ALLEN CAREER INSTITUTE KOTA (RAJASTHAN)

path to success

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GENERAL CHEMISTRY

Recap of Early Classes

In Previous classes we have studied about atoms, molecules, periodic classification of elements, metals, non metal, carbon and it's compounds (IUPAC Nomenclature). In order to escalate our knowledge about chemistry, we will intoduce certain fundamental aspects of chemistry in this chapter called general chemistry. We will introduce basic mole concept to develop a strong foundation through which understanding of subsequent chapters will be easier.

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MOLE CONCEPT

1.0 INTRODUCTION

Chemistry deals with the composition, structure and properties of matter. These aspects can be best described and understood in terms of basic constituents of matter: ***atoms*** and ***molecules***. That is why chemistry is called the science of atoms and molecules ***– THE STUDY OF MATTER.***

2.0 CLASSIFICATION OF MATTER

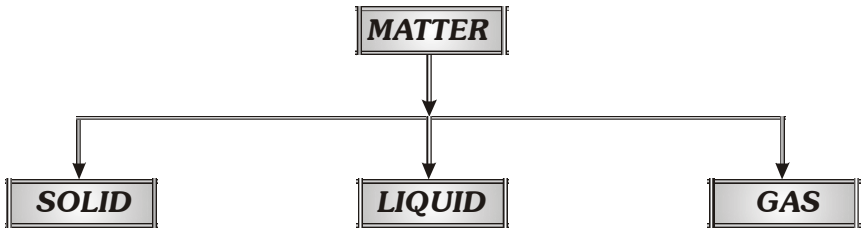
MATTER : Matter is anything that has mass and occupies space.

Two ways of classifying matter :

- ***Physical Classification***
- ***Chemical Classification***

2.1 Physical Classification

SL AL



(i)	Particles held very closely packed in ordered manner.	Particles are less closely packed.	Particles are farthest apart
(ii)	No freedom of movement particles	Particles can move around to some extent	Movement of particles is very of asy and fast
(iii)	Definite shape and volume	Definite volume, indefinite shape	Indefinite shape and volume
(iv)	Exists at low T and high P	Exists at intermediate P & T	Exists at high T and low P

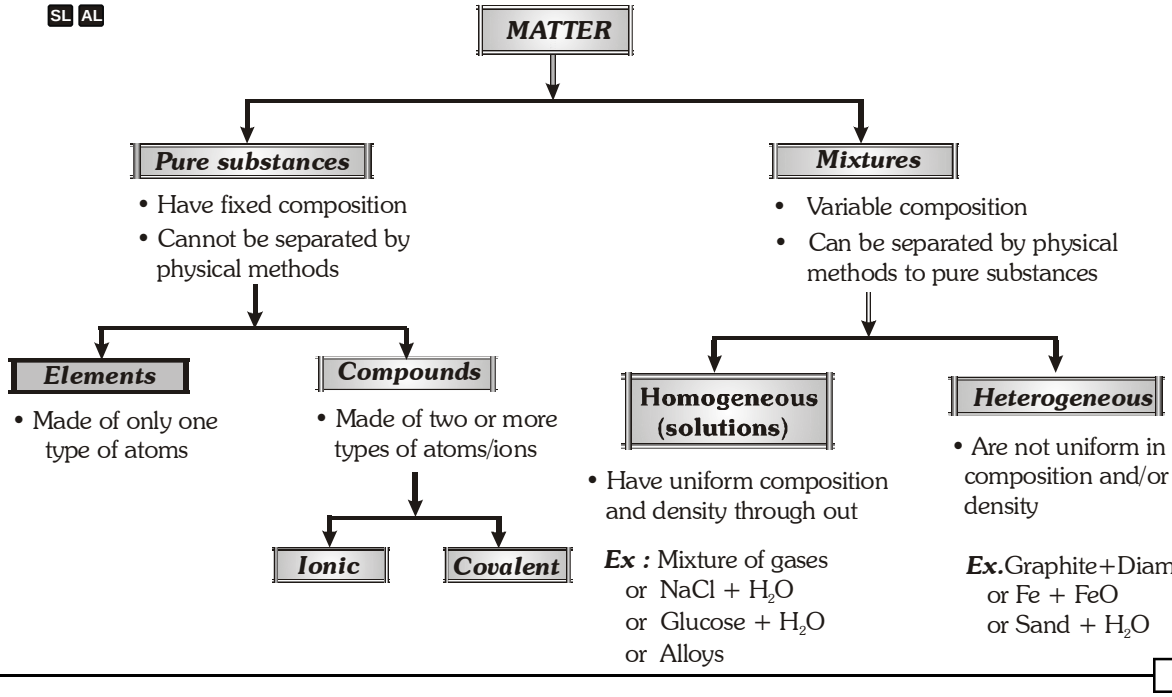
Note : ***For same substance :***

- Solid and Liquid co-exist at ***MELTING POINT***.
- Liquid and gas co-exist at ***BOILING POINT***.
- Solid and gas co-exist at ***SUBLIMATION POINT***.
- Solid, liquid and gas co-exist at ***TRIPLE POINT***.

☞ *Gases do not have any definite volumes. Then what's the meaning of volume of the gas* ***?***

2.2 Chemical Classification

SL AL



☞ ***Note :***

- ***PHASE :*** *It is the state of matter uniform in density and composition.*
- *Homogeneous mixtures have single phase while heterogeneous mixtures are multi-phase.*
  Ex : *$NaCl + H_2O$ mixture has one phase*
  Ex : *Graphite + Diamond mixture has 2 phases.*

SOME SPECIFIC PROPERTIES OF SUBSTANCES

v ***Deliquescence :***

The property of certain compounds of taking up the moisture present in atmosphere and becoming wet when exposed, is known as deliquescence. These compounds are known as deliquescent. Sodium hydroxide, potassium hydroxide, anhydrous calcium chloride, anhydrous magnesium chloride, anhydrous feric chloride, etc., are the examples of deliquescent compounds.

v ***Hygroscopicity :***

Certain compounds combine with the moisture of atmosphere and are converted into hydroxides or hydrates. Such substances are called hygroscopic. Anhydrous copper sulphate, quick lime (CaO), anhydrous sodium carbonate, etc., are of hygroscopic nature.

v ***Efflorescence :***

The property of some crystalline substances of losing their water of crystallisation on exposure and becoming powdery on the surface is called efflorescence and such salts are know as efflorescent. The examples are : Ferrous sulphate ($FeSO_4.7H_2O$), sodium carbonate ($Na_2CO_3.10H_2O$), sodium sulphate ($Na_2SO_4.10H_2O$), potash alum [$K_2SO_4.Al_2(SO_4)_3.24H_2O$], etc.

v ***Malleability :***

This property is shown by metals. When metallic solid is being beaten, it does not break but is converted into thin sheet. It is said to possess the property of malleability. Copper, gold, silver, aluminium, lead, etc., can be easily hammered into sheets. Gold is the most malleable metal.

v ***Ductility :***

The property of metal to be drawn into wires is termed ductility. Copper, silver, gold, aluminium, iron, etc., are ductile in nature. Platinum is the most ductile metal.

v ***Brittleness :***

The solid materials which break into small pieces on hammering are called brittle. The solids of non-metals are generally brittle in nature.

Ex: Ice, Diamond etc.

3.0 THE LAW OF CHEMICAL COMBINATION

SL

Atoine Lavoisier, John Dalton and other scientists formulated certain laws concerning the composition of matter and chemical reactions. These laws are known as the law of chemical combination.

3.1 Law of indestructibility of matter or conservation of Mass

SL

- This law was proposed by ***Lavosier in 1774.***
- According to this law in all chemical changes the total mass of the system remains constant or in a chemical change mass is neither created nor destroyed. Thus, in chemical change-

Total mass of reactant = Total mass of products

Ex. $H_2O(s) \longrightarrow H_2O(\ell)$

Above reaction shows the physical change and the wt. of H_2O (s) = wt. of $(H_2O)(\ell)$

☞ ***Note :***

In case the reacting materials are not completely consumed, the relationship will be

Total masses of reactants = Total masses of product + masses of unreacted reactants

• In nuclear reactions (Mass + energy) is conserved not the mass seperately.

Illustrations

Illustration 1. When 4.2 g $NaHCO_3$ is added to a solution of CH_3COOH weighing 10.0 g, it is observed that 2.2 g CO_2 is released into atmosphere. The residue is found to weigh 12.0 g. Show that these observations are in agreement with the law of conservation of mass.

Solution. $NaHCO_3 + CH_3COOH \longrightarrow CH_3COONa + H_2O + CO_2$

Initial mass = 4.2 + 10 = 14.2

Final mass = 12 + 2.2 = 14.2

Thus, during the course of reaction law of conservation of mass is obeyed.

3.2 Law of constant or definite proportion

SL

- This law was given by ***Joseph Louis proust. in 1799***.
- Chemical compostion of a compound remains constant whether it is obtained by any method or any source.

Ex. In water (H_2O), Hydrogen and Oxygen combine in 1 : 8 mass ratio, the ratio remains constant whether it is tap water, river water or sea water or produced by any chemical reaction.

Illustrations

Illustration 2. 1.80 g of a certain metal burnt in oxygen gave 3.0 g of its oxide. 1.50 g of the same metal heated in steam gave 2.50 g of its oxide. Show that these results illustrate the law of constant proportion.

Solution. In the first sample of the oxide,

wt. of metal = 1.80 g , wt. of oxygen = (3.0 – 1.80) g = 1.2 g

$$\therefore \frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{1.80\text{g}}{1.2\text{g}} = 1.5$$

In the second sample of the oxide,

wt. of metal = 1.50 g , wt. of oxygen = (2.50 – 1.50) g = 1 g

$$\therefore \frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{1.50\text{g}}{1\text{g}} = 1.5$$

Thus, in both samples of the oxide the proportions of the weights of the metal and oxygen are fixed. Hence, the results follows the law of constant proportion.

