestic and industrial effluents.

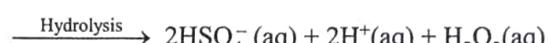
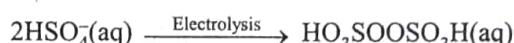
Preparation: Hydrogen peroxide is prepared by the following three main methods :

(i) By the action of cold and dilute sulphuric acid on hydrated barium peroxide

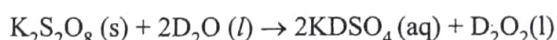


The excess water is removed by evaporation under reduced pressure.

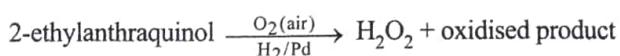
(ii) During the electrolytic oxidation of acidified sulphate solutions at high current density gives peroxodisulphate, which on further hydrolysis gives hydrogen peroxide



The laboratory preparation of D_2O_2 is also done by this method.

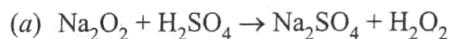


(iii) On the industrial scale, hydrogen peroxide is prepared by the auto-oxidation of 2-ethylanthraquinols

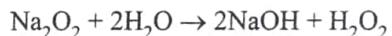


Concentration of Hydrogen Peroxide: In the above case the H_2O_2 obtained is 1%. So, it needs to be concentrated. H_2O_2 is first extracted with water and concentrated to 30% and then 85% (by mass) by distillation under reduced pressure. Then to obtain pure H_2O_2 , the remaining water can be frozen out.

(iv) Treating Na_2O_2 with H_2SO_4



(b) Also by small amount of Na_2O_2 added to ice cold water.



Physical Properties

- Pure hydrogen peroxide is a syrupy liquid. It is colourless but gives a bluish tinge in thick layers.
- It is soluble in water, alcohol and ether in all proportions.
- It is more viscous than water. This is due to the fact that molecules of H_2O_2 are more associated through H-bonding.

Table: Physical Properties of Hydrogen Peroxide

Melting point/K	272.4	Density (liquid at 298 K)/g cm ⁻³	1.44
Boiling point (extrapolated)/K	423	Viscosity (290 K)/centipoise	1.25
Vapour pressure (298 K)/mmHg	1.9	Dielectric constant (298 K)/C ² /N m ²	70.7
Density (solid at 268.5 K)/g cm ⁻³	1.64	Electrical conductivity (298 K) Q ⁻¹ cm ⁻¹	5.1 x 10 ⁻⁸



Strength of Hydrogen Peroxide Solution

The strength of aqueous solution of hydrogen peroxide is usually expressed in the following two ways:

- Percentage strength:** It expresses the amount of H_2O_2 by weight present in 100 ml of the solution. For example, a 30% aqueous solution (w/v) of H_2O_2 implies that 30 grams of H_2O_2 are present in 100 ml of the solution.
- Volume strength:** The most common method of expression of the strength of an aqueous solution of hydrogen peroxide is in terms of the volume (in ml) of oxygen liberated at N.T.P. by the decomposition of 1 ml of the sample of hydrogen peroxide.

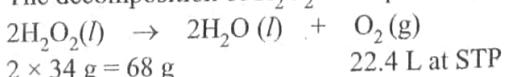


Train Your Brain

Example 15: Calculate the strength of 30V solution of hydrogen peroxide.

Sol. 30V solution of H_2O_2 means that 1L of this H_2O_2 solution will give 30 L of oxygen at STP.

The decomposition of H_2O_2 takes place as follows



From the equation,

22.4 L of O_2 at STP is obtained from H_2O_2 = 68 g

30 L of O_2 at STP is obtained from H_2O_2 ,

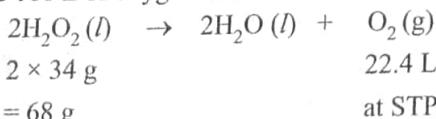
$$= \frac{68}{22.4} \times 30 = 91 \text{ g}$$

Therefore, strength of 30 volume H_2O_2 solution

$$= 91 \text{ g/L}$$

Example 16: What is the percentage strength of a solution of 100V H_2O_2 ?

Sol. 100V solution means that 1L of this H_2O_2 solution will give 100 L of oxygen at STP.



For equation,

22.4L of O_2 at STP is obtained from H_2O_2 = 68 g

$$100\text{L of } \text{O}_2 \text{ at STP is obtained from } \text{H}_2\text{O}_2 = \frac{68}{22.4} \times 100$$

$$= 303.57 \text{ g/L}$$

$$= 30\% \text{ } \text{H}_2\text{O}_2 \text{ solution}$$

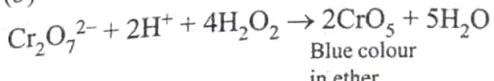
Example 17: When H_2O_2 is added to ice cold solution of acidified potassium dichromate in ether and the contents are shaken and allowed to stand

- a blue colour is obtained in ether due to formation of $\text{Cr}_2(\text{SO}_4)_3$
- a blue colour is obtained in ether due to formation of CrO_5

(c) a blue colour is obtained in ether due to formation of CrO_5

(d) chromyl chloride is formed

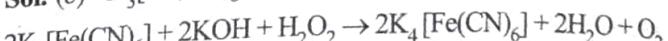
Sol. (b)



Example 18: In alkaline medium, H_2O_2 reacts with Fe^{3+} and Mn^{2+} separately to give

- | | |
|---|---|
| (a) Fe^{4+} and Mn^{4+} | (b) Fe^{2+} and Mn^{2+} |
| (c) Fe^{2+} and Mn^{4+} | (d) Fe^{4+} and Mn^{2+} |

Sol. (c) $\text{K}_3[\text{Fe}(\text{CN})_6]$ is reduced by H_2O_2 in alkaline medium,



$\text{Mn}(\text{OH})_2$ is oxidised by H_2O_2 in alkaline medium



Concept Application

16. Permanent hardness of water cannot be removed by:

- | | |
|-------------------------|---------------------|
| (a) Washing soda method | (b) Permutit method |
| (c) Ion exchange method | (d) Boiling |

17. The formula of calgon is:

- | | |
|---|---|
| (a) $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ | (b) $\text{Na}_4[\text{Na}_2(\text{PO}_3)_6]$ |
| (c) $\text{Na}_4[\text{Na}_2(\text{PO}_3)_3]$ | (d) $\text{Na}_2[\text{Na}_4(\text{PO}_3)_4]$ |

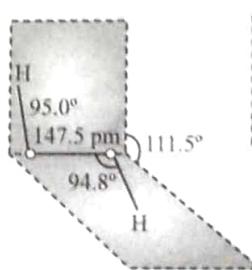
18. In the preparation of H_2O_2 by auto oxidation method the starting substance is:

- | | |
|--------------------------|-------------------------|
| (a) 2-ethylanthraquinone | (b) 2-ethylanthraquinol |
| (c) p-benzoquinone | (d) N-methylaniline |

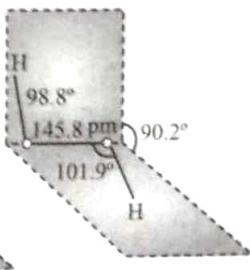
19. Which one of the following is used for laboratory preparation of H_2O_2 ?

- | | |
|--------------------------------------|--------------------------------------|
| (a) $\text{K}_2\text{S}_2\text{O}_8$ | (b) $\text{H}_2\text{S}_2\text{O}_7$ |
| (c) H_2SO_4 | (d) H_2SO_5 |

Structure of H_2O_2 : Hydrogen peroxide is non-linear, non-planar molecule. It has an open book type of structure. The molecular dimensions of H_2O_2 in the gas phase and solid phase slightly differ from each other as shown below.



(a) Gas phase



(b) Solid phase

Figure:

(a) H_2O_2 structure in gas phase, dihedral angle is 111.5° ,

(b) H_2O_2 structure in solid phase at 110 K , dihedral angle is 90.2° .

Chemical Properties

1. Oxidising nature: The oxidising nature of hydrogen peroxide is due to the possession of labile oxygen atom. The potential equation for its oxidising nature can be written as $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + (\text{O})$

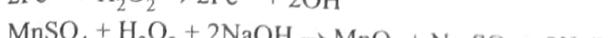
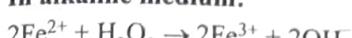
It is a strong oxidising agent. It acts as an electron acceptor in acidic as well as alkaline medium.



In acidic medium



In alkaline medium:



2. Reducing nature: It acts as a reducing agent in both acidic and alkaline medium towards powerful oxidising agents

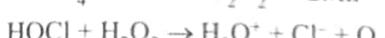


The potential equation when H_2O_2 acts as a reducing agent is expressed as

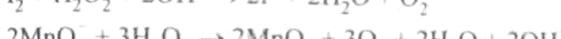
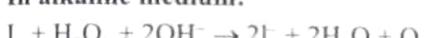


In all the reactions, molecular oxygen is always produced by the combination of H_2O_2 and oxygen atom given by strong oxidising agents.

In acidic medium:



In alkaline medium:



3. Bleaching agent: H_2O_2 also acts as a very good bleaching agent for delicate materials like ivory, silk, wool, feather etc. The bleaching action of H_2O_2 is due to nascent oxygen which it liberates on decomposition.



The nascent oxygen combines with colouring matter which in turn gets oxidised. Thus, the bleaching action of H_2O_2 is due to the oxidation of colouring matter by nascent oxygen and is permanent.

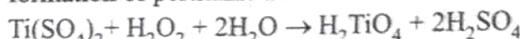
Storage: As the decomposition of H_2O_2 is catalysed by the presence of sunlight, metal surfaces, glass, alkali, dust etc., the storage of H_2O_2 in appropriate containers away from sunlight is necessary. H_2O_2 slowly decomposes on exposure to light in the following way



Therefore, instead of being stored in glass bottles which may contain alkali metal oxides H_2O_2 is stored in wax-lined glass or plastic vessels in dark. Urea is often added as a stabiliser. Precautions are taken to keep away the dust since dust induces explosive decomposition of the compound.

Test for H_2O_2

1. An acidified solution of titanium salt when treated with H_2O_2 , a yellow or orange colour is developed due to formation of pertitanic acid.



2. It liberates iodine from KI solution which give blue colour with starch solution

3. H_2O_2 on shaking with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ with little ether, blue colour is produced.

Uses: Hydrogen peroxide in the form of aqueous solution has many uses like few given below:

(i) In daily life it is used as a material to bleach delicate materials like hair, cotton, wool, silk etc.

(ii) It is used as a mild disinfectant. It is also a valuable antiseptic which is sold under the name of perhydrol.

(iii) In the manufacture of sodium perborate, sodium percarbonate. These are used in high quality detergents.

(iv) In the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.

(v) It is used in industries as a bleaching agent for paper pulp, leather, oils, fats and textiles etc.

(vi) It is also useful in Environmental (green) chemistry. For pollution control of domestic effluents where it restores the aerobic conditions of sewage wastes. For pollution control of industrial effluents containing CN^- ions. H_2O_2 oxidises CN^- ions to harmless products.

HEAVY WATER (D_2O)

Heavy water is chemically deuterium oxide (D_2O). It was discovered by Urey in 1932.

Preparation:

1. It is prepared by the exhaustive electrolysis of ordinary water. It was shown that ordinary water contains very small proportion of D_2O . So, when prolonged electrolysis of water is done, then H_2 is liberated much faster than D_2 and the remaining water becomes enriched in heavy water.

2. It is obtained as a by-product in some fertilizer industries.

Uses: It has some important uses as:

(i) **Moderator:** Heavy water is used as a moderator in nuclear reactors. The job of the moderator is to slow down the fast moving neutrons and therefore controls the nuclear fission process.

(ii) **Tracer compound:** It is used as a tracer compound, in studying the reaction mechanisms.

(iii) **For the preparation of deuterium compounds:** It is used as a starting material for the preparation of a number of deuterium compounds

DIHYDROGEN AS A FUEL

Nowadays, dihydrogen as a fuel is also used because of its various advantages over conventional fuels like petrol, diesel, coal etc.

1. First of all dihydrogen releases large quantities of heat on combustion. The energy released by combustion of fuels like dihydrogen, methane, LPG etc., are compared in terms

of the same amounts in mole, mass and volume as shown in the table below:

It is clear from the above table that on a mass for mass basis, dihydrogen can release about three times more energy than petrol (here octane).

2. Secondly, burning of hydrogen in air yields water as the only product. This way being non-polluting is beneficial in contrast to burning coal in power stations, petrol or diesel in motor engines which release lot of pollutants in the environment.

On the other hand there are certain limitations also. The production of dihydrogen is very costly. Moreover the cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Even the liquefaction of dihydrogen gas requires cooling to 20 K temperature, which is quite expensive. Dihydrogen must be kept out of contact with oxygen or air with which it forms explosive mixtures. So, tanks of metal alloy like those of NaNi_5 , $\text{Ti}-\text{TiH}_2$, $\text{Mg}-\text{MgH}_2$ etc., are used for the storage of dihydrogen.

So, word Hydrogen Economy is used nowadays for the transportation and storage of energy in the form of liquid or gaseous dihydrogen. The further advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. It was for the first time in the history of India that a pilot project using dihydrogen as fuel is launched in Oct, 2005 for running automobiles. Initially 5% dihydrogen was mixed with CNG for use in four-wheeler vehicles. But, now the percentage of dihydrogen appears to increase.

Nowadays, it is also used in fuel cells for generation of electric power. Thus, if a cheap source of large scale production of hydrogen is discovered in the years to come then hydrogen economy will become the common source of energy.

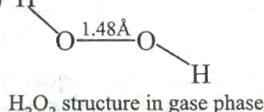
Energy released on combustion (in kJ)	Dihydrogen (in gaseous state)	Dihydrogen (in liquid state)	LPG	CH₄ gas	Octane (in liquid stage)
Per mole	286	285	2220	880	5511
Per gram	143	142	50	53	47
Per litre	12	9968	25590	35	34005



Train Your Brain

Example 19: In H_2O_2 molecule the O–O bond length is (in gas phase).

Sol. (b) H



H₂O₂ structure in gase phase

Example 20: Hydrogen peroxide has a

- (a) Linear structure
 - (b) Closed chain structure
 - (c) Closed book structure
 - (d) Open book structure

Sol. (d) Hydrogen peroxide is non-linear, non-planar molecule. It has an open book type of structure.

Example 21: H_2O_2 changes aqueous KI solution to:

Sol. (b) H_2O_2 liberates iodine from KI solution which gives blue colour with starch solution.

Example 22: Which metal alloy tanks are used for storage of dihydrogen?

- (a) NaNi_5 (b) Ti-TiH_2
 (c) Mg-MgH_2 (d) All of these

Sol. (d) H_2 must be kept out of contact with oxygen or air with which it forms explosive mixture. So tanks of metal alloys like those of $NaNi_5$, $Ti-TiH_2$, $Mg-MgH_2$ etc. are used for the storage of H_2 .

Concept Application

- 20.** Which of the following statement is incorrect?

 - H_2O_2 is an oxidising agent
 - H_2O_2 is a reducing agent
 - H_2O_2 is a bleaching agent
 - H_2O_2 is a dehydrating agent

21. When H_2O_2 act as oxidising agent, one of the end product is generally?

 - O_2
 - H_2O
 - Both (a) and (b)
 - O_3

22. Which of the following is the use of H_2O_2 ?

 - Hair bleach, disinfectant and antiseptic
 - In the synthesis of hydroquinone, tartaric acid, cephalosporin
 - Bleaching agent for textile, paper pup, leather, oilds, fats etc.
 - Treatment of domestic and industrial effluents.
 - i, iii
 - i, ii
 - ii, iv
 - i, ii, iii, iv

23. Some reasons are given regarding the limited use of H_2 as fuel:

 - It's calorific value is low
 - It's availability in free state is less
 - It is difficult to store
 - It's transportation is easy

The correct statement are:

 - I, II and III
 - II, III and IV
 - II and III
 - All of the above

6. Can conc. H_2SO_4 be used for drying H_2 gas? Justify.
- Sol. Conc. H_2SO_4 cannot be used for drying H_2 gas because H_2SO_4 does absorb moisture from moist H_2 , but the process is highly exothermic. The heat so produced causes hydrogen to catch fire because of its inflammable nature.

7. Can dihydrogen act as oxidising agent? If so give chemical reactions to support the statement.

- Sol. Dihydrogen can act as oxidising agent when it forms metal hydrides.

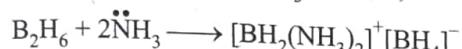


8. What characteristics do you expect from electron deficient hydrides with respect to their structure and chemical reactivity?

- Sol. Electron deficient hydrides do not have sufficient number of electrons to form normal covalent bonds.

They generally exist in polymeric forms such as B_2H_6 , B_4H_{10} , $(AlH_3)_n$, etc.

Due to deficiency of electrons, these hydrides act as Lewis acids and thus, form complex entities with Lewis bases such as : NH_3 , H^- ions, etc.



9. Do you expect the carbon hydride of the type (C_nH_{2n+2}) to act as Lewis acid or base? Justify your answer.

- Sol. Carbon hydride of the type (C_nH_{2n+2}) are electron precise hydrides. In other words, they have exact numbers of electrons required to form covalent bonds. Therefore, they do not have tendency to either gain or lose electrons and hence, they do not act as Lewis acids or Lewis bases.

10. Arrange the following :

- (i) CaH_2 , BeH_2 and TiH_2 in order of increasing electrical conductance.
- (ii) LiH , NaH and CsH in order of increasing ionic character
- (iii) $H-H$, $D-D$ and $F-F$ in order of increasing bond dissociation enthalpy.
- (iv) NaH , MgH_2 and H_2O in order of increasing reducing property.

- Sol. (i) BeH_2 is a covalent hydride, therefore, it does not conduct electricity at all. CaH_2 conducts electricity in the fused state while TiH_2 conducts electricity at room temperature. Thus, the order of increasing electrical conductance is : $BeH_2 < CaH_2 < TiH_2$.
- (ii) Electronegativity decreases down the group from Li to Cs, therefore, the ionic character of their hydrides also increases in the same order, i.e., $LiH < NaOH < CsH$.
- (iii) F – F bond dissociation enthalpy is the minimum. This is due to high concentration of electron density around each F atom in the form of 3 lone pairs which cause significant repulsive interactions.

The bond enthalpy of D–D bond is slightly higher than that of H–H bond. It is due to marginally smaller size of D. Thus, the bond dissociation enthalpy increases in the order : $F-F < H-H < D-D$.

- (iv) Ionic hydrides are powerful reducing agents. Both MgH_2 and H_2O are covalent hydrides but the bond dissociation of O–H bonds in H_2O is much higher than that of Mg–H bond in MgH_2 . Therefore, the reducing character increases in the order : $H_2O < MgH_2 < NaH$.

11. How do you expect the metallic hydrides to be useful hydrogen storage? Explain.

- Sol. In some of the transition metal hydrides, hydrogen is absorbed as H atoms. Due to the inclusion of H atoms, the metal lattice expands and thus becomes less stable. Therefore, when such metallic hydride is heated, it decomposes to release hydrogen gas and very finely divided metal. The hydrogen evolved in this manner can be used as a fuel. Thus, transition metals or their alloys can act as sponge and can be used to store and transport hydrogen to be used as a fuel.

12. Explain the meaning of term hydride gap.

- Sol. Elements of group 7, 8, 9 of d-block do not form hydrides at all. This inability of metals of group 7, 8, 9 of periodic table to form hydrides is referred to as hydride gap of d-block.

13. Explain the following:

- (i) Water is excellent solvent for ionic compounds.
- (ii) Lakes freeze from top to bottom.

- Sol. (i) Water has a high dielectric constant (78.39) due to the polar character of its molecule. Water is an excellent solvent for many ionic as well as covalent compounds. Dissolution of ionic compounds takes place because of ion-dipole interactions. Dissolution of molecular compounds such as alcohols, amides, urea, sugar, glucose, honey, etc., in water takes place because of the tendency of these substances to form hydrogen bonds with water molecules.

- (ii) This is due to the fact that the frozen water does not sink to the bottom but keeps floating at the surface due to its lesser density. This provides thermal insulation to the water below it. The lesser density of ice can be attributed to open cage-like structure on account of hydrogen bonding.

14. What causes the temporary and permanent hardness of water?

- Sol. Temporary hardness is caused by presence of soluble bicarbonates of calcium and magnesium, i.e.

$Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ in water whereas permanent hardness is caused by presence of soluble chlorides and sulphates of calcium and magnesium, i.e. $CaCl_2$, $CaSO_4$, $MgCl_2$ and $MgSO_4$ in water.

15. What is 'demineralised water' and how it can be obtained?

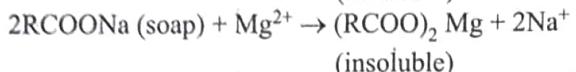
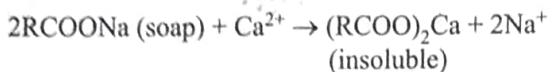
- Sol. Water which is free from all cations and anions is called demineralised water. It is obtained by passing hard water first through cation exchange resin and then through anion exchange resin.

16. Explain the following:

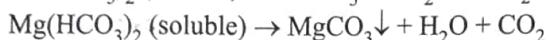
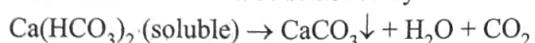
- (i) Soft water lathers with soap but not hard water.
- (ii) Temporary hard water becomes soft on boiling.
- (iii) Water can extinguish most fires but not petrol fire.
- (iv) Hard water is softened before use in boilers.



Sol. (i) Hard water contains calcium and magnesium salts. These react with soap to form insoluble calcium and magnesium salts of fatty acids, i.e., form scum and not lather.



(ii) Temporary hardness of water is due to the presence of soluble bicarbonates of calcium and magnesium. On boiling, the bicarbonates are converted into insoluble carbonates which can be removed by filtration.



(iii) When water poured over petrol fire, petrol being lighter than water floats over water and thus fire spreads instead of being extinguished.

(iv) Hard water consists of bicarbonates and other soluble salts of calcium and magnesium. When hard water is evaporated in boilers, scales of precipitated carbonates of calcium and magnesium along with other salts such as sulphates, chlorides, etc., are formed. In order to avoid the formation of scales hard water is first softened before use in boilers.

17. What happens when?

(i) Heavy water reacts with magnesium nitride.

(ii) Heavy water reacts with sodium.

Sol. (i) $\text{Mg}_3\text{N}_2 + 6\text{D}_2\text{O} \rightarrow \text{Mg}(\text{OD})_2 + 2\text{ND}_3$ (Deutrammonia)

(ii) $\text{Na} + 2\text{D}_2\text{O} \rightarrow 2\text{NaOD} + \text{D}_2$

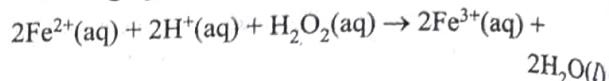
18. Knowing the properties of H_2O and D_2O , do you think that D_2O can be used for drinking purposes?

Sol. Heavy water is injurious to human beings, plants and animals since it slows down the rates of reactions occurring in them. Thus, heavy water does not support life. In fact it retards certain cellular processes, such as mitosis, cell division, etc. Thus, prolonged use of D_2O leads to degeneration of tissues.

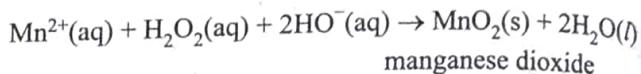
19. Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as a reducing agent.

Sol. H_2O_2 can act as an oxidising as well as a reducing agent both in acidic and basic media as illustrated below.

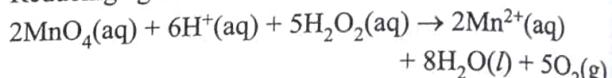
(i) Oxidising agent in acidic medium:



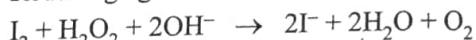
(ii) Oxidising agent in basic medium:



(iii) Reducing agent in acidic medium :



(iv) Reducing agent in basic medium:



20. Explain the following :

(i) Why hydrated barium peroxide is used in the preparation of hydrogen peroxide instead of the anhydrous variety?

(ii) Phosphoric acid is preferred to sulphuric acid in the preparation of H_2O_2 from barium peroxide.

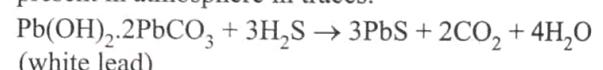
(iii) Statues coated with white lead on long exposure to atmosphere turns black and the original colour can be restored on treatment with H_2O_2 .

Sol. (i) If anhydrous barium peroxide is used in the preparation of hydrogen peroxide the barium sulphate, thus formed, forms an insoluble protective coating on the surface of solid barium peroxide hydrated.

This prevents the further reaction of the acid, i.e., causing the reaction to stop. If, however, hydrated barium peroxide (in the form of the paste) is used, the water causes to dislodge the insoluble BaSO_4 from the surface of BaO_2 . Hence BaSO_4 settles at the bottom of the reaction vessel and the reaction continues without any difficulty.

(ii) When phosphoric acid is used in the preparation of H_2O_2 from BaO_2 , it plays the dual role. It liberates H_2O_2 and also acts as a preservative by retarding its decomposition.

(iii) White lead is used as a pigment. The statues coated with white lead get blackened due to the action of H_2S present in atmosphere in traces.



Exercise-1 (Topicwise)

HYDROGEN & IT'S PROPERTY

1. Hydrogen resembles halogens in many respects for which several factors are responsible. Of the following factors which one is most important in this respect?
 - (a) It's tendency to lose an electron to form a cation.
 - (b) It's tendency to gain a single electron in it's valence shell to attain stable electronic configuration.
 - (c) It's low negative electron gain enthalpy value.
 - (d) It's small size.
2. The colour of hydrogen is:
 - (a) black
 - (b) yellow
 - (c) orange
 - (d) colourless
3. The sum number of neutrons and protons in radioactive isotopes of hydrogen is
 - (a) 3
 - (b) 4
 - (c) 5
 - (d) 6
4. Hydrogen is
 - (a) Electropositive
 - (b) Electronegative
 - (c) Both electropositive as well as electronegative
 - (d) Neither electropositive nor electronegative
5. Atomic hydrogen is obtained by
 - (a) Electrolysis of heavy water
 - (b) Reaction of water with heavy metals
 - (c) Thermal decomposition of water
 - (d) By passing ordinary hydrogen through an electric arc.
6. Which of the following produces hydolith with dihydrogen
 - (a) Mg
 - (b) Al
 - (c) Cu
 - (d) Ca
7. The first ionization energy for (kJ mol^{-1}) H, Li, F, Na has one of the following values 1681, 520, 1312, 495. Which of these values corresponds to that of hydrogen?
 - (a) 1681
 - (b) 1312
 - (c) 520
 - (d) 495
8. Which property of hydrogen does not show resemblance to alkali metals?
 - (a) Hydrogen like alkali metals form stable oxide.
 - (b) Ionisation enthalpy of hydrogen is similar to alkali metals.
 - (c) Like alkali metals hydrogen shows reducing tendency.
 - (d) Like alkali metals hydrogen forms halides.

9. Hydrogen molecule differs from chlorine molecule in the following respect:
 - (a) Hydrogen molecule is non-polar but chlorine molecule is polar.
 - (b) Hydrogen molecule is polar while chlorine molecule is non-polar.
 - (c) Hydrogen molecule can form intermolecular hydrogen bonds but chlorine molecule does not.
 - (d) Hydrogen molecule cannot participate in co-ordinate bond formation but chlorine molecule can.
10. Why does H^+ ion always get associated with other atoms or molecules?
 - (a) Ionisation enthalpy of hydrogen resembles that of alkali metals.
 - (b) It's reactivity is similar to that of halogens.
 - (c) It resembles both alkali metals and halogens.
 - (d) Loss of an electron from hydrogen atom results in a nucleus of very small size as compared to other atoms or ions. Due to small size, it cannot exist free.
11. The ionization energy order for H, H^+ , H^- is
 - (a) $\text{H} < \text{H}^+ < \text{H}^-$
 - (b) $\text{H}^- > \text{H} > \text{H}^+$
 - (c) $\text{H}^- < \text{H}$
 - (d) $\text{H}^+ > \text{H} > \text{H}^-$
12. The oxidation states exhibited by hydrogen in its various compounds are:
 - (a) -1 only
 - (b) Zero only
 - (c) +1, -1 and zero
 - (d) +1 only
13. Which of the following reactions is an example of use of water gas in the synthesis of other compounds?
 - (a) $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow[\text{Ni}]{1270\text{ K}} \text{CO}(\text{g}) + \text{H}_2(\text{g})$
 - (b) $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow[\text{Catalyst}]{673\text{ K}} \text{CO}(\text{g}) + \text{H}_2(\text{g})$
 - (c) $\text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}(\text{g}) \xrightarrow[\text{Ni}]{1270\text{ K}} n\text{CO} + (2n+1)\text{H}_2$
 - (d) $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \xrightarrow[\text{Catalyst}]{\text{Cobalt}} \text{CH}_3\text{OH}(1)$

WATER & HYDRIDES

14. Which of the following hydride is electron-precise hydride?
 - (a) B_2H_6
 - (b) NH_3
 - (c) H_2O
 - (d) CH_4
15. Elements of which of the following group(s) of periodic tables do not form hydrides.
 - (a) Groups 7, 8, 9
 - (b) Group 13
 - (c) Groups 15, 16, 17
 - (d) Group 14
16. Which of the following is an interstitial hydride?
 - (a) $\text{TiH}_{1.5-1.8}$
 - (b) B_2H_6
 - (c) LiH
 - (d) H_2S

- 17.** Heavy water is:
- H_2^{18}O
 - Water obtained by repeated distillation
 - D_2O
 - Water at 4°C .
- 18.** Both temporary and permanent hardness is removed on boiling water with
- $\text{Ca}(\text{OH})_2$
 - Na_2CO_3
 - CaCO_3
 - CaO
- 19.** D_2O is used more in
- Chemical industry
 - Nuclear reactor
 - Pharmaceutical preparations
 - Insecticide preparation
- 20.** Temporary hardness is caused due to the presence of
- CaSO_4
 - CaCl_2
 - CaCO_3
 - $\text{Ca}(\text{HCO}_3)_2$
- 21.** Zeolites are extensively used in
- Softening of water and catalyst
 - Preparing heavy water
 - Increasing the hardness of water
 - Mond's process
- 22.** Permutit is
- Hydrated sodium aluminium silicate
 - Sodium hexametaphosphate
 - Sodium silicate
 - sodium meta-aluminate
- 23.** When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water the sodium ions are exchanged with
- H^+ ions
 - Ca^{2+} ions
 - SO_4^{2-} ions
 - OH^- ions
- 24.** The molarity of pure water at 4°C is
- 1 M
 - 2.5 M
 - 5 M
 - 55.5 M
- 25.** Water softening by Clarke's process uses
- Calcium bicarbonate
 - Sodium bicarbonate
 - Potash alum
 - Calcium hydroxide
- 26.** Ionic hydrides are usually
- Good electrically conductors when solid
 - Easily reduced
 - Good reducing agents
 - Liquid at room temperature
- 27.** Radioactive isotope of hydrogen is :
- Uranium
 - Deuterium
 - Tritium
 - None of these
- 28.** Water is oxidised to oxygen by
- ClO_2
 - KMnO_4
 - H_2O_2
 - Flourine
- 29.** Water obtained by purification with organic ion exchange resins is
- Pure water
 - Free from only Ca^{2+} , Mg^{2+} ions
 - Free from HCO_3^- , SO_4^{2-} and Cl^- ions only
 - None of these
- 30.** The hydride ion (H^-) is a stronger base than hydroxide ion (OH^-). Which of the following reactions will occur if sodium hydride (NaH) is dissolved in water?
- $\text{H}^-(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^-(\text{aq})$
 - $\text{H}^-(\text{aq}) + \text{H}_2\text{O}(l) \rightarrow \text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$
 - $\text{H}^-(\text{aq}) + \text{H}_2\text{O}(l) \rightarrow$ No reaction
 - None of these
- 31.** Temporary hardness may be removed from water by adding
- $\text{Ca}(\text{OH})_2$
 - CaCO_3
 - CaSO_4
 - HCl
- 32.** Which of the following will cause softening of hard water?
- Passing it through anion exchange resin.
 - Passing it through sand.
 - Passing it through cation exchange resin.
 - Passing it through alumina.

H_2O_2 & IT'S PROPERTIES

- 33.** The bleaching properties of H_2O_2 are due to its
- Reducing properties
 - Oxidising properties
 - Unstable nature
 - Acidic nature
- 34.** In which of the following reaction hydrogen peroxide is a reducing agent
- $2\text{FeCl}_2 + 2\text{HCl} + \text{H}_2\text{O}_2 \rightarrow 2\text{FeCl}_3 + 2\text{H}_2\text{O}$
 - $\text{Cl}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{HCl} + \text{O}_2$
 - $2\text{HI} + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{I}_2$
 - $\text{H}_2\text{SO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$
- 35.** The oxide that gives hydrogen peroxide (H_2O_2) on the treatment with a dilute acid (H_2SO_4) is
- MnO_2
 - PbO_2
 - Na_2O_2
 - TiO_2
- 36.** Among KO_2 , NO_2^- , BaO_2 and NO_2^+ unpaired electron is present in
- NO_2^+ and BaO_2
 - KO_2 and BaO_2
 - KO_2 only
 - BaO_2 only
- 37.** H_2O_2 is manufactured nowadays
- By the action of H_2O_2 on BaO_2 .
 - By the action of H_2SO_4 on Na_2O_2 .
 - By electrolysis of 50% H_2SO_4 .
 - By burning hydrogen in excess of oxygen.



38. The compound that gives H_2O_2 on treatment with dilute H_2SO_4 is:

 - PbO_2
 - $BaO_2 \cdot 8H_2O + O_2$
 - MnO_2
 - TiO_2

39. Hydrogen peroxide is obtained by the electrolysis of _____.

 - water
 - sulphuric acid
 - hydrochloric acid
 - fused sodium peroxide

40. H_2O_2 is used as:

 - antiseptic
 - bleaching agent
 - propellant
 - all of the above

41. Which one of the following is used for the laboratory preparation of D_2O_2 ?

 - $K_2S_2O_8$
 - $H_2S_2O_7$
 - H_2SO_4
 - H_2SO_5

42. When CO_2 is bubbled through a solution of barium peroxide in water:

 - O_2 is released
 - Carbonic acid is formed
 - H_2O_2 is formed
 - No reaction occurs

43. H_2O_2 is used but not as:

 - oxidant, reductant
 - bleaching agent
 - antiseptic
 - catalyst

44. The dipole moment of H_2O_2 is 2.1 D. This indicates that the structure of H_2O_2 is:

 - Linear
 - Non-linear
 - Symmetrical
 - None of these

45. Now a day on industrial scale, H_2O_2 is generally prepared by

 - The action of H_2SO_4 on barium oxide.
 - The action of H_2SO_4 on sodium peroxide.
 - By the electrolysis of H_2SO_4 .
 - By burning hydrogen in an excess of O_2 .

46. Moist hydrogen peroxide can-not be dried over concentrated H_2SO_4 because

 - It can catch fire
 - it is reduced by H_2SO_4
 - it is oxidised by H_2SO_4
 - none of these

MISCELLANEOUS



Exercise-2 (Learning Plus)

1. Hydrogen molecule differs from chlorine molecule in the following respect:

 - (a) hydrogen molecule is non-polar but chlorine molecule is polar.
 - (b) hydrogen molecule is polar while chlorine molecule is non-polar.
 - (c) hydrogen molecule can form intermolecular hydrogen bonds but chlorine molecule does not.
 - (d) hydrogen molecule cannot participate in co-ordinate bond formation but chlorine molecule can.

2. Which of the following statements concerning protium, deuterium and tritium is not true?

 - (a) They are isotopes of each other.
 - (b) They have similar electronic configurations.
 - (c) They exist in the nature in the ratio 1 : 2 : 3.
 - (d) Their atomic masses are in the ratio 1 : 2 : 3.

3. Which of the following represents a pair of covalent hydrides?

 - (a) CsH , AlH_3
 - (b) KH , NaH
 - (c) BeH_2 , B_2H_6
 - (d) $\text{VH}_{0.56}$, NH_2

- 27.** Hard water when passed through ion exchange resin containing, RCOOH groups, becomes free from :
- Cl^- ions
 - SO_4^{2-} ions
 - H_3O^+ ions
 - Ca^{2+} ions
- 28.** Hydrogen peroxide is:
- Diamagnetic
 - Paramagnetic
 - Ferromagnetic
 - Ferrimagnetic
- 29.** The volume strength of 1.5N H_2O_2 solution is:
- 8.4L
 - 4.2L
 - 16.8L
 - 5.2L
- 30.** The halogen which has maximum affinity for hydrogen
- F_2
 - Cl_2
 - Br_2
 - I_2
- 31.** The volume of oxygen liberated from 15 ml of 20 volume H_2O_2 is:
- 250 ml
 - 300 ml
 - 150 ml
 - 200 ml
- 32.** The adsorption of hydrogen by metals is called :
- dehydrogenation
 - hydrogenation
 - occlusion
 - adsorption
- 33.** Which of the following metals adsorbs hydrogen?
- Zn
 - Pd
 - Al
 - K
- 34.** The O–H bond energy in water when compared to O – D bond energy in heavy water is
- Greater
 - Lesser
 - Equal
 - two times greater
- 35.** Consider the reactions
- $\text{H}_2\text{O}_2 + 2\text{HI} \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$
 - $\text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- + \text{O}_2$
- Which of the following statements is correct about H_2O_2 with reference to these reactions? Hydrogen peroxide is
- an oxidising agent in both (i) and (ii).
 - an oxidising agent in (i) and reducing agent in (ii).
 - a reducing agent in (i) and oxidising agent in (ii).
 - a reducing agent in both (i) and (ii).
- 36.** Only one element of _____ forms hydride.
- group 6
 - group 7
 - group 8
 - group 9
- 37.** Which metals are used for storage of hydrogen
- Pd, Pt
 - Na, Li
 - W, Mo
 - Fe, Ru
- 38.** Most pure hydrogen is formed by
- $3\text{Fe} + 4\text{H}_2\text{O} \xrightarrow{\text{steam}} \text{Fe}_3\text{O}_4 + 4\text{H}_2$
 - $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$
 - $\text{Ba(OH)}_2 \xrightarrow{\text{Electrolysis}} \text{H}_2 + \text{O}_2$
 - $\text{Dil H}_2\text{SO}_4 \xrightarrow{\text{Electrolysis}} \text{H}_2 + \text{O}_2$
- 39.** Which of the following property is same for both H_2 and D_2 ?
- Enthalpy of fusion
 - Enthalpy of vaporization
 - Internuclear distance
 - Enthalpy of bond dissociation
- 40.** When electric current is passed through an ionic hydride in the molten state?
- Hydrogen is liberated at the anode.
 - Hydrogen is liberated at the cathode.
 - No reaction takes place.
 - Hydride ion migrates towards cathode.
- 41.** Which of the following reactions increases production of dihydrogen from synthesis gas?
- $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow[\text{Ni}]{1270 \text{ K}} \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
 - $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \xrightarrow{1270 \text{ K}} \text{CO}(\text{g}) + \text{H}_2(\text{g})$
 - $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow[\text{Catalyst}]{673 \text{ K}} \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$
 - $\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} \xrightarrow[\text{Ni}]{1270 \text{ K}} 2\text{CO} + 5\text{H}_2$
- 42.** Which one is true about nascent hydrogen?
- More reactive than molecular hydrogen.
 - Can be produced in situ.
 - Shows similarity exactly with hydrogen in reduction reactions.
 - (a) and (b) both.
- 43.** Select the correct statement for heavy water.
- It is less denser than common water.
 - It is an oxide of deuterium.
 - It has a heavy or bad taste.
 - It has a heavier isotope of oxygen.
- 44.** 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.
- 45.** When sodium peroxide is treated with dilute sulphuric acid, we get _____.
- Sodium sulphate and water.
 - Sodium sulphate and oxygen.
 - Sodium sulphate, hydrogen and oxygen.
 - Sodium sulphate and hydrogen peroxide.