☞ ***Note :***

This law is not applicable in case of isotopes.

3.3 The law of multiple proportion

SL

- This law was given by Dalton in 1804.
- If two elements combine to form more than one compound, then the different masses of one element which combine with a fixed mass of the other element, bear a simple ratio to one another.

Ex. Nitrogen and oxygen combine to form five stable oxides –

N_2O	Nitrogen 28 parts	Oxygen 16 parts
N_2O_2	Nitrogen 28 parts	Oxygen 32 parts
N_2O_3	Nitrogen 28 parts	Oxygen 48 parts
N_2O_4	Nitrogen 28 parts	Oxygen 64 parts
N_2O_5	Nitrogen 28 parts	Oxygen 80 parts

The masses of oxygen which combine with same mass of nitrogen in the five compounds bear a ratio 16 : 32 : 48 : 64 : 80 or 1 : 2 : 3 : 4 : 5.

☞ ***Note :***

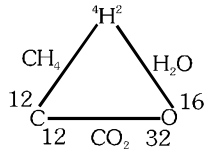
This law is not applicable in case of isotopes & non stoichiometric compounds.

3.4 Law of reciprocal proportion (or law of equivalent wt.)

SL

This law was put forward by ***Richter in 1792***. It states as follows :

The ratio of the weights of two elements A and B which combine separately with a fixed weight of the third element C is either the same or some simple multiple of the ratio of the weights in which A and B combine directly with each other.



This law may be illustrated with the help of the following example.

The elements C and O combine separately with the third element H to form CH_4 and H_2O and they combine directly with each other to form CO_2, as shown in fig.

In CH_4, 12 parts by weight of carbon combine with 4 parts by weight of hydrogen. In H_2O, 2 parts by weight of hydrogen combine with 16 parts by weights of oxygen. Thus the weight of C and O which combine with fixed weight of hydrogen (say 4 parts by weight) are 12 and 32 i.e. they are in the ratio 12 : 32 or 3 : 8. Now in CO_2, 12 parts by weight of carbon combine directly with 32 parts by weight of oxygen i.e. they combine directly in the ratio 12 : 32 or 3 : 8 which is the same as the first ratio.

☞ ***Note :***

This law is also called as law of equivalent wt. due to each element combined in their equivalent wt. ratio.

Illustrations

Illustration 3. Ammonia contains 82.35% of nitrogen and 17.65% of hydrogen. Water contains 88.90% of oxygen and 11.10% of hydrogen. Nitrogen trioxide contains 63.15% of oxygen and 36.85% of nitrogen. Show that these data illustrate the law of reciprocal proportions.

Solution. In NH_3, 17.65g of H combine with N = 82.35g

$\therefore$ 1 g of H combine with N = $\frac{82.35}{17.65}$ g = 4.66 g

In H_2O, 11.10 g of H combine with O = 88.90 g

$\therefore$ 1 g of H combine with O = $\frac{88.90}{11.10}$ g = 8.00 g

$\therefore$ Ratio of the weights of N and O which combine with fixed weight (=1g) of H = 4.66 : 8.00 = 1 : 1.7

In N_2O_3, ratio of weights of N and O which combine with each other = 36.85 : 63.15 = 1 : 1.7

Thus the two ratios are the same. Hence it illustrates the law of reciprocal proportions.

3.5 Law of Gaseous volumes

SL

- This law was given by ***Gay-Lussac.*** in 1808.
- According to this law, gases react with each other in the simple ratio of their volumes. If products are also gases then they are also in simple ratio of volume provided that all volumes are measure at same temp. & pressure.

Illustrations

Illustration 4. For the gaseous reaction, $H_2 + Cl_2 \longrightarrow 2HCl$

If 40 ml of hydrogen completely reacts with chlorine then find out the required volume of chlorine and volume of produced HCl ?

Solution. ***According to Gay Lussac's Law :***

$$H_2 + Cl_2 \longrightarrow 2HCl$$

$\because$ 1 ml of H_2 will react will 1 ml of Cl_2 and 2 ml of HCl will produce.

$\therefore$ 40 ml of H_2 will react with 40 ml of Cl_2 and 80 ml of HCl will produce.

required vol. of Cl_2 = 40 ml, produced vol. of HCl = 80 ml

3.6 Berzelious Hypothesis and Avo-Gadro's Hypothesis

SL

(A) ***Berzelious Hypothesis*** : Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of atoms. The above statements was incorrect and later it was modified by Avo-Gadro.

(B) ***Avo-Gadro's Hypothesis*** : Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.

❖ ***Application of Avogadro's hypothesis : [Details covered later in chapter]***

(a) In finding the atomicity

(b) Relation between molecular weight and vapour density

(c) Relation between molecular weight and volume.

(d) Finding the molecular formula of gas.

BEGINNER'S BOX–1

Matter/Laws of chemical combination

1. Preparation of non stoichiometric compounds follows –

(A) Law of mass conservation (B) Law of definite proportion

(C) Law of multiple proportion (D) Law of reciprocal proportion

2. Two compound AB_2 and AB in which fixed mass of B combine with different masses of A represent–

(A) Law of conservation of mass (B) Law of constant composition

(C) Law of multiple proportion (D) Law of reciprocal proportion

3. Which of the following set of compounds follow law of reciprocal proportion ?

(A) H_2S, H_2O, SO_2 (B) H_2S, H_2O, HNO_3

(C) SO_2, NO_2, H_2S (D) NO_2, NO, N_2O

4. Which of the following is not a mixture–

(A) Iodized table salt (B) Gasoline

(D) L.P.G. (D) Distilled water

5. Which of the following set of compounds illustrate law of multiple proportion–

(A) CO_2, CH_4, H_2O (B) N_2O, N_2O_3, N_2O_5

(C) H_2O, D_2O_3, HOD (D) All of the above

6. Among the following pairs of compounds, the one that illustrates the law of multiple proportions is–

(A) NH_3 and NCl_3 (B) H_2S and SO_2
(C) CuO and Cu_2O (D) CS_2 and $FeSO_4$

7. Law of multiple proportions is illustrated by one of the following pairs-

(A) H_2S and SO_2 (B) NO and N_2O
(C) Na_2S and Na_2O (D) BeO and $BeCl_2$

8*. ***Match the column :***

	Column-I		***Column-II***
(A)	Element	(P)	Can't be decomposed into simpler substances by physical decomposition
(B)	Compound	(Q)	Can be decomposed into simpler substances by chemical methods.
(C)	Mixture	(R)	Can't be decomposed into simpler substances by chemical methods
(D)	H_2O	(S)	Uniform composition
(E)	Fe(s) + S(s) in powdered form	(T)	Consists of one type of atoms
(F)	Sea water	(U)	Consists of 2 or more type of atoms.

4.0 DALTON'S ATOMIC THEORY

SL AL

It was in ***1808, John Dalton***, formulated a precise definition of the indivisible building blocks of matter that we call atoms. Dalton's work marked the beginning of the modern era of chemistry. The hypotheses about the nature of matter on which theory is based is given below.

❖ ***Dalton's atomic theory can be summarized as follows :***

(i) Elements are composed of extremely small particles called atoms.

(ii) All atoms of a given element are identical, having the same size, mass and chemical properties. The atoms of one element are different from the atoms of all other elements.

(iii) Compounds are composed of atoms of more than one element. In any compound, the ratio of the numbers of atoms of any two of the elements present is either an integer or a simple fraction.

(iv) A chemical reaction involves only the separation, combination or rearrangement of atoms ; it does not result in their creation or destruction.

4.1 Limitations of Dalton's atomic theory

According to Dalton's atomic theory, an atom is the ultimate, discrete and indivisible particle of matter. Later researches proved that Dalton's atomic theory was not wholly correct.

❖ ***Dalton's atomic theory suffered from the following drawbacks :***

(i) Atoms of the same or different types have a strong tendency to combine together to form a new 'group of atoms'. For example, hydrogen, nitrogen, oxygen gases exist in nature as 'group of two atoms'. This indicates that the smallest unit capable of independent existence is not an atom, but a 'group of atoms'.

(ii) With the discovery of sub-atomic particles, e.g., electrons, neutrons and protons, the atom can no longer be considered indivisible.

(iii) Discovery of isotopes indicated that all atoms of the same element are not perfectly identical. At least, they differ in their masses. Atoms of the same element having different masses are called isotopes.

Dalton's atomic theory could not explain why certain substances, all containing atoms of the same element, should differ in their properties. For example, charcoal, graphite and diamond all are made up of only Carbon-atoms, but still their properties are quite different.

5.0 USEFUL DEFINITIONS

SL AL

5.1 Fundamental particle's

Atom has many types of particles i.e. electron, proton, neutron, positron, antiproton, neutrino, meson, antineutrino etc. The main fundamental particles are electron, proton, neutron.

❖ ***Properties of fundamental particles :***

Atoms are made up-essentially, of three fundamental particles, which differ in mass and electric charge as follows :

	Electron	***Proton***	***Neutron***
Symbol	e or e^-	p	n
Approximate relative mass	1/1836	1	1
Approximate relative charge	–1	+1	0
Mass in kg	9.10939×10^{-31}	1.67262×10^{-27}	1.67493×10^{-27}
Mass in amu	0.00054	1.00727	1.00867
Actual charge/C	-1.6022×10^{-19}	$+1.6022 \times 10^{-19}$	0

5.2 Other Subatomic Particles

SL AL

Name of Particles	***Mass***	***Charge***
Positron	(same as electron)	same as proton
Anti Proton	(same as proton)	electron
Neutrino	Negligible	Zero
Meson	(200 times than electron)	(+ , –, zero)

5.3 Atomic Number

SL AL

The number of protons present in the nucleus is called atomic number of an element. It is represented by Z. It is also known as nuclear charge.

For neutral atom : Number of protons = Number of electrons

For charged atom : Number of e^- = Z – (charge on atom)

Z = number of protons only

5.4 Mass Number

SL AL

The sum of number of neutrons and protons is called the mass number of element. It is represented by A. It is also known as number of nucleons becuase neutron & proton are present in nucleus.

- ***A = number of protons + number of Neutrons***

☞ ***Note :***

It is always a whole number.

An atom of the element is represented by $_ZX^A$ or ^A_zX.

Where, X = Symbol of element
Z = Atomic number = no. of protons = no. of e^- (If atom is neutral)
A = Mass number = no.of neutrons + Atomic no.

Ex.

$_{11}Na^+$	$_9F^-$	$_6C^{12}$	$_8O^{16}$
($p^+ \rightarrow 11$)	($p^+ \rightarrow 9$)	($p^+ \rightarrow 6$)	($p^+ \rightarrow 8$)
($e^- \rightarrow 10$)	($e^- \rightarrow 9 + 1 = 10$)	($e^- \rightarrow 6$)	($e^- \rightarrow 8$)

Ex.

$_6C^{12}$	$_8O^{16}$
$p^+ \rightarrow 6$	$p^+ \rightarrow 8$
$n^0 \rightarrow 12 - 6 = 6$	$n^0 \rightarrow 16 - 8 = 8$
$e^- \rightarrow 6$	$e^- \rightarrow 8$

Illustrations

Illustration 5. If no. of protons in X^{-2} is 16. then no. of e^- in X^{+2} .

Solution. $\because$ No. of proton in X^{-2} is = 16

$\therefore$ No. of electron in X^{+2} is = 14

Illustration 6. In C^{12} atom if mass of e^- is doubled and mass of proton is halved, then calculate the percentage change in mass no. of C^{12}.

Solution.

	$_6C^{12}$		
e^-	p^+	n°	
6	6	6	$A \rightarrow 12$
12	3	6	$A \rightarrow 9$

$$\% \text{ change} = \frac{3}{12} \times 100 = 25\%$$

Illustration 7*. Assuming that atomic weight of C^{12} is 150 unit from atomic table, then according to this assumption, the weight of O^{16} will be :-

Solution. $\because$ 12 amu = 150

$$\therefore \text{ 1 amu } = \frac{150}{12}$$

$$\therefore \text{ 16 amu} = \frac{150}{12} \times 16 = 200 \text{ Unit}$$

5.5 Isotopes

SL AL

(Given by Soddy) They are atoms of a given element which have the same atomic no. but differ in their mass no.

Ex. $_6C^{12}$, $_6C^{13}$, $_6C^{14}$
$_8O^{16}$, $_{18}O^{17}$, $_{18}O^{18}$
$_1H^1$, $_1H^2$, $_1H^3$

Ex.

	$_6C^{12}$	$_6C^{13}$	$_6C^{14}$
$p^+ \rightarrow$	6	6	6
$e^- \rightarrow$	6	6	6
n° $\rightarrow$	6	7	8

☞ ***Note :***

Isotopes have the same nuclear charge but differ in the number of neutrons in the nucleus.

$_1H^1$	$_1H^2$	$_1H^3$ (Radioactive element)
Protium (H)	Deuterium (D)	Tritium (T)
$p^+ \rightarrow 1$	1	1
$e^- \rightarrow 1$	1	1
n° $\rightarrow 0$	1	2

- Neutron is not available in Protium

5.6 Isotones / Isoneutronic

SL AL

They are atoms of different elements which have the same number of neutrons

Ex.1

		$_6C^{13}$	$_7N^{14}$
n^0	$\rightarrow$	7	7

Ex. 2

		$_{14}Si^{30}$	$_{15}P^{31}$	$_{16}S^{32}$
n^0	$\rightarrow$	16	16	16

5.7 Isodiaphers

SL AL

They are the atoms of different elements which have the same difference between the number of neutrons & protons (n – p).

Ex.1 $_5B^{11}$ $_6C^{13}$

$$\left.\begin{array}{l} p = 5 \\ n = 6 \\ e^- = 5 \end{array}\right] n - p = 1 \qquad \left.\begin{array}{l} p = 6 \\ n = 7 \\ e^- = 6 \end{array}\right] n - p = 1$$

Ex.2 $_7N^{15}$ $_9F^{19}$

$$\left.\begin{array}{l} p = 7 \\ n = 8 \\ e^- = 7 \end{array}\right] n - p = 1 \qquad \left.\begin{array}{l} p = 9 \\ n = 10 \\ e^- = 9 \end{array}\right] n - p = 1$$

5.8 Isosters

SL AL

They are the molecules which have the same number of atoms & electrons.

Ex.1	CO_2	N_2O
Atoms	= 1 + 2	= 2 + 1
	= 3	= 3
Electrons	= 6 + 8 × 2	= 7 × 2 + 8
	= 22 e^-	= 22e^-
Ex.2	CaO	KF
Atoms	2	2
Electrons	20 + 8	19 + 9
	28 e^-	28 e^-
Ex.3	OF_2	HClO
Atoms	= 3	3
Electrons	= 8 + 18	1 + 17 + 8
	= 26 e^-	26 e^-

5.9 Isoelectronic

SL AL

Atoms / molecules / ions possesing the same no. of electrons are called iso electronic.

Ex.1		$_{10}Ne$	$_{11}Na^+$		
	e^-	10	10		
Ex.2		NH_4^+	CH_4	Mg^{+2}	H_2O
	e^-	7 + 4 – 1	6 + 4	12 – 2	2 + 8
		= 10 e^-	= 10 e^-	= 10 e^-	= 10 e^-
Ex.3		Ne	NH_3	NH_2^-	
		10 e^-	10 e^-	1 + 7 + 2	= 10 e^-

6.0 RELATIVE ATOMIC MASS

SL AL

One of the most important concept come out from Dalton's atomic theory was that of relative atomic mass or relative atomic weight. This is done by expressing mass of one atom with respect to a fixed standard. Dalton used hydrogen as the standard (H = 1). Later on oxygen (O = 16) replaced hydrogen as the reference. Therefore relative atomic mass is given as

$$\text{Relative atomic mass (R.A.M.)} = \frac{\text{Mass of one atom of an element}}{\text{mass of one hydrogen atoms}} = \frac{\text{Mass of one atom of an element}}{\frac{1}{16} \times \text{mass of one Oxygen atom}}$$

The present standard unit which was adopted internationally in 1961, is based on the mass of one carbon-12 atom.

7.0 ATOMIC MASS UNIT (OR AMU)

SL AL

The atomic mass unit (amu) is equal to one twelvth $\left(\frac{1}{12}\right)$ the mass of one atom of carbon-12 isotope.

$$\therefore \quad 1 \text{ amu} = \frac{1}{12} \times \text{mass of one C-12 atom} \quad = 1.66 \times 10^{-24} \text{ g or } 1.66 \times 10^{-27} \text{ kg}$$

One amu is also called one Dalton (Da).

Now the relative atomic mass is given as

$$\text{Relative atomic mass} = \frac{\text{mass of one atom of the element}}{\frac{1}{12} \times \text{mass of one C} - 12 \text{ atom}} \qquad \text{R.A.M.} = \text{No. of nucleons.}$$

$$\text{R.A.M.} = \frac{\text{Atomic mass}}{1 \text{ amu}}$$

Atomic mass = R.A.M. × 1 amu

$$\text{Relative molecular mass} = \frac{\text{mass of one molecule of the substance}}{\frac{1}{12} \times \text{mass of one C} - 12 \text{ atom}}$$

$\therefore$ Molecular mass = Relative molecular mass × 1 amu

8.0 MOLE

SL AL

A mole is the amount of a substance that contains as many entities (atoms, molecules or other particles) as there are atoms exactly in 0.012 kg (or 12 g) of the carbon - 12 isotope.

From mass spectrometer we found that there are 6.023×10^{23} atoms are present in 12 g of C-12 isotope. The number of entities in 1 mol is so important that it is given a separate name and symbol known as Avogadro constant denoted by N_A. i.e. on the whole we can say that 1 mole is the collection of 6.02×10^{23} entities. Here entities may represent atoms, ions, molecules or even pens, chair, paper etc.

☞ ***Note :***

1 mole of atom is also termed as 1 g – atom
1 mole of ions is also termed as 1 g – ion
1 mole of molecule is also termed as 1 g – molecule

8.1 Methods of Calculations of mole

(i) If no. of some species is given, then no. of moles $= \frac{\text{Given no.}}{N_A}$

(ii) If weight of a given species is given, then no. of moles $= \frac{\text{Given wt.}}{\text{Atomic wt.}}$ (for atoms),

or, $= \frac{\text{Given wt.}}{\text{Molecular wt.}}$ (for molecules)

(iii) If volume of a gas is given along with its temperature (T) and pressure (P).

use $n = \frac{PV}{RT}$

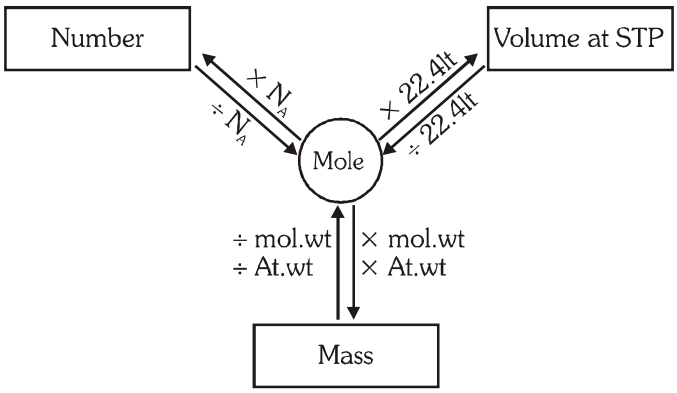
where R = 0.0821 lit-atm/mol-K (when P is in atmosphere and V is in litre)
1 mole of any gas at STP occupies 22.7 litre.