46. Which of the following orders are correct?

(A) $\text{TiH}_2 < \text{BeH}_2 < \text{CaH}_2$ – Electrical conductance.

(B) $\text{LiH} < \text{NaH} < \text{CaH}$ – Ionic character.

(C) $\text{F-F} < \text{H-H} < \text{D-D}$ – Bond dissociation enthalpy.

(D) $\text{H}_2\text{O} < \text{MgH}_2 < \text{NaH}$ – Reducing character.

(a) (A), (B) and (C)

(b) (B), (C) and (D)

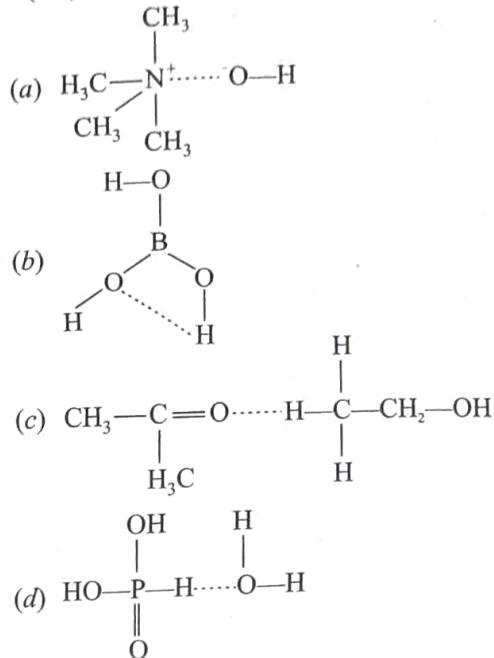
(c) (A), (C) and (D)

(d) (A), (B), (C) and (D)

47. What is false about ice?

 - (a) It has open cage-like structure
 - (b) It has less density than water
 - (c) Each O atom is surrounded by four H atoms
 - (d) Each O atom has four H-bonds around it

48. Which of the following representation of hydrogen bonding is(are) incorrect?



Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

1. Which of the following produces hydrolith with dihydrogen
 - (a) Mg
 - (b) Al
 - (c) Cu
 - (d) Ca
 2. Which process is/are used to remove permanent hardness
 - (a) Boiling
 - (b) Clark's method
 - (c) On reaction with NaOH
 - (d) Permutit process
 3. Ionic hydrides is/are usually
 - (a) Good electrically conductors when solid
 - (b) Easily reduced
 - (c) Good reducing agents
 - (d) Liquid at room temperature
 4. The gas(es) used in the hydrogenation of oils in presence of nickel as a catalyst is/are
 - (a) Methane
 - (b) Ethane
 - (c) Ozone
 - (d) Hydrogen
 5. Ortho-hydrogen and para-hydrogen resembles in which of the following property
 - (a) Thermal conductivity
 - (b) Magnetic properties
 - (c) Chemical properties
 - (d) Heat capacity

6. Ionic hydrides are formed by

 - (a) Transition metals
 - (b) Elements of very high electropositivity
 - (c) Elements of very low electropositivity
 - (d) Metalloids

7. Which hydride is/are an ionic hydride

 - (a) NH_3
 - (b) H_2S
 - (c) $\text{TiH}_{1.73}$
 - (d) NaH

8. Which of the following is/are same for Ortho and Para hydrogen

 - (a) In the number of protons
 - (b) In the molecular mass
 - (c) In the nature of spins of nucleus
 - (d) In the nature of spins of electrons

9. In Bosch's process which gas is NOT utilised for the production of hydrogen

 - (a) Producer gas
 - (b) Water gas
 - (c) Coal gas
 - (d) Natural gas

10. Water softening by Clarke's process does NOT uses

 - (a) Calcium bicarbonate
 - (b) Sodium bicarbonate
 - (c) Potash alum
 - (d) Calcium hydroxide

11. Which of the following will produce hydrogen gas
 (a) Reaction between Fe and dil. HCl.
 (b) Reaction between Zn and conc. H_2SO_4 .
 (c) Reaction between Zn and NaOH.
 (d) Electrolysis of NaCl (aq.) in Nelson's cell.
12. Which of the following statements concerning protium, deuterium and tritium is / are true
 (a) They are isotopes of each other
 (b) They have similar electronic configurations
 (c) They exist in the nature in the ratio of 1 : 2 : 3
 (d) Their mass numbers are in the ratio of 1 : 2 : 3
13. Which of the following statements is/are correct
 (a) Atomic hydrogen is obtained by passing hydrogen gas through an electric arc
 (b) 30% (w/v) or 100V H_2O_2 solution is not called perhydrol.
 (c) Finely divided palladium absorbs large volume of hydrogen gas.
 (d) Ortho and para hydrogen have same physical properties.
14. 100 cm³ of a given sample of H_2O_2 is labelled as "20 volumes". Its percentage strength is:
 (a) 10% (W/V) H_2O_2 (b) 90% (W/V) H_2O_2
 (c) 6% (W/V) H_2O_2 (d) 12% (W/V) H_2O_2
15. Which of the following statements about hydrogen are correct?
 (a) Hydrogen has three isotopes of which protium is the most common.
 (b) Hydrogen never acts as cation in ionic salts.
 (c) Hydrogen ion, H^+ , exists freely in solution.
 (d) Dihydrogen does not act as a reducing agent.
16. Which of the following statement(s) is/are correct?
 (a) Elements of group 15 form electron deficient hydrides.
 (b) All elements of group 14 form electron precise hydrides.
 (c) Electron precise hydrides have tetrahedral geometries.
 (d) Electron rich hydrides can act as Lewis acids.
17. Which of the following statement(s) is/are correct?
 (a) Metallic hydrides are deficient of hydrogen.
 (b) Metallic hydrides conduct heat and electricity.
 (c) Ionic hydrides do not conduct electricity in solid state.
 (d) Ionic hydrides are very good conductors of electricity in solid state.
18. 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.
19. 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.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 20 to 22): Binary compounds of hydrogen with other elements are called hydrides. These hydrides can be classified into different classes depending upon their nature and type of bonding.

20. Which of the following hydrides are generally non-stoichiometric in nature?
 (a) Ionic hydride
 (b) Molecular hydrides
 (c) Interstitial hydride
 (d) Covalent hydrides
21. Among the hydrides given below which is reasonably electron precise hydride?
 (a) NH_3 (b) SiH_4
 (c) NaH (d) H_2S
22. Which of the following statements is false?
 (a) Saline hydrides are formed by the transference of electron from the metal atom to hydrogen atom.
 (b) Along any given row of periodic table, generally the covalent hydrides become increasingly acidic in nature from left to right.
 (c) Metallic hydrides are good conductors of electricity and also have high thermal conductivity.
 (d) None of these

Comprehension (Q. 23 to 25): Hydrogen accounts for approximately 75% of the mass of the universe. Hydrogen serves as the nuclear fuel of our Sun and other stars, and these are mainly composed of hydrogen.

Hydrogen has three isotopes : hydrogen or protium (${}_1^1H$), deuterium or heavy hydrogen (D or ${}_1^2H$), tritium (T or ${}_1^3H$).

23. Which of the following is radioactive in nature?
 (a) hydrogen only
 (b) deuterium only
 (c) tritium only
 (d) deuterium and tritium
24. Hydrogen, H_2 , is very less abundant in the atmosphere due to
 (a) inflammable nature of H_2
 (b) weak earth's gravity which is not able to hold light H_2 molecules
 (c) diatomic nature of hydrogen
 (d) very rapid reaction between hydrogen and atmospheric oxygen

25. Liquid H_2 has been used as rocket fuel as
 (a) its reaction with oxygen is highly exothermic
 (b) it occupies small space
 (c) it has high thrust
 (d) all of the above

Comprehension (Q. 26 to 28): by appropriately matching the information given in the three columns of the following table.

Column - I Name	Column - II Formula	Column - III Specification
(1) Calogen	(P) $\text{Na}_6\text{PO}_6\text{O}_{18}$	(i) Used to Remove temporary Hardness
(2) Permutit	(Q) $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$	(ii) Used to remove permanent hardness
(3) Perhydrol	(R) '100 V' H_2O_2	(iii) Used in Rocket propellant
(4) Washing Soda	(S) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	(iv) Also named as zeolite

26. Which combination is NOT related to removal of $\text{Ca}^{2+}/\text{Mg}^{2+}$ from the sample of water
 (a) (1)-(P)-(i)(ii) (b) (2)-(Q)-(i)(ii)(iv)
 (c) (3)-(R)-(i)(ii) (d) (4)-(S)-(i)(ii)

27. Which of the following is INCORRECT between column-I and column-II
 (a) 1-P (b) 2-Q
 (c) 3-R (d) 2-S
28. Which of the following is INCORRECT matching between column-III & column-II
 (a) (iii) – R (b) (iv) – Q
 (c) (iv) – P (d) none of these

MATCH THE COLUMN TYPE QUESTIONS

29. Match Column-I with Column-II and select the correct answer using the codes given below the lists

Column-I	Column-II	
A. Heavy water	p.	Bicarbonates of Mg and Ca in water
B. Temporary hard	q.	No foreign ions in water
C. Soft water	r.	D_2O
D. Permanent hard	s.	Sulphates and chlorides of Mg and Ca in water

- (a) A \rightarrow r; B \rightarrow p; C \rightarrow q; D \rightarrow s
 (b) A \rightarrow r; B \rightarrow s; C \rightarrow q; D \rightarrow r
 (c) A \rightarrow r; B \rightarrow q; C \rightarrow p; D \rightarrow s
 (d) A \rightarrow q; B \rightarrow r; C \rightarrow p; D \rightarrow s
30. Match Column-I with Column-II and select the correct answer using the codes given below the lists

Column-I	Column-II	
A. Calgon	p.	Metallic hydride
B. Non-stoichiometric compound	q.	Polymetaphosphate of sodium
C. Covalent hydride	r.	Hydrolith
D. Salt-like hydride	s.	Hydrogen compounds of non-metals

- (a) A \rightarrow q; B \rightarrow p; C \rightarrow r; D \rightarrow s
 (b) A \rightarrow r; B \rightarrow s; C \rightarrow q; D \rightarrow r
 (c) A \rightarrow q; B \rightarrow p; C \rightarrow s; D \rightarrow r
 (d) A \rightarrow q; B \rightarrow r; C \rightarrow p; D \rightarrow s

31. Match the column.

(Note: Each statement in column-I has only one match in column-II.)

Column-I	Column-II
A. H	p. Used in the name of perhydrol.
B. H_2	q. Can be reduced to dihydrogen by NaH.
C. H_2O	r. Can be used in hydroformylation of olefin.
D. H_2O_2	s. Can be used in cutting and welding.

- (a) A \rightarrow q; B \rightarrow r; C \rightarrow s; D \rightarrow p
 (b) A \rightarrow s; B \rightarrow r; C \rightarrow q; D \rightarrow p
 (c) A \rightarrow s; B \rightarrow p; C \rightarrow q; D \rightarrow r
 (d) A \rightarrow r; B \rightarrow q; C \rightarrow s; D \rightarrow p

32. Match the column.

(Note: Each statement in column-I has only one match in column-II.)

Column-I	Column-II
A. Electrolysis of water produces	p. atomic reactor
B. Lithium aluminium hydride is used as	q. polar molecule
C. Hydrogen chloride is a	r. recombines on metal surface to generate high temperature
D. Heavy water is used in	s. reducing agent
E. Atomic hydrogen	t. hydrogen and oxygen

- (a) A \rightarrow t; B \rightarrow q, C \rightarrow s; D \rightarrow p; E \rightarrow r
 (b) A \rightarrow t; B \rightarrow r, C \rightarrow q; D \rightarrow p; E \rightarrow s
 (c) A \rightarrow t; B \rightarrow s, C \rightarrow q; D \rightarrow p; E \rightarrow r
 (d) A \rightarrow t; B \rightarrow p, C \rightarrow r; D \rightarrow q; E \rightarrow s

33. Match the column.

(Note: Each statement in column-I has one or more matches in column-II.)

Column-I	Column-II
A. Hydrogen peroxide is used as a	p. Zeolite
B. Used in Calgon method	q. Perhydrol
C. Permanent hardness of hard water is removed by	r. Sodium hexametaphosphate
	s. Propellant

- (a) A \rightarrow q, s; B \rightarrow r; C \rightarrow p, r
 (b) A \rightarrow q; B \rightarrow r; C \rightarrow q, s
 (c) A \rightarrow q; B \rightarrow r; C \rightarrow q, r, s
 (d) A \rightarrow q, s; B \rightarrow r; C \rightarrow p, r

34. Match the column.

(Note: Each statement in column-I has one or more matches in column-II.)

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.	

(a) A \rightarrow p, r, s, t; B \rightarrow q, t; C \rightarrow q; D \rightarrow p, r, s, t
 (b) A \rightarrow q, t; B \rightarrow r; C \rightarrow q, s; D \rightarrow p, q, r, s
 (c) A \rightarrow q, t; B \rightarrow r, t; C \rightarrow q, r, s; D \rightarrow p, r, s
 (d) A \rightarrow q, t; B \rightarrow r, s; C \rightarrow p, r; D \rightarrow p, r, s, t

NUMERICAL TYPE QUESTIONS

35. Find the volume of oxygen gas liberated at STP, when 25 ml of '30 volumes' H_2O_2 is completely decomposed.

36. Find out the value of 'a'. [a = x + y]
 $\text{H}_2\text{S}_2\text{O}_8$ on completely hydrolysis givesx.....mole of H_2SO_4 &y..... mole of H_2O_2 .

37. Calculate the total no. of Peroxy linkage in the following compounds $\text{H}_2\text{S}_2\text{O}_8$, CrO_5 , H_2TiO_4

38. Find out the sum of protons, electrons and neutrons in the heaviest isotope of hydrogen.

39. Find out the number of following orders which are correct against the mentioned properties:

 - (i) $\text{H}_2 < \text{D}_2 < \text{T}_2$ (Number of protons)
 - (ii) $\text{H}_2 < \text{D}_2$ (Bond energy)
 - (iii) $\text{H}_2 < \text{D}_2 < \text{T}_2$ (Boiling point)
 - (iv) $\text{H}_2 < \text{D}_2 < \text{T}_2$ (No. of neutrons)

40. Find out the number of following orders which are NOT correct against the mentioned properties:

(i) $\text{CaH}_2 < \text{BeH}_2$	(Electrical conductance in molten condition)
(ii) $\text{LiH} < \text{NaH} < \text{CsH}$	(Ionic character)
(iii) $\text{H}_2 < \text{D}_2 < \text{F}_2$	(Bond dissociation enthalpy)
(iv) $\text{NaH} < \text{MgH}_2 < \text{H}_2\text{O}$	(Reducing property)

41. Find out the value of 'x' in ion $[\text{H}_x\text{O}_4]^{+}$:

Exercise-4 (Past Year Questions)

JEE MAIN

7. In which of the following reaction, hydrogen peroxide acts as an oxidizing agent? (2017)
- $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$
 - $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$
 - $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$
 - $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$
8. Hydrogen peroxide oxidises $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in acidic medium but reduces $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ in alkaline medium. The other products formed are, respectively: (2014)
- $(H_2O + O_2)$ and $(H_2O + OH^-)$
 - H_2O and $(H_2O + O_2)$
 - H_2O and $(H_2O + OH^-)$
 - $(H_2O + O_2)$ and H_2O
9. The temporary hardness of water is due to (2019)
- Na_2SO_4
 - $NaCl$
 - $Ca(HCO_3)_2$
 - $CaCl_2$
10. The correct statements among (a) to (d) regarding H_2 as fuel are:
- It produces less pollutants than petrol
 - A cylinder of compressed dihydrogen weighs ~30 times more than a petrol tank producing the same amount of energy
 - Dihydrogen is stored in tanks of metal alloys like $NaNi_5$
 - On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively.
- (2019)
- (II) and (IV) only
 - (I) and (IV) only
 - (II), (III) and (IV) only
 - (I), (II) and (III) only
11. The temporary hardness of a water sample is due to compound X. Boiling this sample converts X to compound Y. X and Y, respectively, are (2019)
- $Ca(HCO_3)_2$ and CaO
 - $Mg(HCO_3)_2$ and $MgCO_3$
 - $Mg(HCO_3)_2$ and $Mg(OH)_2$
 - $Ca(HCO_3)_2$ and $Ca(OH)_2$
12. The temporary hardness of water is due to: (2019)
- $Ca(HCO_3)_2$
 - $NaCl$
 - Na_2SO_4
 - $CaCl_2$
13. The hardness of a water sample (in terms of equivalents of $CaCO_3$) containing $10^{-3} M$ $CaSO_4$ is: (molar mass of $CaSO_4$ = 136 g mol⁻¹) (2019)
- 100 ppm
 - 50 ppm
 - 10 ppm
 - 90 ppm
14. The isotopes of hydrogen are: (2019)
- Tritium and protium only
 - Deuterium and tritium only
 - Protium and deuterium only
 - Protium, deuterium and tritium
15. Among the following reactions of hydrogen with halogens, the one that requires a catalyst is: (2019)
- $H_2 + I_2 \rightarrow 2HI$
 - $H_2 + F_2 \rightarrow 2HF$
 - $H_2 + Cl_2 \rightarrow 2HCl$
 - $H_2 + Br_2 \rightarrow 2HBr$
16. The chemical nature of hydrogen peroxide is: (2019)
- Oxidising and reducing agent in acidic medium, but not in basic medium.
 - Oxidising and reducing agent in both acidic and basic medium
 - Reducing agent in basic medium, but not in acidic medium
 - Oxidising agent in acidic medium, but not in basic medium.
17. The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively, are: (2019)
- 2 and 0
 - 3 and 2
 - 3 and 1
 - 2 and 1
18. The hydride that is NOT electron deficient is: (2019)
- B_2H_6
 - AlH_3
 - SiH_4
 - GaH_3
19. NaH is an example of: (2019)
- Electron-rich hydride
 - Molecular hydride
 - Saline hydride
 - Metallic hydride
20. The synonym for water gas when used in the production of methanol is: (2019)
- natural gas
 - laughing gas
 - syn gas
 - fuel gas
21. The metal that gives hydrogen gas upon treatment with both acid as well as base is: (2019)
- zinc
 - iron
 - magnesium
 - mercury
22. In comparison to the zeolite process for the removal of permanent hardness, the synthetic resins method is: (2020)
- More efficient as it can exchange both cations as well as anions
 - Less efficient as it exchanges only anions
 - More efficient as it can exchange only cations
 - Less efficient as the resins cannot be regenerated
23. Among statements (a)-(d), the correct ones are: (2020)
- Decomposition of hydrogen peroxide gives dioxygen
 - Like hydrogen peroxide, compounds, such as $KClO_3$, $Pb(NO_3)_2$ and $NaNO_3$ when heated liberate dioxygen.
 - 2-Ethylanthraquinone is useful for the industrial preparation of hydrogen peroxide.
 - Hydrogen peroxide is used for the manufacture of sodium perborate.
- (a), (c) and (d) only
 - (a), (b), (c) and (d)
 - (a), (b) and (c) only
 - (a) and (c) only

JEE ADVANCED

38. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a (2014)

 - (a) Reducing agent, oxidising agent
 - (b) Reducing agent, reducing agent
 - (c) Oxidising agent, oxidising agent
 - (d) Oxidising agent, reducing agent

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (d) | 3. (c) | 4. (c) | 5. (b) | 6. (b) | 7. (c) | 8. (a) | 9. (d) | 10. (b) |
| 11. (c) | 12. (d) | 13. (b) | 14. (d) | 15. (b) | 16. (d) | 17. (a) | 18. (b) | 19. (c) | 20. (d) |
| 21. (b) | 22. (d) | 23. (c) | | | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (d) | 3. (a) | 4. (c) | 5. (d) | 6. (d) | 7. (b) | 8. (b) | 9. (d) | 10. (d) |
| 11. (c) | 12. (c) | 13. (d) | 14. (d) | 15. (a) | 16. (a) | 17. (c) | 18. (b) | 19. (b) | 20. (d) |
| 21. (a) | 22. (a) | 23. (b) | 24. (d) | 25. (d) | 26. (c) | 27. (c) | 28. (d) | 29. (b) | 30. (b) |
| 31. (a) | 32. (c) | 33. (b) | 34. (b) | 35. (c) | 36. (c) | 37. (c) | 38. (b) | 39. (b) | 40. (d) |
| 41. (a) | 42. (c) | 43. (d) | 44. (b) | 45. (c) | 46. (c) | 47. (c) | 48. (d) | 49. (c) | 50. (d) |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (c) | 3. (c) | 4. (b) | 5. (b) | 6. (c) | 7. (a) | 8. (b) | 9. (d) | 10. (d) |
| 11. (b) | 12. (a) | 13. (c) | 14. (a) | 15. (c) | 16. (a) | 17. (b) | 18. (c) | 19. (a) | 20. (d) |
| 21. (b) | 22. (c) | 23. (c) | 24. (a) | 25. (c) | 26. (c) | 27. (d) | 28. (a) | 29. (a) | 30. (a) |
| 31. (b) | 32. (c) | 33. (b) | 34. (b) | 35. (b) | 36. (a) | 37. (a) | 38. (d) | 39. (c) | 40. (a) |
| 41. (c) | 42. (d) | 43. (b) | 44. (d) | 45. (d) | 46. (b) | 47. (c) | 48. (a) | | |

EXERCISE-3 (JEE ADVANCED LEVEL)

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|-------------|-------------|-----------|-----------|-----------|---------------------------------------|-------------|-------------|---------------|-------------|
| 1. (d) | 2. (d) | 3. (c) | 4. (d) | 5. (c) | 6. (b) | 7. (d) | 8. (a,b,d) | 9. (a,c,d) | 10. (a,b,c) |
| 11. (a,c,d) | 12. (a,b,d) | 13. (a,c) | 14. (c,d) | 15. (a,b) | 16. (b,c) | 17. (a,b,c) | 18. (a,b,c) | 19. (a,b,c,d) | |
| 20. (c) | 21. (b) | 22. (d) | 23. (c) | 24. (b) | 25. (d) | 26. (c) | 27. (d) | 28. (c) | 29. (a) |
| 30. (c) | 31. (b) | 32. (c) | 33. (d) | 34. (a) | 35. [750 ml of O ₂ at NTP] | | | 36. [3] | 37. [4] |
| 38. [4] | 39. [3] | 40. [3] | 41. [9] | | | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (b) | 3. (c) | 4. (a) | 5. (c) | 6. (c) | 7. (c) | 8. (b) | 9. (c) | 10. (d) |
| 11. (c) | 12. (a) | 13. (a) | 14. (d) | 15. (a) | 16. (b) | 17. (c) | 18. (c) | 19. (c) | 20. (c) |
| 21. (a) | 22. (a) | 23. (b) | 24. (d) | 25. (c) | 26. (d) | 27. (b) | 28. (b) | 29. (c) | 30. (b) |
| 31. (a) | 32. (d) | 33. (b) | 34. (a) | 35. (a) | 36. (d) | 37. (c) | | | |

JEE Advanced

38. (a)

CHAPTER

10

The s-Block Elements

INTRODUCTION

In this chapter, we will study the general characteristics of the alkali and alkaline earth metals and their compounds. We will also study the compounds of s-block elements, their uses and importance, commercially and industrially. The biological significance of sodium, potassium, calcium and magnesium will also be discussed in this chapter.

The s-Block Elements

Those elements in which last electron enters in s-orbital are called s-block elements. These are located at extreme left hand side of the periodic table. Since s orbital can accommodate only two electrons, the elements having one electron in their outermost s-orbital are grouped into group-1 and those having two electrons are grouped into group-2 of periodic table.

Group-1 Elements : Alkali Metals

- (i) Group 1 elements are called alkali metals because their oxides and hydroxides when treated with water, form alkaline solutions.
- (ii) This includes the typical or representative elements of IA such as Li and Na as well as K, Rb, Cs and Fr.
- (iii) They are never found in the free state, because of their high reactivity,
- (iv) Francium is a radioactive element.
- (v) All are silvery white, light, soft, malleable and ductile metals with metallic lustre.

1. Electronic Configuration: The alkali metals have one valence electron outside the noble gas core therefore, configuration is

$$[\text{Noble gas}]ns^1; \text{ where } n = 2 \text{ to } 7$$

Since the outermost electron is loosely held, alkali metals readily lose electron to give monovalent (M^+) ions, that is why they are most electropositive metals.

The electronic configurations of alkali metals are given below:

Element	Symbol	Electronic configuration
Lithium	Li	$[\text{He}]2s^1$
Sodium	Na	$[\text{Ne}]3s^1$
Potassium	K	$[\text{Ar}]4s^1$
Rubidium	Rb	$[\text{Kr}]5s^1$
Caesium	Cs	$[\text{Xe}]6s^1$
Francium	Fr	$[\text{Rn}]7s^1$

2. Atomic and Ionic Radii: The atoms of alkali metals have the largest size in their respective periods. The atomic radius increases on moving down the group.

Size order : $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$

Ionic radii : $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$

3. Ionization Enthalpy: The first ionisation enthalpies of alkali metals are low as compared to the elements of other groups belonging to the same period. However, within the group the ionization enthalpies of the alkali metals decrease down the group.

IE order : $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$

4. Hydration Enthalpy: The alkali metal ions are extensively hydrated in aqueous solutions. Smaller the ion, more is the extent of hydration. The hydration enthalpies of alkali metal ions decrease with increase in ionic size.

$\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ (Hydration energy Decreases)

Li^+ has maximum degree of hydration and for this reason many lithium salts exist as hydrated salts. For example, $\text{LiCl} \cdot 2\text{H}_2\text{O}$.

5. Melting point and Boiling point:

(a) Weak interatomic bonds due to their large atomic radii and presence of only one valence electron. Hence, melting point and boiling point are low.

(b) Decreasing order of melting point and boiling point is $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$

(c) With the increase in the size of metal atom, the repulsion of the non-bonding electrons increases and therefore, melting point and boiling point decreases from Li to Cs.

6. **Density:** $d = \frac{\text{mass}}{\text{volume}}$

In a group, atomic volume also increase along with atomic weight but atomic weight increases more than atomic volume, so density increases from Li to Cs.

Exception: Density of Na is higher than K as empty d-orbitals are present in K. Maximum capacity of M shell is of 18 electrons but it contains only 8 electron, which decreases its density. Increasing order of density is:



7. Standard oxidation potential:

- (a) All the alkali metals have high positive values of standard oxidation potential (tendency of releasing electrons in water or self ionic solutions).
- (b) So these are good reducing agent, having upper most positions in the electro chemical series.
- (c) Li has highest standard oxidation potential (+3.05 eV) due to its high hydration energy. Such that it converts into Li^+ ion by losing one electron.

Order of standard oxidation potential of s-block elements



Hydration energy \propto Charge density on ion

Note: Li is the strongest reducing agent among all elements of periodic table due to high hydration energy.

8. Complex formation tendency:

- (a) Only those elements can form complex compounds which have:

- (i) Small cation size
- (ii) High charge density
- (iii) Vacant d-orbital to accept electrons

(b) Only Li^+ can form complex compound due to its small size, rest alkali metals have very less tendency to form complex compounds.

9. **Flame Colouration:** When alkali metals and their salts are heated in the oxidizing flame of a Bunsen burner, they impart characteristic colours to the flame. This happens because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region as given below.

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Golden Yellow	Violet	Red violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

This particular property of alkali metals is helpful in detecting them by respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy.

10. **Photoelectric Effect:** Alkali metals (except Li) exhibit photoelectric effect (a phenomenon of emission of electrons from surface by exposing it to visible light). These elements when irradiated with light, the light energy absorbed may be sufficient to make an atom lose electron. This property makes caesium and potassium useful as electrodes in photoelectric cells.

Table: Atomic and Physical Properties of the Alkali Metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	$[\text{He}] 2\text{s}^1$	$[\text{Ne}] 3\text{s}^1$	$[\text{Ar}] 4\text{s}^1$	$[\text{Kr}] 5\text{s}^1$	$[\text{Xe}] 6\text{s}^1$	$[\text{Rn}] 7\text{s}^1$
Ionization enthalpy/kJ mol ⁻¹	520	496	419	403	376	~375
Hydration enthalpy/kJ mol ⁻¹	-506	-406	-330	-310	-276	—
Metallic radius / pm	152	186	227	248	265	—
Ionic radius M^+ / pm	76	102	138	152	167	(180)
m.p. / K	454	371	336	312	302	—
b.p/K	1615	1156	1032	961	944	—
Density/g cm ⁻³	0.53	0.97	0.86	1.53	1.90	—
Standard potentials $E^\circ / \text{V for } (\text{M}^+/\text{M})$	-3.04	-2.714	-2.925	-2.930	-2.927	—
Occurrence in lithosphere*	18*	2.27**	1.84**	78-12*	2-6*	$\sim 10^{-18}* \text{}$

* ppm(part per million), ** percentage by weight; Lithosphere : The Earth's outer layer: its crust and part of the upper mantle





Train Your Brain

Example 1: Why the alkali metals are never found in free state in nature?

Sol. The alkali metals readily lose electron to give monovalent M^+ ions, hence they are highly reactive and therefore they are never found in free state in nature.

Example 2: Among the following which element is the rarest of all?

- (a) Na
- (b) Fr
- (c) Cs
- (d) K

Sol. (b) Fr is radioactive and less abundant therefore rarest of all.

Example 3: What is the correct order of density?

- (a) Li > Na > K
- (b) Na > K > Li
- (c) K > Na > Li
- (d) Na = K > Li

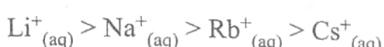
Sol. (b) Density of K is less than Na due to presence of vacant d-orbitals.

Example 4: The ionic radii of alkali metal ions in water (hydrated radii) are in the order:

- (a) $Li^+ > Na^+ > K^+ > Rb^+ < Cs^+$
- (b) $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
- (c) $Li^+ < Na^+ > K^+ > Rb^+ > Cs^+$
- (d) $Li^+ > Na^+ < K^+ < Rb^+ < Cs^+$

Sol. (b) Hydrated radii $\propto \frac{\text{Charge}}{\text{Ionic radii}}$

Therefore, order of hydrated radii is:



- (a) Violet, red violet, golden yellow and crimson red, respectively.
- (b) Red violet, violet, golden yellow and crimson red, respectively.
- (c) Crimson red, golden yellow, violet and red violet lilac, respectively.
- (d) Crimson red, golden yellow, lilac and red violet, respectively.

3. Which of the following increases in magnitude as the atomic number of alkali metals increases?

- (a) Electronegativity
- (b) First ionisation potential
- (c) Ionic radius
- (d) Melting point

4. In view of their ionisation energies, the alkali metals are:

- (a) Weak oxidising agents
- (b) Strong reducing agents
- (c) Strong oxidising agents
- (d) Weak reducing agents

CHEMICAL PROPERTIES

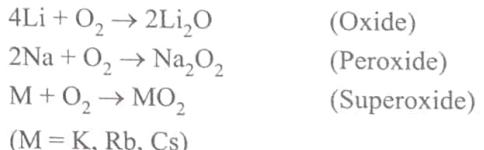
The alkali metals are highly reactive elements. The cause for their high chemical reactivity is:

1. Low value of first ionisation enthalpy
2. Large size
3. Low heat of atomisation

The reactivity of these metals increases down the group.

(i) **Reactivity towards air:** You might have seen that alkali metals tarnish in dry air because of formation of their oxides and when these oxides react with moisture they form hydroxides.

Alkali metals burn very fast in oxygen and form different kind of oxides like monoxides, peroxides and superoxides. Lithium forms monoxide, sodium forms peroxide and other metals form superoxides. The superoxide O_2^- ion generally remains stable only in the presence of large cations like K, Rb, Cs. This stability is related to the compatibility of size and higher lattice energy.



- In all compounds formed by alkali metals with oxygen, their oxidation state is +1.
- The temperature required for the reaction to take place decreases on descending the group.
- The stability of peroxide or superoxide increases as the size of the alkali metal increases. This is due to stabilization of large anions by large cations through lattice energy effects.



Concept Application

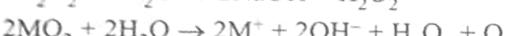
1. The elements of group 1 are called alkali metals because:
 - (a) Their oxides form acidic solutions on treating with water.
 - (b) Their peroxides form alkaline solution on treating with water.
 - (c) Their oxides and hydroxides form alkaline solutions on treating with water.
 - (d) Their hydroxides form acidic solution on treating with water.
2. The metals Li, Na, K and Rb and their salts when introduced into flame give the following characteristic colour to flame:



- The oxides and peroxides are colourless when pure but superoxides are yellow or orange in colour, peroxides are diamagnetic whereas superoxide are paramagnetic in nature.
- The normal oxides of alkali metals dissolve readily in water to form hydroxides and a large amount of heat is produced.



The peroxides and superoxides are also readily hydrolysed by water as shown below:



The higher oxides generally act as good oxidising agent, sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

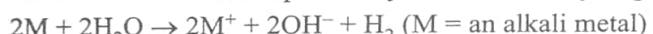
- The hydroxides which are obtained by reaction of the oxides with water are white crystalline solids. The hydroxides of alkali metals are strong bases. The basic character of alkali metal hydroxides increases in going down the group.



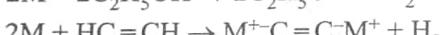
Alkali metal hydroxides are freely soluble in water and their dissolution in water is accompanied by evolution of much heat due to intense hydration.

Note: Alkali metals are generally kept immersed in kerosene oil because they are highly reactive towards air and water but due to less density, Li is kept wrapped in paraffin wax.

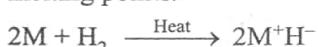
- (ii) **Reactivity towards water:** The alkali metals on reaction with water form their respective hydroxide and dihydrogen.



They also react with proton donors or acidic hydrogen such as alcohol, gaseous ammonia, hydrogen halide and alkynes.

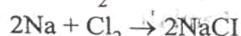
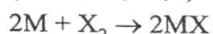


- (iii) **Reactivity towards dihydrogen:** Alkali metals react with dry dihydrogen at about 673 K (lithium at 1073 K) to form crystalline hydrides which are ionic in nature and have high melting points.



- (iv) **Reactivity towards halogens:** The alkali metals combine with halogens to form metal halides, which are ionic, colourless, crystalline solids having high melting point and general formula, MX.

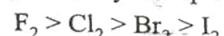
(X = F, Cl, Br, I)



Reactivity with particular halogen:



Reactivity with particular alkali metal, M:



The alkali metal halides can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX).

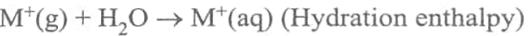
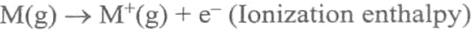
- All of these halides have high negative enthalpies of formation, the $\Delta_f H^\circ$ value for fluorides become less negative as we go down the group, while the reverse is true for $\Delta_f H^\circ$ for chlorides, bromides and iodides.
- For a given metal, $\Delta_f H^\circ$ always becomes less negative from fluoride to iodide. The melting and boiling points always follow the trend:



- All halides of the alkali metals except lithium fluoride (LiF) are freely soluble in water. The low solubility of lithium fluoride is attributed to greater force of attraction between lithium ions and fluoride ions in the crystal lattice or high lattice enthalpy.
- Caesium iodide (CsI) also has relatively low solubility in water. This is attributed to smaller hydration energy of its large sized ions.
- LiCl, LiBr and LiI are soluble in ethanol, acetone and other solvents of low polarity. This is due to predominant covalent character of these halides. The predominant covalent character of lithium halides is due to greater polarizing power of Li^+ ion.

Among lithium halides, LiI has maximum covalent character due to large polarizability of iodide ion. LiCl is soluble in pyridine also.

- (v) **Reducing Nature:** The alkali metals have strong tendency to get oxidised that is why they act as strong reducing agents, among these lithium is the strongest and sodium is the least powerful reducing agent. The standard electrode potential (E°) measures the reducing power and represents the changes:



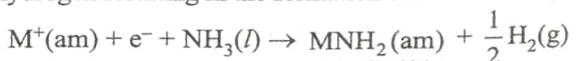
- Since lithium ion has small size, it has the highest hydration enthalpy which gives an explanation for its high negative E° value and its high reducing power.

- Higher the negative value of E° , more reducing will be the ionic species.