☞ ***Note :***

STP & NTP conditions are different.
NTP = 1 atm pressure & 273 K and STP = 1 bar pressure & 273 K.
However since the difference is very small, it can be neglected.

8.2 Y-map

SL AL



9.0 GRAM ATOMIC MASS

SL AL

The atomic mass of an element expressed in gram is called gram atomic mass of the element.

OR

It is also defined as mass of 6.02×10^{23} atoms.

OR

It is also defined as the mass of one mole atoms.
For example for Sodium atom :
Atomic mass of 'Na' atom = mass of one 'Na' atom = 23 amu
gram atomic mass = mass of 6.02×10^{23} 'Na' atoms
$= 23 \text{ amu} \times 6.02 \times 10^{23}$
$= 23 \times 1.66 \times 10^{-24} \text{ g} \times 6.02 \times 10^{23} = 23 \text{ g}$
($\because$ $1.66 \times 10^{-24} \times 6.02 \times 10^{23} \simeq 1$)
Now see the table given below and understand the definition given before.

Element	***R.A.M. (Relative Atomic Mass)***	***Atomic mass (mass of one atom)***	***Gram Atomic mass/weight***
N	14	14 amu	14 gm
He	4	4 amu	4 gm
C	12	12 amu	12 gm

☞ ***Note :***

Average atomic weight = Σ % of isotopes X molar mass of isotopes.

Illustrations

Illustration 8 ***The atomic mass of an element is 50***

(i) Calculate the mass of one atom, in amu

(ii) Calculate the mass of 6.022×10^{23} atoms, in gm

(iii) Calculate the number of atoms in its 10 gm

(iv) What mass of the element contains 3.011×10^{20} atoms

Sol. (i) 50 amu (ii) 50 gm

(iii) Q 50 gm of element contains 6.022×10^{23} atoms

$\therefore$ 10 gm of element will contain $\frac{6.022 \times 10^{23}}{50} \times 10 = 1.2044 \times 10^{22}$ atoms

(iv) Q 6.022×10^{23} atoms weighs 50 gm

$\therefore 3.011 \times 10^{20}$ atoms weighs $\frac{50}{6.022 \times 10^{23}} \times 3.011 \times 10^{20} = 0.025$ gm

Illustration 9 ***An element exist in nature in two isotopic forms : X^{30} (90%) and X^{32}(10%). What is the average atomic mass of element ?***

Sol. Av. atomic mass $= \frac{\Sigma(\%\text{abundance} \times \text{atomic mass})}{100} = \frac{90 \times 30 + 10 \times 32}{100} = 30.2$

10.0 GRAM MOLECULAR MASS

SL AL

The molecular mass of a substance expressed in gram is called the gram-molecular mass of the substance.

OR

It is also defined as mass of 6.02×10^{23} molecules

OR

It is also defined as the mass of one mole molecules.

For example for 'O_2' molecule :

Molecular mass of '$\boldsymbol{O_2}$' molecule = mass of one '$\boldsymbol{O_2}$' molecule

$= 2 \times$ mass of one 'O' atom

$= 2 \times 16$ amu

$= 32$ amu

gram molecular mass = mass of 6.02×10^{23} '$\boldsymbol{O_2}$' molecules

$= 32 \text{ amu} \times 6.02 \times 10^{23}$

$= 32 \times 1.66 \times 10^{-24}\text{g} \times 6.02 \times 10^{23}$

$= 32$ gm

☞ ***Note :***

Average molecular wt. $= \frac{\Sigma n_i m_i}{\Sigma n_i}$ where n_i = no. of moles of compound

m_i = molecular mass of compound

Illustrations

Illustration 10. The molecular mass of a compound is 75

(i) Calculate the mass of 100 molecules, in amu.

(ii) Calculate the mass of 5000 molecules, in gm.

(iii) What is the mass of 6.022×10^{20} molecules, in gm

(iv) How many molecules are in its 2.5 mg

Sol. (i) mass of 1 molecules = 75 amu

$\therefore$ mass of 100 molecules = 7500 amu

(ii) Mass of 5000 molecules = 5000 × 75 amu

= $5000 \times 75 \times 1.67 \times 10^{-24} = 6.26\,25 \times 10^{-19}$ gm

(iii) $\therefore$ 6.022×10^{23} molecules weighs 75 gm

Q 6.022×10^{20} molecules weighs $\frac{75}{6.022 \times 10^{23}} \times 6.022 \times 10^{20} = 0.075$ gm

(iv) $\therefore$ 75 gm compound contains 6.022×10^{23} molecules

Q 2.5×10^{-3} gm will contain $\frac{6.022 \times 10^{23}}{75} \times 2.5 \times 10^{-3} = 2.007 \times 10^{19}$ molecules.

Illustration 11. A gaseous mixture contains 40% H_2 and 60% He, by volume. What is the average molecular mass of mixture ?

Sol. $M_{av} = \frac{\Sigma(\%\text{ by vol.} \times \text{molecular mass})}{100} = \frac{40 \times 2 + 60 \times 4}{100} = 3.20$

Illustration 12. Calculate no. of molecules and number of oxygen atoms in 53 gram of Na_2CO_3.

Solution No. of gm molecules = $\frac{\text{given wt. in gm}}{\text{gm molecular mass}} = \frac{53}{106} = 0.5$ gm molecules

($\because$ gm moleucular mass of Na_2CO_3 = 106)

number of molecules = $0.5 \times 6.023 \times 10^{23} = 3.011 \times 10^{23}$ molecules

no. of oxygen atoms = $3 \times 0.5 \times 6.023 \times 10^{23} = 9.033 \times 10^{23}$ oxygen atoms

BEGINNER'S BOX–2

Given data : At wt. Si = 28, H = 1, O = 16, Na = 23, Cl = 35.5, P = 31, Cu = 64

1. Calculate the number of g-molecules (mole of molecules) in the following : [$N_A = 6 \times 10^{23}$]

(i) 3.2 gm CH_4 (ii) 70 gm nitrogen (iii) 4.5×10^{24} molecules of ozone

(iv) 2.4×10^{21} atoms of hydrogen (v) 11.2 L ideal gas at 0°C and 1 atm

(vi) 4.54 ml SO_3 gas at STP (vii) 8.21 L C_2H_6 gas at 400K and 2atm

(viii) 164.2 ml He gas at 27°C and 570 torr

2. Find no. of protons in 180 ml H_2O. Density of water = 1 gm/ml.

3. What mass of $Na_2SO_4.7H_2O$ contains exactly 6.023×10^{22} atoms of oxygen ?

4. What is number of atoms and molecules in 112 L of O_3(g) at 0°C and 1atm ?

5. How many g of element are present in 10 g atom of Si. (Given at. wt. of Si = 28.)

6. Calculate the no. of molecules in a drop of water weighing 0.09 g.

7. Calculate no. of each atom present in 106.5 g of $NaClO_3$.

8. Find the no. of mole of phosphorus in 93 g of phosphorus assuming that molecular formula of phosphorus is P_4. Also determine the no. of atoms and molecules of phosphorus in the sample.

9. Calculate the number of moles in 5.75 g of sodium. (Atomic mass of sodium = 23.)

10. How many grams of each of the following elements must be taken to get 1 mol of substance in which element generally exists ?

(a) Sodium (b) Chlorine (c) Copper

11*. The density of liquid mercury is 13.6gm/cm^3. How many moles of mercury are there in 1 litre of the metal? (Atomic mass of Hg = 200)

12*. The charge on 1 gram ions of Al^{3+} is : [$e = 1.6 \times 10^{-19}$]

(A) $\frac{1}{27} N_A e$ coulomb (B) $\frac{1}{3} \times N_A e$ coulomb (C) $\frac{1}{9} \times N_A e$ coulomb (D) $3 \times N_A e$ coulomb

13. Which of the following contains greatest number of oxygen atoms :

(A) 1 g of O (B) 1 g of O_2

(C) 1 g of O_3 (D) all have the same number of atoms

14. A sample of ammonium phosphate, $(NH_4)_3PO_4$, contains 3.18 mol of hydrogen atoms. The number of moles of oxygen atoms in the sample is :

(A) 0.265 (B) 0.795 (C) 1.06 (D) 3.1

15. Four 1 litre flasks are separately filled with the gases H_2, He, O_2 and O_3 at the same temperature and pressure. The ratio of total number of atoms of these gases present in different flask would be :

(A) 1 : 1 : 1 : 1 (B) 1 : 2 : 2 : 3 (C) 2 : 1 : 2 : 3 (D) 3 : 2 : 2 : 1

◻ *DENSITY :*

It is of two types.

I. Absolute density

II. Relative density

❖ *For liquids and solids :*

$$\text{Absolute density} = \frac{\text{mass}}{\text{volume}}$$

$$\textbf{\textit{Relative density or specific gravity}} = \frac{\text{density of the substance}}{\text{density of water at } 4°C\ (1\,gm\,ml^{-1})}$$

❖ *For gases :*

$$\text{Absolute density} = \frac{\text{mass}}{\text{volume}} = \frac{PM}{RT}$$

where P is pressure of gas, M = mol. wt. of gas, R is the gas constant, T is absolute temperature.

Vapour Density :

Vapour density is defined as the density of the gas with respect to hydrogen gas at the same temperature and pressure.

$$\text{Vapour density} = \frac{d_{gas}}{d_{H_2}} = \frac{PM_{gas}/RT}{PM_{H_2}/RT}$$

$$\text{V.D.} = \frac{M_{gas}}{M_{H_2}} = \frac{M_{gas}}{2} \Rightarrow \boxed{\mathbf{M_{gas} = 2 \times V.D.}}$$

Example. A gaseous mixture of H_2 and NH_3 gas contains 68 mass % of NH_3. The vapour density of the mixture is –

Sol. No. of moles of NH_3 in 100g mixture = $\frac{68}{17} = 4$

No. of moles of H_2 in 100g mixture = $\frac{32}{2} = 16$

$$M_{average} = \frac{\text{Total mass}}{\text{Total moles}} = \frac{100}{4+16} = 5$$

$$V.d = \frac{5}{2} = 2.5$$

11.0 PERCENTAGE COMPOSITION AND MOLECULAR FORMULA

SL AL

Here we are going to find out the percentage of each element in the compound by knowing the molecular formula of compound. We know that according to law of definite proportions any sample of a pure compound always possess constant ratio with their combining elements.

Illustrations

Illustration 1. Every molecule of ammonia always has formula NH_3 irrespective of method of preparation or sources. i.e. 1 mole of ammonia always contains 1 mol of N and 3 mole of H. In other wards 17 g of NH_3 always contains 14 g of N and 3 g of H. Now find out % of each element in the compound.

Solution Mass % of N in NH_3 = $\frac{\text{Mass of N in 1 mol } NH_3}{\text{Mass of 1 mol of } NH_3} \times 100 = \frac{14\text{ g}}{17} \times 100 = 82.35\ \%$

Mass % of H in NH_3 = $\frac{\text{Mass of H is 1 mol } NH_3}{\text{Mass of 1 mol of } NH_3} \times 100 = \frac{3}{17} \times 100 = 17.65\%$

Illustration 2. Chlorophyll the green colouring material of plants contains 3.68 % of magnesium by mass. Calculate the number of magnesium atom in 5.00 g of the complex.

Solution Mass of magnesium in 5.0 g of complex = $\frac{3.68}{100} \times 5.00 = 0.184$ g

Atomic mass of magnesium = 24

24 g of magnesium contain = 6.023×10^{23} atoms

$\therefore$ 0.184 g of magnesium would contain = $\frac{6.023 \times 10^{23}}{24} \times 0.184 = 4.617 \times 10^{21}$ atom

Therefore, 5.00 g of the given complex would contain 4.617×10^{21} atoms of magnesium.

11.1 Empirical and Molecular formula

SL AL

We have just seen that knowing the molecular formula of the compound we can calculate percentage composition of the elements. Conversely if we know the percentage composition of the elements initially, we can calculate the relative number of atoms of each element in the molecules of the compound. This gives as the empirical formula of the compound. Further if the molecular mass is known then the molecular formula can be easily determined. Thus, the empirical formula of a compound is a chemical formula showing the relative number of atoms in the simplest ratio, the molecular formula gives the actual number of atoms of each element in a molecule.

- ***Empirical formula :*** Formula depicting constituent atom in their simplest ratio.
- ***Molecular formula :*** Formula depicting actual number of atom in one molecule of the compound. The molecular formula is generally an integral multiple of the empirical formula.

i.e. molecular formula = empirical formula × n ; where n = $\frac{\text{molecular formula mass}}{\text{empirical formula mass}}$

Illustrations

Illustration 10. An organic substance containing carbon, hydrogen and oxygen gave the following percentage composition.

C = 40.687 % ; H = 5.085 % and O = 54.228 %

The molecular weight of the compound is 118. Calculate the molecular formula of the compound.

Solution ***Step-1***

To calculate the empirical formula of the compound.

Element	***Symbol of element***	***Percentage of element***	***At. mass of atoms =*** $\frac{\text{Percentage}}{\text{At.mass}}$	***Relative no. atomic ratio***	***Simplest no. atomic ratio***	***Simplest***
Carbon	C	40.687	12	$\frac{40.687}{12}=3.390$	$\frac{3.390}{3.389}=1$	2
Hydrogen	H	5.085	1	$\frac{5.085}{1}=5.035$	$\frac{5.085}{3.389}=1.5$	3
Oxygen	O	54.228	16	$\frac{54.228}{16}=3.389$	$\frac{3.389}{3.389}=1$	2

$\therefore$ Empirical formula is $C_2H_3O_2$

Step - 2

To calculate the empirical formula mass.

The empirical formula of the compound is $C_2H_3O_2$.

Empirical formula mass = (2 × 12) + (3 × 1) + (2 × 16) = 59.

Step - 3

To calculate the value of 'n'

$$n = \frac{\text{molecular mass}}{\text{Empirical formula mass}} = \frac{118}{59} = 2$$

Step - 4

To calculate the molecular formula of the salt

Molecular formula = n × (Empirical formula) = $2 \times C_2H_3O_2 = C_4H_6O_4$

Thus the molecular formula is $C_4H_6O_4$.

Example. ***An organic compound contains 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Molecular formula of compound is :-***

Sol. V.D. = 73 $\Rightarrow$ M = 2 × 73 = 146

$$C = 146 \times \frac{49.3}{100} = 71.978 \text{ g} \simeq 6 \text{ mole}$$

$$H = 146 \times \frac{6.84}{100} = 9.9864 \text{ g} \simeq 10 \text{ mole}$$

$$O = 146 \times \frac{43.86}{100} = 64.86 \text{ g} \approx 4 \text{ mol}$$

M.F. = $C_6H_{10}O_4$

Example. ***The empirical formula of an organic compound containing carbon & hydrogen is CH_2. The mass of 1 litre of organic gas is exactly equal to mass of 1 litre N_2 therefore molecular formula of organic gas is.***

Sol. Empirical Mass of CH_2 = 12 + 2 = 14

$\because$ Mass of 1 litre of organic gas = Mass of 1 litre of N_2

Since V, P, T, n are same.

Therefore $PV = \frac{m}{M}RT$

implies that molar mass should also be same.

$\therefore$ Molecular mass of organic compound will be 28 g

$$n = \frac{\text{Molecular mass}}{\text{Empirical mass}} = \frac{28}{14} = 2$$

So molecular formula = $2 \times CH_2 = C_2H_4$

BEGINNER'S BOX–3

Isotope, Average Molecular mass, E.F. and M.F.

1. A compounds was found to contain 5.37% nitrogen. What is the minimum molecular wt. of compound :
(A) 26.07 g (B) 2.607 (C) 260.7 (D) none

2*. The atomic weight of Cu is 63.546. There are only two naturally occurring isotopes of copper ^{63}Cu and ^{65}Cu. The natural abundance of the ^{63}Cu isotope must be approximately :
(A) 10% (B) 30% (C) 50% (D) 70%

3. A certain alkaloid has 70.8% carbon, 6.2% hydrogen, 4.1% nitrogen and the rest oxygen. What is its empirical formula:
(A) $C_{20}H_{21}NO_4$ (B) $C_{20}H_{20}NO_4$ (C) $C_{21}H_{20}NO_3$ (D) $C_{20}H_{19}NO_3$

4. The total number of neutrons in dipositive zinc ions with mass number 70 is
(A) 34 (B) 40 (C) 36 (D) 38

5. Number of gm-atoms of sulphur present in SO_2 gas which occupy 22.7 ml at S.T.P.
(A) 0.001 (B) 0.01 (C) 1 (D) 10

6*. In an organic compound of molar mass greater than 100 containing only C, H and N, the percentage of C is 6 times the percentage of H while the sum of the percentages of C and H is 1.5 times the percentage of N. What is the least molar mass :
(A) 175 (B) 140 (C) 105 (D) 210

7. The simplest formula of a compound containing 50% of element X (atomic mass = 10) and 50% of the element Y (atomic mass = 20) by weight is :
(A) XY (B) X_2Y (C) XY_2 (D) X_2Y_3

8. Cortisone is a molecular substance containing 21 atoms of carbon per molecule. The mass percentage of carbon in cortisone is 69.98 %. Its molar mass is :
(A) 176.5 (B) 252.2 (C) 287.6 (D) 360.1

9*. Sample I has higher O^{18}/O^{16} ratio of atoms are compared to Sample II. The average mass of oxygen in Sample I is .....that of Sample II :
(A) equal to (B) greater than (C) less than (D) None of these

10. Calculate the change in percentage of C (by weight) when all H-atoms are replaced by 'T' in CH_4 molecule. (Given atomic weight - C : 12, H : 1, T : 3)
(A) 75% (B) 50% (C) 25% (D) 40%

QUANTUM NUMBERS

Quantum numbers give complete information about an electron or orbital in an atom.

1. *Principal Quantum number (n) :*

(i) Permissible value of $n \rightarrow 1$ to ∞

(ii) It represents shell number/energy level

(iii) The energy states corresponding to different principal quantum numbers are denoted by letters K,L,M, N etc.

n :	1	2	3	4	5	6
Designation of shell :	K	L	M	N	O	P

(iv) It indicates the distance of an electron from the nucleus.

(v) It also determines the energy of the electron. In general higher the value of 'n', higher is the energy of a electron.

(vi) It give an idea of total number of orbitals & electron (which may) present in a shell & that equal to n^2 & $2n^2$ respectively.

2. *Azimuthal Quantum number (l) :*

(i) The values of *l* depends upon the value of 'n' and possible values are '0' to (n –1) .

(ii) It gives the name of subshells associated with the energy level and number of subshells within an energy level.

(iii) The different value of '*l*' indicates the shape of orbitals and designated as follows :

Value	***Notation***	***Name***	***Shape***
$l = 0$	s	Sharp	Spherical
$l = 1$	p	Principal	Dumbell
$l = 2$	d	Diffused	Double Dumbell
$l = 3$	f	Fundamental	Complex

(iv) It also determines the energy of orbital along with n.

For a particular energy level/shell energy of subshell is in the following order $\rightarrow s < p < d < f$

(v) It gives the total number of orbitals in a subshell & that equals to $(2l + 1)$ and number of electron in a subshell = $2(2l + 1)$

3. *Magnetic Quantum number (m or m_l) :*

(i) The value of m depends upon the value of *l* and it may have integral value $-l$ to $+l$ including zero.