- (vi) **Solutions in liquid ammonia:** All alkali metals dissolve in liquid ammonia and give deep blue colour solution which are conducting in nature. These solutions contain ammoniated cations and ammoniated electrons as shown below:



- The blue colour of the solution is considered to be due to ammoniated electrons which absorb energy corresponding to red region of visible light for their excitation to higher energy levels. The transmitted light thus imparts blue colour to the solution. The electrical conductivity of the solution is due to both ammoniated cations and ammoniated electrons. The blue solution on standing slowly liberates hydrogen resulting in the formation of amide.



(where 'am' denotes solution in ammonia).

ANOMALOUS PROPERTIES OF LITHIUM

Lithium shows properties which are very different from the other members of its group. This is due to: (i) exceptionally small size of its atom and ion and (ii) greater polarizing power of lithium ion (i.e., high charge/radius ratio). Due to these factors, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

Points of difference between Lithium and other Alkali Metals:

- (i) As compared to other alkali metals, lithium is harder and its melting point and boiling point are higher.
- (ii) Among all the alkali metals, lithium is least reactive but the strongest reducing agent. When burnt in air it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.
- (iii) LiCl is deliquescent and crystallises as a hydrate, $\text{LiCl} \cdot 2\text{H}_2\text{O}$ whereas other alkali metal chlorides do not form hydrates.
- (iv) Except for lithium, rest of alkali metal's hydrogencarbonates are obtained in the solid form.
- (v) Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.
- (vi) Lithium nitrate when heated gives lithium oxide, Li_2O whereas other alkali metal nitrates decompose to give the corresponding nitrite.



- (vii) LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

Points of similarities between Lithium and Magnesium

The similarities between lithium and magnesium are because of their similar sizes, comparable atomic radii and electronegativities.

$$\text{Li} = 152 \text{ pm} \quad \text{Li}^+ = 76 \text{ pm}$$

$$\text{Mg} = 160 \text{ pm} \quad \text{Mg}^{2+} = 72 \text{ pm}$$

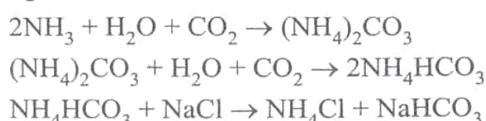
The major similarities are

- (i) Both lithium and magnesium are harder and lighter than other elements of their respective groups.
- (ii) Both lithium and magnesium react slowly with water. Their oxides and hydroxides are less soluble and their hydroxides decompose on heating. Both lithium and magnesium form nitride, Li_3N and Mg_3N_2 by direct combination with nitrogen.
- (iii) Their oxides like Li_2O and MgO do not combine with excess oxygen to give their superoxide.
- (iv) The carbonates of both decompose easily on heating to form oxides and CO_2 and do not form solid hydrogencarbonates.
- (v) Both LiCl and MgCl_2 are soluble in ethanol, are deliquescent and crystallise from aqueous solution as hydrates, $\text{LiCl} \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

SOME IMPORTANT COMPOUNDS OF SODIUM

Sodium Carbonate (Washing Soda), $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

It is prepared by **Solvay process** which exploits the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate. The ammonium hydrogencarbonate is prepared by passing CO_2 to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogencarbonate are formed.



Sodium hydrogencarbonate crystals separate. These are heated to give sodium carbonate.



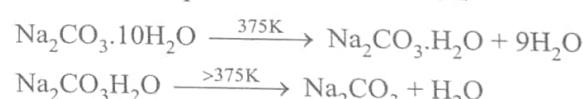
When solution having NH_4Cl is treated with $\text{Ca}(\text{OH})_2$, NH_3 is produced and recovered and CaCl_2 is obtained as a by-product.



Potassium carbonate cannot be manufactured by solvay process because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

Properties of Sodium Carbonate

Sodium carbonate is a white coloured, crystalline solid which is found as a decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. This is also called as washing soda. It is easily soluble in water. When heated, decahydrate loses its water of crystallisation and forms monohydrate. Above 375 K, the monohydrate becomes completely anhydrous and changes to a white powder called **soda ash**.



Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.



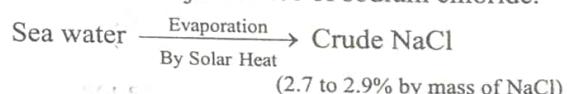
Uses of Sodium Carbonate

- (i) It is used for softening hard water, for washing purposes in laundry and cleaning.
- (ii) It is used in the manufacture of glass, soap, borax and caustic soda.
- (iii) It is used in paper, paints and textile industries.
- (iv) It is an important laboratory reagent both in qualitative and quantitative analysis.
- (v) For making fusion mixture i.e. $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$.

Sodium Chloride, NaCl

Preparation:

Sea water is the major source of sodium chloride.



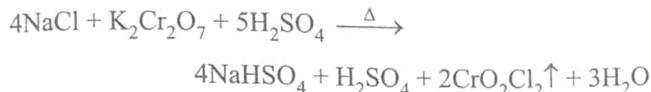
- (i) It contains impurities of Na_2SO_4 , MgCl_2 , CaCl_2 etc.
- (ii) Insoluble impurities are removed by filtration.
- (iii) Filtrate $\xrightarrow{\text{HCl gas passed}}$ Pure NaCl (ppt)

Then HCl gas is passed through the solution to get saturated solution, due to common ion effect, the crystals of pure NaCl separate out.

- (iv) MgCl_2 and CaCl_2 being more soluble remain in the solution.

Properties

- (i) FCC structure of solid.
- (ii) Its solubility in water is 36 g in 100 g of water at 0°C .
- (iii) Pure sodium chloride is non-hygroscopic but due to the impurities of CaCl_2 and MgCl_2 it behaves as hygroscopic.
- (iv) Reaction with $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ (conc.)

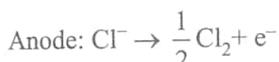
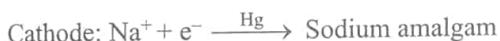


Uses of Sodium Chloride

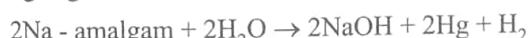
- (i) It is an essential constituent of our food. It is used as common salt or table salt for domestic purposes.
- (ii) It is used for the preparation of Na_2O_2 , NaOH and Na_2CO_3 .
- (iii) It is used in freezing mixture.

Sodium Hydroxide (Caustic Soda), NaOH

Sodium hydroxide is manufactured by the electrolysis of sodium chloride solution (brine) in a specially designed cell called **Castner-Kellner cell**. A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.

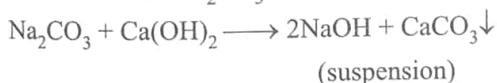


The amalgam is treated with water to give sodium hydroxide and hydrogen gas.



(Gossage's method)

Caustication of Na_2CO_3



Since the $K_{\text{sp}}(\text{CaCO}_3) < K_{\text{sp}}(\text{Ca}(\text{OH})_2)$, the reaction shifts towards right.

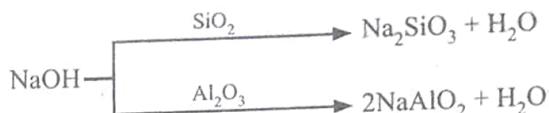
Properties of sodium hydroxide

Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. On prolonged exposure, CO_2 is absorbed resulting in the formation of a layer

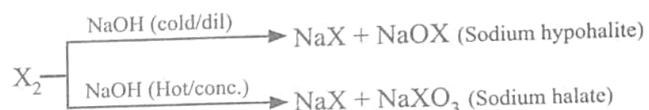
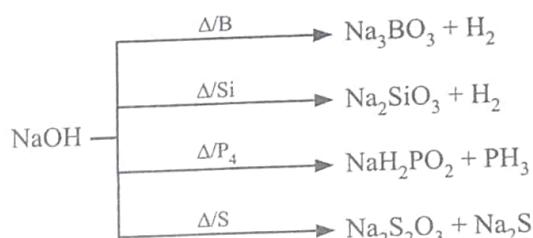
of Na_2CO_3 at the surface. It is highly soluble in water and the solution has a very corrosive action on animal tissue.

Reactions of NaOH

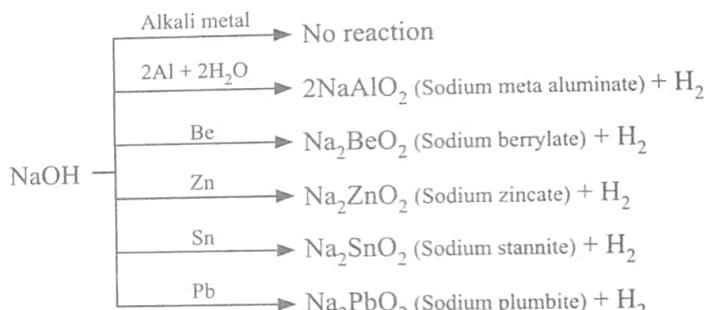
- (i) NaOH is a strong base.



- (ii) Reaction with non metals: No reaction with H_2 , N_2 and C.



- (iii) Reaction with metal:



Uses of Sodium Hydroxide

- (i) It is used in the manufacture of paper, soap and artificial silk.
- (ii) It is used for petroleum refining.
- (iii) It is used for mercerizing cotton fabrics.
- (iv) It is used in purification of bauxite.
- (v) It is used for the preparation of pure fats and oils.
- (vi) It is used as a laboratory reagent.

Sodium Hydrogen Carbonate (Baking Soda), NaHCO_3

Sodium hydrogencarbonate is obtained as an intermediate product in **Solvay's process** for the manufacture of sodium carbonate. It can also be made by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium hydrogencarbonate being less soluble gets separated out.



Uses of Sodium Hydrogen Carbonate

- (i) It is used as a component of baking powder.
- (ii) It is used in fire extinguishers.
- (iii) It is used in medicines. It acts as a mild antiseptic for skin infections and also used as an antacid.

BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals. They also regulate flow of water across cell membranes and in transport of sugars and amino acids into the cells.

Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP (adenosine triphosphate), potassium ions in combination with sodium ions are responsible for transmission of nerve signals.

There is a considerable variation in the concentrations of Na^+ and K^+ ions found on the opposite sides of cell membranes. The functional features of nerve cells depend upon the sodium-potassium ion gradient that is established on the cell. These ionic gradients are maintained by sodium-potassium pumps that operate across the cell membranes. As a typical example, in blood plasma, sodium is present to the extent of 143 mmol L^{-1} whereas the potassium level is only 5 mmol L^{-1} within the red blood cells. These concentration change to 10 mmol L^{-1} (Na^+) and 105 mmol L^{-1} (K^+). Sodium-potassium pump consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

A typical 70 kg man contains about 90 g of Na and 170 g of K, compared with only 5 g of iron and 0.06 g of copper.

Uses of Alkali Metals

1. Lithium is used as a metal in a number of alloys. Its alloy with magnesium containing about 14% lithium is extremely tough and corrosion resistant which is used for armour plate and aerospace components.
 2. Lithium hydroxide is used in the ventilation systems of space crafts and submarines to absorb carbon dioxide.
 3. Lithium aluminium hydride (LiAlH_4) is a powerful reducing agent which is commonly used in organic synthesis.
 4. Liquid sodium or its alloy with potassium is used as a coolant in nuclear reactors.
 5. Sodium-lead alloy is used for the preparation of tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$, which is used as an antiknocking agent in petrol.
$$(\text{Pb} + 4\text{Na}) + 4\text{C}_2\text{H}_5\text{Cl} \rightarrow (\text{C}_2\text{H}_5)_4\text{Pb} + 4\text{NaCl}$$
Lead-sodium alloy : tetraethyl lead
 6. Sodium is used in the production of sodium vapour lamps.
 7. Potassium chloride is used as fertilizer.
 8. Potassium hydroxide is used in the manufacture of soft soaps and also as an absorbent of carbon dioxide.
 9. Potassium ions play a vital role in biological systems.
 10. Caesium is used in photoelectric cells.



Train Your Brain

Example 9: An aqueous solution of soda lime is

(d) Initially acidic changes to alkaline after some time.

Sol. (b) Soda lime is mixture of NaOH and CaO, both are basic in nature.

Example 10: The aqueous solution of baking soda is

Sol. (b) $\text{NaHCO}_3 \xrightarrow{\text{H}_2\text{O}} \text{NaOH} + \text{H}_2\text{O} + \text{CO}_2$

Example 11: Washing soda is manufactured by

- (a) Denni's process (b) Hall's process
 (c) Castener's process (d) Solvay's process

Sol. (d) It is prepared by Solvay's process which exploits the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate.

Example 12: The reaction that is least feasible is:

- (a) $\text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2$
 (b) $4\text{Li} + \text{O}_2 \rightarrow 2\text{Li}_2\text{O}$
 (c) $6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N}$
 (d) $2\text{C}_6\text{H}_5\text{C}\equiv\text{CH} + 2\text{Li} \rightarrow 2\text{C}_6\text{H}_5\text{C}\equiv\text{CLi} + \text{H}_2$

Sol. (d)



Concept Application

9. On commercial scale, sodium hydroxide is prepared by
(a) Dow's process (b) Solvay process
(c) Castner-Kellner cell (d) Hall-Heroult process

10. Fire extinguisher contains H_2SO_4 and
(a) Na_2CO_3 (b) NaHCO_3 solution
(c) NaHCO_3 and Na_2CO_3 (d) CaCO_3

11. Sodium carbonate on heating gives
(a) CO_2
(b) Water vapours
(c) Carbon dioxide + Water vapour
(d) None of these

12. K^+ ions are essential for
(a) Metabolism of glucose inside the cell.
(b) The synthesis of proteins.
(c) Activation of certain enzymes.
(d) All of the above

Group-2 Elements: Alkaline Earth Metals

The elements of group-2 are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). Except Be, rest are known as alkaline earth metal, because these are alkaline in nature and exist in the earth's crust.

Beryllium is not considered alkaline earth metal because its

oxide i.e., BeO is amphoteric in nature, which can be explained by its reaction with acids as well as alkalis.



Sodium beryllate

Table: Atomic and Physical Properties of the Alkaline Earth Metals

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	$[\text{He}] 2s^2$	$[\text{Ne}] 3s^2$	$[\text{Ar}] 4s^2$	$[\text{Kr}] 5s^2$	$[\text{Xe}] 6s^2$	$[\text{Rn}] 7s^2$
Ionization enthalpy (I)/kJ mol ⁻¹	899	737	590	549	503	509
Ionization enthalpy (II)/kJ mol ⁻¹	1757	1450	1145	1064	965	979
Hydration enthalpy (kJ mol)	-2494	-1921	-1577	-1443	-1305	—
Metallic Radius / pm	111	160	197	215	222	—
Ionic radius M^{2+} / pm	31	72	100	118	135	148
m.p. / K	1560	924	1124	1062	1002	973
b.p / K	2745	1363	1767	1655	2078	(1973)
Density / g cm ⁻³	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potentials E'/V for (M^{2+} / M)	-1.97	-2.36	-2.84	-2.89	-2.92	-2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390*	$10^{-6}*_{\text{pm}}$

*ppm (parts per million); ** percentage by weight

- Electronic Configuration:** The alkaline earth metals have 2 electrons in the s-orbital of the valence shell. Their general electronic configuration may be represented as [Noble gas] ns^2 ; where n = 2 to 7

Element	Symbol	Electronic Configuration
Beryllium	Be	$[\text{He}] 2s^2$
Magnesium	Mg	$[\text{Ne}] 3s^2$
Calcium	Ca	$[\text{Ar}] 4s^2$
Strontium	Sr	$[\text{Kr}] 5s^2$
Barium	Ba	$[\text{Xe}] 6s^2$
Radium	Ra	$[\text{Rn}] 7s^2$

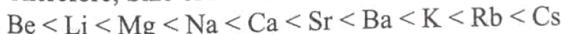
2. Atomic and Ionic Radii

- These are smaller than IA group elements, since extra charge on nucleus attracts the electron cloud. Order of atomic radii is:



- In s-block elements, Be is the smallest while Cs is the biggest.

Therefore, Size order is:



- Ionization Enthalpies:** The first ionisation enthalpies of the alkaline earth metals are higher than those of the

corresponding group 1 metals due to stable, fully filled s² configuration. Order of ionisation energy is:



- Hydration Enthalpies:** The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Therefore, compounds of alkaline earth metals are more extensively hydrated, for example, magnesium chloride and calcium chloride exist as hexahydrates ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) whereas sodium chloride and potassium chloride do not form such hydrates. Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.



- Physical Properties:** The alkaline earth metals are silvery white, lustrous and relatively soft but harder than the alkali metals.

Beryllium and magnesium appear to be somewhat greyish. The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes, but this trend is not systematic because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba.

6. Flame Test:

- + Be and Mg atoms due to small size bind their electrons more strongly, so are not excited to higher level, hence do not give flame test.
- + Other elements that give characteristic colour to flame are:
Ca - Brick red
Sr - Dark red (Crimson red)
Ba - Green (Apple green)

7. Photo-Electric Effect: These elements do not show this property as their atomic size is small hence ionisation potential is higher than IA group.

8. Standard Oxidation Potential:

- + They have lower values of standard oxidation potential due to their small size.
- + Increasing order of standard oxidation potential is
 $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$
- + Tendency of loosing electron increases down the group.
Hydration energy \propto Charge density on ion

9. Complex Formation Tendency: Less tendency to form complex compounds, but due to small size of cations, Be and Mg form complex compounds like $[\text{BeF}_4]^{2-}$, $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$, Mg – Chlorophyll.



Concept Application

13. Which of the following statement is incorrect?
 - (a) The atomic radius of Na is greater than that of Mg.
 - (b) Metallic bond in Mg is stronger than the metallic bond in Na.
 - (c) Melting and boiling points of Mg are greater than those of Ca.
 - (d) Mg and Ca both impart characteristic colour to the flame.
14. Among the alkaline earth metals, the element forming predominantly covalent compounds is
 - (a) Ba
 - (b) Sr
 - (c) Ca
 - (d) Be
15. From Be to Ba, electropositive or metallic character
 - (a) Increases
 - (b) Decreases
 - (c) Remains same
 - (d) Cannot be predicted
16. Which of the following has maximum ionisation energy?
 - (a) $\text{Ba} \rightarrow \text{Ba}^{2+} + 2e^-$
 - (b) $\text{Be} \rightarrow \text{Be}^+ + e^-$
 - (c) $\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$
 - (d) $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$

Chemical Properties

(i) Reaction with air

- (a) Except Be and Mg, these metals are easily tarnished in air, as a layer of oxide is formed on the surface.
- (b) Barium in powdered form, burst into flame on exposure to air.
- (c) In moist air, except Be, all the elements convert into carbonates.
- (d) In dry air both Be and Mg give nitride and oxide while others give only oxides.

(ii) Reaction with oxygen

- (a) Alkaline earth metals react with O_2 to form 'MO' type oxides. ($M = \text{Be}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$)
- (b) But Ca, Sr and Ba due to low ionisation potential and more reactivity form MO_2 (peroxides) at low temperature. Ex: CaO_2 , SrO_2 , BaO_2
- (c) BeO shows amphoteric property.
 $\text{MgO} \rightarrow$ weak base
 $\text{CaO}, \text{SrO} \& \text{BaO} \rightarrow$ Strong base
- (d) Basic property increases from Be to Ba.

(iii) Reaction with hydrogen

- (a) Except Be, all the alkaline earth metals form MH_2 type hydrides (MgH_2 , CaH_2 , SrH_2 , BaH_2) on heating directly with H_2 .
- (b) BeH_2 is prepared by action of BeCl_2 with LiAlH_4 .
$$2\text{BeCl}_2 + \text{LiAlH}_4 \rightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$$
- (c) BeH_2 and MgH_2 are covalent, others are ionic.
- (d) Be and Mg hydride have tendency of polymerisation.



Train Your Brain

Example 13: The crimson colour imparted to flame is due to salt of

- (a) Barium
- (b) Copper
- (c) Calcium
- (d) Strontium

Sol. (d) Strontium element gives crimson colour in flame test. It is due to the excitation of electron by thermal energy, which is then followed by de-excitation of electron to ground state along with liberation of light in the visible region.

Example 14: The IIA group metal ion having $6s^2 6p^6$ as outer electron configuration is:

- (a) Ca^{2+}
- (b) Sr^{2+}
- (c) Ba^{2+}
- (d) Ra^{2+}

Sol. (d) It is noble gas electronic configuration. Electronic configuration of Ra is $[\text{Rn}]7s^2$. After loss of two electrons it shows same electronic configuration as Rn.

Example 15: The most abundant element among the following is

- (a) Mg
- (b) Ca
- (c) Sr
- (d) Ra

Sol. (b) The order of abundance (% by weight) is:

$$\text{Ca} > \text{Mg} > \text{Ba} > \text{Sr} > \text{Be}$$

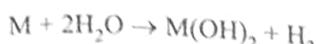
Example 16: Alkaline earth metal salts are:

- (a) Paramagnetic
- (b) Diamagnetic
- (c) Ferromagnetic
- (d) All of the above

Sol. (b) In Alkaline earth metal salts, metal is present in M^{2+} form which relates to the noble gas electronic configuration. Thus, these are diamagnetic.

(iv) Reaction with water

- (a) These metals react slowly with water to give H₂ and metal hydroxides.



- (b) Be does not react with water.

- (c) Mg reacts only with hot water.

- (d) Ca, Sr, Ba react with cold water but not as energetically as alkali metals.

Order of reactivity: Ba > Sr > Ca > Mg > Be

- (e) From Be(OH)₂ to Ba(OH)₂, basic property and stability increases.

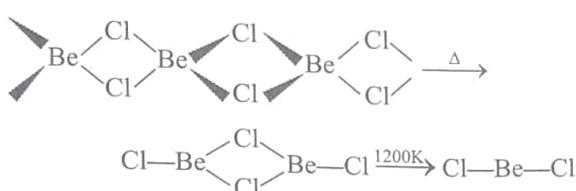
(v) Reaction with Halogens

- (a) Alkaline earth metals react with X₂ (Halogen) to form MX₂. Ex; BeCl₂, MgCl₂, CaCl₂, etc.

- (b) Ionic nature of MX₂ increases from BeCl₂ to BaCl₂.

- (c) Ba burns in contact with Cl₂.

- (d) Beryllium forms covalent halides, all other members forms ionic halides. Beryllium halides are soluble in organic solvents. Beryllium chloride has a chain structure.



BeCl₂ in vapour phase forms a chloro-bridged dimer which at high temperature of the order of 1200 K dissociates into linear monomer.

The tendency to form halide hydrates gradually decreases (for example, MgCl₂.8H₂O, CaCl₂.6H₂O, SrCl₂.6H₂O and BaCl₂.2H₂O) down the group. The hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be dehydrated by heating but the corresponding hydrated halides of Be and Mg on heating undergo hydrolysis.

The fluorides of alkaline earth metals are less soluble than chlorides due to their high lattice energies.

- (e) BeCl₂ and MgCl₂ are covalent in nature.

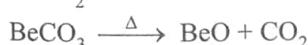
Order of ionic nature is:



(vi) Carbonates

- (a) All the alkaline metals form MCO₃ type carbonates.

- (b) Except BeCO₃, all the carbonates are stable towards heat. Therefore, BeCO₃ is kept stored in atmosphere of CO₂.



- (c) Order of stability:



(vii) Nitrates

- (a) Alkaline earth metals forms M(NO₃)₂ type nitrates. (M-Alkaline earth metals).

- (b) Stability increases from Be(NO₃)₂ to Ba(NO₃)₂ but these are less stable than IA group, due to smaller atomic size.

- (c) All alkaline metal nitrates on heating give metal oxides and NO₂ + O₂.



- (d) Be(NO₃)₂ forms a layer of BeO on its surface so reaction stops.

(viii) Nitrides

- (a) Only Be and Mg burns in N₂ to give M₃N₂ (Be₃N₂, Mg₃N₂)



(ix) Sulphates

- (a) Alkaline earth metals form MSO₄ type sulphates.

- (b) Ionic nature of alkaline earth metal sulphates increases from Be to Ba.



- (c) Solubility decreases from BeSO₄ to BaSO₄. As Be²⁺ and Mg²⁺ are of small size, their hydration energy is high.

Hydration Energy > Lattice energy

- (d) Order of solubility:



- (e) Order of thermal stability:



As Ionic nature increases, thermal stability increases.

ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium shows different behaviour from the rest members of its group and shows diagonal relationship to aluminium due to reasons discussed below:

- (i) Beryllium has exceptionally small atomic and ionic size and therefore does not compare well with other members of the group. Because of high ionisation enthalpy and small size, it forms compounds which are largely covalent and get easily hydrolysed.

- (ii) Beryllium does not exhibit coordination number more than four as in its valence shell, there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of d-orbitals.

- (iii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

Diagonal Relationship between Beryllium and Aluminium

The ionic radius of Be^{2+} is approximately 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Similarities between Al and Be are given below:

- Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
- Beryllium hydroxide dissolves in excess of alkali to give beryllate ions, $[\text{Be}(\text{OH})_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[\text{Al}(\text{OH})_4]^-$.
- The chlorides of both beryllium and aluminium have Cl^- bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong lewis acids. They are used as Friedel Crafts catalysts.
- Beryllium and aluminium ions have strong tendency to form complexes, $[\text{BeF}_4]^{2-}$, $[\text{AlF}_6]^{3-}$.



Train Your Brain

Example 17: Halides of Be dissolve in organic solvent while that of Ba do not. This is due to

- High hydration energy of Be halides.
- High lattice energy of barium halides.
- Large size of Ba^{2+} .
- Halides of Be are covalent but that of Ba are ionic.

Sol. (d) Halides of Be are covalent but that of Ba are ionic. Like dissolves like, therefore covalent halide of Be dissolve in organic solvent while ionic halide of Ba dissolve in water.

Example 18: The ratio of moles of water as water of crystallisation in LiCl and BaCl_2 is:

- | | |
|---------|---------|
| (a) 1:1 | (b) 1:2 |
| (c) 1:4 | (d) 1:3 |

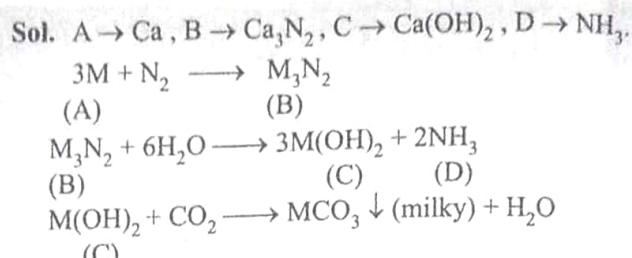
Sol. (a) $\text{LiCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, have water of crystallisation in 1:1 ratio.

Example 19: Which of the following statement is not correct?

- KOH is a stronger alkali than NaOH.
- Milk of magnesia is aqueous suspension of $\text{Mg}(\text{OH})_2$.
- MgO is a refractory material used for lining electrical furnaces.
- $\text{Mg}(\text{OH})_2$ precipitates on heating hydrated MgCl_2 .

Sol. (d) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta} \text{Mg}(\text{OH})\text{Cl} \xrightarrow{\Delta} \text{MgO}$

Example 20: Element (A) burns in nitrogen to give an ionic compound B. Compound B reacts with water to give (C) and (D). A solution of (C) becomes milky on bubbling CO_2 . The chloride of element (A) imparts brick red colour to Bunsen flame. Identify (A) to (D).



As the colour of the flame is brick red, metal (A) can be Ca.



Concept Application

- The hybridisation of BeCl_2 in solid state and above 1200 K, respectively is:

(a) sp^3 , sp^3	(b) sp^3 , sp^2
(c) sp^2 , sp^2	(d) sp^3 , sp
- Which of the following is not correctly matched?
 - Basic strength of oxides
 $\text{Cs}_2\text{O} < \text{Rb}_2\text{O} < \text{K}_2\text{O} < \text{Na}_2\text{O} < \text{Li}_2\text{O}$
 - Stability of peroxides
 $\text{Na}_2\text{O}_2 < \text{K}_2\text{O}_2 < \text{Rb}_2\text{O}_2 < \text{Cs}_2\text{O}_2$
 - Stability of bicarbonates
 $\text{LiHCO}_3 < \text{NaHCO}_3 < \text{KHCO}_3 < \text{RbHCO}_3 < \text{CsHCO}_3$
 - Melting point
 $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$

(a) (i) and (iv)	(b) (i) and (iii)
(c) (i) and (ii)	(d) (ii) and (iii)
- Magnesium metal burns in air to give:

(a) MgO	(b) Mg_3N_2
(c) MgCO_3	(d) MgO and Mg_3N_2 both
- $\text{BeCl}_2 + \text{LiAlH}_4 \longrightarrow \text{X} + \text{LiCl} + \text{AlCl}_3$

(a) X is LiH	(b) X is BeH_2
(c) X is $\text{BeCl}_2 \cdot 2\text{H}_2\text{O}$	(d) None of these

SOME IMPORTANT COMPOUNDS OF CALCIUM

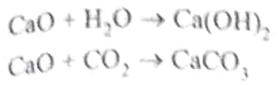
Calcium Oxide or Quick Lime (CaO)

It is prepared on a commercial scale by heating limestone (CaCO_3) in a rotatory kiln at 1070 - 1270 K.

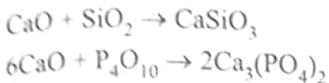


The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion.

Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.



When small amount of water is added to lime it breaks the lump, this process is called slaking of lime. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.



Uses of Calcium Oxide

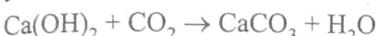
- (i) Calcium oxide is the cheapest form of alkali, it is also important primary material for manufacturing cement.
- (ii) It is used in the manufacture of sodium carbonate from caustic soda.
- (iii) It is used in the purification of sugar and in the manufacture of dye stuffs.

Calcium Hydroxide (Slaked Lime), $\text{Ca}(\text{OH})_2$

Calcium hydroxide is prepared by adding water to quick lime (CaO).

Calcium hydroxide is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as **lime water** and a suspension of slaked lime in water is known as **milk of lime**.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.



When excess of CO_2 is passed, the precipitate dissolves to form calcium hydrogencarbonate.



Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching power.

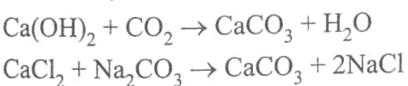


Uses of Calcium Hydroxide

- (i) It is used in preparation of building material called mortar.
- (ii) Due to its disinfectant nature, it is used in white wash.
- (iii) It is used in making glass, in tanning industry, for the preparation of bleaching powder and for the purification of sugar.

Calcium Carbonate, CaCO_3 (Lime Stone)

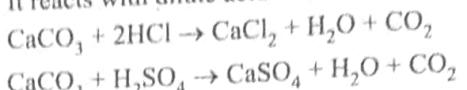
Calcium carbonate is found in various forms like limestone, chalk, marbles, etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.



In this preparation, excess of carbon dioxide is avoided because it will lead to the formation of water soluble calcium hydrogencarbonate. Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.



It reacts with dilute acid to liberate carbon dioxide.



Uses of Calcium Carbonate, CaCO_3

In the form of marble and in the manufacture of quick lime, it is used as a building material. It is used as flux in extraction of iron when mixed with magnesium. Specially precipitated CaCO_3 is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and as a filler in cosmetics.

Calcium Sulphate, (Plaster of Paris) $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is heated at 393 K.



Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, CaSO_4 is formed. This is known as '**dead burnt plaster**'.

It has a unique property of setting with water. On mixing with a sufficient quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

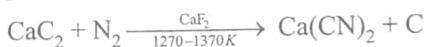
Uses of Plaster of Paris

Used in building industry and in plasters. It is used for immobilising the affected part of organ where there is a bone fracture or sprain. It is also used in dentistry, in ornamental work and for making casts of statues and busts.

Calcium Cyanamide, $\text{Ca}(\text{CN})_2$

Preparation

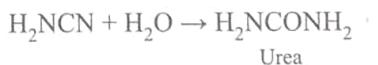
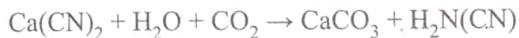
Calcium cyanamide, $\text{Ca}(\text{CN})_2$ is prepared by heating a mixture of CaC_2 in an atmosphere of N_2 at 1270–1370 K with CaF_2 .



Its trade name is Nitrolim.

Uses of Calcium Cyanamide

- ❖ Calcium cyanamide, $\text{Ca}(\text{CN})_2$ is a slow acting manure and is preferred to soluble compounds like NaNO_3 or $(\text{NH}_4)_2\text{SO}_4$ since it confers fertility of permanent nature. It is a nitrogenous fertiliser and undergoes a series of changes giving cyanamide, urea, NH_3 and finally the nitrates which are assimilable by plants.



Calcium Hydroxyapatite

Hydroxyapatite, $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{Ca}(\text{OH})_2$ is the main component of tooth enamel. Cavities are formed when acids decompose this enamel. This can be prevented by converting the hydroxyapatite to more resistant enamel-fluorapatite, $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaF}_2$.

Hydrolith

Hydrolith (CaH_2) is calcium hydride and on hydrolysis gives calcium hydroxide and liberates hydrogen.

Cement

Cement was first introduced in England in 1824 by Joseph Aspdin. It is also called Portland cement because it resembles with the natural limes tone quarried in the Isle of Portland, England.

Cement is obtained by combining CaO with clay, which contains silica, SiO₂, along with oxides of aluminium, iron and magnesium. The average composition of Portland cement is

CaO	→ 50 to 60%
SiO ₂	→ 20 - 25%
Al ₂ O ₃	→ 5 to 10%
MgO	→ 2 - 3%
Fe ₂ O ₃	→ 1 - 2%
SO ₃	→ 1 - 2%

For a good quality cement, the ratio of silica (SiO₂) to alumina (Al₂O₃) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO₂), aluminium (Al₂O₃) and iron (Fe₂O₃) should be close as possible to 2.

During manufacture of cement, clay and lime are strongly heated together, they fuse and react to form cement clinker. This clinker is mixed with 2-3% by weight of gypsum (CaSO₄.2H₂O) to form cement. Thus, important ingredient present in Portland cement are dicalcium silicate Ca₂SiO₄ (26%), tricalcium silicate Ca₃SiO₅ (51%) and tricalcium aluminate Ca₃Al₂O₆ (11%).

Setting of Cement: When mixed with water, the setting of cement takes place, which gives a hard mass. This is due to hydration of the molecules of the constituents and their rearrangement. The reason of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

Uses of Cement

- (i) It has become an important commodity next to iron and steel.
- (ii) It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200-300 mg.

All enzymes that use ATP in phosphate transfer require magnesium as the cofactor. The chlorophyll contains magnesium. About 99% of body calcium is present in bones and teeth.

It also plays important role in neuromuscular function, inter neuromal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated at about 100 mg L⁻¹. It is maintained by two hormones: calcitonin and parathyroid. Bone is continuously solubilised and redeposited to the extent of 400 mg per day in man.

Uses of Alkaline Earth Metals

- (i) Beryllium is used in the manufacture of alloys. Copper-Beryllium alloys are used in the making of high strength springs.

- (ii) Metallic beryllium is used for making windows of X-ray tubes.
- (iii) Magnesium, being a light metal, forms many light alloys with aluminum, zinc, manganese and tin.
- (iv) Magnesium (Powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals.
- (v) Magnesium-aluminium alloys are used in aircraft construction.
- (vi) Magnesium is used as sacrificial anode for the prevention of corrosion of iron.
- (vii) A suspension of magnesium hydroxide in water (called milk of magnesia) is used as an antacid to control excess acidity in stomach.
- (viii) Magnesium carbonate is an ingredient of toothpaste.
- (ix) Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon.
- (x) Calcium and barium metals are used to remove air from vacuum tubes due to their tendency to react with oxygen and nitrogen at high temperature.
- (xi) Radium salts are used for radio therapy of cancer.

Important Compounds and Their Formula

1.	Active nitrogen	N (Atomic nitrogen)
2.	Alums	M ₂ 'SO ₄ .M ₂ '''(SO ₄) ₃ .24H ₂ O M' = K ⁺ , NH ₄ ⁺ , Na ⁺ etc. M''' = Cr ³⁺ , Al ³⁺ , Fe ³⁺ etc.
3.	Asbestos	CaMg ₃ (SiO ₃) ₄
4.	Arsine	AsH ₃
5.	Aquaregia	Conc.HNO ₃ + Conc. HCl (1:3 part)
6.	Anhydrene	Mg(ClO ₄) ₂
7.	Argentoferrous galena	PbS + Ag ₂ S
8.	Borax	Na ₂ B ₄ O ₇ .10H ₂ O
9.	Blue vitriol	CuSO ₄ .5H ₂ O
10.	Barytes	BaSO ₄
11.	Baryta water	Ba(OH) ₂ solution
12.	Baryta	BaO
13.	Baking soda	NaHCO ₃
14.	Bleaching powder	CaOCl ₂
15.	Boranes	Hydride of borone
16.	Brine	NaCl solution
17.	Calgon	Na ₂ [Na ₄ (PO ₃) ₆]
18.	Coinage metals	Cu, Ag and Au
19.	Carborundum	SiC
20.	Cementite	FeC
21.	Caliche	NaNO ₃ + NaIO ₃

22.	Caustic soda	NaOH
23.	Caustic potash	KOH
24.	Calomel	Hg ₂ Cl ₂
25.	Corrosive sublimate	HgCl ₂
26.	Deuterium	² H or D
27.	D.D.T.	p-dichlorodiphenyltrichloroethane
28.	Dry ice	Solid CO ₂
29.	Freon	CF ₂ Cl ₂
30.	Ferric Alum	K ₂ SO ₄ .Fe ₂ (SO ₄) ₃ .24H ₂ O
31.	Fenton's reagent	H ₂ O ₂ + few drops of FeSO ₄
32.	Fusion mixutre	Na ₂ CO ₃ + K ₂ CO ₃
33.	Fluid magnesia	12% solution of Mg(OH) ₂
34.	Fehling solution	CuSO ₄ .5H ₂ O+NaOH+Na, K tartarate
35.	King of metals	Gold
36.	Horn Silver	AgCl
37.	Green vitriol	FeSO ₄ .7H ₂ O
38.	Graphite	An allotrope of carbon
39.	Gun powder	75% KNO ₃ + 12%S + 13% charcoal (explosive)
40.	Glauber salt	Na ₂ SO ₄ .10H ₂ O
41.	Hydrolith	CaH ₂
42.	Heavy water	D ₂ O
43.	Hypo (sodium thiosulphate)	Na ₂ S ₂ O ₃ .5H ₂ O
44.	Heavy hydrogen	D ₂
45.	King of chemicals	H ₂ SO ₄
46.	Lime (quick lime or burnt lime)	CaO
47.	Lead pencil	Graphite
48.	Lime water	Ca(OH) ₂
49.	Laughing gas	N ₂ O
50.	Lunar Caustic	AgNO ₃
51.	Litharge (Masscote)	PbO
52.	Lithopone	(ZnS + BaSO ₄), a pigment
53.	Mortar	Slaked lime + sand (1 : 3 in water)
54.	Mica	K ₂ O.Al ₂ O ₃ .6SiO ₂ .2H ₂ O
55.	Mohr salt	FeSO ₄ .(NH ₄) ₂ SO ₄ .6H ₂ O
56.	Matte	Cu ₂ S + FeS

57.	Milk of lime	Ca(OH) ₂ in water
58.	Minium	Pb ₃ O ₄
59.	Micro cosmic salt	NaNH ₄ .HPO ₄ .4H ₂ O (used in test of silicates)
60.	Milk of magnesia	Paste of Mg(OH) ₂ in water (Antacid)
61.	Magnesia	MgO
62.	Marsh gas	CH ₄
63.	Nitrolim	Ca(CN) ₂ + C (a fertilizer)
64.	Nascent Hydrogen	H at the moment of generation
65.	Nessler's reagent	(K ₂ HgI ₄ + KOH) aqueous solution
66.	Indian saltpetre, Bengal salt petre	KNO ₃
67.	Oil of vitriol	Conc.H ₂ SO ₄
68.	Ozone	O ₃
69.	Oleum	H ₂ S ₂ O ₇
70.	Permutit (Zeolite)	Na ₂ Al ₂ SiO ₈ .XH ₂ O
71.	Pearl ash (Potash)	K ₂ CO ₃
72.	Plaster of paris	CaSO ₄ .½ H ₂ O or 2CaSO ₄ .H ₂ O
73.	Philospher's wool	ZnO (Zinc white) (chinese white)
74.	Phosgene	COCl ₂
75.	Phosphine	PH ₃
76.	Pig iron	Impure form of iron
77.	Producer gas	A mixture of CO + N ₂ + H ₂
78.	Quartz	SiO ₂
79.	Refrigerant	CO ₂ , NH ₃ , CF ₂ Cl ₂ etc.
80.	Red lead	Pb ₃ O ₄
81.	Rochelle salt	Sodium - potassium tartarate
82.	Rust	Fe ₂ O ₃ .xH ₂ O
83.	Sorel's cement (Magnesia cement)	MgCl ₂ .5MgO.XH ₂ O
84.	Soda - lime	NaOH + CaO
85.	Soda ash	Na ₂ CO ₃ (anhydrous)
86.	Slaked lime	Ca(OH) ₂
87.	Stainless steel	An alloy of Fe, Cr and C
88.	Salt cake	Na ₂ SO ₄ (anhydrous)
89.	Super phosphate	Ca(H ₂ PO ₄) + 2CaSO ₄
90.	TNT	Trinitrotoluene (an explosive)
91.	TNB	Trinitrobenzene (an explosive)

92.	Tincal	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
93.	Talc	$3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ or $\text{Mg}_2(\text{Si}_2\text{O}_3)_2 \cdot \text{Mg}(\text{OH})_2$
94.	Tritium	${}^1\text{H}^3$ (an isotope of H)
95.	Water glass	Na_2SiO_3
96.	Water gas	$\text{CO} + \text{H}_2$
97.	White vitriol	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
98.	Wrought iron	Pure form of iron
99.	Washing soda	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
100.	Willemite\Zincite	ZnO
101.	Zinc white	ZnO
102.	Zinc blend	ZnS



Train Your Brain

Example 21: On heating gypsum above 393 K, the product formed is

- (a) $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (b) $\text{CaSO}_4 \cdot \text{H}_2\text{O}$
 (c) $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (d) Dead burnt plaster

Sol. (d) Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, CaSO_4 is formed. This is known as '**dead burnt plaster**'.

Example 22: Antacid formula is

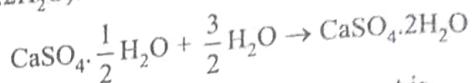
- (a) $\text{Ca}(\text{OH})_2$ (b) $\text{Mg}(\text{OH})_2$
 (c) $\text{Zn}(\text{OH})_2$ (d) $\text{Be}(\text{OH})_2$

Sol. (b) Most commercially available antacids are combinations of aluminum and magnesium hydroxide.

Example 23: Plaster of Paris in contact with water sets to a hard mass whose composition is

- (a) CaSO_4 (b) $\text{CaSO}_4 \cdot \text{H}_2\text{O}$
 (c) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (d) $\text{CaSO}_4 \cdot \text{Ca}(\text{OH})_2$

Sol. (c) When plaster of paris comes in contact with water it sets into a hard mass which is called gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).



Example 24: The role of gypsum in cement is

- (a) To increase setting time.
 (b) To increase porous nature.
 (c) To decrease setting time.
 (d) To decrease porous nature.

Sol. (a) Gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.



Concept Application

21. Portland cement is:

- (a) Calcium aluminium silicate
 (b) Alumina
 (c) Gypsum
 (d) Calcium carbonate

22. Identify the correct statement

- (a) Gypsum contains a lower percentage of calcium than plaster of paris.
 (b) Gypsum is obtained by heating plaster of paris.
 (c) Plaster of paris is obtained by hydration of gypsum.
 (d) Plaster of paris is obtained by partial oxidation of gypsum.

23. Hydrated calcium sulphate when heated at 120°C , loses:

- (a) $1/2\text{H}_2\text{O}$ (b) H_2O
 (c) $3/2\text{H}_2\text{O}$ (d) $2\text{H}_2\text{O}$

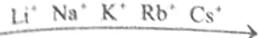
24. The ATP forms a complex with:

- (a) Mg^{2+} (b) Ca^{2+}
 (c) Be^{2+} (d) Ba^{2+}

Short Notes

General properties of alkali metals

- General electronic configuration is [Noble gas]ns¹; n = 2 to 7



- On moving down the group:

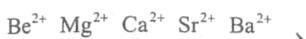
- Degree of hydration decreases.
- Hydration energy decreases.
- Hydrated ion size decreases.
- Ionic conductance increases.

- On dissolving Metal in NH₃

- $\text{M(s)} \xrightarrow{\text{NH}_3} \text{M}^+ + \text{e}^-$
- $\text{M}^+ + x(\text{NH}_3) \rightarrow [\text{M}(\text{NH}_3)_x]^+$ Ammoniated cation
- $\text{e}^- + y(\text{NH}_3) \rightarrow [\text{e}(\text{NH}_3)_y]^-$ Ammoniated electron
- The blue colour is due to → Ammoniated electron
- The paramagnetic nature is due to → Ammoniated electron
- The conducting nature is due to M⁺ + Ammoniated electron

General properties of alkaline earth metals

- General electronic configuration is [Noble gas]ns²; n = 2 to 7

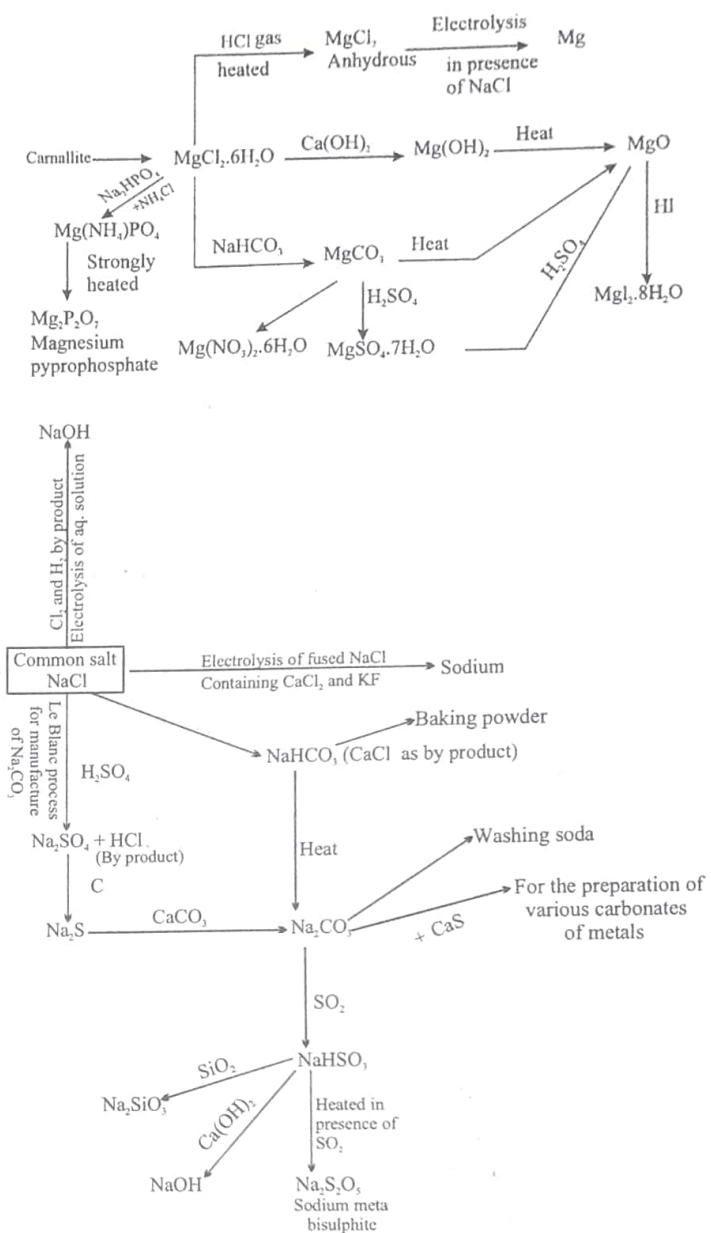
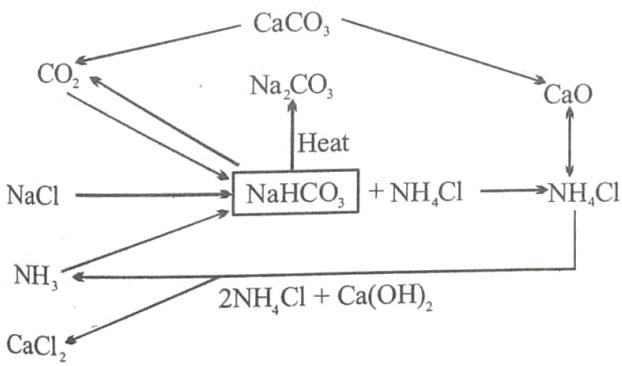


- On moving down the group:

- Atomic radii increases.
- Degree of hydration decreases.
- Hydration energy decreases.
- Hydrated ion size decreases.
- Ionic conductance increases.

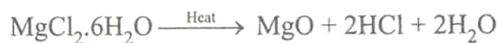
Important compounds of s-block elements

Flow Sheet of Solvay Process



Chlorides of Alkaline Earth Metal

- BeCl₂ in the vapour phase above 900°C is monomeric, below 900°C exists as dimer and in the solid state exists as a polymeric chain structure. When dissolved in a coordinating solvent it exists as a monomer.
- Anhydrous MgCl₂ cannot be prepared by simple heating of hydrated magnesium chloride, MgCl₂.6H₂O as it gets hydrolysed to magnesium oxide.



- Out of the oxides of group 2 elements only BeO is extremely hard, non volatile, has high melting point and is amphoteric.

Oxide of Calcium

Quick lime (CaO) is obtained when limestone is heated at about 1000°C . On adding water, quick lime gives a hissing sound and forms calcium hydroxide, known as slaked lime. The paste of lime in water is called milk of lime while the filtered and clear solution is known as lime water. Chemically, both are $\text{Ca}(\text{OH})_2$.

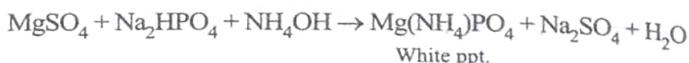
Quick lime is used for making caustic soda, bleaching powder, calcium carbide, mortar, cement, glass, dye stuffs and purification of sugar.

Mortar: It is a building material. It consists of slaked lime and silica in the ratio of 1:3. The mixture makes a paste with water. It is called mortar.

Analytical Detection of Mg

(i) Charcoal cavity test: On heating charcoal cavity with one drop of $\text{Co}(\text{NO}_3)_2$, a pink colour is imparted to the residue, $\text{CoO} \cdot \text{MgO}$.

(ii) The salt solution when mixed with NH_4Cl and NH_4OH and finally treated with soluble phosphates forms a white precipitate of magnesium ammonium phosphate.



Solved Examples

Explain the orders given in (Q. 1 to 21) for the property mentioned after each question:

1. $\text{MgO} < \text{SrO} < \text{K}_2\text{O} < \text{Cs}_2\text{O}$ (Basic character).

Sol. Increasing electropositive nature of the element makes its oxide more basic.

2. $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$ (Ionic radii in water).

Sol. Smaller the size of the ion, greater is the extent of hydration, so the size of hydrated ions becomes larger for smaller size ions.

3. $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ (Molar conductivity in water).

Sol. Li^+ ion is heavily hydrated, so has lowest mobility while Cs^+ ion is least hydrated, so has the highest mobility.

4. $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ (Reactivity with water).

Sol. Reactivity with water increases down the group, due to decrease in ionisation energy.

5. $\text{Cs} < \text{Rb} < \text{K} < \text{Na} < \text{Li}$ (Reactivity with hydrogen).

Sol. The ease of formation of hydrides decreases down the group.

6. $\text{Cs} < \text{Rb} < \text{K} < \text{Na} < \text{Li}$ (Melting point).

Sol. Melting point decreases down the group due to decrease in strength of metallic bond as size of atom increases.

7. $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$ (Basic nature of hydroxides).

Sol. Basic nature of hydroxides increases down the group the strength of a base depends on ionisation of the hydroxide which in turns depends on the polarity of bond and internuclear distance between the oxygen of the hydroxide and metal atom.

8. $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$ (Thermal stability of hydroxides).

Sol. Thermal stability of hydroxides increases down the group. Bigger cation is stabilised by bigger anion and vice-versa.

9. $\text{LiCl} < \text{LiBr} < \text{LiI}$ (Covalent character).

Sol. According to Fajan's rule, Li^+ ion polarizes the larger anion more, giving larger covalent character.

10. $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{SrCl}_2 < \text{BaCl}_2$ (Ionic character).

Sol. According to Fajan's rule, larger size cation has less polarising power, giving larger ionic character.

11. $\text{BaCO}_3 < \text{CaCO}_3 < \text{MgCO}_3 < \text{BeCO}_3$ (Solubility).

Sol. On moving down the group, the lattice energy of carbonates does not decrease more while the degree of hydration decreases more, so solubility decreases down the group.

12. $\text{BeF}_2 < \text{MgF}_2 < \text{CaF}_2 < \text{BaF}_2$ (Solubility).

Sol. Decrease in lattice energy is more as compared to hydration energy down the group.

13. $\text{Be}(\text{OH})_2 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Ba}(\text{OH})_2$ (Solubility).

Sol. L.E. is dominating factor. (Refer to Q. 12)

14. $\text{Be}(\text{OH})_2 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Ba}(\text{OH})_2$ (Basicity).

Sol. Basicity of hydroxides increases down the group. (Refer to Q. 7)

15. $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+}$ (Hydration of ions):

Sol. The extent of hydration of ion decreases with increase in ionic size.

16. $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ (Reactivity with water).

Sol. Reactivity with water increases down the group due to decrease in ionisation energy.

17. $\text{BaSO}_4 < \text{SrSO}_4 < \text{CaSO}_4 < \text{MgSO}_4 < \text{BeSO}_4$ (Solubility).

Sol. Decrease in hydration energy is more as compared to lattice energy down the group.

18. $\text{CaI}_2 < \text{CaBr}_2 < \text{CaCl}_2 < \text{CaF}_2$ (Melting point).

Sol. As the size of anion increases, its polarisation by the cation increases, so covalent character increases.

19. $\text{CsH} < \text{KH} < \text{NaH} < \text{LiH}$ (Stability of hydrides).

Sol. Stability of hydrides decreases down the group due to decrease in lattice energy.

20. $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{BaCO}_3$ (Thermal stability).

Sol. BeO is more stable than BaO , so BeCO_3 has a greater tendency to decompose to give stable BeO . Hence, BeCO_3 is least stable and BaCO_3 is most stable.

21. $\text{LiBr} < \text{NaBr} < \text{KBr} < \text{RbBr} < \text{CsBr}$ (Ionic character).

Sol. Larger the difference between the electronegativities, greater the ionic character.

Exercise-1 (Topicwise)

PROPERTIES OF ALKALI METALS

1. Which of the following is not a s-block element?
(a) [Ar] $4s^2 3d^{10} 4p^6 5s^1$ (b) $1s^2 2s^2 2p^1$
(c) [He] $2s^2 2p^6 3s^1$ (d) None of these

2. The alkali metals which form normal oxide, peroxide as well as super oxides are
(a) Na, Li (b) K, Li
(c) Li, Cs (d) K, Rb

3. Potassium is kept in
(a) Alcohol (b) Water
(c) Kerosene (d) Liquid ammonia

4. In aqueous solution, the largest ion is:
(a) Na^+ (aq.) (b) Cs^+ (aq.)
(c) Rb^+ (aq.) (d) Li^+ (aq.)

5. Which of the following statement is correct regarding alkali metals?
(a) Cation is less stable than the atom
(b) Cation is smaller than the atom
(c) Size of cation and atom is the same
(d) Cation is greater in size than the atom

6. On flame test, K gives colour.
(a) Golden yellow (b) Crimson red
(c) Violet (d) Apple green

7. Which of the following alkali metal is smallest in size?
(a) Rb (b) K
(c) Na (d) Li

8. Which one does not form a peroxide on heating in air?
(a) Na (b) Ba
(c) Ca (d) Li

9. The alkaline earth metals, which do not impart any colour to Bunsen flame are
(a) Be and Mg (b) Mg and Ca
(c) Be and Ca (d) Be and Ba

10. The hydration energy of Mg^{2+} is greater than that of:
(a) Al^{3+} (b) Na^+
(c) Be^{2+} (d) Mg^{3+}

11. Most reactive metal among the following is:
(a) K (b) Li
(c) Na (d) Cs

12. Sodium metal can be stored under:
(a) Benzene (b) Kerosene
(c) Alcohol (d) Water

PROPERTIES OF COMPOUNDS OF ALKALI METALS

19. Na_2CO_3 can be manufactured by Solvay's process but K_2CO_3 cannot be prepared because

 - (a) K_2CO_3 is more soluble.
 - (b) K_2CO_3 is less soluble.
 - (c) KHCO_3 is more soluble than NaHCO_3 .
 - (d) KHCO_3 is less soluble than NaHCO_3 .

20. Which metal forms amide with NH_3 at 300°C ?
- Mg
 - Pb
 - Al
 - Na
21. Which of the compound does not exist in solid state?
- LiHCO_3
 - CaCO_3
 - NaHCO_3
 - Na_2CO_3
22. Which of the following alkali metal carbonate is the least stable and decomposes readily?
- Li_2CO_3
 - Na_2CO_3
 - K_2CO_3
 - Cs_2CO_3
23. A solid compound 'X' on heating gives CO_2 gas and a residue. The residue mixed with water forms 'Y'. On passing an excess of CO_2 through 'Y' in water, a clear solution, 'Z' is obtained. On boiling 'Z', compound 'X' is reformed. The compound 'X' is:
- Na_2CO_3
 - K_2CO_3
 - $\text{Ca}(\text{HCO}_3)_2$
 - CaCO_3
24. Amongst LiCl , RbCl , BeCl_2 and MgCl_2 , the compound with the greatest and least ionic character respectively are:
- LiCl and RbCl
 - MgCl_2 and BeCl_2
 - RbCl and BeCl_2
 - RbCl and MgCl_2
25. Which of the following pair can't exist in solution?
- NaHCO_3 and NaOH
 - Na_2CO_3 and NaOH
 - Na_2CO_3 and NaCl
 - NaHCO_3 and NaCl
26. The chemical formula of soda ash is:
- NaOH
 - $\text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$
 - Na_2CO_3
 - $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
27. Anode in the middle compartment of castner kellner cell is made with
- Mercury
 - Graphite
 - Iron
 - Steel
28. A blue coloured solution of sodium in liquid NH_3 acts as strong reducing agent, because of
- Ammoniated sodium
 - Ammonia dissociates
 - Sodium nitride is formed
 - Ammoniated electrons
29. The alkali halide that is soluble in pyridine is:
- NaCl
 - LiCl
 - KCl
 - CsI
30. Excess of sodium hydroxide reacts with zinc to form:
- ZnH_2
 - Na_2ZnO_2
 - ZnO
 - $\text{Zn}(\text{OH})_2$
31. The stability of the following alkali metal chlorides follows the order?
- $\text{LiCl} > \text{KCl} > \text{NaCl} > \text{CsCl}$
 - $\text{CsCl} > \text{KCl} > \text{NaCl} > \text{LiCl}$
 - $\text{NaCl} > \text{KCl} > \text{LiCl} > \text{CsCl}$
 - $\text{KCl} > \text{CsCl} > \text{NaCl} > \text{LiCl}$
32. A metal M reacts with N_2 to give a compound 'A' (M_3N). 'A' on heating at high temperature gives back 'M' and 'A' on reacting with H_2O gives a gas B. 'B' turns CuSO_4 solution blue on passing through it. A and B can be
- Al and NH_3
 - Li and NH_3
 - Na and NH_3
 - Mg and NH_3
33. The oxide that gives hydrogen peroxide on treatment with a dilute cold acid is
- PbO_2
 - Na_2O_2
 - MnO_2
 - SnO_2
34. An alkali metal nitrate on heating decomposes and liberates two different gases along with an oxide. The alkali metal is
- Li
 - Na
 - K
 - Cs

PROPERTIES OF ALKALINE EARTH METALS

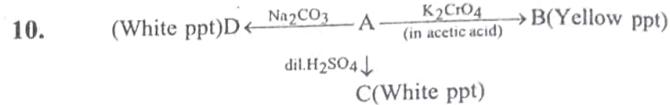
35. The metal which gives brick red colour in flame test is:
- Barium
 - Calcium
 - Strontium
 - Radium
36. The element with atomic number 12 belongs to group and period.
- IA, third
 - IIIA, third
 - IIA, third
 - IIIA, second
37. The correct order of hydration energy of alkaline earth metal ions is:
- $\text{Be}^{+2} > \text{Mg}^{+2} > \text{Ca}^{+2} > \text{Sr}^{+2} > \text{Ba}^{+2}$
 - $\text{Ba}^{+2} > \text{Be}^{+2} > \text{Ca}^{+2} > \text{Mg}^{+2} > \text{Sr}^{+2}$
 - $\text{Mg}^{+2} > \text{Be}^{+2} > \text{Ba}^{+2} > \text{Ca}^{+2} > \text{Sr}^{+2}$
 - None of these
38. Beryllium differs from rest of the members of its family (Group-IIA) in many ways. The reason for this is its:
- Small size and higher electronegativity
 - Small size and lower electronegativity
 - Large size and lower ionisation energy
 - Large size and largest ionic radius
39. A ribbon of magnesium was heated to redness in an atmosphere of nitrogen and on cooling, water was added, the gas evolved was
- Ammonia
 - Hydrogen
 - Nitrogen
 - Oxygen
40. Which of the following statement is incorrect?
- The atomic radius of Na is greater than that of Mg.
 - Metallic bond of Mg is stronger than the metallic bond in Na.
 - Melting and boiling points of Mg are less than those of Ca.
 - Mg and Ca both impart characteristic colour to the flame.

PROPERTIES OF COMPOUNDS OF ALKALINE EARTH METALS

41. Mg is present in
- Chlorophyll
 - Haemoglobin
 - Vitamin-B₁₂
 - Vitamin-B₂

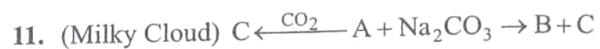
Exercise-2 (Learning Plus)

1. Alkali metals are not characterised by
 - Good conductor of heat and electricity
 - High oxidation potentials
 - High melting points
 - Solubility in liquid ammonia
2. Cs^+ ion impart violet colour to Bunsen flame. This is due to the fact that the emitted radiations are of:
 - High energy
 - Lower frequencies
 - Longer wave-lengths
 - Zero wave number
3. Na and Li are placed in dry air. We get:
 - NaOH , Na_2O , Li_2O
 - Na_2O , Li_2O
 - Na_2O , Li_2O , Li_3N , NH_3
 - Na_2O , Li_3N , Li_2O
4. Which one of the following electrolyte is used in Down's process of extracting sodium metal?
 - $\text{NaCl} + \text{CaCl}_2 + \text{KF}$
 - NaCl
 - $\text{NaOH} + \text{KCl} + \text{KF}$
 - $\text{NaCl} + \text{NaOH}$
5. A solution of sodium in liquid ammonia is strongly reducing and highly conducting due to the presence of:
 - Sodium atoms
 - Sodium hydride
 - Sodium amide
 - Solvated electrons
6. The reaction of an element A with water produces combustible gas B and an aqueous solution of C. When another substance D reacts with this solution, C also produces the same gas B. D also produces the same gas even on reaction with dilute H_2SO_4 at room temperature. Element A imparts golden yellow colour to Bunsen flame. Then A, B, C and D may be identified as:
 - Na , H_2 , NaOH and Zn
 - K , H_2 , KOH and Zn
 - K , H_2 , NaOH and Zn
 - Ca , H_2 , CaCOH_2 and Zn
7. Which salt on heating does not give brown coloured gas?
 - LiNO_3
 - KNO_3
 - $\text{Pb}(\text{NO}_3)_2$
 - AgNO_3
8. The order of solubility of lithium halides in non-polar solvents follows the order:
 - $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$
 - $\text{LiF} > \text{LiI} > \text{LiBr} > \text{LiCl}$
 - $\text{LiCl} > \text{LiF} > \text{LiI} > \text{LiBr}$
 - $\text{LiBr} > \text{LiCl} > \text{LiF} > \text{LiI}$
9. $\text{Na} + \text{Al}_2\text{O}_3 \xrightarrow{\text{High temperature}} \text{X} \xrightarrow[\text{water}]{\text{CO}_2 \text{ in}} \text{Y};$
Compound Y is:
 - NaAlO_2
 - NaHCO_3
 - Na_2CO_3
 - Na_2O_2



If A is the metallic salt, then the white ppt. of D must be of:

- Strontium carbonate
- Red lead
- Barium carbonate
- Calcium carbonate



The chemical formulae of A and B are:

- NaOH and $\text{Ca}(\text{OH})_2$
- $\text{Ca}(\text{OH})_2$ and NaOH
- NaOH and CaO
- CaO and $\text{Ca}(\text{OH})_2$

12. A fire work gave bright crimson light. It probably contained a salt of:

- Ca
- Sr
- Ba
- Mg

13. A piece of magnesium ribbon was heated to redness in an atmosphere of nitrogen and on cooling, water was added, the gas evolved was:

- Ammonia
- Hydrogen
- Nitrogen
- Oxygen

14. EDTA is used in the estimation of:

- Mg^{2+} ions
- Ca^{2+} ions
- Both Ca^{2+} and Mg^{2+} ions
- Mg^{2+} ions but not Ca^{2+} ions

15. A metal M readily forms water soluble sulphate MSO_4 , water insoluble hydroxide M(OH)_2 and oxide MO . The oxide and hydroxide are soluble in NaOH . The M is:

- Be
- Mg
- Ca
- Sr

16. Which of the following salts on heating gives a mixture of two gases?

- $\text{Ba}(\text{NO}_3)_2$
- NaNO_3
- KNO_3
- RbNO_3

17. A compound X on heating gives a colourless gas. The residue is dissolved in water to obtain Y. Excess CO_2 is bubbled through aqueous solution of Y, Z is formed. Z on gently heating gives back X. The compound X is:

- CaCO_3
- Na_2CO_3
- $\text{Ca}(\text{HCO}_3)_2$
- K_2CO_3

18. Amongst the following hydroxides, the one which has the lowest value of K_{sp} is:

- $\text{Mg}(\text{OH})_2$
- $\text{Ca}(\text{OH})_2$
- $\text{Ba}(\text{OH})_2$
- $\text{Be}(\text{OH})_2$

19. Explain the following:
- Why should an alkali metal never be put into a burette?
 - LiF has the lowest solubility of the group 1st metal halides.
 - BeCl₂ in aqueous solution exists as [Be(H₂O)₄]²⁺ rather than Be²⁺.
 - None of these.
20. Plaster of Paris hardens by :
- Giving off CO₂
 - Utilising water
 - Changing into CaCO₃
 - Giving out water
21. Sodium forms Na⁺ and not Na²⁺ because
- Sodium contains only one electron in outer most shell.
 - First ionisation potential is small and the difference in first and second ionisation potentials is very large.
 - Radius of Na²⁺ is much larger than Na⁺.
 - None of these.
22. Sodium and potassium occur:
- In native state
 - In combined state
 - In gaseous state
 - All of these
23. An atom of an element has electronic structure 2, 8, 1 which statement is correct for it?
- It has a valency of 7.
 - It exists as a diatomic molecule.
 - The element is of non-metallic nature.
 - It forms a basic oxide.
24. Potassium when heated strongly in oxygen, it forms
- K₂O
 - KO₂
 - K₂O₂
 - KO
25. NaOH is manufactured by the electrolysis of brine solution. The products of reaction are:
- Na & Cl₂
 - Cl₂ & O₂
 - Cl₂ & H₂
 - Na & O₂
26. Caustic soda is:
- Efflorescent
 - Deliquescent
 - Hygroscopic
 - Oxidant
27. Sodium carbonate is not used
- In soap making
 - In paper making
 - In tyre making
 - In baking of bread
28. Baking soda is:
- Washing soda
 - Caustic soda
 - Soda ash
 - Sodium bicarbonate
29. K⁺ ions are essential for:
- Metabolism of glucose inside the cell.
 - The synthesis of proteins.
 - Activation of certain enzymes.
 - All of the above.
30. In cell fluid, the most abundant cation is:
- Na⁺
 - K⁺
 - Mg²⁺
 - Ca²⁺
31. Chlorophyll, the green component of plants contains:
- Ca²⁺
 - Be²⁺
 - Mg²⁺
 - Ba²⁺
32. Sulphates and carbonates of alkaline earth metals are insoluble in water due to:
- Hydration energy > lattice energy
 - Hydration energy < lattice energy
 - Hydration energy = lattice energy
 - All are correct
33. In the Solvay process of manufacture of sodium carbonate, the raw materials used are :
- Aqueous NaOH, NH₃ and CO₂
 - Molten NaOH, NH₃ and CO
 - Brine NaCl, NH₃ and CO
 - Brine NaCl, NH₃ and CO₂
34. Which of the following group II sulphates has hydration enthalpy higher than the lattice enthalpy?
- SrSO₄
 - CaSO₄
 - BeSO₄
 - BaSO₄
35. Solution of K₂O in water is basic, because it contains a significant concentration of :
- O₂²⁻
 - O₂
 - OH
 - K⁺
36. A doctor by mistake administers a dilute Ba(NO₃)₂ solution to a patient for radiographic investigations. Which of the following should be the best to prevent the absorption of soluble barium and subsequent barium poisoning?
- NaCl
 - Na₂SO₄
 - Na₂CO₃
 - NH₄Cl
37. Which salt hydrolyses to minimum extent?
- Mg(NO₃)₂
 - Ba(NO₃)₂
 - Ca(NO₃)₂
 - NaNO₃
38. Which of the following statement is incorrect ?
- The effective component of bleaching powder is OCl⁻.
 - CaCO₃ is obtained when quick lime is heated with coke in an electric furnace.
 - Anhydrous CaSO₄ is dead burnt plaster.
 - BaCO₃ is obtained on fusion of BaSO₄ and Na₂CO₃.
39. The metal which does not react with nitrogen is
- Li
 - K
 - Ca
 - Mg
40. Which of the following shows maximum solubility in LiqNH₃?
- Li
 - Na
 - K
 - Fe
41. When NaNO₃ is treated with Na⁻
- NaNO₃ is formed.
 - Na₂O and N₂ are formed.
 - Na₂O₂ and N₂ are formed.
 - Na₂O and Na₃N are formed.
42. A + H₂O → NaOH; A $\xrightarrow[400^\circ\text{C}]{\text{O}_2}$ B $\xrightarrow{\text{H}_2\text{O}}$ NaOH + O₂
B is used for purification of air in submarines. A and B are
- Na₂O₂ and Na₂O
 - Na₂O and Na₂O₂
 - Na₂O₂ and O₂
 - Na₂O and O₂

43. Out of AgF , CaF_2 , BeF_2 and MgF_2
- AgF and BeF_2 are insoluble, and CaF_2 and MgF_2 are soluble in water.
 - AgF and BeF_2 are soluble, and CaF_2 and MgF_2 are insoluble in water.
 - CaF_2 , BeF_2 , MgF_2 soluble, AgF is insoluble.
 - All are insoluble
44. The metallic luster exhibited by sodium is explained by
- Diffusion of Na^+
 - Oscillation of loose electrons
 - Excitation of free protons
 - Existence of BCC lattice
45. In solid KHCO_3 , HCO_3^- ions exist as
- Monomers
 - Dimers
 - Polymers
 - $\text{H}^+ & \text{CO}_3^{2-}$
46. Reactivity of Na with water is more than Li because of
- Higher oxidation potential of Na.
 - Lesser hydration energy of Na^+ .
 - Lower melting point of Na.
 - Lesser density of Li.
47. During electrolysis of NaCl(aq) , using Hg cathode, Na is formed at cathode because
- SRP of Na is high.
 - SOP of Na is high.
 - Hydrogen tends to form HCl.
 - Ovvoltage for H_2 liberation is high with Hg electrode.
48. Following are the ionisation potential values of 899KJmol^{-1} (I_1), 1757KJmol^{-1} (I_2), 15000KJmol^{-1} (I_3)
- Na
 - Be
 - K
 - Ne
49. KO_2 (potassium super oxide) is used in oxygen cylinders in space and submarines because it
- Absorbs CO_2 and increases O_2 content
 - Eliminates moisture
 - Absorbs CO_2
 - Produces ozone
50. Which one of the following processes will produce hard water?
- Saturation of water with MgCO_3
 - Saturation of water with CaSO_4
 - Addition of Na_2SO_4 to water
 - Saturation of water with CaCO_3
51. In curing cement plasters, water is sprinkled from time to time. This helps in
- Developing interlocking needle-like crystals of hydrated silicates.
 - Hydrating sand and gravel mixed with cement.
 - Converting sand into silicic acid.
 - Keeping it cool.
52. The substance not likely to contain CaCO_3 is
- Calcined gypsum
 - Seashells
 - Dolomite
 - A marble statue
53. What is the best description of the change that occurs when $\text{Na}_2\text{O(s)}$ is dissolved in water?
- Oxide ion accepts a pair of electrons.
 - Oxide ion donates a pair of electrons.
 - Oxidation number of oxygen increases.
 - Oxidation number of sodium decreases.
54. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be
- 2.55 eV
 - 10.2 eV
 - 5.1 eV
 - +2.55 eV
55. Several blocks of magnesium are fixed to the bottom of a ship to
- Make the ship lighter.
 - Prevent action of water and salt.
 - Prevent puncturing by under-sea rocks.
 - Keep away the sharks.
56. Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements gives the correct picture?
- The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group.
 - In both the alkali metals and the halogens the chemical reactivity decreases with increase in atomic number down the group.
 - Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens.
 - In alkali metals, the reactivity increases but in the halogens it decreases with increase in atomic number down the group.
57. Sodium does not normally react with
- Ammonia gas
 - Ethyne
 - But-2-yne
 - Propyne
58. BeCl_2 reacts with LiAlH_4 to give
- $\text{Be} + \text{Li}[\text{AlCl}_4] + \text{H}_2$
 - $\text{Be} + \text{AlH}_3 + \text{LiCl} + \text{HCl}$
 - $\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$
 - $\text{BeH}_2 + \text{Li}[\text{AlCl}_4]$

Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

1. The metallic lustre exhibited by sodium is explained by
 (a) Diffusion of sodium ions.
 (b) Oscillation of mobile valence electrons.
 (c) Existence of free protons.
 (d) Existence of body centered cubic lattice.

2. Alkali metals give colour in Bunsen flame due to :
 (a) Low electronegativity
 (b) One electron in outer most orbit
 (c) Smaller atomic radii
 (d) Low ionisation energy

3. Consider the following statements;

S1 : Among alkali metal halides, lithium iodide is the most covalent in nature.

S2 : Potassium has greater photoelectric work function than sodium.

S3 : The blue solution of alkali metals in liquid ammonia is stable at room temperature, where ammonia is still a liquid, in the presence of Fe.

S4 : The melting and boiling points of alkali metal halides always follow the trend : chloride > fluoride > bromide > iodide.

and arrange in the order of true/false.