(ii) It gives the number of orbitals in a given subshell and orientation of different orbitals in space.

e.g. for n = 4, *l* = 0 to 3.

l	0	1	2	3
m	0	+1, 0, – 1	+2, 1, 0, –1, –2	+3, +2, +1, 0, –1, –2, –3
Possible Orientation	1	3	5	7
Orbitals	s	p_x, p_y, p_z	$d_{z^2}, d_{x^2-y^2}$ d_{xy}, d_{yz}, d_{xz}	Not in syllabus

(iii) The orbitals having same value of n and *l* but different value of m, have same energy in absence of external electric & magnetic field. These orbitals having same energy of a particular subshell is known as Degenerate orbitals.

4. *Spin Quantum number (s) & magnetic spin quantum number (m_s) :*

(i) While moving around the nucleus, the electron always spins about its own axis either clockwise or anticlockwise. The magnetic spin quantum number represents the direction of electron spin (rotation) around its own axis (clockwise or anticlockwise).

(ii) There are two possible values of m_s are $+\frac{1}{2}$ & $-\frac{1}{2}$ and represented by the two arrows ↑ (spin up) and ↓ (spin down).

RULES FOR FILLING ELECTRONS

1. *Pauli's exclusion principle*

'No two electrons in an atom can have same values of all the four quantum numbers.

An orbital accommodates two electron with opposite spin. These two electrons have same values of principal, azimuthal and magnetic quantum number but the fourth, i.e. magnetic spin quantum number will be different. i.e.

For K, shell (n = 1)

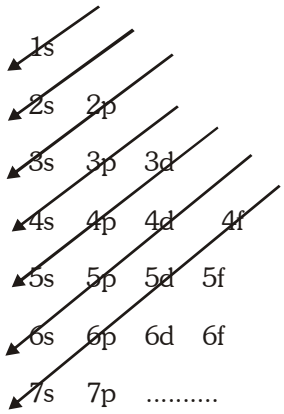
$l = 0$, m = 0

For 1st Electron $n = 1, l = 0, m = 0, m_s = +\frac{1}{2}$

For 2nd Electron $n = 1, l = 0, m = 0, m_s = -\frac{1}{2}$

2. *Aufbau Principle (Means Building up) :*

The electrons are added progressively to the various orbitals in the order of increasing energies starting with the orbital of the lowest energy



1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p

Alternatively, the order of increase of energy of orbitals can be calculated from (n + l) rule.

(i) Lower the value of (n + l) for an orbital, the lower will be its energy.

(ii) If two orbitals have the same (n + l) value, then orbital with lower value of n has the lower energy.

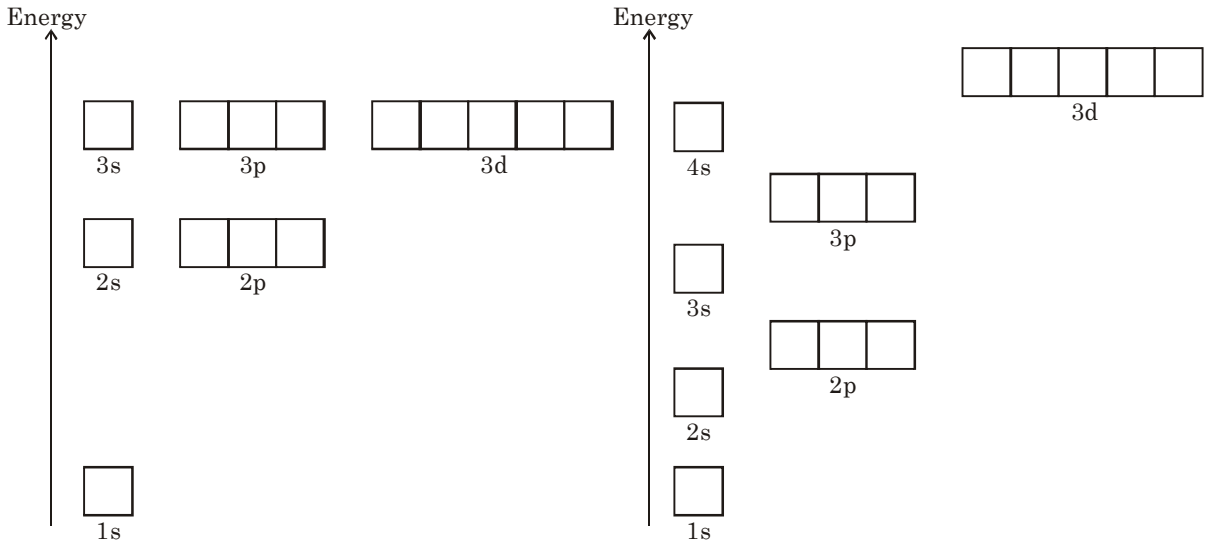
e.g. 2p & 3s

For 2p, n = 2, l = 1, (n + l) = 2 + 1 = 3

For 3s, n = 3, l = 0, (n + l) = 3 + 0 = 3

Then for 2p, n is lesser than for 3s, so 2p has lower energy than 3s.

(iii) 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f .... energy order of different orbitals for single electron system like H, He^+, Li^{+2} etc.



(A) For single electron or hydrogenic atom (B) Multi electronic atoms

Energy level diagram for few electronic shells

Example.4 Write the increasing order of energies of 4s, 3p, 4p and 3d.

Ans. For 4s, n = 4, l = 0, (n + l) = 4

For 3p, n = 3, l = 1, (n + l) = 4

For 4p, n = 4, l = 1, (n + l) = 5

For 3d, n = 3, l = 2, (n + l) = 5

$\Rightarrow$ 3p < 4s < 3d < 4p increasing order

3. *Hund's rule of maximum multiplicity :*

This rule deals with the filling of electrons into the orbitals belonging to the same subshell i.e. orbitals of equal energy, called degenerate orbitals.

"Electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electron with parallel spins. "

"Pairing of electrons in the orbitals belonging to the same subshell (p, d, f) does not take place until each orbital belonging to that subshell has got one electron each i.e. singly occupied. Moreover, the singly occupied orbitals must have the electrons with the parallel spin multiplicity"

Multiplicity = 2|S| + 1, where S = Total spin.

i.e. $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ (+1/2 +1/2 +1/2) Find total spin & multiplicity

$$\text{Total spin S} = \frac{1}{2}+\frac{1}{2}+\frac{1}{2}=\frac{3}{2}$$

$$\text{Multiplicity} = 2\times\frac{3}{2}+1=4$$

i.e. $\boxed{\uparrow}\boxed{\downarrow}\boxed{\uparrow}$ (+1/2 +1/2 +1/2)

$$\text{Total spin S} = \frac{1}{2}-\frac{1}{2}+\frac{1}{2}=\frac{1}{2}$$

$$\text{Multiplicity} = 2\times\frac{1}{2}+1=2$$

i.e. [↑↓] [↑] [↑] [↑] [ ]
+1/2 +1/2 +1/2

Total spin S = $\frac{1}{2}+\frac{1}{2}+\frac{1}{2}=\frac{3}{2}$

Multiplicity = $2\times\frac{3}{2}+1=4$

i.e. [↑] [↑] [↑] [↑] [↑]

Total spin = $5\times\frac{1}{2}=\frac{5}{2}$

Multiplicity = $2\times\frac{5}{2}+1=6$

ELECTRONIC CONFIGURATION OF ATOMS

The distribution of electrons in various shells, subshells and orbitals, in an atom of an element, is called its electronic configuration.

x ← no. of electrons in subshell
n*l*
↑ ↑ — represents subshell
(represents shell)

$2p^5$ ← no. of electrons in p-subshell
↑ ↑ — p subshell
Second shell

$_3Li$; $1s^2, 2s^1$ or [He] $2s^1$ or 1s [↑↓] 2s [↑] or 2s [He] [↑]

Electronic configuration :

Example.5 Nitrogen

Ans. $_7N$: $1s^2, 2s^2\, 2p^3$ [Orbital notation method]

$1s^2, 2s^2\, 2p_x^1 2p_y^1 2p_z^1$

or

1s [↑↓] 2s [↑↓] 2p [↑] [↑] [↑] [Orbital diagram method]

or

[He] $2s^2\, 2p^3$ [Condensed form]

Extra stability of Half-filled and fully-filled orbitals.

The electronic configuration of most of the atoms follows the Aufbau's rule. However, in certain elements such as Cr, Cu etc. Where the two subshells (4s and3d) differ slightly in their energies (4s < 3d), an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half-filled.

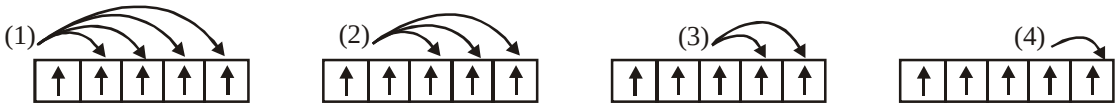
$_{24}Cr \rightarrow$ [Ar] $3d^5, 4s^1$ and not [Ar] $3d^4\, 4s^2$

$_{29}Cu \rightarrow$ [Ar] $3d^{10}, 4s^1$ and not [Ar] $3d^9\, 4s^2$

It has been found that there is extra stability associated with these electronic configuration. This stabilization is due to the following two factors.

(i) ***Symmetrical distribution of electron :*** It is well known that symmetry leads to stability. The completely filled or half-filled subshell have symmetrical distribution of electron in them and are therefore more stable. This effect is more dominant in d and f-orbitals. This means three or six electrons in p-subshell, 5 or 10 electrons in d-subshell and 7 or 14 in f-subshell forms a stable arrangement.

(ii) ***Exchange energy :*** This stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. these electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or fully filled. As result the exchange energy is maximum and so is the stability.

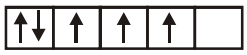


4-exchanges by electron 1 | 3-exchanges by electron 2 | 2-exchanges by electron 3 | 1-exchanges by electron 4

Total exchange pairs = 10

$\frac{n(n-1)}{2} \rightarrow$ Number of exchange pairs

n $\rightarrow$ Number of electron with parallel spins.

e.g. 