- | | |
|-------------|-------------|
| (a) T F F F | (b) T T F F |
| (c) T F T T | (d) T T T F |

4. Which of the following alkali metal has the highest reactivity towards water?

- | | |
|--------|--------|
| (a) Na | (b) Rb |
| (c) Li | (d) K |

5. Which of the following compound can exist in aqueous solution?

- | | |
|---------------------------|------------------------------|
| (i) Na_2O | (ii) Na_2O_2 |
| (iii) KO_2 | (iv) K_2CO_3 |
| (a) i, ii | (b) ii, iv |
| (c) i, ii, iii | (d) Only iii |

6. Which of the following salts are composed of isoelectronic cation and anion?

- | | |
|----------------------|----------------------|
| (I) NaCl | (II) BaCl_2 |
| (III) MgF_2 | (IV) CaS |
| (a) I and II | (b) II and III |
| (c) III & IV | (d) None of these |

7. Which of the following compound liberates H_2 with cold water ?

- | | |
|----------------------------|------------------|
| (a) H_2O_2 | (b) NaH |
| (c) NaOH | (d) Mg |

8. Low solubility of CsI in water is due to
 (a) Smaller hydration enthalpy of Cs^+
 (b) Smaller hydration enthalpy of I^-
 (c) Lower lattice enthalpy of its two ions
 (d) Both (a) and (b)

9. Select the correct statement.

- | | |
|--|---|
| (a) Among the alkali metals, only lithium reacts with nitrogen directly at room temperature to form metal nitride. | (b) Among the alkali metal carbonates, Li_2CO_3 has the lowest thermal stability. |
| (c) Among the alkali metal hydroxide, CsOH has the highest solubility in water. | (d) All of these |

10. In the synthesis of sodium carbonate, the recovery of ammonia is done by treating NH_4Cl with $\text{Ca}(\text{OH})_2$. The byproduct obtained in this process is :

- | | |
|---------------------|----------------------|
| (a) CaCl_2 | (b) NaCl |
| (c) NaOH | (d) NaHCO_3 |

11. Which of the following can not decompose on heating to give CO_2 in a dry test tube?

- | | |
|------------------------------|------------------------------|
| (a) Li_2CO_3 | (b) Na_2CO_3 |
| (c) KHCO_3 | (d) BeCO_3 |

12. NaNO_3 is not used as gun powder because it is:

- | | |
|-----------------|----------------------|
| (a) Hygroscopic | (b) Very costly |
| (c) Amorphous | (d) Soluble in water |

13. The chemistry of Li is very similar to that of Mg even though they belong to different groups. This is due to the fact that:

- | | |
|--|---|
| (a) Both occur in nature as compounds. | (b) Both have same electronic configuration. |
| (c) Both have nearly the same size. | (d) Both have charge to size ratio nearly the same. |

14. Crystals of washing soda lose nine molecules of water when exposed to dry air. This phenomenon is known as:

- | | |
|-------------------|-------------------|
| (a) Dehydration | (b) Efflorescence |
| (c) Deliquescence | (d) Evaporation |

15. The correct statement for crystalline CsI_3 is:

- | | |
|---|---|
| (a) It contains Cs^+ , I^- and molecular I_2 . | (b) It is a covalent compound. |
| (c) It contains Cs^+ and I_3^- . | (d) It contains Cs^{3+} and I^- . |

16. In the Down's method for the extraction of sodium, the melting point of the electrolyte is lowered by adding:

- | | |
|------------------------|----------------------|
| (a) Potassium chloride | (b) Calcium chloride |
| (c) Potassium fluoride | (d) Cryolite |

17. Select correct statements:

- (a) Li_2CO_3 is only sparingly soluble in water and no LiHCO_3 has been isolated.
- (b) K_2CO_3 cannot be made by a method similar to the ammonia-soda (Solvay) process.
- (c) Li_2CO_3 and MgCO_3 both are thermally stable.
- (d) $\text{Na}_3\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ is a mineral called trona.

18. KO_2 finds use in oxygen cylinders used for space and submarines. The fact(s) related to such use of KO_2 is/are:

- (a) It produces O_2
- (b) It produces O_3
- (c) It absorbs CO_2
- (d) It absorbs both CO and CO_2

19. The compound(s) which have $-\text{O}-\text{O}-$ bond(s) is/are

- (a) BaO_2
- (b) Na_2O_2
- (c) CrO_5
- (d) Fe_2O_3

20. Highly pure dilute solution of sodium in ammonia:

- (a) Shows blue colouration due to solvated electrons
- (b) Shows electrical conductivity due to both solvated electrons as well as solvated sodium ions
- (c) Shows red colouration due to solvated electrons but a bad conductor of electricity
- (d) Produces hydrogen gas or carbonate

21. Select correct statements amongst the following:

- (a) Stability of peroxides and superoxides of alkali metals increases with increase in size of the cation.
- (b) Increase in stability in (a) is due to stabilisation of large anions by larger cations through lattice energy effects.
- (c) The low solubility of LiF is due to its high lattice energy whereas low solubility of CsI is due to smaller hydration energy.
- (d) NaOH does not form hydrated salt.

22. Which of the following disproportionate(s) on heating with sodium hydroxide?

- (a) P_4 (white)
- (b) S_8
- (c) Cl_2
- (d) B

23. Select correct statement:

- (a) Oxides (M_2O) and peroxides (M_2O_2) of alkali metals are diamagnetic and colourless.
- (b) Superoxides (MO_2) of alkali metals are paramagnetic.
- (c) Li and Na do not form superoxides.
- (d) All are correct.

24. Which of the following substance(s) is/are used in laboratory for drying purposes?

- (a) Anhydrous P_2O_5
- (b) Graphite
- (c) Anhydrous CaCl_2
- (d) Na_3PO_4

25. Na_2SO_4 is water soluble but BaSO_4 is insoluble because:

- (a) The hydration energy of Na_2SO_4 is higher than that of its lattice energy.
- (b) The hydration energy of Na_2SO_4 is less than that of its lattice energy.
- (c) The hydration energy of BaSO_4 is less than that of its lattice energy.
- (d) The hydration energy of BaSO_4 is higher than that of its lattice energy.

26. Which of the following are ionic carbides?

- (a) CaC_2
- (b) Al_4C_3
- (c) SiC
- (d) Be_2C

27. Slaked lime, $\text{Ca}(\text{OH})_2$ is used:

- (a) In the manufacture of sodium hydroxide.
- (b) In the manufacture of bleaching powder.
- (c) In the preparation of ammonia from ammonium salts.
- (d) In the detection of carbon dioxide gas.

28. Be and Al resemble in:

- (a) Both become passive on reaction with HNO_3 due to formation of oxide layer.
- (b) Their chlorides are Lewis acids.
- (c) Chlorides exist in polymeric form.
- (d) Hydroxides are soluble in alkali as well as in acid.

29. The pair of compounds which cannot exist together in aqueous solution is

- (a) Na_2CO_3 and NaHCO_3
- (b) NaHCO_3 and NaOH
- (c) NaOH and NaH_2PO_4
- (d) $\text{NaOH} + \text{Na}_2\text{HPO}_4$

30. Select the wrong statements amongst the following:

- (a) CaF_2 is soluble in water
- (b) BaSO_4 is soluble in water
- (c) $\text{Ba}(\text{OH})_2$ is insoluble in water
- (d) MgSO_4 is soluble in water

31. Sulphate salt which gives metal oxide and SO_3 (or $\text{SO}_2 + 1/2 \text{O}_2$) on heating is

- (a) K_2SO_4
- (b) CaSO_4
- (c) MgSO_4
- (d) $(\text{NH}_4)_2\text{SO}_4$

32. Which of the following are soluble in water?

- (a) Na_2CO_3
- (b) BaC_2O_4
- (c) MgCO_3
- (d) BeCl_2

33. The correct statement about sodium and its compound would include that

- (a) Sodium forms an ionic hydride NaH
- (b) Sodium nitrate decomposes to the nitrite on heating
- (c) Sodium is a hard metal
- (d) Sodium carbonate decomposes easily on heating

34. Which of the following will release CO_2 when heated to 1000°C ?

- (a) KHCO_3
- (b) Li_2CO_3
- (c) K_2CO_3
- (d) PbCO_3

35. Select the correct statements amongst the following:

- (a) Sodium can be prepared by electrolyzing aqueous solution of NaCl .
- (b) Sodium can be prepared by electrolyzing fused NaCl .
- (c) Density of sodium is less than that of Li.
- (d) Sodium is a soluble in liquid ammonia.



- 36.** Which of the following properties show an increasing trend on moving from Li to Cs within the group?
 (a) Ionic mobility in aqueous solution.
 (b) Reactivity towards water.
 (c) Solubility of bromide salt.
 (d) Thermal stability of carbonate salt.

37. Which of the following statement regarding the oxides of alkali and alkaline metals is correct?
 (a) The reactivity of K_2O towards water is more than that of $2NaO$.
 (b) The oxides of alkaline earth metals are more basic than those of alkali metals.
 (c) MgO is used as a refractory material for lining of electric furnace.
 (d) The milk of lime and lime water are two different solutions.

38. Which of the following statements is /are true?
 (a) All alkali metals are soft and can be cut with knife.
 (b) Alkali metals do not occur in free state in nature.
 (c) Alkali metals are highly electropositive elements.
 (d) Alkali metal hydrides are covalent in character.

39. Select the incorrect statement (s) amongst the following:
 (a) Cs^+ is more hydrated than the other alkali metal ions.
 (b) Among the alkali metals Li, Na, K and Rb, lithium has the highest melting point.
 (c) Ionic mobility of Li^+ is maximum among alkali metal cations.
 (d) Ionisation potential of Li is lower than that of Na.

40. Li does not resemble other alkali metals in following properties
 (a) Li_2CO_3 decomposes into oxides while other alkali carbonates are thermally stable.
 (b) $LiCl$ has high covalent character.
 (c) Li_3N is stable.
 (d) $LiCl$ is non-conducting in molten state.

41. Be and Al show diagonal relationship hence both have
 (a) Same degree of electronegativity.
 (b) Basic nature of oxides.
 (c) Approximately same charge radius ratio.
 (d) $BeCl_2$ and $AlCl_3$ are volatile and fume in moist air.

42. Going down to the IIA group following properties increase except
 (a) Solubility of sulphates in H_2O
 (b) Hydration energy
 (c) Thermal stability of carbonates
 (d) Ionic radius

43. Sodium oxide cannot be obtained by heating
 (a) Na_2CO_3
 (b) $NaNO_3$
 (c) $NaHCO_3$
 (d) $NaOCl$

44. Choose the correct statements amongst the following:
 (a) $BeCO_3$ is kept in the atmosphere of CO_2 because it is less stable thermally.
 (b) Be dissolve in alkali forming $[Be(OH_4)]^{2-}$.
 (c) BeF_2 forms complexion with NaF in which Be goes with cation.
 (d) BeF_2 forms complex ion with NaF in which Be goes with anions.

45. Which can be used to generate H_2 ?
 (a) $Al + NaOH$
 (b) $Zn + NaOH$
 (c) $Mg + NaOH$
 (d) $LiH + H_2O$

46. Select correct statements amongst the following:
 (a) Beryllium & magnesium hydride are covalent and polymeric.
 (b) CaH_2 , SrH_2 and BaH_2 are ionic.
 (c) BeH_2 contains 3 centre 2 electron bond.
 (d) Ionic hydrides react with H_2O or acid forming H_2 .

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 47 to 49): Bleaching powder is considered as a mixed salt of hydrochloric acid and hypochlorous acid. It is a pale yellow powder. It shows oxidising and bleaching properties. A good sample of bleaching powder contains 35-38 % of available chlorine. bleaching powder can be prepared by reacting $Ca(OH)_2$ with Cl_2 .

47. Which of the following is formed by the reaction of bleaching powder with acetone?
 (a) CCl_4
 (b) $CHCl_3$
 (c) CCl_3CHO
 (d) CH_3Cl

48. Maximum percentage of available chlorine on the basis of $CaOCl_2 \cdot H_2O$ formula is:
 (a) 35 (b) 40 (c) 45 (d) 49

49. On long standing, bleaching powder undergoes autoxidation. The products formed are:
 (a) $CaCl_2$ and $HClO$
 (b) $Ca(ClO_3)_2$ and $CaCl_2$
 (c) $Ca(ClO_4)_2$ and $CaCl_2$
 (d) $Ca(ClO_3)_2$ and $Ca(ClO_4)_2$

Comprehension (Q. 50 to 51): On treatment with cold water, an element (A) reacts readily liberating a colourless, odourless gas (B) and forms a solution (C). Li is reacted with (B) yielding a solid product (D) which gives strongly basic solution (E), in water. When CO_2 gas is bubbled through solution (C), a white ppt. (F) is formed but it redissolve forming solution (G) when more CO_2 is passed. F gives deep red colouration to a Bunsen burner flame. (F) on heating with excess of carbon at $2000^\circ C$ gives (H).

50. Metal (A) may be
 (a) Be (b) Ca
 (c) Sr (d) Ba

51. Solution (G) contains a salt which
 (i) Causes permanent hardness of water.
 (ii) Cannot be obtained in solid state.
 (iii) Causes temporary hardness of water.
 (iv) Can be obtained in solid state.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 47 to 49): Bleaching powder is considered as a mixed salt of hydrochloric acid and hypochlorous acid. It is a pale yellow powder. It shows oxidising and bleaching properties. A good sample of bleaching powder contains 35-38 % of available chlorine. bleaching powder can be prepared by reacting $\text{Ca}(\text{OH})_2$ with Cl_2 .

- (b) Li has the highest melting point.

(c) Ionic mobility of Li^+ is maximum among alkali metal cations.

(d) Ionisation potential of Li is lower than that of Na.

40. Li does not resemble other alkali metals in following properties

 - (a) Li_2CO_3 decomposes into oxides while other alkali carbonates are thermally stable.
 - (b) LiCl has high covalent character.
 - (c) Li_3N is stable.
 - (d) LiCl is non-conducting in molten state.

41. Be and Al show diagonal relationship hence both have

 - (a) Same degree of electronegativity.
 - (b) Basic nature of oxides.
 - (c) Approximately same charge radius ratio.
 - (d) BeCl_2 and AlCl_3 are volatile and fume in moist air.

42. Going down to the IIA group following properties increase except

 - (a) Solubility of sulphates in H_2O
 - (b) Hydration energy
 - (c) Thermal stability of carbonates
 - (d) Ionic radius

43. Sodium oxide cannot be obtained by heating

 - (a) Na_2CO_3
 - (b) NaNO_3

47. Which of the following is formed by the reaction of bleaching powder with acetone?

 - (a) CCl_4
 - (b) CHCl_3
 - (c) CCl_3CHO
 - (d) CH_3Cl

48. Maximum percentage of available chlorine on the basis of $\text{CaOCl}_2 \cdot \text{H}_2\text{O}$ formula is:

 - (a) 35
 - (b) 40
 - (c) 45
 - (d) 49

49. On long standing, bleaching powder undergoes autoxidation. The products formed are:

 - (a) CaCl_2 and HClO
 - (b) $\text{Ca}(\text{ClO}_3)_2$ and CaCl_2
 - (c) $\text{Ca}(\text{ClO}_4)_2$ and CaCl_2
 - (d) $\text{Ca}(\text{ClO}_3)_2$ and $\text{Ca}(\text{ClO}_4)_2$

Comprehension (Q. 50 to 51): On treatment with cold water, an element (A) reacts readily liberating a colourless, odourless gas (B) and forms a solution (C). Li is reacted with (B) yielding a solid product (D) which gives strongly basic solution (E), in water. When CO_2 gas is bubbled through solution (C), a white ppt. (F) is formed but it redissolve forming solution (G) when more CO_2 is passed. F gives deep red colouration to a Bunsen burner flame. (F) on heating with excess of carbon at 2000°C gives (H).

50. Metal (A) may be

 - (a) Be
 - (b) Ca
 - (c) Sr
 - (d) Ba

51. Solution (G) contains a salt which

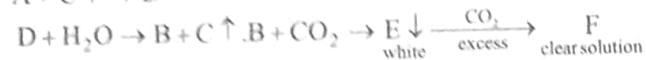
 - (i) Causes permanent hardness of water.
 - (ii) Cannot be obtained in solid state.
 - (iii) Causes temporary hardness of water.

Correct statements are:

Comprehension (Q. 52 to 54):



C is colorless & odourless gas and A is an element.



54. Compound D is
 (a) NaHSO_4 (b) NaClO_3
 (c) Na_2SO_4 (d) Na_2S

MATCH THE COLUMN TYPE QUESTIONS

- 55.** Match the particulars/name of process listed in **Column-I** with the formula of the compounds listed in **Column-II**

Column-I	Column-II
A. Solvay process	p. Na_2O
B. Evolve CO_2 on heating	q. Na_2O_2
C. Aqueous solution is not neutral towards litmus	r. NaHCO_3
D. Used as air purifier in submarine	s. Na_2CO_3

- (a) $A \rightarrow r, s; B \rightarrow r; C \rightarrow p, q, r, s; D \rightarrow q$
 (b) $A \rightarrow r, s; B \rightarrow r; C \rightarrow p, r, q, s; D \rightarrow q$
 (c) $A \rightarrow s; B \rightarrow p; C \rightarrow r; D \rightarrow q$
 (d) $A \rightarrow p, s; B \rightarrow r; C \rightarrow q, r; D \rightarrow p$

- 56.** Match the reactions given in **Column-I** with the main products obtained and given in **Column-II**.

Column-I	Column-II
A. $\text{Ca(OH)}_2 + \text{Cl}_2 \xrightarrow[35^\circ\text{C}]{\text{below}}$ (slaked lime)	p. Calcium chloride and oxygen gas.
B. $\text{Ca(OH)}_2 + \text{Cl}_2 \xrightarrow{\text{cold (below } 25^\circ\text{C)}} \text{ (milk of lime)}$	q. Calcium chloride and calcium chlorate

C.	$\text{Ca}(\text{OH})_2 + \text{Cl}_2 \xrightarrow{\text{heat (above } 35^\circ\text{C)}}$	r.	Bleaching powder.
D.	$\text{Ca}(\text{OH})_2 + \text{Cl}_2 \xrightarrow{\text{red hot}}$ (slaked lime)	s.	Calcium chloride and calcium hypochlorite.
		t.	Calcium chloride & calcium chlorite.

- (a) $A \rightarrow s; B \rightarrow p; C \rightarrow r; D \rightarrow q$
 - (b) $A \rightarrow r, s, t; B \rightarrow r; C \rightarrow q, s; D \rightarrow p$
 - (c) $A \rightarrow r; B \rightarrow s; C \rightarrow q; D \rightarrow p$
 - (d) $A \rightarrow r; B \rightarrow s; C \rightarrow p; D \rightarrow q$

NUMERICAL TYPE QUESTIONS

57. How many X–O–X linkages are present in the structure of calgon (NaPO_3)₆?
 58. How many of the following are correctly matched?

Element	Colour in flame test
K	Violet/Lilac
Na	Yellow
Be	Crimson red
Ca	Brick red
Sr	Apple green
Mg	No colour
Rb	Red violet
Cs	Blue
Li	Crimson red

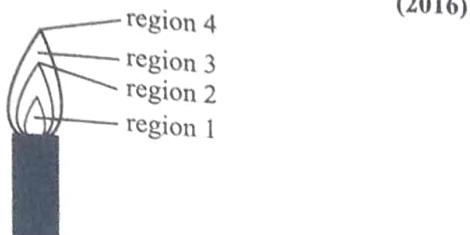
59. How many of the following form polymeric chains?
 BeCl_2 , AlCl_3 , NaHCO_3 , Li_2CO_3 , BeH_2 , Na_2CO_3

60. $\text{NaOH} + \text{PbO} \xrightarrow{\Delta} x + \text{H}_2\text{O}$
 $\text{NaOH} + \text{SnO}_2 \xrightarrow{\Delta} y + \text{H}_2\text{O}$
 $\text{NaOH} + \text{H}_2\text{O} + \text{Al} \xrightarrow{\Delta} z + \text{H}_2$
 Sum of the number of atoms present in one molecule each of x, y, z is _____.
 61. Molecular formula of Glauber's salt in $\text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$. The value of x is _____.

Exercise-4 (Past Year Questions)

JEE MAIN

1. The hottest region of Bunsen flame shown in the figure below is:



(2016)

- (a) Region 2 (b) Region 3
 (c) Region 4 (d) Region 1

2. The main oxides formed on combustion Li, Na and K in excess of air are, respectively:
- (a) Li_2O , Na_2O and KO_2 (b) LiO_2 , Na_2O_2 and K_2O
 (c) Li_2O_2 , Na_2O_2 and KO_2 (d) Li_2O , Na_2O_2 and KO_2

3. Both lithium and magnesium display several similar properties due to the diagonal relationship; however, the one which is incorrect is:
- (a) Both form basic carbonates.
 (b) Both form soluble bicarbonates.
 (c) Both form nitrides.
 (d) Nitrates of both Li and Mg yield NO_2 and O_2 on heating.

4. When metal 'M' is treated with NaOH , a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH . Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is:
- (a) Ca (b) Al (c) Fe (d) Zn

5. 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:
- (a) Na (b) Rb (c) Mg (d) Li

6. The metal used for making X-ray tube window is:
- (a) Mg (b) Na (c) Be (d) Ca

7. Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of:
- (a) Sodium - ammonia complex
 (b) Sodamide
 (c) Sodium ion-ammonia complex
 (d) Ammoniated electrons

8. NaH is an example of:
- (a) Electron rich hydride (b) Metallic hydride
 (c) Saline hydride (d) Molecular hydride

9. The alkaline earth metal nitrate that does not crystallise with water molecules is:

- (a) $\text{Mg}(\text{NO}_3)_2$ (b) $\text{Sr}(\text{NO}_3)_2$
 (c) $\text{Ca}(\text{NO}_3)_2$ (d) $\text{Ba}(\text{NO}_3)_2$

10. The metal that forms nitride by reacting directly with N_2 of air is:

- (a) K (b) Li (c) Rb (d) Cs

11. The amphoteric hydroxide is:

- (a) $\text{Be}(\text{OH})_2$ (b) $\text{Ca}(\text{OH})_2$
 (c) $\text{Mg}(\text{OH})_2$ (d) $\text{Sr}(\text{OH})_2$

12. The correct order of hydration enthalpies of alkali metal ions is:

- (a) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$
 (b) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{Rb}^+$
 (c) $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$
 (d) $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Cs}^+ > \text{Rb}^+$

13. Magnesium powder burns in air to give:

- (a) MgO only (b) MgO and $\text{Mg}(\text{NO}_3)_2$
 (c) MgO and Mg_3N_2 (d) $\text{Mg}(\text{NO}_3)_2$ and Mg_3N_2

14. The covalent alkaline earth metal halide ($X = \text{Cl}, \text{Br}, \text{I}$) is:

- (a) CaX_2 (b) SrX_2 (c) BeX_2 (d) MgX_2

15. Among the following, the energy of 2s orbital is lowest in:

- (a) K (b) Na (c) Li (d) H

16. The INCORRECT statement is:

- (a) Lithium is least reactive with water among the alkali metals.
 (b) LiCl crystallises from aqueous solution as $\text{LiCl} \cdot 2\text{H}_2\text{O}$.
 (c) Lithium is the strongest reducing agent among the alkali metals.
 (d) LiNO_3 decomposes on heating to give LiNO_2 and O_2 .

17. When gypsum is heated to 393 K, it forms:

- (a) Anhydrous CaSO_4
 (b) $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$
 (c) $\text{CaSO}_4 \cdot 5 \text{H}_2\text{O}$
 (d) Dead burnt plaster

18. A metal 'A' on heating in nitrogen gas gives compound B. B on treatment with H_2O gives a colorless gas which when passed through CuSO_4 solution gives a dark blue-violet coloured solution. A and B respectively, are:

- (a) Mg and Mg_3N_2 (b) Na and NaNO_3
 (c) Mg and $\text{Mg}(\text{NO}_3)_2$ (d) Na and Na_3N

19. Among the statements A – D, the correct ones are: (2020)
- Lithium has the highest hydration enthalpy among the alkali metals.
 - Lithium chloride is insoluble in pyridine.
 - Lithium cannot form ethynide upon its reaction with ethyne.
 - Both lithium and magnesium react slowly with H_2O .
- (a) A, B and D only (b) B and C only
 (c) A and D only (d) A, C and D only
20. Two elements A and B have similar chemical properties. They don't form solid hydrogencarbonates, but react with nitrogen to form nitrides. A and B, respectively, are: (2020)
- (a) Li and Mg (b) Cs and Ba
 (c) Na and Rb (d) Na and Ca

21. Among the statements (I – IV), the correct ones are: (2020)
- Be has smaller atomic radius compared to Mg.
 - Be has higher ionization enthalpy than Al.
 - Charge/radius ratio of Be is greater than that of Al.
 - Both Be and Al form mainly covalent compounds.
- (a) (I), (III) and (IV) (b) (I), (II) and (IV)
 (c) (I), (II) and (III) (d) (II), (III) and (IV)

22. An alkaline earth metal 'M' readily forms water soluble sulphate and water insoluble hydroxide. Its oxide MO is very stable to heat and does not have rock-salt structure. M is: (2020)
- (a) Ca (b) Mg (c) Sr (d) Be

23. Match the following compounds (Column-I) with their uses (Column-II): (2020)

Column-I		Column-II	
A.	$Ca(OH)_2$	p.	Casts of statues
B.	NaCl	q.	White wash
C.	$CaSO_4 \cdot \frac{1}{2} H_2O$	r.	Antacid
D.	$CaCO_3$	s.	Washing soda preparation

- (a) A → q; B → r; C → s; D → p
 (b) A → q; B → s; C → p; D → r
 (c) A → r; B → s; C → q; D → p
 (d) A → s; B → p; C → r; D → q

24. Among the sulphates of alkaline earth metals, the solubilities of $BeSO_4$ and $MgSO_4$ in water, respectively, are: (2020)
- (a) Poor and poor (b) Poor and high
 (c) High and poor (d) High and high

25. Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A): Lithium salts are hydrated.

Reason (R): Lithium has higher polarising power than other alkali metal group members.

In the light of the above statements, choose the most appropriate answer from the options given below: (2021)

- (a) Both (A) and (R) are correct but (R) is not the correct explanation of (A).
 (b) (A) is correct but (R) is not correct.

- (c) (A) is not correct but (R) is correct.
 (d) Both (A) and (R) are correct and (R) is the correct explanation of (A).

26. The number of water molecules in gypsum, dead burnt plaster and plaster of Paris, respectively are: (2021)

- (a) 2, 0 and 1 (b) 0.5, 0 and 2
 (c) 5, 0 and 0.5 (d) 2, 0 and 0.5

27. What are the products formed in sequence when excess of CO_2 is passed in slaked lime? (2021)

- (a) $Ca(HCO_3)_2$, $CaCO_3$ (b) $CaCO_3$, $Ca(HCO_3)_2$
 (c) CaO , $Ca(HCO_3)_2$ (d) CaO , $CaCO_3$

28. Match Column-I with Column-II: (2021)

	Column-I		Column-II
A.	Li	p.	Photoelectric cell
B.	Na	q.	Absorbent of CO_2
C.	K	r.	Coolant in fast breeder nuclear reactor
D.	Cs	s.	Treatment of cancer
		t.	Bearings for motor engines

Choose the correct answer from the options given below:

- (a) A → t; B → p; C → q; D → s
 (b) A → t; B → q; C → s; D → p
 (c) A → s; B → r; C → p; D → q
 (d) A → t; B → r; C → q; D → p

29. Which one of the following compounds is used as a chemical in certain type of fire extinguishers? (2022)

- (a) Baking Soda (b) Soda ash
 (c) Washing Soda (d) Caustic Soda

30. Match the Column-I with Column-II:

Column-I (Metal)		Column-II (Emitted light)	
A.	Li	p.	670.8
B.	Na	q.	589.2
C.	Rb	r.	780.0
D.	Cs	s.	455.5

Choose the most appropriate answer from the options given below: (2022)

- (a) A → p; B → q; C → r; D → s
 (b) A → r; B → q; C → p; D → s
 (c) A → r; B → p; C → q; D → s
 (d) A → s; B → q; C → p; D → r

31. Choose the correct order of density of the alkali metals: (2022)

- (a) $Li < K < Na < Rb < Cs$ (b) $Li < Na < K < Rb < Cs$
 (c) $Cs < Rb < K < Na < Li$ (d) $Li < Na < K < Cs < Rb$

32. An element A of group 1 shows similarity to an element B belonging to group 2. If A has maximum hydration enthalpy in group 1, then B is: (2022)

- (a) Mg (b) Be (c) Ca (d) Sr

33. Portland cement contains 'X' to enhance the setting time.

What is 'X'? (2022)

- (a) $CaSO_4 \cdot \frac{1}{2} H_2O$ (b) $CaSO_4 \cdot 2H_2O$
 (c) $CaSO_4$ (d) $CaCO_3$

JEE ADVANCED

34. The species present in solution when CO_2 is dissolved in water are (2006)
- (a) CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-}
(b) H_2CO_3 , CO_3^{2-}
(c) CO_3^{2-} , HCO_3^-
(d) $\text{CO}_2\text{H}_2\text{CO}_3$
35. MgSO_4 on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula? (2006)
- (a) $\text{Mg}(\text{NH}_4)\text{PO}_4$ (b) $\text{Mg}_3(\text{PO}_4)_2$
(c) $\text{MgCl}_2 \cdot \text{MgSO}_4$ (d) MgSO_4
36. **Statement-I:** Alkali metals dissolve in liquid ammonia to give blue solutions.
- Statement-II:** Alkali metals in liquid ammonia give solvated species of the type $[\text{M}(\text{NH}_3)_n]^+$ (M = alkali metals). (2007)
- (a) Both Statement-I & Statement-II are true & the Statement-II is a correct explanation of the Statement-I.
(b) Both Statement-I & Statement-II are true but Statement-II is not a correct explanation of the Statement-I.
(c) Statement-I is true but Statement-II is false.
(d) Statement-I is false but Statement-II is true.
37. A solution of colourless salt, H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are) (2008)
- (a) NH_2NO_3 (b) NH_4NO_2
(c) NH_4Cl (d) $(\text{NH}_4)_2\text{SO}_4$
38. White phosphorus on reaction with NaOH gives PH_3 , as one of the products. This is a (2008)
- (a) Dimerization reaction (b) Disproportionation reaction
(c) Condensation reaction (d) Precipitation reaction
39. Aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ on reaction with Cl_2 gives (2008)
- (a) $\text{Na}_2\text{S}_4\text{O}_6$ (b) NaHSO_4
(c) NaCl (d) NaOH
40. The compound(s) formed upon combustion of sodium metal in excess air is (are) (2009)
- (a) Na_2O_2 (b) Na_2O
(c) NaO_2 (d) NaOH
41. Which of the following will liberate O_2 upon hydrolysis? (2020)
- (a) Pb_3O_4 (b) KO_2
(c) Na_2O_2 (d) Li_2O_2

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (d) | 3. (c) | 4. (b) | 5. (b) | 6. (d) | 7. (c) | 8. (c) | 9. (c) | 10. (b) |
| 11. (d) | 12. (d) | 13. (d) | 14. (d) | 15. (a) | 16. (d) | 17. (d) | 18. (a) | 19. (d) | 20. (b) |
| 21. (a) | 22. (a) | 23. (c) | 24. (a) | | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (d) | 3. (c) | 4. (d) | 5. (b) | 6. (c) | 7. (d) | 8. (d) | 9. (a) | 10. (b) |
| 11. (d) | 12. (b) | 13. (a) | 14. (b) | 15. (b) | 16. (c) | 17. (c) | 18. (c) | 19. (c) | 20. (d) |
| 21. (a) | 22. (a) | 23. (d) | 24. (c) | 25. (a) | 26. (c) | 27. (b) | 28. (d) | 29. (b) | 30. (b) |
| 31. (d) | 32. (b) | 33. (b) | 34. (a) | 35. (b) | 36. (c) | 37. (a) | 38. (a) | 39. (a) | 40. (d) |
| 41. (a) | 42. (b) | 43. (d) | 44. (b) | 45. (a) | 46. (d) | 47. (a) | 48. (a) | 49. (c) | 50. (b) |
| 51. (b) | 52. (b) | 53. (b) | 54. (a) | 55. (d) | 56. (d) | 57. (c) | 58. (b) | | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (a) | 3. (d) | 4. (a) | 5. (d) | 6. (a) | 7. (b) | 8. (a) | 9. (c) | 10. (c) |
| 11. (b) | 12. (b) | 13. (a) | 14. (c) | 15. (a) | 16. (a) | 17. (a) | 18. (d) | 19. (a) | 20. (b) |
| 21. (b) | 22. (b) | 23. (d) | 24. (b) | 25. (c) | 26. (b) | 27. (d) | 28. (d) | 29. (d) | 30. (b) |
| 31. (c) | 32. (b) | 33. (d) | 34. (c) | 35. (c) | 36. (b) | 37. (d) | 38. (b) | 39. (b) | 40. (c) |
| 41. (b) | 42. (b) | 43. (b) | 44. (b) | 45. (c) | 46. (c) | 47. (d) | 48. (b) | 49. (a) | 50. (b) |
| 51. (a) | 52. (a) | 53. (b) | 54. (b) | 55. (b) | 56. (d) | 57. (c) | 58. (c) | | |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|-------------|-------------|-------------|-------------|-------------|---------------|---------------|---------------|-------------|-------------|
| 1. (b) | 2. (d) | 3. (a) | 4. (b) | 5. (c) | 6. (c) | 7. (b) | 8. (a) | 9. (d) | 10. (a) |
| 11. (b) | 12. (a) | 13. (d) | 14. (a) | 15. (c) | 16. (c) | 17. (a,b,d) | 18. (a,c) | 19. (a,b,c) | 20. (a,d) |
| 21. (a,b,c) | 22. (a,b,c) | 23. (a,b,d) | 24. (a,c) | 25. (a,c) | 26. (a,b,d) | 27. (a,b,c,d) | 28. (a,b,c,d) | 29. (b,c) | 30. (a,b) |
| 31. (b,c) | 32. (a,d) | 33. (a,b) | 34. (a,b,d) | 35. (b,d) | 36. (a,b,d) | 37. (a,c,d) | 38. (a,b,c) | 39. (a,c,d) | 40. (a,b,c) |
| 41. (a,c,d) | 42. (a,b) | 43. (a,c,d) | 44. (a,b,d) | 45. (a,b,d) | 46. (a,b,c,d) | 47. (b) | 48. (d) | 49. (b) | 50. (b) |
| 51. (c) | 52. (c) | 53. (a) | 54. (c) | 55. (a) | 56. (c) | 57. [6] | 58. [7] | 59. [3] | 60. [15] |

61. [10]

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

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

JEE Advanced

- | | | | | | | | |
|---------|---------|---------|-----------|---------|---------|-----------|---------|
| 34. (a) | 35. (a) | 36. (b) | 37. (a,b) | 38. (b) | 39. (b) | 40. (a,b) | 41. (b) |
|---------|---------|---------|-----------|---------|---------|-----------|---------|

CHAPTER

11

The p-Block Elements

INTRODUCTION

The elements in which last electron enters into p-subshell are called as p-block elements. The number of p-orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of p-orbitals is six, hence p-block contains six groups. The general electronic configuration of these elements is $ns^2 np^1\text{--}6$ (except for He). There are six groups in p-block.

Boron (of group 13) forms three covalent bonds in its compounds hence need two more electrons to complete its octet, hence its compounds are electron deficient or Lewis acid. Highly toxic element of Boron family is Tl.

Carbon (of group 14) occurs both in free state and combined state in nature. All living systems contain carbon. Carbohydrates, fats, proteins, vitamins, hormones, nucleic acids etc. all contain carbon.

The first member of each of these groups also displays the ability of forming $p\pi$ - $p\pi$ bonds to itself ($C=C$, $C\equiv C$, $N=N$) and also to other elements of second period ($C=O$, $C\equiv N$, $N=O$ and so on)

Table: General Electronic Configuration and Oxidation state of p-block elements.

Group	13	14	15	16	17	18
General electronic configuration	$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$	$ns^2 np^4$	$ns^2 np^5$	$ns^2 np^6$ (1s ² for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, -4	+3, -3	+4, +2, -2	+5, +3, +1, -1	+6, +4, +2

BORON FAMILY

Group III A contains six elements: Boron, Aluminium, Gallium, Indium, Thallium and Nihonium.

The heavier members of this group show inert pair effect. Boron compounds, especially the hydrides are electron deficient compounds which can accept a lone pair of electrons hence behave as Lewis acids.

Physical Properties

General electronic configuration is $ns^2 np^1$.

Atomic Number	Atomic Radii	Element Character	Configuration	Metallic
5	85 pm	B	[He] 2s ² 2p ¹	Non-metal
13	143 pm	Al	[Ne] 3s ² 3p ¹	Metal
31	135 pm	Ga	[Ar] 3d ¹⁰ 4s ² 4p ¹	Metalloid
49	167 pm	In	[Kr] 4d ¹⁰ 5s ² 5p ¹	Metal
81	170 pm	Tl	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	Metal
113	—	Nh	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	Metal

Irregularity in metallic character in gallium is because of shielding effect. In Gallium 10 electrons are filled in d orbitals hence have less shielding so size decreases and metallic character decreases.

Aluminium is most metallic among boron family due to its least electronegativity.

Atoms	B	Al	Ga	In	Tl
Electronegativity	2	1.5	1.6	1.7	1.8

Due to poor shielding of 3d and 4d and Lanthanoid contraction

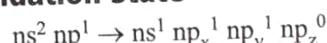
Atomic Size: Atomic size of boron family is smaller than alkaline and larger than carbon family. Down the group atomic size increases irregularly. Gallium is smaller than aluminium due to poor shielding of 3d orbital.

Ionization Energy: Ionization enthalpy, the general trend do not decrease smoothly down the group. Ionization energy decreases from B to Al, but increases from Al to Ga.

Decreasing order of 1st ionization energy is as follows

B > Tl > Ga > Al > In

Oxidation State



G.S. E.S.

- (a) Only covalent bonds are formed with valency = 3 & oxidation state = ± 3
- (b) Generally Compounds are formed by sp^2 hybridisation and have trigonal planar geometry.

- (c) Compounds of B are more covalent than compound of Al because charge/size ratio of B is more than Al.
- (d). The charge density of B is more because polarising power of B is more, \therefore more covalent character in Boron compound is observed.
- (e) $B \rightarrow Tl$ Covalent character decreases due to decrease in charge density or polarising power.
- (f) Trivalent compounds of group are electron deficient
eg. BF_3 acts as a lewis acid.
- (g) In general B shows oxidation state of +3 and -3
eg. Mg_3B_2 the oxidation state of B is -3.
 BF_3 the oxidation state of B is +3.
- (h) $6s\ e^-$ of Tl {Inert pair effect} are same as duplet configuration of He and so $6s\ e^-$ are inert and does not take part in chemical reaction.
- (i) Tl has valency = 1, 3 & oxidation state = +1 & +3.
- (j) Tl^{+3} is strong oxidising agent.
- (k) Tl^{+3} is highly unstable.
- (l) Tl^+ Compounds resemble compounds of alkali metals Thallous Tl^{+1} compounds will be more stable as compared to Tallic compounds (Tl^{+3})
- (m) Ga, In, Tl show inert pair effect in their compounds.
- (n) Indium in +1 oxidation state is reducing agent.

Melting and Boiling Points

- (a) B has very high melting point & boiling point due to giant molecular structure.
B.p. order : $B > Al > In > Tl > Ga$
M.p. order : $B > Al > Ga < In < Tl$
- (b) Ga has least melting point among all these.
- (c) Ga exists in liquid state in summer (m.p. = 303K)
- (d) Main use of Ga is in high temperature thermometer.



Train Your Brain

Example 1: The stable oxidation state of Tl is +1 hence its hydroxide is similar to:

- (a) $Ca(OH)_2$ (b) $Al(OH)_3$
(c) $Mg(OH)_2$ (d) $NaOH$

Sol. (d) Tl^{+1} stable i.e. $Na^+ OH^-$

Example 2: Choose the incorrect option;

- (a) Tendency of form ionic compound increases from B to Tl.
(b) Boron forms only covalent compound.
(c) Thallium forms only ionic compounds.
(d) Group 13 elements have less tendency to form complexes than the s-block elements.

Sol. (d) Group 13 element have more tendency to form complex than s-block element
→ due to their small size more effective nuclear charge as well as vacant orbitals to accept electrons.

Example 3: Boron cannot form which one of the following anions?

- (a) $B(OH)_4^-$ (b) BO_2^-
(c) BF_6^{3-} (d) BH_4^-

Sol. (c) Boron cannot form BF_6^{3-} anions due to absence of 2d orbitals in boron. Since 2d orbitals are not present in boron, it cannot expand its octet beyond 8. BF_6^{3-} anion will have 12 valence electrons around B.

Example 4: Melting point is higher for

- (a) B (b) Al
(c) Ga (d) In

Sol. (a) B has very high melting point and boiling point due to giant molecular structure.

M.p. order: $B > Al > Ga < In < Tl$

Example 5: TlI_3 is an ionic compound which furnishes the following ions in solution:

- (a) Tl^{3+} and I^- ions (b) Tl^+ and I_3^- ions
(c) Tl^+ , I^- ions and I^2- (d) Tl^+ and I^- ions

Sol. (b) TlI_3 exist as $\rightarrow Tl^+$ and I_3^- ions due to inert pair effect.



Concept Application

1. The increasing order of atomic radii of the following group 13 elements is:

- (a) $Al < Ga < In < Tl$
(b) $Ga < Al < In < Tl$
(c) $Al < In < Ga < Tl$
(d) $Al < Ga < Tl < In$

2. **Statement-I:** Boron always forms covalent bond Because:

Statement-II: The small size of B^{3+} favours formation of covalent bond.

- (a) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I

- (b) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-I

- (c) Statement-I is True, Statement-II is False
(d) Statement-I is False, Statement-II is True

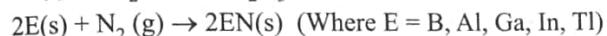
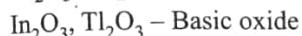
3. Boron compounds behave as Lewis acids because of their

- (a) Acidic nature
(b) Covalent nature
(c) Electron deficient character
(d) Ionising property

4. Boron has an extremely high melting point because of:
- The strong vander Waals forces between its atoms
 - The strong binding forces in the covalent polymer
 - Its ionic crystal structure
 - Allotropy
5. Which one of the following has the lowest m.p.?
- B
 - Al
 - Ga
 - Tl

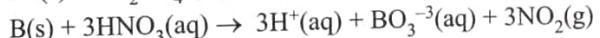
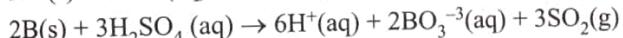
CHEMICAL PROPERTIES

1. **Reactivity towards air:** Amorphous boron and aluminium metal on heating in air forms trioxide and forms nitride at very high temperature. Gallium and indium are not affected with air while thallium does.

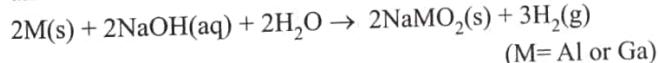


B_2O_3 is called boric anhydride as it is anhydride of boric acid.

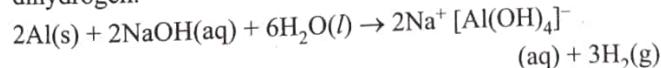
2. **Reactivity towards acids:** Boron is not affected by non-oxidising agents like HCl and dil. H_2SO_4 while all other elements react with conc. H_2SO_4 and HNO_3 . Ga and Al develop protective layer of oxide with conc. HNO_3 .



3. **Reactivity towards alkalies:** Except Indium and Thallium all other elements react with alkali solutions



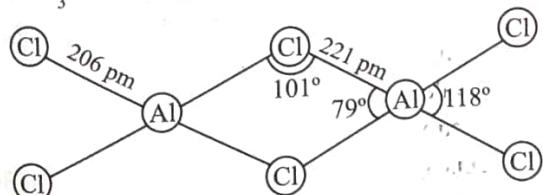
Example, Al also reacts with aq. Alkali and liberates dihydrogen.



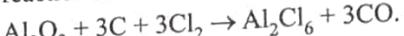
Sodium tetrahydroxoaluminate (III)

4. **Reactivity towards halogens:** Trihalides are formed when these elements react with halogens. All these halides exist as discrete molecular species which are sp^2 hybridised and covalently bonded. TlI_3 is unstable (Tl^{3+}I^-) but TlI_3 (Tl^+I_3^-) can exist.

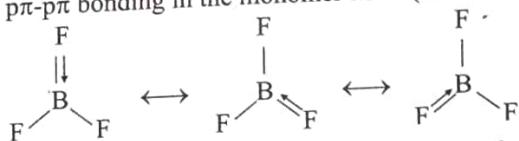
AlCl_3 achieves stability by forming a dimer.



(i) Al_2O_3 on heating with coke & Cl_2 forms Al_2Cl_6 and this reaction is called as **Reductive Chlorination**.

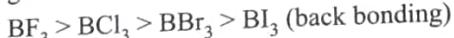


(ii) BF_3 do not form dimer while other forms because, the energy released by the formation of an additional bond to another boron atom is not sufficient to compensate for the loss in energy to the system in overcoming the B-F π - π bonding in the monomer itself (back bonding).

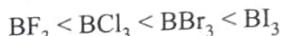


(iii) Al, Ga, In & Tl do not show back bonding because of increase in the size of the element. Actually they make use of vacant p-orbitals to complete their octet by forming dimers.

(iv) Acidic strength is inversely proportional to back-bonding, as back-bonding decreases from BF_3 to BI_3 as given below



Hence, Lewis acidic strength will increase as under



π - π back-bonding is strongest in BF_3 because both B and F involve 2p orbital in back-bonding.

Stability of halides in +3 oxidation state decreases down the group.

FACTS ABOUT ALUMINIUM CHLORIDE (AlCl_3)

- ❖ Anhydrous AlCl_3 can be prepared by passing dry Cl_2 or HCl gas over hot Al. It may also be prepared by passing dry Cl_2 gas over a hot mixture of alumina & Coke (McAfee process).
- ❖ Anhydrous AlCl_3 is hygroscopic in nature & for $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ which is deliquescent in nature.
- ❖ Anhydrous AlCl_3 gives out HCl fumes when exposed to moist air (due to rapid hydrolysis).
- ❖ In organic solvents AlCl_3 exists as a dimer Al_2Cl_6 .
- ❖ In AlCl_3 , Al is sp^2 hybridised while in Al_2Cl_6 its state of hybridisation is sp^3 .
- ❖ AlCl_3 does not conduct current in the fused state.

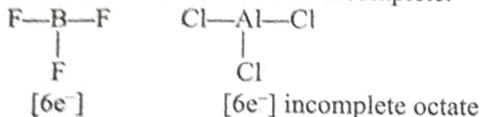


Train Your Brain

Example 6: Boron compounds behave as Lewis acids because of their:

- Acidic nature
- Covalent nature
- Electron deficient character
- Ionising property

Sol. (c) Boron compound behave as lewis acid character because in Boron group it valence shell electron is three. Thus its octet is incomplete.



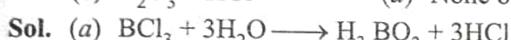
Example 7: Boron reacts with nitric acid to form:

- (a) Sodium borate, H_2 (b) Boric acid
 (c) Diborane (d) Borax



Example 8: Which of the following compounds are formed when boron trichloride is treated with water.

- (a) $\text{H}_3\text{BO}_3 + \text{HCl}$ (b) $\text{B}_2\text{H}_6 + \text{HCl}$
 (c) $\text{B}_2\text{O}_3 + \text{HCl}$ (d) None of these

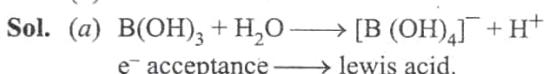


Except BF_3 all tri halides are readily hydrolysed by water.

Example 9: In the following reaction:



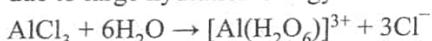
- (a) $\text{B}(\text{OH})_3$ is a Lewis acid.
 (b) $\text{B}(\text{OH})_3$ is a Lewis base.
 (c) $\text{B}(\text{OH})_3$ is amphoteric.
 (d) None is correct.



Example 10: Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives:

- (a) $\text{Al}^{3+} + 3\text{Cl}^-$ (b) $[\text{Al}(\text{H}_2\text{O})_6]^{3+} + 3\text{Cl}^-$
 (c) $[\text{Al}(\text{OH})_6]^{3-} + 3\text{HCl}$ (d) $\text{Al}_2\text{O}_3 + 6\text{HCl}$

Sol. (b) AlCl_3 is covalent but in water, it becomes ionic due to large hydration energy of Al^{3+} .



Concept Application

6. The formation of molecular complex BF_3 and NH_3 results in a change in hybridisation of boron :
 (a) From sp^3 to sp^3d (b) From sp^2 to dsp^2
 (c) From sp^3 to sp^2 (d) From sp^2 to sp^3
7. In the following sets of reactants which two sets best exhibit the amphoteric character of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$?
 Set-1 : $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (s) and OH^- (aq)
 Set-2 : $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (s) and H_2O (l)
 Set-3 : $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (s) and H^+ (aq)
 Set-4 : $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (s) and NH_3 (aq)

- (a) 1 and 2 (b) 2 and 4
 (c) 1 and 3 (d) 3 and 4

8. Heating an aqueous solution of aluminium chloride to dryness will give:

- (a) AlCl_3 (b) Al_2Cl_6
 (c) Al_2O_3 (d) $\text{Al}(\text{OH})\text{Cl}_2$

9. Aluminium is industrially prepared by:

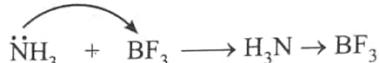
- (a) Fused cryolite (b) Bauxite ore
 (c) Alunite (d) Borax

10. Aluminium is not acted upon by pure water as –

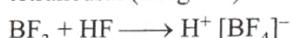
- (a) Impurities in water are essential for the reaction to occur.
 (b) It is light metal.
 (c) It is protected by a film of aluminium oxide.
 (d) It is not a reactive metal.

IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

Trihalides of these elements are covalent in nature and are hydrolysed in water and produces species like tetrahedral $[\text{M}(\text{H}_2\text{O})_4]^-$ and octahedral $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ except in boron.



In this reaction, hybridisation of BF_3 changes to sp^3 as one more bond is formed with nitrogen. Here shape changes to tetrahedral (irregular).



Here F^- reacts with BF_3 as F^- is nucleus-loving (nucleophile) and H^+ is electron-loving (electrophile) and BF_3 itself wants electrons.

$[\text{BF}_4]^-$ is a complex anion.

In above reaction, $[\text{BF}_4]^-$ is having sp^3 hybridisation with tetrahedral geometry.

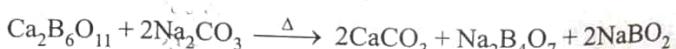
Due to absence of d-orbital maximum covalency of B is 4 while other elements of that group have d-orbitals hence, maximum covalency can be expected beyond 4.

SOME IMPORTANT COMPOUNDS OF BORON

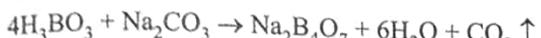
1. Borax or Tincal

- (i) Common Indian name is Suhaga.
 (ii) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ is known as Jeweller's Boron. also named as sodium tetra borate penta hydrate.
 (iii) $\text{Na}_2\text{B}_4\text{O}_7$ is known as Boron glass.

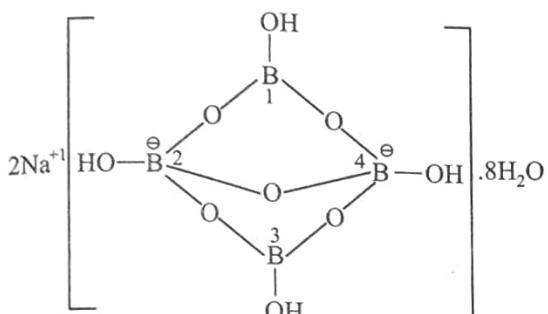
Preparation from Colemanite



Borax is a white crystalline solid and can be prepared by boric acid.



Formula: $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ or $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$



Number of B in sp^2 hybridisation = 2 (1, 3)

Number of B in sp^3 hybridisation = 2 (2, 4)

Oxidation state of all boron present = +3 state

n-factor = 2

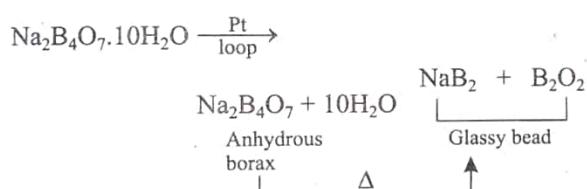
Number of B—O—B bonds = 5

Number of B—O bonds = 14

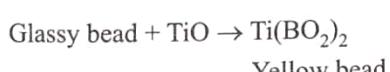
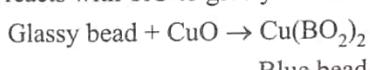
Number of bridging oxygen between two boron = 5

It furnishes two OH from 2nd and 4th, then octet of B cannot be completed. After cleavage it will be highly unstable structure.

On heating borax first loses water molecules and swells up and gives sodium metaborate which on further heating turns into a transparent liquid which solidifies into glassy bead. It is also called borax bead test.



This glassy bead reacts with CuO or CoO to give blue bead and reacts with TiO to give yellow bead of metaborate.



Colour of meta borates

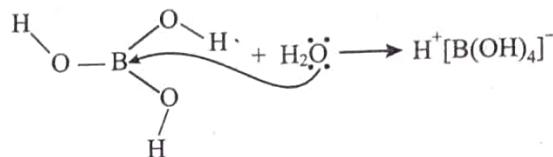
Cu and Co - Blue

Fe and Cr - Green

Ni - Brown

2. Orthoboric acid (H_3BO_3): It is white, soft, needle-like crystals having a soapy touch.

It does not give 3H^+ but accepts one lone pair from H_2O , so n-factor = 1. This is a monobasic Lewis acid as oxygen gives one electron pair to boron, so it acquires positive charge and becomes unstable, so it furnishes 1H^+ and gets stable.

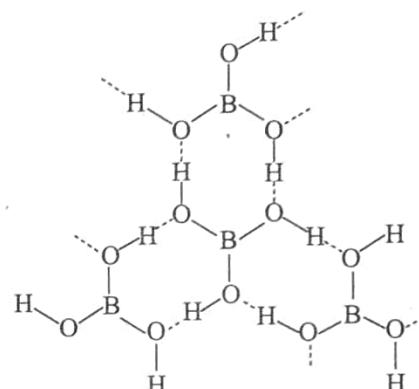
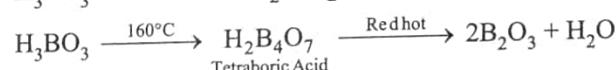
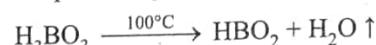


In $\text{H}^+[\text{B}(\text{OH})_4]^-$ hybridisation of boron is sp^3 .

It is prepared by treating concentrated sulphuric acid with borax.



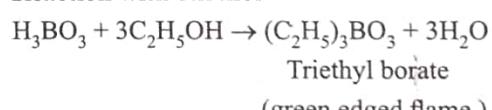
On heating to 100°C it gives metaboric acid which on further heating to 160°C gives $\text{H}_2\text{B}_4\text{O}_7$ which on extremely high temperature gives boric oxide.



Structure of boric acid; the dotted lines represent hydrogen bonds.

Boric acid is layered structure. $\text{B}(\text{OH})_3$ units are joined by hydrogen bonds and form two dimensional sheet.

Reaction with ethanol



Note: This is also called an Alcohol test.

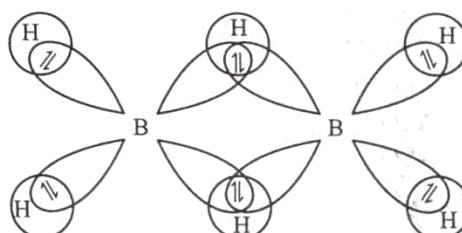
Uses

(i) As a antiseptic, as eye wash (eye-lotion) and as food preservatives.

(ii) In leather - industry.

(iii) In the preparation of glass and enamels.

3. Hydrides of boron



It is 3 centre 2 electron bonding called banana bonding or bridge bonding.

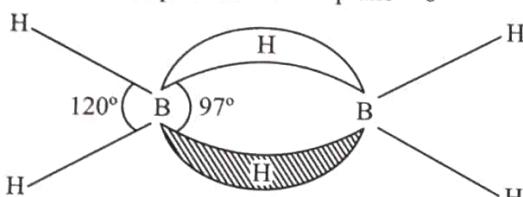
Number of bonds of bond length 119 pm = 4

Number of bonds of bond length 134 pm = 4

Number of bonds of bond angle 97° = 2

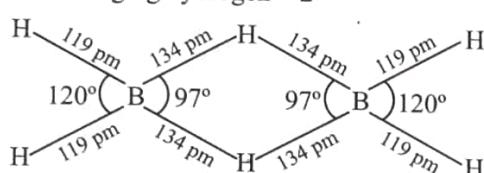
Number of bonds of bond angle 120° = 2

Number of atoms present in same plane = 6

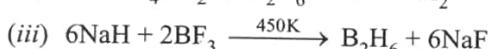
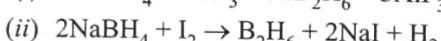
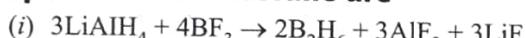


Number of terminal hydrogen = 4

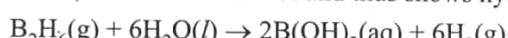
Number of bridging hydrogen = 2



Preparations of Diborane are



Since boranes have vacant p-orbitals in central boron atom hence, it reacts with water and thus shows hydrolysis.



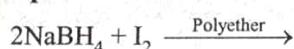
Boron hydride reacts with excess ammonia to give $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ which is white ionic solid and consists of $[\text{H}_3\text{N}]^+ \rightarrow \text{BH}_2^- \leftarrow \text{NH}_3]^+$ and $[\text{BH}_4]^-$.

When boron hydride reacts with excess ammonia at higher temperature then it gives boron nitride that has graphite-like structure $(\text{BN})_n$ but when diborane and ammonia react in ratio 1 : 2 at higher temperature then it gives borazine ($\text{B}_3\text{N}_3\text{H}_6$) which is known as **inorganic benzene or borazine**.

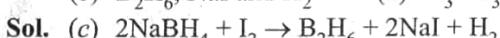


Train Your Brain

Example 11: Products formed are

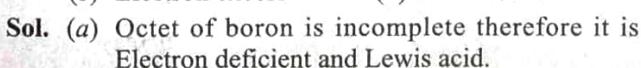


- (a) HI, NaI and H_2
- (b) B_2H_6 , NaI and HI
- (c) B_2H_6 , NaI and H_2
- (d) $\text{H}_3\text{BO}_3 + \text{H}_2$



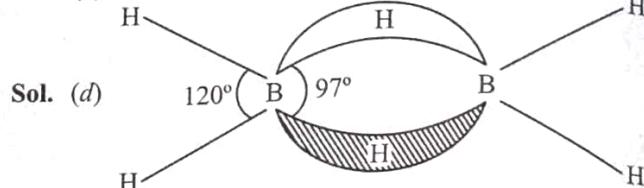
Example 12: Which type of hydride is BH_3 ?

- (a) Electron deficient
- (b) Electron precise
- (c) Electron excess
- (d) Lewis base



Example 13: Which of the following statement is correct regarding B_2H_6 ?

- (a) Each boron atom is sp^3 hybridised
- (b) B_2H_6 is electron deficient
- (c) B_2H_6 has banana bond
- (d) All of these



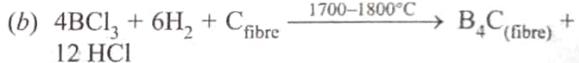
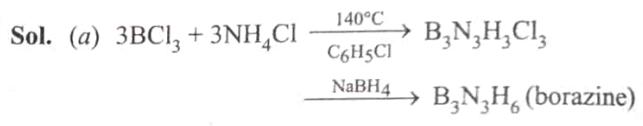
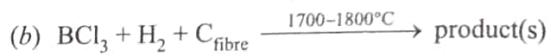
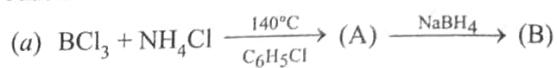
Sol. (d)

Example 14: Diborane belongs to the:

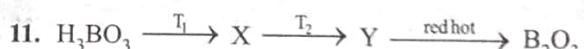
- (a) B_nH_{n+6} series
- (b) B_nH_{n+1} series
- (c) B_nH_{n+4} series
- (d) B_nH_{n+8} series

Sol. (c) Boranes have general formula of B_nH_{n+4} are called nidoboranes. Thus diborane i.e. n = 2, i.e. B_2H_6

Example 15: Complete the following reactions and identify the products formed.



Concept Application



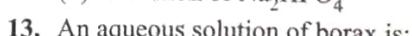
If $T_1 < T_2$ then X and Y respectively are

- (a) X = Metaboric acid and Y = Tetraboric acid
- (b) X = Tetraboric acid and Y = Metaboric acid
- (c) X = Borax and Y = Metaboric acid
- (d) X = Tetraboric acid and Y = Borax



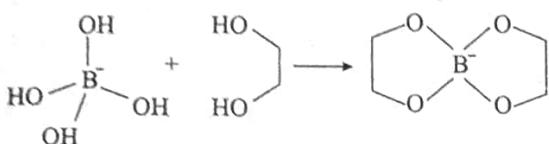
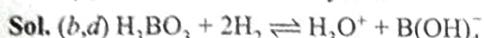
How can this reaction proceed in forward direction?

- (a) Addition of cis 1,2 diol
- (b) Addition of borax
- (c) Addition of trans 1,2 diol
- (d) Addition of Na_2HPO_4



- (a) Neutral
- (b) Amphoteric
- (c) Basic
- (d) Acidic

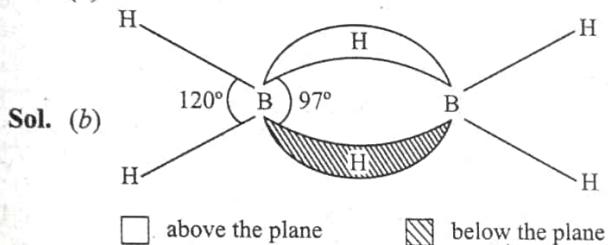
- (c) It has a three dimensional structure due to hydrogen bonding.
 (d) It is a weak electrolyte in water



⇒ On addition of glycol, equilibrium shift in forward direction ⇒ it's acidity increases.

Example 18: In which of the following compounds banana bond is present?

- (a) BCl_3
- (b) B_2H_6
- (c) $\text{B}(\text{OH})_3$
- (d) All of these



Example 19: H_3BO_3 is

- (a) Monobasic acid and weak Lewis acid
- (b) Monobasic and weak Bronsted acid
- (c) Monobasic and strong Lewis acid
- (d) Tribasic and weak Bronsted acid

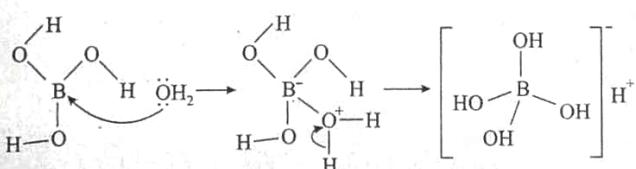


(Monobasic weak Lewis Acid)

Example 20: Statement-I: In water, orthoboric acid behaves as a weak monobasic acid.

Statement-II: In water, orthoboric acid acts as a proton donor.

- (a) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I
- (b) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-I
- (c) Statement-I is True, Statement-II is False
- (d) Statement-I is False, Statement-II is True



Concept Application

16. In alums, each metal ion is surrounded by

- (a) Two water molecules
- (b) Four water molecules
- (c) Six water molecules
- (d) Eight water molecules

17. When a solution of sodium hydroxides is added in excess to the solution of potash alum, we obtain

- (a) A white precipitate
- (b) Bluish white precipitate
- (c) A clear solution
- (d) A crystalline mass

18. Which of the following is not an ionic trihalide

- | | |
|--------------------|--------------------|
| (a) AlF_3 | (b) BF_3 |
| (c) InF_3 | (d) GaF_3 |

19. Alum is found to contain hydrated monovalent cation $[\text{M}(\text{H}_2\text{O})_6]^+$, trivalent cation $[\text{M}'(\text{H}_2\text{O})_6]^{3+}$ and in the ratio of:

- | | |
|---------------|---------------|
| (a) 1 : 1 : 1 | (b) 1 : 1 : 2 |
| (c) 1 : 2 : 2 | (d) 1 : 2 : 3 |

20. Aqueous solution of potash alum is:

- | | |
|--------------|------------|
| (a) Alkaline | (b) Acidic |
| (c) Neutral | (d) Soapy |

GROUP 14 ELEMENTS: THE CARBON FAMILY

Group IV A contains six elements: Carbon, Silicon, Germanium, Tin, Lead and Flerovium.

General electronic configuration is ns^2np^2 .

All elements of this family except carbon have tendency to show maximum covalency of six due to absence of vacant d-orbitals.

Silicon is second most abundant element in earth crust (27.7%). Carbon is the seventeenth most abundant element in earth crust. Carbon is important element of all living organisms. Till yet more than 5 million organic compounds have been discovered, 40,000 new organic compounds are discovering every year.

Note: Most abundant element in earth crust is oxygen (46.6%) by mass. Second most abundant element is silicon (27.7%). Third most abundant element is aluminium (8%) and fourth abundant element is iron.

Silicon is used in cement, glass, transistors, semiconductors.

Tin is used in alloys. Tin mainly occurs as cassiterite (SnO_2) and lead occurs as galena (PbS).

Germanium is used in transistors.

Lead is used in glass, paints and varnish

Physical Properties

Atomic Number	Element	Atomic radii (pm)	Electronic configuration	Metallic character
6	C	77	[He] 2s ² 2p ²	Non-metal
14	Si	117	[Ne] 3s ² 3p ²	Metalloid
32	Ge	122	[Ar] 3d ¹⁰ 4s ² 4p ²	Metalloid
50	Sn	140	[Kr] 4d ¹⁰ 5s ² 5p ²	Metals
82	Pb	146	[Xe] 5d ¹⁰ 6s ² 6p ²	Metals
114	Fl	—	[Rn] 6d ¹⁰ 7s ² 7p ²	Metals

The elements of this group form covalent bonds with each other and therefore there are strong binding forces between their atoms in both solid and liquid states.

Consequently the melting and boiling points of group 14 elements are much higher in comparison to group 13 elements. The atomic radius, ionic radius and density increase when one moves from top to bottom in a group in periodic table while melting point decreases from B to Ga and then increases from (Ga to In).

Atomic Size: Size of this family is smaller than boron family but larger than nitrogen family, down the group atomic size increases regularly. There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb, a small increase in radius is observed. This is due to the presence of completely filled d & f orbitals in heavier members.

Still properties of silicon differs from germanium due to poor shielding effect of 3d subshell and properties of germanium differs from tin due to poor shielding effect of 4f subshell (Lanthanoid contraction).

Properties of tin are different from lead due to poor shielding effect of 5f subshell (Actinoid contraction).

Ionization Energy and Electronegativity: Ionization energy of this group is higher than boron family and lower than nitrogen family. Down the group ionization energy decreases irregularly.

Decreasing order of first ionization energy is as follows:



Large decrease in ionization potential from C to Si is due to increase in size of atom. Ionization energy decreases from silicon is due to less screening effect of d¹⁰ electrons in Ge and Sn, and due to d¹⁰f¹⁴ electrons in Pb.

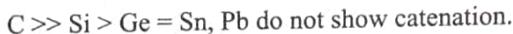
Ionization energy increases from Sn to Pb, it increases slightly due to Lanthanide contraction and increase of 32 units of nuclear charge in Pb over Sn.

Element	Electronegativity
C	2.5
Si	1.8
Ge	1.8
Sn	1.8
Pb	1.9

Order of electronegativities is C > Pb > Si = Ge = Sn

Catenation: Catenation power of carbon family is higher than boron family and nitrogen family. Down the group, catenation tendency decreases.

Catenation tendency is highest in carbon among all elements of family while silicon has second highest tendency of catenation among all elements of family and the decreasing tendency of catenation is as follows:



Oxidation State: They can form M⁺⁴ or M⁻⁴ ions. But due to high I.E. they do not form M⁺⁴. C and Si show +4 oxidation state while Ge, Sn and Pb shows +4 and +2 oxidation state due to inert pair effect.

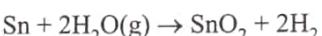
Chemical Properties

- Reactivity towards air:** All members of this group form monoxide of the general formula MO such as CO, SiO, SnO and PbO. All members of this group form dioxides of molecular formula MO₂ such as CO₂, SiO₂, GeO₂, SnO₂ and PbO₂.

CO₂ is monomeric, SiO₂ is 3-D network solid.

Dioxides (CO₂, SiO₂ and GeO₂) are acidic whereas dioxides (SnO₂ and PbO₂) and mono-oxides (SnO and PbO) are amphoteric. Mono-oxide CO is neutral while GeO is distinctly acidic.

- Reactivity towards water:** In this family carbon, silicon and germanium are unaffected by water while lead becomes inert towards water due to formation of protective oxide film. Tin is converted into tin dioxide and hydrogen gas is liberated on reaction with steam.



- Reactivity towards halogen:** On moving down the group from carbon to lead stability of +4 oxidation state decreases while stability of +2 oxidation state increases and hence decreases oxidising power decreases down the group due to inert pair effect.

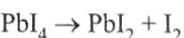
These elements form two types of halides - MX₂ and MX₄. Most of the MX₄ are covalent. SnF₄ and PbF₄ are ionic in nature.

Thermal stability decreases with increasing atomic size or molecular mass of tetrahalide or due to decreasing polarity.



CF₄ > CCl₄ > CBr₄ > CI₄ In these compounds:

PbI₄ is not stable as I⁻ is strong reducing agent which reduces Pb⁺⁴ to Pb⁺² and also stability of +4 oxidation state of Pb is lesser than +2 state.



Hydrolysis of Halides

The chlorides except CCl₄ are hydrolysed readily by water



Silicic acid

Hydrolysis of silicon tetrafluoride gives silica and fluorosilicic acid



(Silica) (Fluorosilicic acid)

Due to unavailability of vacant d-orbitals, carbon tetrahalides cannot increase its co-ordination number hence does not form complexes while those having vacant d-orbitals form.

ANOMALOUS BEHAVIOUR OF CARBON

Carbon shows anomalous behaviour due to its smaller size, higher electronegativity, higher ionization enthalpy and unavailability of d-orbitals.

Carbon atom forms double or triple bonds involving $\text{p}\pi$ - $\text{p}\pi$ bonding. Carbon has also the property to form closed chain compounds with O, S and N atoms as well as forming $\text{p}\pi$ - $\text{p}\pi$ multiple bonds with other elements particularly N, S and O.

CCl_4 is stable, while other chloride can hydrolyse due to presence of vacant d-orbital.



Train Your Brain

Example 21: The tendency for catenation in the group 14 elements is in the order:

- (a) C <<< Si < Ge <<< Sn < Pb
 (b) C >>> Si > Ge >>> Sn > Pb
 (c) C <<< Si < Ge ≈ Sn < Pb
 (d) C >>> Si > Ge ≈ Sn >>> Pb

Sol. (d) C >> Si > Ge \approx Sn >>> Pb

Small size of carbon

Example 22: Elements of group 14

- (a) Exhibit oxidation state of + 4 only
 - (b) Exhibit oxidation state of +2 and +4 only
 - (c) Form M^{2-} and M^{4+} ions
 - (d) Form M^{2+} and M^{4+} ions

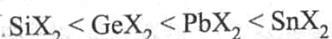
Sol. (d) General electronic configuration of elements of group 14 is $ns^2 np^2$; they form M^{+2} and M^{+4} ions.

Example 23: The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence:

- (a) $\text{GeX}_2 \ll \text{SiX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$
 (b) $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{PbX}_2 \ll \text{SnX}_2$
 (c) $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$
 (d) $\text{PbX}_2 \ll \text{SnX}_2 \ll \text{GeX}_2 \ll \text{SiX}_2$

Sol. (c) Due to the inert pair effect (the reluctance of ns₂ electrons of outermost shell to participate in bonding) the stability of M²⁺ ions (of group IV elements) increases as we go down the group.

The stability of dihalides increases down the group:



Concept Application

ALLOTROPES OF CARBON

All the elements of the carbon family with the exception of lead exhibit allotropy and this tendency decreases from C to Pb. It is due to decreasing bond energy.

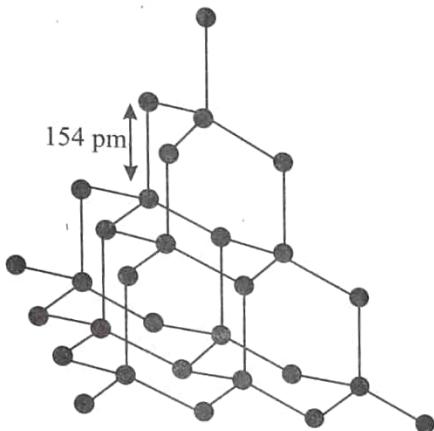
Bond	C—C	Si—Si	Ge—Ge	Sn—Sn
Bond energy (kJ/mol)	348	297	260	240

Carbon shows allotropism due to catenation and $p\pi-p\pi$ bond formation. Carbon exists in two allotropic forms - crystalline and amorphous. The crystalline forms are diamond and graphite while the amorphous forms are coal, charcoal and lamp-black. The third form is fullerenes discovered by Kroto, Smalley and Curl.

Tin has maximum number of allotropes.

DIAMOND

In diamond each carbon is joined to other four carbon tetrahedrally and carbon-carbon bond length is 1.54 \AA and bond angle is $109^{\circ}28'$ having sp^3 hybridisation on each carbon. All four electrons in carbon are involved in bonding hence, it is bad conductor of heat and electricity



The structure of diamond

It is purest form of carbon and hardest natural substance known. It is transparent and has a specific gravity 3.52 and its refractive index is high (2.45).

- (i) 1 carat of diamond = 200 miligram.
- (ii) Diamond powder if consumed is fatal and causes death in minutes.

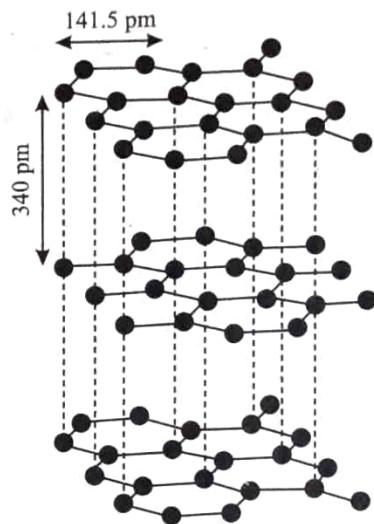
It is difficult to break due to extented covalent bonding.

Diamond is used for making cutters. Blades of diamond are used in eye surgery and as an abrasive for sharpening hard tools. Impure diamonds (black) are used in knives for cutting glass.

GRAPHITE

Each carbon is sp^2 hybridised. It has layered structure. These layers are attracted by van der Waals force. Each carbon has one free electron in p-orbital, so it is a good conductor of electricity. All electrons get delocalized in one layer and form π -bond. Graphite is aromatic. Electron jumps from one orbital to another hence it is a good conductor of heat and electricity. In graphite carbon-carbon bond length is 141.5 pm and distance between adjacent graphite layer is 340 pm .

Graphite is used as a lubricant at high temperature. Oil gets burn or denatured at high temperature but graphite does not get denatured even at high temperature so, preferred over oil and grease.



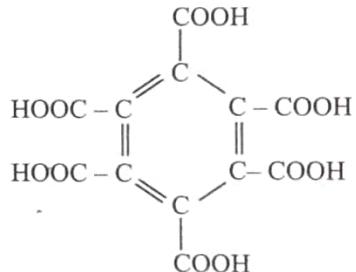
The structure of graphite

Graphite marks the paper black so it is called Black lead or plumbago and so it is used in pencil lead.

Composition of pencil lead is graphite + clay. The percentage of lead in pencil lead = 0%

Graphite has high melting point so it is employed in manufacture of crucible.

Graphite when heated with oxidising agents like alkaline $KMnO_4$ forms mellitic acid.



Benzene hexa carboxylic acid

Graphite on oxidation with conc. HNO_3 gives acid i.e. known as **Graphite acid ($C_{12}H_6O_{12}$)**.

Important points: Graphite is of two forms : α and β .

In α -graphite, layers are arranged in sequence ABAB... with the third layer exactly above first layer.