Only 6 total exchange possible

Exceptional electronic configuration

S.No.	Element	Z	Configuration
1	Cr	24	$[Ar]4s^1 3d^5$
2.	Cu	29	$[Ar]4s^1 3d^{10}$
3.	Nb	41	$[Kr]5s^1 4d^4$
4.	Mo	42	$[Kr]5s^1 4d^5$
5.	Ru	44	$[Kr]5s^1 4d^7$
6.	Rh	45	$[Kr]5s^1 4d^7$
7.	Pd	46	$[Kr]4d^{10}$
8.	Ag	47	$[Kr]5s^1 4d^{10}$
9.	La	57	$[Xe]6s^2 5d^1$
10.	Ce	58	$[Xe]6s^2 4f^1 5d^1$
11.	Gd	64	$[Xe]6s^2 4f^7 5d^1$
12.	Pt	78	$[Xe]6s^1 4f^{14} 5d^9$
13.	Au	79	$[Xe]6s^1 4f^{14} 5d^{10}$
14.	Ac	89	$[Rn]7s^1 6d^1$
15.	Th	90	$[Rn]7s^2 6d^2$

MAGNETIC PROPERTIES

❖ ***Paramagnetism :***

(i) The substances which are weakly attracted by magnetic field are paramagnetic and this phenomenon is known as paramagnetism.

(ii) Their magnetic character is retained till they are in magnetic field and lose their magnetism when removed from magnetic field.

❖ ***Diamagnetism :***

(i) The substances which are weakly repelled by magnetic field are diamagnetic and this phenomenon is known as diamagnetism.

(ii) Diamagnetic substances lack unpaired electrons and their spin magnetic moment is zero e.g., NaCl, N_2O_4 etc.

❖ ***Spin magnetic moment :***

The spin magnetic moment of electron (excluding orbit magnetic moment) is given by :

$$\mu = \sqrt{[n(n+2)]}\ B.M.$$

Where n is number of unpaired electron in species.

The magnetic moment is expressed in Bohr magneton (B.M.)

Example.6 A compound of vanadium has magnetic moment of 1.73 BM. Work out the electronic configuration of vanadium ion in the compound.

Ans. Vanadium belongs to 3d series with Z = 23. The magnetic moment of 3d series metal is given by spin only formula.

$$\mu = \sqrt{n(n+2)}\ \text{BM (BM = Bohr's magneton)}$$

$\because$ $\sqrt{1.73} = \sqrt{3}$

$\Rightarrow$ $n(n+2) = 3 \Rightarrow n = 1$

$\Rightarrow$ Magnetic moment correspond to one unpaired electron.

$\Rightarrow$ Electronic configuration of vanadium atom $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$.

For one unpaired electron 4 electron must be removed in which first 2 electron are lost from 4s orbital (outermost).

Electronic configuration of V^{+4}

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^1$

Nodal Planes of different orbitals

Nodal plane is a plane at which the probability of finding an electron becomes zero.

eg.

Orbital	***Nodal plane***	***Orbital***	***Nodal plane***
s	None	d_{xy}	XZ & YZ planes
p_x	YZ plane	d_{yz}	XZ & XY planes
p_y	XZ plane	d_{xz}	XY & YZ planes
p_z	XY plane	$d_{x^2-y^2}$	Planes perpendicular to XY plane, passing through origin (nucleus) and inclined at 45° to X & Y axis.
		d_{z^2}	None (two nodal cones are available)

BEGINNER'S BOX–4

Quantum Numbers

1. Which d -orbital does not have four lobes?

(A) $d_{x^2-y^2}$ (B) d_{xy} (C) d_{yz} (D) d_{z^2}

2 The total number of subshells in n^{th} main energy level are :

(A) n^2 (B) $2n^2$ (C) (n–1) (D) n.

3. Which of the following orbital does not make sense?

(A) 3d (B) 3f (C) 5p (D) 7s.

4. The maximum number of electrons in s, p and d-subshells are :

(A) 2 in each (B) 2, 6 and 6 (C) 2, 6 and 10 (D) 2, 6 and 12.

5*. Any p-orbital can accommodate up to :

(A) four electrons (B) two electrons with parallel spin

(C) six electrons (D) two electrons with opposite spin.

6. Which of the following sets of quantum numbers represent an impossible arrangement

	n	l	m	m_s		n	l	m	m_s
(A)	3	2	–2	$\frac{1}{2}$	(B)	4	0	0	$\frac{1}{2}$
(C)	3	2	–3	$\frac{1}{2}$	(D)	5	3	0	$\frac{1}{2}$

7*. Which quantum number will determine the shape of the subshell

(A) Principal quantum number (B) Azimuthal quantum number

(C) Magnetic quantum number (D) Spin quantum number

Electronic Configuration and Miscellaneous

8. A d-block element has total spin value of +3 or –3, then the magnetic moment of the element is approximately:

(A) 2.83 B.M. (B) 3.87 B.M. (C) 5.9 B.M. (D) 6.93 B.M.

9*. Magnetic moment of $_{25}Mn^{x+}$ is $\sqrt{15}$ B.M then the value of x is :

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

10. Magnetic moment of $_{26}Fe^{2+}$ ion is same as

(A) $_{26}Fe$ (B) $_{24}Cr^{2+}$ (C) $_{28}Ni^{4+}$ (D) All of these

11. Orbital angular momentum of an electron is $\sqrt{3}\frac{h}{\pi}$, then the number of orientations of this orbital in space are

(A) 3 (B) 5 (C) 7 (D) 9

12. The correct order of the magnetic moment of $[_{25}Mn, _{24}Cr, _{26}Fe]$ is :

(A) $Fe^{3+} > Cr^{+3} = Mn^{+4}$ (B) $Fe^{3+} > Cr^{3+} > Mn^{4+}$ (C) $Cr^{3+} = Mn^{4+} > Fe^{3+}$ (D) $Fe^{3+} > Mn^{+4} > Cr^{3+}$

13. Magnetic moment of X^{n+} (Z = 26) is $\sqrt{24}$ B.M. Hence number of unpaired electrons and value of n respectively are -

(A) 4, 2 (B) 2, 4 (C) 3, 1 (D) 0, 2

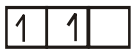
14. Magnetic moments of V (Z = 23), Cr (Z = 24), Mn (Z = 25) are x, y, z respectively. Hence :

(A) x = y = z (B) x < y < z (C) x < z < y (D) z < y < x

15. Predict total spin for each configuration.

(a) $1s^2$ (b) $1s^2, 2s^2\ 2p^6$ (c) $1s^2, 2s^2\ 2p^5$ (d) $1s^2, 2s^2\ 2p^3$ (e) $1s^2\ 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^2$.

16*. The electronic configuration of a carbon atom is $1s^2, 2s^2, 2p^2$ and consider the following four arrangements of the 2p electrons. Which arrangement have lowest energy ?

(A) (B) (C)  (D)

SOME WORKED OUT EXAMPLES

Illustration 1. A certain compound has the molecular formula X_4O_6. If 10 g of X_4O_6 has 5.72 g of X, atomic mass of X is

Solution. atoms of X : atom of O = 4 : 6

$$\frac{5.72}{X} : \frac{4.28}{16} = 4 : 6$$

$$\frac{5.72}{X} \times 6 = \frac{4.28}{16} \times 4$$

X = 32.07

Illustration 2. A sample of water contains only H^1 and H^2 atoms in 4 : 1 atomic ratio and O^{16} and O^{17} in 5 : 2 atomic ratio. The average molecular mass of such water is :

Solution. Average atomic mass of 'H' = $\frac{1\times4+2\times1}{5} = 1.2$

Average atomic mass of 'O' = $\frac{16\times5+2\times17}{7} = 16.28$

So Average molecular mass of H_2O = 1.2 + 1.2 + 16.28 = 18.68

Illustration 3. A sample of $Mg_3(PO_4)_2$ contains 72 gm Magnesium in the sample, then calculate the number of gm molecule of oxygen in the same sample.

Solution. 72 gm Mg is present in
1 mole $Mg_3(PO_4)_2$
∴ 8 moles of O atoms
4 moles of O_2 molecules
4 gm molecules of O_2 are present.

Illustration 4. A 448 *l* vessel contains $O_2(g)$ & $CO_2(g)$ in 2 : 3 ratio at 1 atm & 0°C. Calculate the number of moles of $CO_2(g)$ present in the vessel.

Solution. 448 ℓ O_2 & $CO_2(g)$ 2 : 3

Volume of CO_2 = $\frac{3}{5}\times448 = 268.8\ell$

Number of moles of CO_2 = 12 *l*

Illustration 5. A sample of $K_2SO_4.Al_2(SO_4)_3.24\,H_2O$ contains 6.4 kg oxygen then calculate mass of sulphur (in gm) in same sample ?

Solution. $K_2SO_4.Al_2(SO_4)_3.24H_2O$
6.4 kg oxygen
[moles of substance × 40] number of oxygen
40 × x × 16 = 6400 gram
x = 10 moles
number of moles of s = 4 × 10 moles = 40 moles
weight of sulphur = 1280 gm

Illustration 6. 'X' is molecular substance containing 21 atoms of carbon per molecule. The weight % of C in 'X' is 50.4%. What is molecular weight of X.

Solution. Mass of carbon in 1 molecule of X = 21 × 12 = 252 amu
if % weight of carbon is 50.4 % in molecule then

Molecular mass of X = $\frac{252\times100}{50.4} = 500\text{amu}$

Illustration 7. The number of gram-molecules of oxygen which can be obtained from 5g-molecules of $H_2S_2O_8$ are

Solution. 5 g molecule of $H_2S_2O_8$ = 5 mole $H_2S_2O_8$
= 40 gm atom of oxygen
= 20 gm molecule of O_2.

Illustration 16.