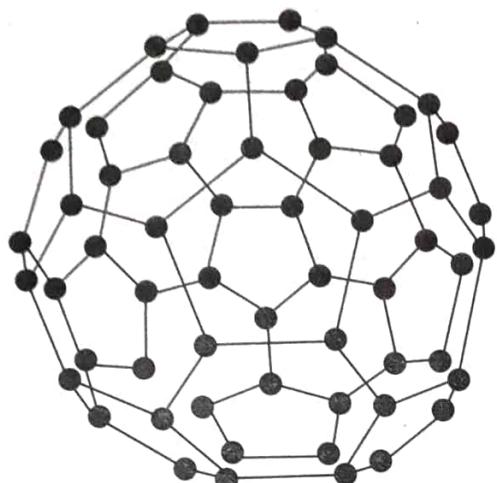
In β -graphite, the layers are arranged as ABCABC... the two forms are interconvertible.

Graphite is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less, than diamond. However entropy of graphite is more than diamond.

FULLERENE

It was made as a result of action of a laser beam or strong heating of a sample of graphite in presence of inert atmosphere. The sooty material mainly contains C_{60} with C_{70} (small amount).

Most common fullerene is C_{60} called Buckminsterfullerene which has football-like structure. It contains 20 hexagonal six-membered ring and 12 pentagonal five-membered ring. Every ring in this structure is aromatic. It is used to make ball bearings.



The structure of C_{60} , Buckminsterfullerene
Molecule of Fullerene has the shape of a soccer ball (football).

COAL

It is the crude form of carbon. It has been formed in nature as a result of slow decomposition of vegetable matter under the influence of heat, pressure and limited supply of air.

The successive stages of transformation are : peat, lignite, bituminous, steam coal and anthracite.

Bituminous is hard stone, burns with smoky flame. The superior quality is anthracite which burns with non-smoky flame.
Lamp black or carbon black: It is obtained by burning substances rich in carbon content such as kerosene, petroleum, turpentine oil, acetylene etc. in a limited supply of air.

Uses of Carbon

- (i) **Graphite:** In making lead pencils, electrodes of electric furnaces, as a moderator in nuclear reactor, as a lubricant in machinery.
- (ii) **Charcol:** In removing offensive odour from air, in removing fused oil from crude spirit, in decolorising sugar syrup, in gas masks etc.
- (iii) **Carbon black:** For making printing inks, black paints, Indian inks, boot polishes and ribbons of typewriters.
Coal : For the manufacture of coal gas, coal tar, coke and synthetic petrol.



Train Your Brain

Example 24: Various allotropes of carbon?

- (a) Diamond is the hardest and graphite is the softest
- (b) Diamond is the hardest and coke is the softest
- (c) Diamond is the hardest and lamp black is the softest
- (d) Coke is the hardest and diamond is the softest

Sol. (c) Fact based

Example 25: Different layers in graphite are held together by:

- | | |
|----------------------|-------------------------|
| (a) Ionic bonding | (b) Metallic bonding |
| (c) Covalent bonding | (d) Vander waals forces |

Sol. (d) Different layers in graphite are held together by Vander waals forces.

Example 26: Which of the following is a good conductor of electricity?

- | | |
|-------------|--------------|
| (a) Diamond | (b) Graphite |
| (c) Coal | (d) None |

Sol. (b) Graphite is a good conductor of electricity?

Example 27: Most stable allotrope of carbon thermodynamically is

- | | |
|---------------|-------------|
| (a) Fullerene | (b) Diamond |
| (c) Graphite | (d) Coke |

Sol. (c) Graphite is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less, than diamond.

Example 28: Graphite conducts electricity because of the:

- (a) Highly polarized nature of π -electrons.
- (b) Highly delocalized nature of π -electrons.
- (c) Highly localized nature of π -electrons.
- (d) None of these

Sol. (b) In graphite there is sp^2 hybridized carbon. thus due to Highly delocalized π electrons it possess electrical conductivity.



Concept Application

28. In which of the following there exists a $\pi\pi - d\pi$ bonding:

- (a) Diamond
- (b) Graphite
- (c) Dimethylamine
- (d) Trisilylamines

29. Bucky ball or buckminsterfullerene is:

- (a) An allotrope of carbon
- (b) It is referred as $C-60$
- (c) It has sp^2 -hybridised nature and resembles with soccer ball
- (d) All of these

30. Inert form of carbon is :

- (a) Diamond
- (b) Graphite
- (c) Coal
- (d) Charcoal

31. Thermodynamically the most stable form of carbon is:

- (a) Diamond
- (b) Graphite
- (c) Fullerenes
- (d) Coal

Carbides of Carbon

Compounds of C with less electronegative element are known as carbides.

A. Ionic or Salt like carbides:

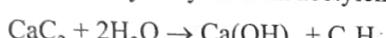
(i) Formed by ionic bonding and exists as crystalline solids.

Ionic carbide = Carbon + Highly Electropositive metal

(a) **Methanides:** In these carbon is in - 4 oxidation state. When subjected for hydrolysis form methane.



(b) **Acetylates:** In these carbon is in -1 oxidation state. These on hydrolysis form acetylene



(c) **Allylates:** Carbon is in $-\frac{4}{3}$ oxidation state. They form propyne on hydrolysis



Note: Calcium carbide react with nitrogen to form nitrolime (Calcium cyanamide). It releases NH_3 on hydrolysis so it is mainly used as fertilizer.



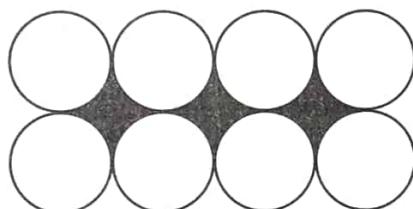
B. Covalent Carbides:

(a) C + Non metals = Covalent carbides (Small discrete molecules) eg : CH_4 , CCl_4 etc.

(b) Carbides consist of giant molecules. eg SiC (carborundum) etc.

These are very hard & used for cutting

C. Interstitial carbides or Refractory Carbides:



- (i) Interstitial sites are occupied by carbon.
- (ii) Carbon are held by weak vander waal force in interstitial carbides eg. Steel
- (iii) Iron carbides having atomic radii $< 1.37 \text{ \AA}$ is not a interstitial carbides \therefore Interstices are very less.
- (iv) Ti, Zr, Hg, W, Mo, V : Forms Interstitial carbides, while Co, Ni, Fe do not form interstitial carbides.
Rest of transition metal forms interstitial carbides
- (v) Characteristics of interstitial compounds :
 - (a) Density is high so very hard & have high m.p. & b.p.
 - (b) They are employed in cutting of tools especially tungustun carbide.
- (vi) Interstitial compounds are non stoichiometric compounds (here ratio is not fixed and is in fraction.)



Train Your Brain

Example 29: Which of the following is neutral oxide?

- | | |
|--------------------|-------------------|
| (a) CO | (b) CO_2 |
| (c) SiO_2 | (d) NO_2 |

Sol. (a) CO_2 , SiO_2 , NO_2 are acidic.

Example 30: Carbon suboxide C_3O_2 has

- (a) Linear structure
- (b) Bent structure
- (c) Trigonal planar structure
- (d) Distorted tetrahedral structure

Sol. (a) Carbon suboxide C_3O_2 is linear $\text{O} = \text{C} = \text{C} = \text{O}$

Example 31: Allylates are ionic carbides. They contains :

- | | |
|----------------------------|----------------------------|
| (a) C^{4-} ions | (b) C_2^{2-} ions |
| (c) C_3^{3-} ions | (d) C_3^{4-} ions |

Sol. (d) Allylates contain C_3^{4-} ions.

Example 32: Methanides are :

- (a) Mg_2C_3 , Be_2C , Al_4C_3 and CaC_2
- (b) Mg_2C_3 , Be_2C and Al_4C_3
- (c) Be_2C , Al_4C_3 and CaC_2
- (d) Be_2C and Al_4C_3

Sol. (d) Methanides contains C^{4-} .

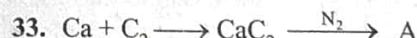
Example 33: The ions present in Al_4C_3 , CaC_2 and Mg_2C_3 are respectively:

- | | |
|---|---|
| (a) C^{4-} , C_2^{2-} , C_3^{4-} | (b) C_2^{2-} , C^{4-} , C_3^{4-} |
| (c) C_3^{4-} , C_3^{2-} , C^{4-} | (d) C_3^{4-} , C^{4-} , C_2^{2-} |

Sol. (a) The ions present in Al_4C_3 , CaC_2 and Mg_2C_3 are C^{4-} , C_2^{2-} , C_3^{4-} respectively.



Concept Application



Compound (A) is used as a/an

- (a) Fertilizer
- (b) Dehydrating agent
- (c) Oxidising agent
- (d) Reducing agent

34. Carbon reacts with metal to form:

- | | |
|---------------|---------------|
| (a) Carbide | (b) Carbonate |
| (c) Hydroxide | (d) Oxide |

35. Which gas is responsible for green house effect :

- | | |
|-------------------|-------------------|
| (a) CO_2 | (b) SO_2 |
| (c) CO | (d) SO_3 |

36. Which of the following statement is false:

- (a) Dry ice is solid CO_2
- (b) CO_2 is weakly acidic
- (c) CO_2 and SiO_2 are linear molecules
- (d) CO_2 is a gas while SiO_2 is solid

37. On hydrolysis CaC_2 gives a gas which on trimerisation gives:

- (a) C_2H_2
- (b) C_6H_6
- (c) C_2H_4
- (d) C_3H_8

FUELS OF CARBON

Calorific value: It is the total quantity of heat liberated by the complete combustion of a unit mass of the fuel in air

Unit = Kcal / m³

(a) Water gas:

- (i) It is a mixture of $\text{CO} + \text{H}_2$ with a small amount of CO_2 & also known as synthesis gas.
- (ii) A mixture of water gas and producer gas is used for manufacture of NH_3 by Haber's process
- (iii) Water gas is also known as blue gas because it burns with blue flame.
- (iv) Contains maximum percentage of CO.

(b) Producer gas:

- (i) It is a mixture of $\text{CO} + \text{N}_2$
- (ii) Cheapest gaseous fuel

(c) Coal gas: It is a mixture of $\text{H}_2 + \text{CH}_4 + \text{CO}$ and other gases like $\text{N}_2, \text{C}_2\text{H}_4, \text{O}_2$ etc.

(d) Oil gas: It is a mixture of $\text{H}_2 + \text{CH}_4 + \text{C}_2\text{H}_4 + \text{CO}$ and other gases like CO_2 .

(e) Gobar gas: or Bio gas: $\text{CH}_4 + \text{CO} + \text{H}_2$

(f) Natural gas: $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8 + \text{C}_4\text{H}_{10}$

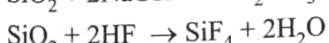
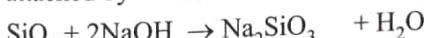
(g) L.P.G. (Liquified Petroleum Gas):

Butane + Isobutane

SILICON DIOXIDE

It is commonly known as silica and is nearly non-reactive because of its very high silicon-oxygen bond enthalpy. It is resistant to acids, halogens, metals and dihydrogen.

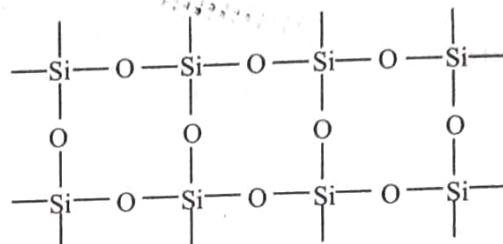
It is attacked by HF and NaOH.



The entire solid crystal may be considered as giant molecule in which eight-membered rings are formed with alternate silicon and oxygen atoms.

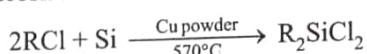
Uses:

SiO_2 (silica gel) is used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

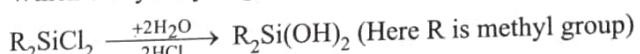


SILICONES

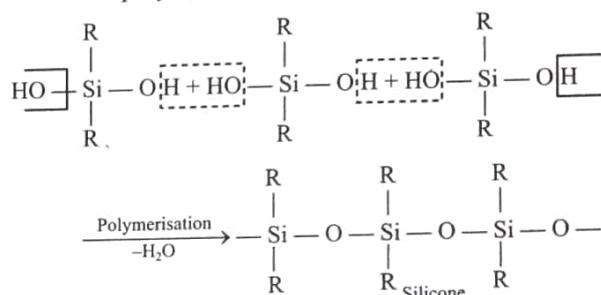
Alkyl chloride reacts with silicon at 537K in presence of copper catalyst to give dialkyl dichlorosilane with other substituted chlorosilane.



Which on hydrolysis gives dialkyl dihydroxy silane.



Which on polymerisation gives silicones.



Silicones are water repellants, good electrical insulators, stable towards heat, non-toxic resistant to chemicals. Silicone oils remain viscous at different temperature.

These can be used in surgical and cosmetic plants. It is a polymer having $-\left(\text{Si}-\text{O}\right)_n-$ monomer. It can be used as lubricant.

SILICATES

Oxide anion of silicon is known as silicates. There are following five types of Silicate.

(i) **Orthosilicates:** These do not share any corner. The anions are discrete SiO_4^{4-} units.

Examples - Zircon (ZrSiO_4) and Forestrite (Mg_2SiO_4).

(ii) **Pyrosilicate:** Here, two tetrahedral share one corner to form $\text{Si}_2\text{O}_7^{6-}$ anion. The structure possessed by them is called island structure.

Example - Thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$).

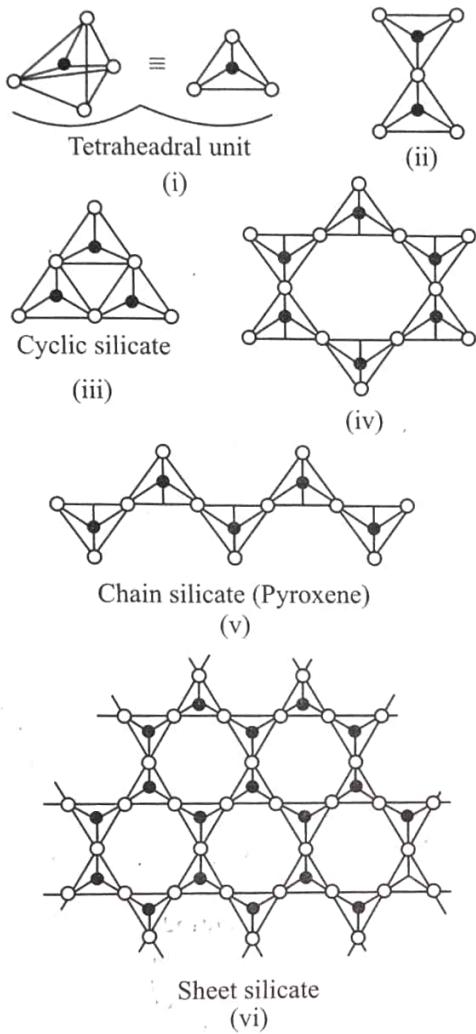
(iii) **Cyclic or ring silicates:** Here two corners of each tetrahedron are shared to form closed rings. The anionic unit are $(\text{SiO}_3^{2-})_n$.

Examples: Wollastonite- $\text{Ca}_3\text{Si}_3\text{O}_9$,

Beryl - $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$.

(iv) **Chain silicates:** Here two corners of each tetrahedron are shared to form a linear chain. The anionic unit is again

$(\text{SiO}_3^{2-})_n$. Linear silicate chain is present in pyroxenes. Example - Spodumene - $\text{LiAl}(\text{SiO}_3)_2$. If two chains are cross linked, the double strand silicates $(\text{Si}_4\text{O}_{11}^{6-})_n$ are called amphiboles. Example - asbestos.



(v) **Sheet silicates:** These silicates are formed by the sharing of three corners of each tetrahedron. The anion has a two dimensional sheet structure with general formula $(\text{Si}_2\text{O}_5^{2-})_n$. Example - Clay

(vi) **Three dimensional silicates:** These are formed by the sharing of all the four corners. Example - All the crystalline forms of silica. Example : Zeolites, Feldspar

ZEOLITES

If Al atoms replace few silicon atoms in 3D-network of SiO_2 , overall structure known as aluminosilicates acquires a negative charge.

Cations such as Na^+ , K^+ , Ca^{2+} etc balance the negative charge, e.g., feldspar (CaF_2) and Zeolites.

Uses

- Softening hard water by ion-exchanging.
- Converting alcohols directly into gasoline (ZSM-5).
- As catalyst in petrochemical industries.

GLASS

It is a transparent or translucent amorphous supercooled solid solution of silicates and borates. Its composition is variable as it is not a true compound it is also referred as pseudo solid.



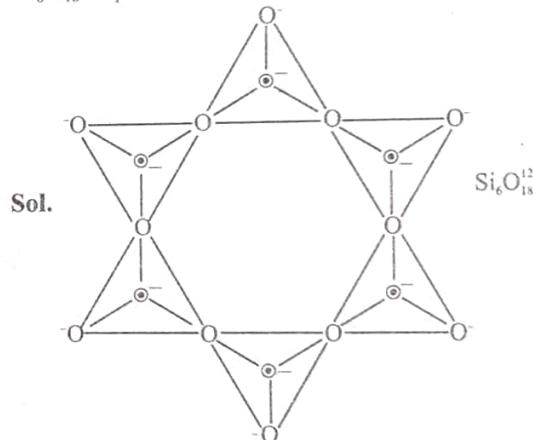
Train Your Brain

Example 34: In silicon dioxide:

- Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms.
- Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms.
- Silicon atom is bonded to two oxygen atoms
- There are double bonds between silicon and oxygen atoms.

Sol. (a) Each Si atom is surrounded by four O atoms and each oxygen atom is bonded to two Si atoms.

Example 35: Draw the structure of cyclic silicate containing $\text{Si}_6\text{O}_{18}^{12-}$ ion.

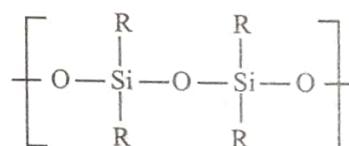


Example 36: $\text{RCl} \xrightarrow[\text{Si}]{\text{Cu-powder}} \text{R}_2\text{SiCl}_2 \xrightarrow{\text{H}_2\text{O}}$

$\text{R}_2\text{Si}(\text{OH})_2 \xrightarrow{\text{condensation}}$ A Compound (A) is:

- A linear silicone
- A chlorosilane
- A linear silane
- A network silane

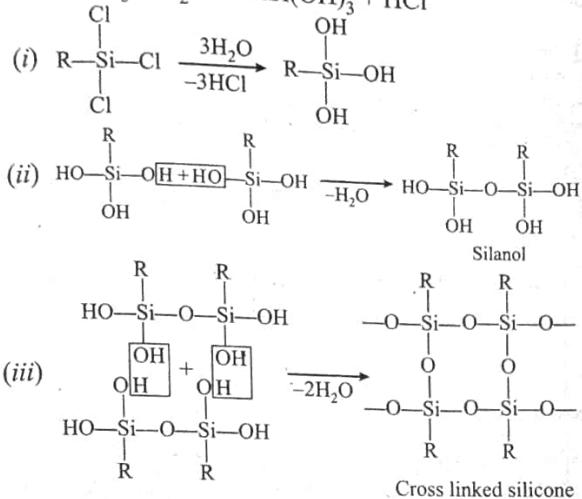
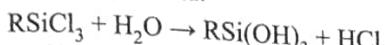
Sol. (a) It form linear silicon



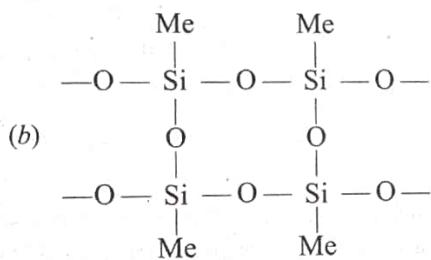
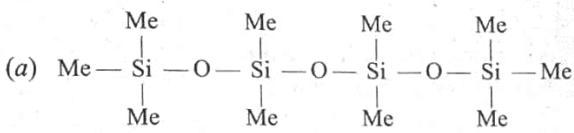
Example 37: Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is

- | | |
|-------------------------------|-----------------------------|
| (a) R_4Si | (b) RSiCl_3 |
| (c) R_2SiCl_2 | (d) R_3SiCl |

Sol. (b) Trichlorosilane is the basic ingredient used in the production of purified cross linked silicon polymer. In water, it rapidly decomposes to produce a silicone polymer while giving off hydrochloric acid.



Example 38: If we start with $MeSiCl_3$ as the starting material, silicones formed is:



(c) Both of the above

(d) None of the above



We get silicon in which '3' oxygen atom connected with each silicon.

Concept Application

38. $(Me)_2SiCl_2$ on hydrolysis will produce

(a) $(Me)_2Si(OH)_2$ (b) $(Me)_2Si = O$

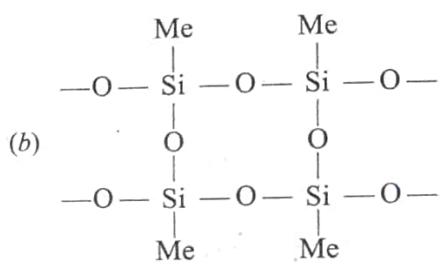
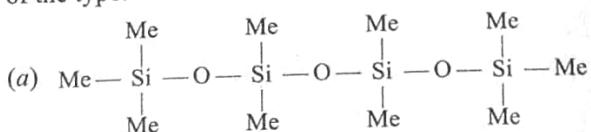
(c) $[-O-(Me)_2Si-O-]_n$ (d) $Me_2SiCl(OH)$

39. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be:

(a) Sodium (b) Magnesium

(c) Mercury (d) Tin

40. If we mix Me_3SiCl with Me_2SiCl_2 , we get silicones of the type:



(c) Both of the above

(d) None of the above

41. Lead pipes are readily corroded by:

(a) Dil. H_2SO_4 (b) Conc. H_2SO_4

(c) Acetic acid (d) Water

42. Silicone resins are made by :

(a) Dissolving a mixture of $PhSiCl_3$ and $(Ph)_2SiCl_2$ in toluene and then hydrolysis with water.

(b) Hydrolysing a mixture of $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$.

(c) Hydrolysis of $(CH_3)_2SiCl_2$

(d) None of these

Short Notes

13th-Group

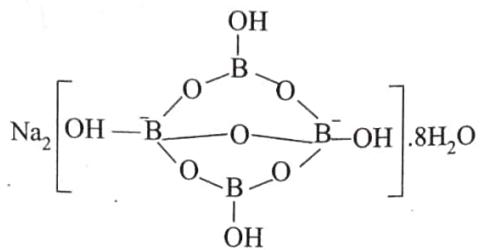
❖ Some important ores of Boron are given as under.

- (i) Boric acid, H_3BO_3
- (ii) Borax, $Na_2B_4O_7 \cdot 10H_2O$
- (iii) Colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$

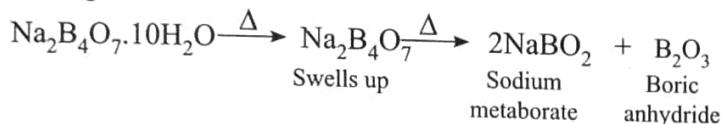
❖ Some important minerals of aluminium are given as under.

- (i) Corundum, Al_2O_3
- (ii) Bauxite, $Al_2O_3 \cdot 2H_2O$
- (iii) Cryolite, Na_3AlF_6
- (iv) Feldspar, $KAlSi_3O_8$

BORAX $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$

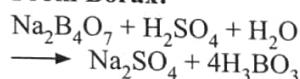


(i) Heating

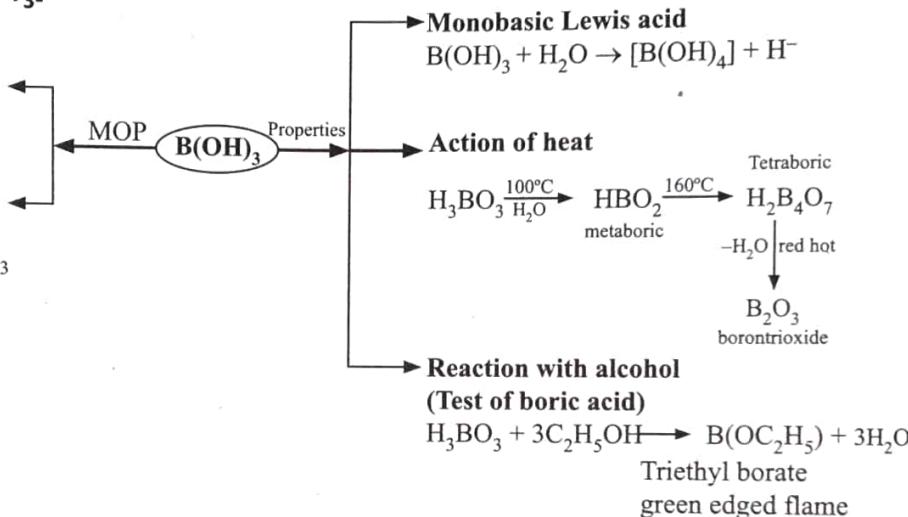
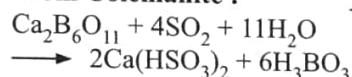


Orthoboric Acid [H_3BO_3 or $\text{B}(\text{OH})_3$]

From Borax:

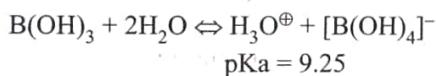


From Colemanite :

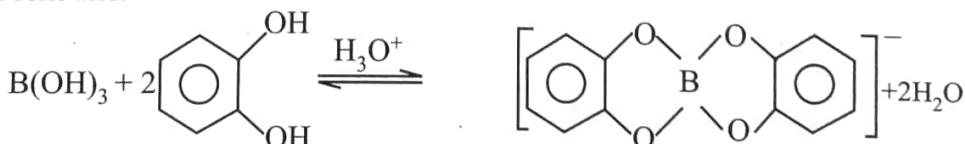


Properties

❖ Boric acid is a weak monobasic acid



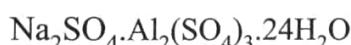
❖ It is difficult to titrate boric acid against NaOH solutions and the end point cannot be located correctly. However, it can be successfully titrated in the presence of polyhydroxy alcohols (e.g. Glycerol, mannitol, catechol or sugar). The presence of these compounds greatly increase the acidity of boric acid.



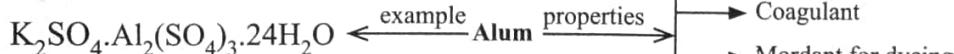
Boron is complex by these compounds. These complex ions cannot interact with H^+ ions as boron atom has already acquired its maximum covalency of four. Consequently, boric acid in presence of polyhydroxy alcohols can be titrated against NaOH to a definite end point.

Alums [$\text{M}_2\text{SO}_4 \cdot \text{M}'(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$]

Soda alum



Potash alum

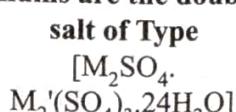


Ammonium alum



- aq. solution acidic
- Coagulant
- Mordant for dyeing
- Tanning of leather

Alums are the double salt of Type



M : Monovalent Cation:
 $\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$

M' : Trivalent Cation:
 $\text{Al}^{3+}, \text{Fe}^{3+} \& \text{Cr}^{3+}$

14th-Group Elements

- The common oxidation exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states.
- Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).
- Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.
- SiO only exists at high temperature.
- The dioxides – CO_2 , SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.
- Tin decomposes steam to form dioxide and dihydrogen gas.
- All halide of 14th group are covalent. Exceptions are SnF_4 and PbF_4 , which are ionic in nature.
- Stability of dihalides increases down the group.
- The order of catenation is $\text{C} > \text{Si} > \text{Ge} \approx \text{Sn}$. Lead does not show catenation.

- Catenation is the unique tendency of 14 group elements to form long chains of different sizes and shapes. The tendency to show catenation is directly related to the strength of bond. The bond energies of 14 group elements decrease as under:

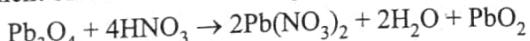
Catenation	C–C	Si–Si	Ge–Ge	Sn–Sn	Pb–Pb
Bond energy (kJ mole ⁻¹)	348	222	167	155	–

This is the reason why carbon forms many chains, Si, a few and Ge and Sn form practically no chains.

- CO_2 is a gas while SiO_2 is a solid at room temperature.
- SiO only exists at high temperature.
- CO_2 SiO_2 GeO_2 , GeO are acidic, PbO , PbO_2 is SnO and SnO_2 are amphoteric an CO is neutral
- ⇒ Among 14th group element only Sn reacts with steam to produce H_2 gas.
- ⇒ Tetrahalide of 14th group elements are covalent except SnF_4 and PbF_4 .
- Stability of oxidation state.
- ⇒ $\text{C}^{+4} \rightarrow \text{Pb}^{+4}$ (Stability)
- ⇒ $\text{C}^{+2} \rightarrow \text{Pb}^{+2}$ (Stability)
- ⇒ Pb^{+4} compounds are strong oxidizing agent.
- ⇒ PbI_4 does not exist.

Oxide of Lead

- Red lead (Pb_3O_4)** is considered to be mixture of lead monoxide and lead dioxide and it is written as $(\text{PbO}_2 \cdot 2\text{PbO})$.
- Lead dioxide (PbO_2)**. It is a brown powder obtained by the treatment of red lead with HNO_3 .



It is used as an active material of the positive plate in storage cells and finds use in match industry as an oxidizing agent.

Reaction of Lead Oxides

Oxide	ex NaOH	HCl	H_2SO_4	HNO_3
PbO	Na_2PbO_2	PbCl_2	PbSO_4	$\text{Pb}(\text{NO}_3)_2$
PbO_2	Na_2PbO_3	$\text{PbCl}_2 + \text{Cl}_2$	$\text{PbSO}_4 + \text{O}_2$	$\text{Pb}(\text{NO}_3)_2$
Pb_2O_3	$\text{Na}_2\text{PbO}_2 + \text{NaPbO}_1$	$\text{PbCl}_2 + \text{Cl}_2$	$\text{PbSO}_4 + \text{O}_2$	$\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2$
Pb_3O_4	$\text{Na}_2\text{PbO}_2 + \text{Na}_2\text{PbO}_3$	$\text{PbCl}_2 + \text{Cl}_2$	$\text{PbSO}_4 + \text{O}_2$	$\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2$

Tin and Its Compound

❖ Action of conc. HNO_3 on tin

- (a) Dilute HNO_3



- (b) Hot conc. HNO_3



Metastannic acid

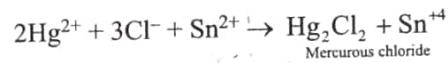
❖ Action of conc. NaOH on tin

- (a) $\text{Sn} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SnO}_3 + 2\text{H}_2\uparrow$

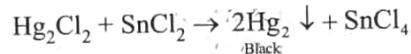
SnCl_2

- $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ on heating undergoes to form its basic chloride $\text{Sn}(\text{OH})\text{Cl}$. The anhydrous salt, therefore, be obtained by heating the hydrated salt in the presence of HCl vapour.

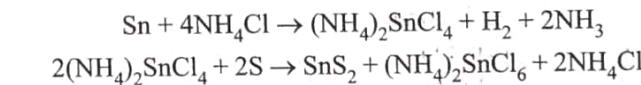
- Stannous chloride reduces mercuric chloride (HgCl_2) to a white precipitate of mercurous chloride (Hg_2Cl_2)



which finally turns to metallic mercury (dark grey or black)



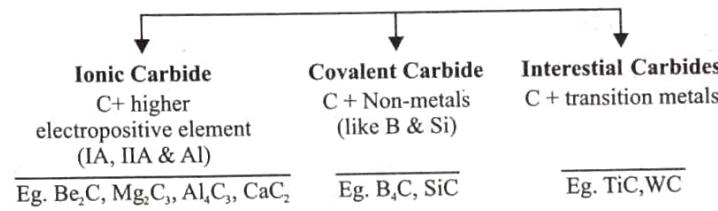
- Mosaic gold (SnS_2)**: Stannic sulphide exists in yellow glistening scales which is used for decorative purposes under and the name mosaic gold. It is prepared by heating mixture of tin fillings, sulphur and NH_4Cl in a retort.



Carbides

Binary compounds of carbon with other elements (except hydrogen) are known as carbides

CARBIDES



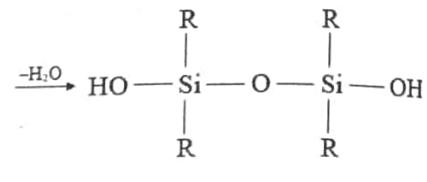
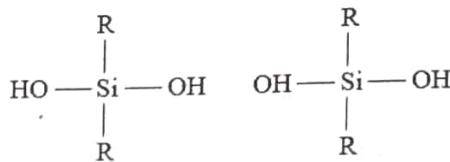
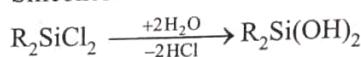
Solved Examples

- White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.
- Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.
- Boron is unable to form BF_6^{3-} ion. Explain.
- Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.
- Why is boric acid considered as a weak acid?
- Because it is not able to release H^+ ions on its own. It receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions.
- Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.
- (i) Carbon
(ii) Lead
(iii) Silicon and germanium
- $[\text{SiF}_6]^{2-}$ is known whereas $[\text{SiCl}_6]^{2-}$ not. Give possible reasons.
- The main reasons are:
(i) Six large chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.
(ii) Interaction between lone pair of chloride ion and Si^{4+} is not very strong.
- Diamond is covalent, yet it has high melting point. Why?
- Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.
- SiH_4 is more reactive than CH_4 . Explain Reasons
- The main reasons are:
(i) $\text{Si}^{\delta+} - \text{H}^{\delta-}$ in $\text{C}^{\delta-} - \text{H}^{\delta+}$
C – more electronegative than H
Si less electronegative than H
So bond polarity is reversed when Nu– attacks, it faces repulsion in C but not in Si
(ii) Silicon is having vacant d orbital which is not in case of carbon
(iii) Silicon is larger in size compared to C. By which the incoming Nu– doesn't face any steric hindrance to attack at Si whereas CH_4 is tightly held from all sides.
- Regular use of which of the following fertilizer increases the acidity of soil:
(a) Potassium nitrate
(b) Urea
(c) Superphosphate of lime
(d) Ammonium sulphate

Sol. (d) Regular use of ammonium sulphate increases the acidity of soil. The hydrolysis of ammonium sulphate produces sulphuric acid which increases the acidity of soil.
 $(\text{NH}_4)_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O} + \text{H}_2\text{SO}_4$
To prevent acidity, slaked lime is added to neutralize the acid.

- The hydrolysis of alkyl substituted chlorosilanes given.....

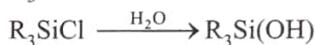
Sol. Silicones



(Silicone)

- The hydrolysis of trialkylchlorosilane R_3SiCl , yields

Sol. $\text{R}_3\text{Si}(\text{OH})$



- One recently discovered allotrope of carbon (e.g., C_{60}) is commonly known as

Sol. Buckminster fullerene

- Which of the following is used in high temperature thermometry ?

- | | |
|--------|--------|
| (a) Na | (b) Ga |
| (c) Tl | (d) Hg |

Sol. (d) Mercury is used in high temperature thermometry.

- Boron form covalent compound due to

- | |
|------------------------------|
| (a) Higher ionization energy |
| (b) Lower ionization energy |
| (c) Small size |
| (d) Both (a) and (c) |

Sol. (d) Due to small size and higher ionization energy boron form covalent compound.

- Which of the following is a non-metal

- | |
|---------------|
| (a) Gallium |
| (b) Indium |
| (c) Boron |
| (d) Aluminium |

Sol. (c) Boron is non-metal.

- 15.** Aluminium is more reactive than iron. But aluminium is less easily corroded than iron because:

 - Oxygen forms a protective oxide layer on aluminium
 - Aluminium is a noble metal
 - Iron undergoes reaction easily with water
 - Iron forms mono and divalent ions

Sol. (a) On reacting with water Oxygen forms a protective oxide layer of Al(OH)_3 on aluminium.

16. Inorganic benzene (borazole) is :

 - BH_3O_3
 - $\text{B}_3\text{N}_3\text{H}_6$
 - B_2H_6
 - B_6H_{10}

Sol. (b) $\text{B}_3\text{N}_3\text{H}_6$ is known as borazine or borazole or inorganic benzene.

17. The hydrides of boron are called

 - Boron hydrogen compounds
 - Hydrogen borides
 - Boranes
 - Hydroboric acids

Sol. (c) The hydrides of boron are known as boranes.

18. Which one of the following does not exist in the free form?

 - BF_3
 - BCl_3
 - BBr_3
 - BH_3

Sol. (d) BH_3 exist as a dimer form (B_2H_6).

19. Which of the following is most acidic?

 - Na_2O
 - MgO
 - Al_2O_3
 - CaO

Sol. (c) Na_2O , MgO , CaO are basic in nature while Al_2O_3 is amphoteric in nature.

20. Borax is:

 - $\text{Na}_2\text{B}_4\text{O}_7$
 - $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$
 - $\text{Na}_2\text{B}_4\text{O}_7 \cdot 7\text{H}_2\text{O}$
 - $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

Sol. (d) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is known as borax.

21. Boric acid is polymeric due to

 - Its acidic nature
 - The presence of hydrogen bonds
 - Its monobasic nature
 - Its geometry

Sol. (b) Boric acid is layered structure. $\text{B}(\text{OH})_3$ units are joined by hydrogen bonds and form two dimensional sheet polymer.

22. Which of the following element has exceptionally high melting point?

 - Al
 - Ga
 - B
 - In

Sol. (c) B has very high melting point and boiling point due to giant molecular structure.
M.p. order : $\text{B} > \text{Al} > \text{Ga} < \text{In} < \text{Tl}$

- 23.** In group 14, which element show inert pair effect?
 (a) Si (b) Pb (c) C (d) Ge

Sol. (b) Group 13th, 14th, and 15th Tl, Pb and Bi shows inert pair effect respectively.

24. The catenation tendency of C, Si and Ge is in the order Ge < Si < C. The bond energies (in kJ mol⁻¹) of C—C, Si—Si and Ge—Ge bonds are respectively:
 (a) 348, 260, 297 (b) 348, 297, 260
 (c) 297, 348, 260 (d) 260, 297, 348

Sol. (b) The catenation tendency of C, Si and Ge is in the order Ge < Si < C. The bond energies (in kJ mol⁻¹) of C—C, Si—Si and Ge—Ge bonds are 348, 297, 260 respectively. Ge has lowest bond energy, hence lowest catenation tendency. C has highest bond energy, hence highest catenation tendency.

25. Difference between diamond and graphite is due to:
 (a) Graphite combines with oxygen to form carbon dioxide but diamond does not
 (b) The atoms in each have different masses
 (c) The crystal structure in diamond is different from that in graphite
 (d) All of these

Sol. (c) The crystal structure in diamond is different from that in graphite.

26. Which of the following halide cannot hydrolysed?
 (a) CCl_4 (b) SiCl_4
 (c) GeCl_4 (d) SiF_4

Sol. (a) CCl_4 is stable, while other chloride can hydrolyse due to presence of vacant d-orbital.

27. On heating oxalic acid with H_2SO_4 , we get
 (a) H_2CO_3 (b) CO_2 and O_2
 (c) CO_2 and CO (d) $\text{H}_2\text{CO}_3 + \text{CO}_2 + \text{O}_2$

Sol. (c) $\text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\text{H}_2\text{SO}_4} \text{H}_2\text{O} + \text{CO} + \text{CO}_2$

28. In what respect the reaction of N_2 with (i) CaC_2 (calcium carbide) (ii) BaC_2 (barium carbide) differ from each other.

Sol. (i) CaC_2 reacts with N_2 to form calcium cyanamide.
 $\text{CaC}_2(\text{s}) + \text{N}_2(\text{g}) \xrightarrow{1373\text{K}} \text{CaCN}_2(\text{s}) + \text{C}(\text{s})$
 Calcium cyanamide

(ii) BaC_2 reacts with N_2 to form barium cyanide
 $\text{BaC}_2(\text{s}) + \text{N}_2(\text{g}) \xrightarrow{\text{Heating}} \text{Ba}(\text{CN})_2(\text{s})$
 Barium cyanide

29. Complete the following reactions

(a) $\text{CO} + \text{H}_2 \xrightarrow[420-670\text{k}, 300\text{atm}]{\text{ZnO}+\text{Cu}} \dots$

(b) $\text{R}_3\text{SiOH} + \text{OHSiR}_3 \longrightarrow \dots + \dots$

(c) $\text{Na}_2\text{CO}_3 + \text{Si} \longrightarrow \dots + \dots$

Sol. (a) $\text{CO} + 2\text{H}_2 \xrightarrow[420-670\text{k}, 300\text{atm}]{\text{ZnO}+\text{Cu}} \text{CH}_3\text{OH}$

(b) $\text{R}_3\text{SiOH} + \text{OHSiR}_3 \longrightarrow \text{R}_3\text{Si—O—SiR}_3 + \text{H}_2\text{O}$

(c) $\text{Na}_2\text{CO}_3 + \text{Si} \longrightarrow \text{Na}_2\text{SiO}_3 + \text{C}$

Exercise-1 (Topicwise)

BORON

1. TlI_3 is an ionic compound which furnishes the following ions in solution:
 - Tl^{3+} and I^- ions
 - Tl^+ and I_3^- ions
 - Tl^+ , I^- ions and I_2
 - Tl^+ and I^- ions
2. Which is true for an element R present in III group of the periodic table
 - It is gas at room temperature
 - It has oxidation state of +4
 - It forms R_2O_3
 - It forms RX_2

PROPERTIES OF BORON

3. In diborane
 - 4 bridged hydrogens and two terminal hydrogen are present
 - 2 bridged hydrogens and four terminal hydrogen are present
 - 3 bridged and three terminal hydrogen are present
 - None of the above
4. A mixture of boric acid with ethyl alcohol burns with green edged flame due to the formation of
 - Ethyl borax
 - Ethyl borate
 - Methyl borax
 - Methyl borate
5. Which of the following is known as inorganic benzene
 - Borazine
 - Boron nitride
 - p-dichlorobenzene
 - Phosphonitrilic acid
6. BCl_3 does not exist as dimer but BH_3 exist as dimer (B_2H_6) because
 - Chlorine is more electronegative than hydrogen
 - There is $p\pi-p\pi$ back bonding in BCl_3 but BH_3 does not contain such multiple bonding
 - Large sized chlorine atoms do not fit in between the small boron atoms whereas small sized hydrogen atoms get fitted in between boron atoms
 - None of the above
7. Which of the following is the electron deficient molecule
 - B_2H_6
 - C_2H_6
 - PH_3
 - SiH_4
8. Acidic strength of Boron trihalide are in order of
 - $BF_3 < BCl_3 < BBr_3 < BI_3$
 - $BI_3 < BBr_3 < BCl_3 < BF_3$
 - $BBr_3 < BCl_3 < BF_3 < BI_3$
 - $BF_3 < BI_3 < BCl_3 < BBr_3$

PROPERTIES OF ALUMINIUM

9. Aluminium is a self-preserving metal, because
 - It is not tarnished by air
 - A thin film of basic carbonate on its surface
 - A non-porous layer of oxide is formed on its surface
 - It is not affected by salt water
10. In the thermite process the reducing agent is

<i>(a) Al</i>	<i>(b) C</i>
<i>(c) Mg</i>	<i>(d) Na</i>

COMPOUNDS OF ALUMINIUM

11. Alum is found to contain hydrated monovalent cation $[M(H_2O)_6]^{+}$, trivalent cation $[M'(H_2O)_6]^{+3}$ and SO_4^{2-} in the ratio of:
 - 1 : 1 : 1
 - 1 : 1 : 2
 - 1 : 2 : 2
 - 1 : 2 : 3
12. Aluminium hydroxide is soluble in excess of sodium hydroxide forming the ion

<i>(a) AlO_2^{+3}</i>	<i>(b) AlO_2^{-3}</i>
<i>(c) AlO_2^-</i>	<i>(d) AlO_3^-</i>
13. Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives
 - $[Al(OH)_6]^{3-} + 3HCl$
 - $[Al(H_2O)_6]^{3+} + 3Cl^-$
 - $Al^{3+} + 3Cl^-$
 - $Al_2O_3 + 6HCl$
14. Aluminium vessels should not be washed with materials containing washing soda since
 - Washing soda is expensive
 - Washing soda is easily decompose
 - Washing soda reacts with aluminium to form soluble aluminate
 - Washing soda reacts with aluminium to form insoluble aluminium oxide
15. Aluminium (III) chloride forms a dimer because
 - Higher coordination number can be achieved by aluminium
 - Aluminium has high ionization energy
 - Aluminium belongs to III group
 - It cannot form a trimer

GENERAL CHARACTERISTIC OF C-FAMILY

16. Amongst the elements of group 14, the reducing power of the divalent species decreases in the order

 - (a) Ge > Sn > Pb
 - (b) Sn > Ge > Pb
 - (c) Pb > Sn > Ge
 - (d) Sn > Pb > Ge

CHEMISTRY OF CARBON

17. Carbon-60 contains:

 - (a) 20 pentagons and 12 hexagons
 - (b) 12 pentagons and 20 hexagons
 - (c) 30 pentagons and 30 hexagons
 - (d) 24 pentagons and 36 hexagons

COMPOUNDS OF CARBON

18. Suppose you have to determine the percentage of carbon dioxide in a sample of a gas available in a container. Which is the best absorbed material for the carbon dioxide:

 - (a) Heated copper oxide
 - (b) Cold, solid calcium chloride
 - (c) Cold, solid calcium hydroxide
 - (d) Heated charcoal

19. Which is used to produce smoke screens

 - (a) Calcium phosphide
 - (b) Zinc sulphide
 - (c) Sodium carbonate
 - (d) Zinc phosphide

CHEMISTRY OF SILICON

TIN AND LEAD



Exercise-2 (Learning Plus)

1. The decrease in stability of higher oxidation state in p-block with increasing atomic number is due to:

 - (a) Increase in bond energy as going down the group.
 - (b) The reluctance of s-subshell electrons to participate in the chemical bonding.
 - (c) Both are correct.
 - (d) None is correct.

2. Crystalline boron in small amounts may be obtained by:

 - (a) Reducing BCl_3 with H_2
 - (b) Pyrolysis of BI_3
 - (c) Thermal decomposition of diborane
 - (d) All of these

- 3.** Borax is:
- (a) $\text{Na}_2\text{B}_4\text{O}_7$
 - (b) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$
 - (c) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 7\text{H}_2\text{O}$
 - (d) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
- 4.** $\text{H}_3\text{BO}_3 \xrightarrow{T_1} X \xrightarrow{T_2} Y \xrightarrow{\text{red hot}} \text{B}_2\text{O}_3$
if $T_1 < T_2$ then X and Y respectively are
- (a) X = Metaboric acid and Y = Tetraboric acid
 - (b) X = Tetraboric acid and Y = Metaboric acid
 - (c) X = Borax and Y = Metaboric acid
 - (d) X = Tetraboric acid and Y = Borax
- 5.** Borax bead test is responded by:
- (a) Divalent metals
 - (b) Heavy metals
 - (c) Light metals
 - (d) Metal which forms coloured metaborates
- 6.** H_2S gas can be obtained by the action of water on:
- (a) CuS
 - (b) FeS
 - (c) Flower of sulphur
 - (d) Al_2S_3
- 7.** Which of the following is only acidic in nature:
- (a) $\text{Be}(\text{OH})_2$
 - (b) $\text{Mg}(\text{OH})_2$
 - (c) $\text{B}(\text{OH})_3$
 - (d) $\text{Al}(\text{OH})_3$
- 8.** Aluminium does not react with:
- (a) NaOH
 - (b) conc. HCl
 - (c) N_2
 - (d) conc. HNO_3
- 9.** Aqueous solution of potash alum is:
- (a) Alkaline
 - (b) Acidic
 - (c) Neutral
 - (d) Soapy
- 10.** Which mixed sulphate is not an alum:
- (a) $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 - (b) $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 - (c) $\text{Na}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 - (d) $\text{CuSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- 11.** An aqueous solution of BCl_3 is:
- (a) Weak acid
 - (b) Weak base
 - (c) Neutral
 - (d) Strong base
- 12.** Elements of group 14:
- (a) Exhibit oxidation state of +4 only
 - (b) Exhibit oxidation state of +2 and +4
 - (c) Form M^{-2} and M^{4+} ions
 - (d) Form M^{2+} and M^{4+} ions
- 13.** Methanides are:
- (a) Mg_2C_3 , Be_2C , Al_4C_3 and CaC_2
 - (b) Mg_2C_3 , Be_2C and Al_4C_3
 - (c) Be_2C , Al_4C_3 and CaC_2
 - (d) Be_2C and Al_4C_3
- 14.** When oxalic acid reacts with conc. H_2SO_4 , two gases produced are of neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases. The product formed during this absorption and the gas which gets absorbed are respectively.
- (a) K_2CO_3 and CO_2
 - (b) KHCO_3 and CO_2
 - (c) K_2CO_3 and CO
 - (d) KHCO_3 and CO
- 15.** Coal gas is a mixture of:
- (a) CO and H_2
 - (b) H_2 , saturated and unsaturated hydrocarbons, CO , CO_2 , N_2 and O_2
 - (c) saturated and unsaturated hydrocarbons
 - (d) CO , CO_2 and CH_4
- 16.** The ions present in Al_4C_3 , CaC_2 and Mg_2C_3 are respectively:
- (a) C^4- , C_2^{2-} , C_3^{4-}
 - (b) C_2^{2-} , C^4- , C_3^{4-}
 - (c) C_3^{4-} , C_2^{2-} , C^4-
 - (d) C_3^{4-} , C^4- , C_2^{2-}
- 17.** Select incorrect statement:
- (a) Interstitial carbides are formed by metalloids like Si and B
 - (b) SiC is called carborundum
 - (c) CO and CN^- both are fatal due to complex formation with Fe(III) present in blood
 - (d) CO is obtained as by-product when carbon and SiO_2 is used in reduction processes of phosphate rock to give phosphorus.
- 18.** The hydroxide of which metal ion is soluble in excess of sodium hydroxide solution:
- (a) Fe^{3+}
 - (b) Cr^{3+}
 - (c) Sn^{2+}
 - (d) Cu^{2+}
- 19.** Unlike PbCl_4 , PI_4 and PBr_4 are not found because:
- (a) Bromine and iodine are more electronegative than chlorine.
 - (b) Iodine and bromine are smaller in size.
 - (c) Larger iodine and bromine are able to reduce Pb^{4+} to Pb^{2+} or Pb.
 - (d) The statement is incorrect.
- 20.** Which of the following halides is least stable and has doubtful existence?
- (a) Cl_4
 - (b) GeI_4
 - (c) SnI_4
 - (d) PbI_4

Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

1. Which of the following facts regarding boron and silicon is/are true?
 - Boron is used to make boron steel or boron carbide control rods for nuclear reactor.
 - Boron and silicon form halides which are not hydrolysed.
 - Boron and silicon react with magnesium to form magnesium boride and magnesium silicide which are decomposed by acids to give volatile borane and silane, respectively.
 - Both boron and silicon react with alkali to form borates and silicates containing BO_3^{3-} and SiO_4^{4-} tetrahedral units, respectively.
2. Which species exist?
 - $[\text{BF}_6]^{3-}$
 - $[\text{AlF}_6]^{3-}$
 - $[\text{GaF}_6]^{3-}$
 - $[\text{InF}_6]^{3-}$
3. Which of the following statement(s) is/are correct?
 - The oxide, B_2O_3 and $\text{B}(\text{OH})_3$ are acidic
 - The halides of B (except BF_3) and Si are readily hydrolysed.
 - The hydrides of B and Si are volatile, spontaneously flammable and readily hydrolysed.
 - Aluminium hydride is a polymer, $(\text{AlH}_3)_n$.
4. Which is/are the correct statement(s)?
 - BeF_2 readily coordinates two additional F^- ions forming the $[\text{BeF}_4]^{2-}$ complex.
 - One mole of borax in aqueous solution reacts with two moles of acid.
 - HCOONa as well as solid $\text{K}_3[\text{Fe}(\text{CN})_6]$ both on heating with concentrated sulphuric acid evolve carbon monoxide gas.
 - Carbon mono oxide when passed through a solution of iodine pentaoxide, I_2O_5 liberates iodine and carbon dioxide gases.
5. Which of the following statements about anhydrous aluminium chloride is/are incorrect ?
 - It exists as AlCl_3 molecule in gaseous phase
 - It is a strong Lewis base
 - It sublimes at 100°C under vacuum
 - It is not easily hydrolysed
6. Select the correct statement(s)
 - The graphite is diamagnetic and diamond is paramagnetic in nature.
 - Graphite acts as a metallic conductor along the layers of carbon atoms and as semi-conductor perpendicular to the layers of the carbon atoms.
 - Graphite is less denser than diamond
 - C_{60} is called as Buckminster fullerene

7. Consider the following statements and which of the following are correct?
 - $\text{B}_4\text{O}_7^{2-}$ on hydrolysis with acid / water yields $\text{B}(\text{OH})_3$
 - SiO_4^{4-} on hydrolysis with acid / water yields $\text{Si}_2\text{O}_7^{6-}$
 - MeSiCl_3 on hydrolysis and then condensations gives a complex cross-linked polymer of silicones.
 - Among CO_2 , CuO , CaO and H_2O , CO_2 is most acidic oxide while CaO is most basic oxide.
 - $\text{S}_1 \text{S}_2 \text{S}_3$ only
 - $\text{S}_1 \text{S}_3 \text{S}_4$ only
 - $\text{S}_1 \text{S}_2 \text{S}_3 \text{S}_4$
 - $\text{S}_2 \text{S}_3 \text{S}_4$ only
8. Carbon monoxide is prepared by:
 - Heating formic acid with conc. H_2SO_4
 - Heating potassium ferrocyanide with conc H_2SO_4
 - Heating malonic acid with P_4O_{10}
 - Hydrolysis of Mg_2C_3
9. Which of the following statement(s) is/are false for soluble bicarbonates?
 - They give pink colour with phenolphthalein.
 - They do not liberate carbondioxide with phenol.
 - They give white precipitate with magnesium nitrate in cold.
 - They liberate carbondioxide on reaction with dil. H_2SO_4 .
10. A complex cross-linked polymer (silicone) is formed by
 - Hydrolysis of $(\text{CH}_3)_3\text{SiCl}$.
 - Hydrolysis of a mixture of $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CH}_3)_2\text{SiCl}_2$
 - Hydrolysis of CH_3SiCl_3
 - Hydrolysis of SiCl_4 .

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 11 to 13): Compound (A) on reaction with iodine in the solvent diglyme gives a hydride (B) and hydrogen gas. The product (B) is instantly hydrolysed by water or aqueous alkali forming compound (C) and liberating hydrogen gas. The compound (C) in aqueous solution behaves as a weak mono basic acid. But in presence of certain organic polyhydroxy compound behaves as a strong monobasic acid. The hydride (B) in air catches fire spontaneously forming oxide which gives coloured beads with transition metal compounds.

11. Which of the following statement is correct for the product (C)?
 - It is an odd electron molecule.
 - It in water acts as proton donor.
 - It in solid state have hydrogen bonding.
 - It is a useful primary standard for titrating against acids.

12. Aqueous solution of product (C) can be titrated against sodium hydroxide using phenolphthalein indicator only in presence of:

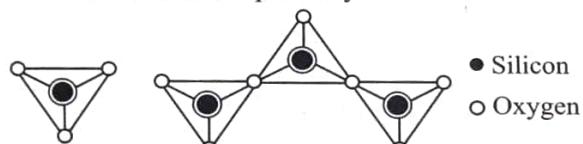
- (a) cis-1, 2 diol
- (b) trans-1, 2 diol
- (c) borax
- (d) Na_2HPO_4

13. Which of the following statement is correct for hydride (B)?

- (a) One mole of it react with two moles of HCl .
- (b) It reacts with excess of ammonia at low temperature to form an ionic compound.
- (c) One mole of it reacts with one mole of trimethylamine.
- (d) It reacts with methyl alcohol to form a trimethyl compound liberating oxygen gas.

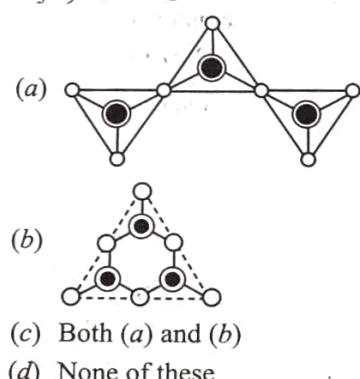
Comprehension (Q. 14 to 16): Read name 'silica' covers an entire group of minerals, which have the general formula SiO_2 , the mole common of which is quartz. Quartz is form work silicane with SiO_4 tetrahedral arranged in spirals. The spirals can turn in a clockwise or anticlockwise direction a feature that results in there being two mirror images, optically active, varieties of quartz.

14. The following pictures represent various silicate anions. Their formulae are respectively



- (a) $\text{SiO}_3^{2-} \text{Si}_3\text{O}_7^{2-}$
- (b) $\text{SiO}_4^{4-} \text{Si}_3\text{O}_{10}^{8-}$
- (c) $\text{SiO}_4^{2-} \text{Si}_3\text{O}_9^{2-}$
- (d) $\text{SiO}_3^{4-} \text{Si}_3\text{O}_7^{8-}$

15. $\text{Si}_3\text{O}_9^{6-}$ (having three tetrahedral) is represented as :



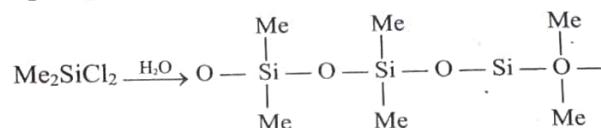
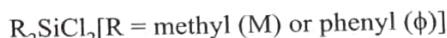
16. The silicate anion in the mineral kinotite is a Chain of three SiO_4 tetrahedra that share corners with adjacent tetrahedra. The mineral also contains Ca^{2+} ions, Cu^{2+} ions and water molecule in a 1 : 1 : 1 ratio mineral is represented as:

- (a) $\text{CaCuSi}_3\text{O}_{10}\cdot\text{H}_2\text{O}$
- (b) $\text{CaCuSi}_3\text{O}_{10}\cdot2\text{H}_2\text{O}$
- (c) $\text{Ca}_2\text{Cu}_2\text{Si}_2\text{O}_{10}\cdot2\text{H}_2\text{O}$
- (d) None of these

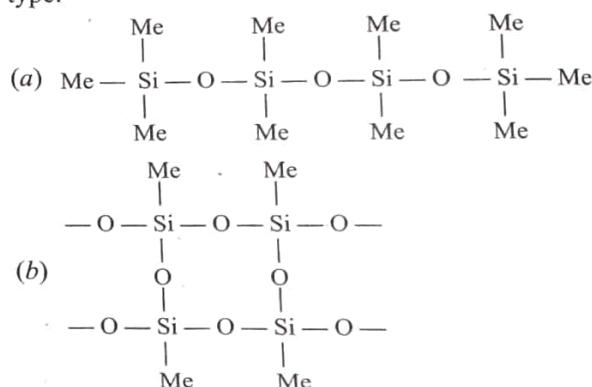
Comprehension (Q. 17 to 18): Read the following write-ups and answer the questions at the end of it.

Silicons are synthetic polymers containing represented R_2SiO units. Since, the empirical formula is that of acetone (R_2CO) the same silicone has been given to these. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of



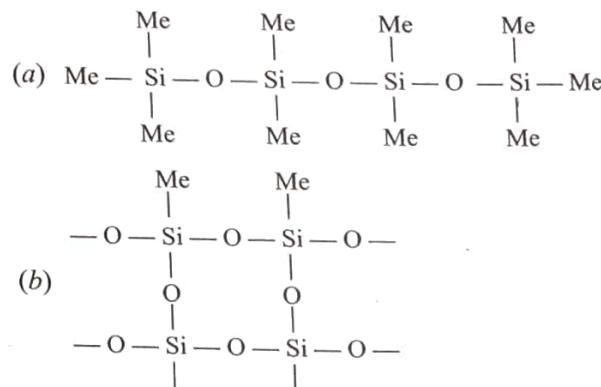
17. If we mix Me_3SiCl with Me_2SiCl_2 , we get silicones of they type:



(c) Both of the above

(d) None of the above

18. If we start with MeSiCl_3 as the starting material, silicones formed is:



(c) Both of the above

(d) None of the above

MATCH THE COLUMN TYPE QUESTIONS

19. Match the reactions listed in column-I with characteristic(s)/ type of reactions listed in column-II.

Column-I	Column-II
A. $\text{Al}_2(\text{C}_2)_3 + \text{H}_2\text{O} \rightarrow$	p. One of the products contains both σ and π bonds
B. $\text{CH}_2(\text{COOH})_2 + \text{P}_4\text{O}_{10} \rightarrow$	q. Hydrolysis
C. $\text{CH}_3\text{SiCl}_3 + \text{H}_2\text{O} \rightarrow$	r. Dehydration
D. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow[\text{standing}]{\text{on}}$	s. Complex crosslinked polymer

- (a) A-(p); B-(p,r); C-(r,s); D-(q)
- (b) A-(p,q); B-(p,r); C-(q,s); D-(q)
- (c) A-(p,q); B-(q,s); C-(p,r); D-(r)
- (d) A-(r); B-(p,s); C-(q,s); D-(p)

20. Match the reactions listed in column-I with characteristic(s)/ type of reactions listed in column-II.

Column-I	Column-II
A. $\text{BBr}_3 + \text{H}_2 \rightarrow \text{B}$	p. Borax bead test
B. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{CuSO}_4 \rightarrow \text{Cu}(\text{BO}_2)_2$	q. Reduction
C. $\text{AlCl}_3 + \text{H}_2\text{O} \rightarrow \text{HCl}$	r. White fumes
D. $\text{Cr}_2\text{O}_3 + \text{Al} \rightarrow \text{Cr}$	s. Hydrolysis

- (a) A-(p,s); B-(q,r); C-(r); D-(p)
- (b) A-(p,q); B-(q); C-(s); D-(q)
- (c) A-(q); B-(p); C-(r,s); D-(q)
- (d) A-(p); B-(q,r); C-(r,p); D-(r)

NUMERICAL TYPE QUESTIONS

21. Find the maximum number of atoms are lying in the same plane for B_2H_6 .

22. Which of following substance is having higher lattice energy than NaBr .

$\text{CaCl}_2, \text{NaI}, \text{CsBr}, \text{LiF}, \text{MgO}, \text{Al}_2\text{O}_3, \text{TiO}_2$

23. 1 mole of B_2H_6 (g) on hydrolysis yields moles of H_2 (g).

24. How many of the following statements are correct regarding allotropes of carbon:

- (a) Graphite is not a good conductor of electricity in perpendicular direction of layers at ordinary temperatures.
- (b) Coke is the impure form of carbon.
- (c) Anthracite is the purest form of Carbon.
- (d) Buckminster fullerene contains 12 five membered rings and 20 six-membered rings.
- (e) Diamond is a good conductor of Heat.
- (f) Graphite is diamagnetic in nature.
- (g) Graphite is thermodynamically more stable than diamond

25. For Boron family (B, Al, Ga, In and Tl)

x : Number of elements which are solid at 40°C .

y : Period number of element which has greater ionization energy than element just above and below it in periodic table.

z : Period number of most abundant element of group 13.
Report your answer $x + 2y + 3z$

26. Consider a prototypical fullerene, C_{60} .

Let, a = Number of 5-membered rings

b = Number of 6-membered rings

c = Number of π -bonds in C_{60}

Find the value of $(3a - 2b + c)$

27. $\text{B}_{10}\text{C}_2\text{H}_{12}$ is isostructural & isoelectronic with borate ion of formula $\text{B}_x\text{H}_y^{Z-}$ give $x + y + z$.

28. Which of the following salts are amphoteric in nature.

$\text{PbO}, \text{PbO}_2, \text{SnO}, \text{SnO}_2, \text{Al}_2\text{O}_3, \text{ZnO}, \text{BeO}, \text{Ca}_2\text{O}_3, \text{B}_2\text{O}_3$

29. $\text{Mg} + \text{B} \rightarrow \text{Mg}_x\text{B}_y \xrightarrow{\text{HCl}} \text{Diborane}$

Report your answer as $(x + y)$.

Exercise-4 (Past Year Questions)

JEE MAIN

1. The reaction of zinc with dilute and concentrated nitric acid, respectively, produces: (2016)

- (a) N_2O and NO_2
- (b) NO_2 and NO
- (c) NO and N_2O
- (d) NO_2 and N_2O

2. The pair in which phosphorous atoms have a formal oxidation state of +3 is: (2016)

- (a) Orthophosphorous and pyrophosphorous acids
- (b) Pyrophosphorous and hypophosphorous acids
- (c) Orthophosphorous and hypophosphorous acids
- (d) Pyrophosphorous and Pyrophosphoric acids

3. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are: (2017)
- (a) ClO^- and ClO_3^- (b) ClO_2^- and ClO_3^-
 (c) Cl^- and ClO^- (d) Cl^- and ClO_2^-
4. Which of the following are Lewis acids? (2018)
- (a) AlCl_3 and SiCl_4 (b) PH_3 and SiCl_4
 (c) BCl_3 and AlCl_3 (d) PH_3 and BCl_3
5. The element that does NOT show catenation is: (2019)
- (a) Ge (b) Si (c) Sn (d) Pb
6. Correct statements among (i) to (iv) regarding silicones are
- (i) They are polymers with hydrophobic character
 (ii) They are biocompatible
 (iii) In general, they have high thermal stability and low dielectric strength
 (iv) Usually they are resistant to oxidation and used as greases. (2019)
- (a) (i), (ii), (iii) and (iv) (b) (i), (ii) and (iii)
 (c) (i) and (ii) only (d) (i), (ii) and (iv)
7. The hydride that is NOT electron deficient is: (2019)
- (a) SiH_4 (b) B_2H_6
 (c) GaH_3 (d) AlH_3
8. Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce, respectively (2019)
- (a) HBO_2 and H_3BO_3 (b) H_3BO_3 and B_2O_3
 (c) B_2O_3 and H_3BO_3 (d) B_2O_3 and $[\text{BH}_4]^-$
9. The amorphous form of silica is: (2019)
- (a) Quartz (b) Kieselguhr
 (c) Cristobalite (d) Tridymite
10. The correct statements among I to III regarding group 13 element oxides are (2019)
- (I) Boron trioxide is acidic.
 (II) Oxides of aluminium and gallium are amphoteric.
 (III) Oxides of indium and thallium are basic.
 (a) (I), (II) and (III) (b) (II) and (III) only
 (c) (I) and (III) only (d) (I) and (II) only
11. The basic structural unit of feldspar, zeolites, mica and asbestos is: (2019)
- (a) $(\text{SiO}_3)^{2-}$ (b) SiO_2
 (c) $(\text{SiO}_4)^{4-}$ (d) $\begin{array}{c} \text{R} \\ | \\ -\text{Si}-\text{O}- \\ | \\ \text{R} \quad (\text{R}=\text{Me}) \end{array}$
12. The reaction of $\text{H}_3\text{N}_3\text{B}_3\text{Cl}_3$ (A) with LiBH_4 in tetrahydrofuran gives inorganic benzene (B). Further, the reaction of (A) with (C) leads to $\text{H}_3\text{N}_3\text{B}_3(\text{Me})_3$. Compounds (B) and (C) respectively, are: (2020)
- (a) Boron nitride and MeBr
 (b) Borazine and MeMgBr
 (c) Borazine and MeBr
 (d) Diborane and MeMgBr
13. Which one of the following is having highest melting point? (2020)
- (a) AgCl (b) AgBr
 (c) AgF (d) AgI
14. Reaction of an inorganic sulphite X with dilute H_2SO_4 generates compound Y. Reaction of Y with NaOH gives X. Further, the reaction of X with Y and water affords compound Z. Y and Z, respectively, are (2020)
- (a) S and Na_2SO_3 (b) SO_2 and NaHSO_3
 (c) SO_2 and Na_2SO_3 (d) SO_3 and NaHSO_3
15. Which one of the following is formed (mainly) when red phosphorus is heated in a sealed tube at 803K? (2021)
- (a) White phosphorus
 (b) Yellow phosphorus
 (c) β -Black phosphorus
 (d) α -Black phosphorus
16. Column-I (compound) Column-II (effect/affected species)
- | Column-I | Column-II |
|------------------------------|--------------------------------|
| A. Carbon monoxide | p. Carcinogenic |
| B. Sulphur dioxide | q. Metabolized by pyrus plants |
| C. Polychlorinated biphenyls | r. Haemoglobin |
| D. Oxides of Nitrogen | s. Stiffness of flower buds |

(2021)

Choose the correct answer from the options given below:

- (a) A-(r); B-(s); C-(p); D-(q)
 (b) A-(s); B-(p); C-(r); D-(q)
 (c) A-(p); B-(q); C-(r); D-(s)
 (d) A-(r); B-(s); C-(q); D-(p)

17. Given below are two statements: one is labelled as Assertion A and the other is labelled as Reason R.

Assertion (A): $\text{SO}_2(g)$ is absorbed to a large extent than $\text{H}_2(g)$ on activated charcoal.

Reason (R): $\text{SO}_2(g)$ has a higher critical temperature than $\text{H}_2(g)$.

In the light of the above statements, choose the most appropriate answer from the options given below. (2021)

- (a) Both A and R are correct but R is not the correct explanation of A.
 (b) Both A and R are correct and R is the correct explanation of A.
 (c) A is not correct but R is correct.
 (d) A is correct but R is not correct.

18. The product obtained from the electrolytic oxidation of acidified sulphate solutions, is: (2021)

- (a) HSO_4^- (b) $\text{H}_2\text{S}_2\text{O}_8$
 (c) $\text{H}_2\text{S}_2\text{O}_5$ (d) $\text{H}_2\text{S}_2\text{O}_7$

19. Number of electron deficient molecules among the following PH_3 , B_2H_6 , CCl_4 , NH_3 , LiH and BCl_3 is (2022)

(a) 0 (b) 1
(c) 2 (d) 3

20. Match the Column-I with Column-II (2022)

Column-I		Column-II
A. Cs	p.	High temperature thermometer
B. Ga	q.	Water repellent sprays
C. B	r.	Photoelectric cells
D. Si	s.	Bullet proof vest

Choose the most appropriate answer from the option given below:

- (a) A-(r); B-(p); C-(s); D-(q)
(b) A-(s); B-(r); C-(q); D-(p)
(c) A-(q); B-(r); C-(s); D-(p)
(d) A-(p); B-(s); C-(q); D-(r)

21. Consider the following reaction:



If B is an oxoacid of phosphorus with no P-H bond, then A is: (2022)

- (a) White P_4 (b) Red P_4
(c) P_2O_3 (d) H_3PO_3

22. The interhalogen compound formed from the reaction of bromine with excess of fluorine is a: (2022)

- (a) Hypohalite
(b) Halate
(c) Perhalate
(d) Halite

23. White phosphorus reacts with thionyl chloride to give (2022)

- (a) PCl_5 , SO_2 and S_2Cl_2
(b) PCl_3 , SO_2 and S_2Cl_2
(c) PCl_3 , SO_2 and Cl_2
(d) PCl_5 , SO_2 and Cl_2

24. When borax is heated with CoO on a platinum loop, blue coloured bead formed is largely due to: (2022)

- (a) B_2O_3 (b) $\text{Co}(\text{BO}_2)_2$
(c) CoB_4O_7 (d) $\text{CO}[\text{B}_4\text{O}_5(\text{OH})_4]$

JEE ADVANCED

25. The correct statement(s) for orthoboric acid is/are (2014)

- (a) It behaves as a weak acid in water due to self ionization.
(b) Acidity of its aqueous solution increases upon addition of ethylene glycol.
(c) It has a three dimensional structure due to hydrogen bonding.
(d) It is weak electrolyte in water.

26. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is (2015)

27. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are: (2015)

- (a) CH_3SiCl_3 and $\text{Si}(\text{CH}_3)_4$
(b) $(\text{CH}_3)_2\text{SiCl}_2$ and $(\text{CH}_3)_3\text{SiCl}$
(c) $(\text{CH}_3)\text{SiCl}_2$ and CH_3SiCl_3
(d) SiCl_4 and $(\text{CH}_3)_3\text{SiCl}$

28. The crystalline form of borax is (2016)

- (a) Tetrานuclear $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ unit
(b) All boron atoms in the same plane
(c) Equal number of sp^2 and sp^3 hybridized boron atoms
(d) One terminal hydroxide per boron atom

29. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10} (2016)

- (a) Can also be prepared by reaction of P_4 and HNO_3
(b) Is diamagnetic
(c) Contains one N-N bond
(d) Reacts with Na metal producing a brown gas

30. Which of the following liberates O_2 upon hydrolysis? (2020)

- (a) Pb_3O_4 (b) KO_2 (c) Na_2O_2 (d) Li_2O_2

31. Choose the correct statement(s) among the following. (2020)

- (a) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is a reducing agent.
(b) SnO_2 reacts with KOH to form $\text{K}_2[\text{Sn}(\text{OH})_6]$.
(c) A solution of PbCl_2 in HCl contains Pb^{2+} and Cl^- ions.
(d) The reaction of Pb_3O_4 with hot dilute nitric acid to give PbO_2 is a redox reaction.

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (a) | 3. (c) | 4. (b) | 5. (c) | 6. (d) | 7. (c) | 8. (c) | 9. (b) | 10. (c) |
| 11. (a) | 12. (a) | 13. (c) | 14. (b) | 15. (c) | 16. (c) | 17. (c) | 18. (b) | 19. (b) | 20. (b) |
| 21. (a) | 22. (c) | 23. (d) | 24. (c) | 25. (d) | 26. (a) | 27. (b) | 28. (d) | 29. (d) | 30. (a) |
| 31. (b) | 32. (a) | 33. (a) | 34. (a) | 35. (a) | 36. (c) | 37. (b) | 38. (c) | 39. (c) | 40. (a) |
| 41. (c) | 42. (a) | | | | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (b) | 4. (b) | 5. (a) | 6. (c) | 7. (a) | 8. (a) | 9. (c) | 10. (a) |
| 11. (b) | 12. (c) | 13. (b) | 14. (c) | 15. (a) | 16. (a) | 17. (b) | 18. (c) | 19. (a) | 20. (c) |
| 21. (b) | 22. (c) | 23. (b) | 24. (b) | 25. (c) | 26. (c) | 27. (c) | 28. (a) | 29. (a) | 30. (d) |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (d) | 3. (d) | 4. (a) | 5. (d) | 6. (d) | 7. (c) | 8. (d) | 9. (b) | 10. (d) |
| 11. (a) | 12. (b) | 13. (d) | 14. (a) | 15. (b) | 16. (a) | 17. (a) | 18. (c) | 19. (c) | 20. (d) |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|------------|------------|--------------|--------------|------------|------------|----------|----------|----------|---------|
| 1. (a,c,d) | 2. (b,c,d) | 3. (a,b,c,d) | 4. (a,b,c,d) | 5. (a,b,d) | 6. (b,c,d) | 7. (c) | 8. (a,b) | 9. (a,c) | 10. (c) |
| 11. (c) | 12. (a) | 13. (b) | 14. (b) | 15. (b) | 16. (c) | 17. (a) | 18. (b) | 19. (b) | 20. (c) |
| 21. [6] | 22. [5] | 23. [6] | 24. [4] | 25. [21] | 26. [26] | 27. [26] | 28. [8] | 29. [5] | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (a) | 3. (c) | 4. (c) | 5. (d) | 6. (d) | 7. (a) | 8. (c) | 9. (b) | 10. (a) |
| 11. (c) | 12. (b) | 13. (c) | 14. (b) | 15. (d) | 16. (a) | 17. (b) | 18. (b) | 19. (d) | 20. (a) |
| 21. (b) | 22. (b) | 23. (b) | 24. (b) | | | | | | |

JEE Advanced

- | | | | | | | | | | |
|-----------|---------|---------|-------------|-----------|---------|--------------------|--|--|--|
| 25. (b,d) | 26. [6] | 27. (b) | 28. (a,c,d) | 29. (b,d) | 30. (b) | 31. (a,b or a,b,c) | | | |
|-----------|---------|---------|-------------|-----------|---------|--------------------|--|--|--|

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