The orbital angular momentum of a d-electron is :-

(A) $\sqrt{6}\hbar$ (B) $\sqrt{2}\hbar$ (C) $\hbar$ (D) $2\hbar$

Solution.

For d–electron, $\ell = 2$, orbital angular momentum $= \sqrt{\ell(\ell+1)\hbar} = \sqrt{2(2+1)\hbar} = \sqrt{6}\hbar$

So, ***(A)*** is the correct answer

Illustration 17.

The following electron configuration of an atom in the ground state is not correct because :-

3s 3p 3d

(A) the energy of the atom is not minimum (B) Pauli's exclusion principle is violated
(C) Hund's rule is violated (D) Aufbau principle is not followed

Ans. (C)

Illustration 19.

The electronic configuration of an element is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$. This represents its :-

(A) excited state (B) ground state (C) cationic form (D) anionic form

Solution.

The given electronic configuration is ground state for chromium.

So, ***(B)*** is the correct answer

Illustration 20.

Which of the following sets of quantum number is/are incorrect ?

(A) $n = 3, \ell = 3, m = 0, s = \frac{1}{2}$ (B) $n = 3, \ell = 2, m = 2, s = -\frac{1}{2}$

(C) $n = 3, \ell = 1, m = 2, s = -\frac{1}{2}$ (D) $n = 3, \ell = 0, m = 0, s = +\frac{1}{2}$

Solution.

When $n = 3$, ℓ cannot be 3, so (A) is incorrect when $l = 1$, m cannot be $= +2$.

So, ***(C)*** is incorrect

So, ***(A)*** and ***(C)*** is the correct answer.

Illustration 21.

Select the pairs of ions which have same electronic configuration ?

(A) Cr^{3+}, Fe^{3+} (B) Fe^{3+}, Mn^{2+} (C) Fe^{3+}, Co^{3+} (D) Se^{3+}, Cr^{3+}

Solution.

Fe^{3+} and Mn^{2+} have same electronic configuration

So ***(B)*** is the correct answer.

Illustration 24.

Principal, azimuthal and magnetic quantum numbers are respectively related to :-

(A) size, orientation and shape (B) size, shape and orientation
(C) shape, size and orientation (D) none of these

Solution.

Principal gives size, i.e. azimuthal gives shape and magnetic quantum number gives the orientation.

Illustration 31.

Which of the following is the ground state electronic configuration of nitrogen :-

(A) [↑↓] [↑↓] [↑] [↑] [↑] (B) [↑↓] [↑↓] [↑] [↓] [↑]

(C) [↑↓] [↑↓] [↑] [↓] [↓] (D) [↑↓] [↑↓] [↓] [↓] [↓]

Solution.

In (A) and (D), the unpaired electrons have spin in the same direction.

So, ***(A)*** and ***(D)*** are the correct answer.

Illustration 32.

Select the wrong statement (s) from the following ?

(A) If the value of $\ell = 0$, the electron distribution is spherical

(B) The shape of the orbital is given by magnetic quantum number

(C) Angular momentum of 1s, 2s, 3s electrons are equal

(D) In an atom, all electrons travel with the same velocity

Solution.

(B) is wrong because shape is given by azimuthal quantum number and magnetic quantum number tells the orientation. (D) is wrong because electrons in different shells travel with different velocities.

So, (A) and (C) are the correct answer.

Illustration 33.

For the energy levels in an atom, which one of the following statement/s is/are correct ?

(A) There are seven principal electron energy levels

(B) The second principal energy level can have four sub-energy levels and contain a maximum of eight electrons

(C) The M energy level can have a maximum of 32 electrons.

(D) The 4s sub-energy level is at a lower energy than the 3d sub-energy level.

Solution.

(A) and (D) are true. (B) is wrong because for $n = 2$, $\ell = 0, 1$ (two sub-energy levels). (C) is wrong because M shell means $n = 3$. Maximum electrons it can have $= 2n^2 = 2 \times 3^2 = 18$

So, ***(A)*** and ***(D)*** is the correct answer.

Illustration 34.

Which of the following statement (s) is (are) correct ?

(A) The electronic configuration of Cr is $[Ar]3d^5, 4s^1$ (Atomic No. of Cr = 24)

(B) The magnetic quantum number may have a negative value

(C) In silver atom 23 electrons have spin of one type and 24 of the opposite type (Atomic No. of Ag = 47)

(D) The oxidation state of nitrogen in HN_3 is –3

Solution.

Only (D) is wrong because oxidation state of N in HN_3 is –1/3.

So, ***(A)***, ***(B)*** and ***(C)*** are the correct answer.

Illustration 35.

Many elements have non-integral atomic masses because :-

(A) they have isotopes

(B) their isotopes have non-integral masses

(C) their isotopes have different masses

(D) the constituents, neutrons, protons and electrons combine to give rational masses

Solution.

Non-integral atomic masses are due to isotopes which have different masses.

So, ***(A)*** and ***(C)*** are the correct answer.

Illustration 36.

How many sub-shells are there in N shell ? How many orbitals are there in d sub-shell ?

Solution

For N shell, principal quantum number, n = 4.

Number of sub-shells, in an energy level = n

∴ Number of sub-shells, in N shell = 4

For d subshell $l = 2$

Number of orbitals in a sub-shell = $2l + 1$

Number of orbitals in a d-sub-shell = $2 \times 2 + 1 = 5$

Illustration 37.

State which of the following sets of quantum numbers would be possible and which would not be permissible for an electron in an atom.

(i) $n = 3, l = 3, m_l = +3, m_s = +\frac{1}{2}$ (ii) $n = 3, l = 0, m_l = +1, m_s = -\frac{1}{2}$

(iii) $n = 5, l = 4, m_l = +3, m_s = 1$ (iv) $n = 0, l = 0, m_l = 0, m_s = +\frac{1}{2}$

(v) $n = 4, l = 3, m_l = -2, m_s = -\frac{1}{2}$

Solution

(i) Not possible because when n = 3, l cannot be equal to 3. The value of l cannot be numerically equal to the value of n.

(ii) Not possible because when $l = 0$, m_l cannot be +1. The value of m_l cannot be numerically more than the value of l.

(iii) Not possible because s cannot be 1. The only allowed values of m_s are $+\frac{1}{2}$ and $-\frac{1}{2}$.

(iv) Not possible because n cannot be 0.

(v) This set is permitted because when n = 4, l can be 3. When $l = 3$, m_l can be –2. m_s can have $-\frac{1}{2}$ value.

Illustration 38.

Give the sets of quantum numbers that describe an electron in a 3p orbital.

Solution

$n = 3, l = 3, m_l = +1, 0 \text{ or } -1, m_s = +\frac{1}{2} \text{ or } +\frac{1}{2}$.

Illustration 39.

Which of the following set of Quantum number not possible ?

	(i)	***(ii)***	***(iii)***
	$n = 2$	$n = 3$	$n = 4$
	$\ell = 0$	$\ell = 2$	$\ell = 3$
	$m = -1$	$m = 0$	$m = -2$
	$s = -\frac{1}{2}$	$s = \pm\frac{1}{2}$	$s = \pm\frac{1}{2}$
Solution	not possible	possible	possible

Illustration 40.

What is the maximum number of electrons that can be accommodated :

(i) in the shell with n = 3

(ii) in the subshell with $l = 3$

(iii) in an orbital with $m_l = +3$

Solution

(i) For a shell with n = 3 the number of orbitals = $n^2 = 3^2 = 9$

$\therefore$ Number of electrons = 9 × 2 = 18

(ii) Number of orbitals = $2l + 1 = 2 \times 3 + 1 = 7$

$\therefore$ Number of electrons = 7 × 2 = 14

(iii) This corresponds to only one orbital and hence it can accomodate only 2 electrons.

Illustration 41.

Which of the following orbitals are not possible ?

2d, 4f, 4g and 6d

Solution

2d is not possible. For d sub-shell $l = 2$. When n = 2, l can be 0 and 1. Since l cannot be 2 for n = 2 hence 2d sub-shell is not possible.

4f is possible. For f-sub-shell $l = 3$. When n = 4, l can be equal to 3.

4g is not possible. For g-sub-shell $l = 4$. When n = 4, l cannot be equal to 4.

6d is possible. For d-sub-shell $l = 2$. When n = 6, l can be equal to 2.

Illustration 42.

What are the possible values of m_ℓ for an electron with $\ell = 2$?

Solution

The value of m_ℓ can vary from $-\ell$ to $+\ell$; in this case m_ℓ can have values –2, –1, 0, +1 and +2.

Illustration 43.

What are the possible values of m_s for an electron with $m_\ell = 0$?

Solution

m_s must be –1/2 or +1/2. These are the only permitted values, regardless of the values of the other quantum numbers.

Illustration 44.

Match each of the following quantum number values with the proper letter designation (K , L , M , N , s , p , d , f) :

(a) n = 1 ***(b) ℓ = 2*** ***(c) ℓ = 0*** ***(d) n = 3***

Solution

(a) K (b) d (c) s (d) M

Illustration 45.

What is the orbital angular momentum of an electron in 3p orbital.

Solution

Angular momentum (L) $= \sqrt{\ell(\ell+1)}\dfrac{h}{2\pi} = \sqrt{2}\dfrac{h}{2\pi} = ...$

Illustration 46.

What is spin angular momentum of an electron.

Solution

Spin Angular momentum $= \sqrt{s(s+1)}\dfrac{h}{2\pi}$

$$\sqrt{\left(\frac{1}{2}\right)\frac{3}{2}}\frac{h}{2\pi} = \sqrt{\frac{3}{4}} \times \frac{h}{2\pi}$$

Illustration 47.

What is orbital angular momentum of an electron in 3d orbital.

(A) $\sqrt{3}\dfrac{h}{2\pi}$ (B) $\sqrt{5}\dfrac{h}{2\pi}$ (C) $\dfrac{3h}{2\pi}$ (D) $\sqrt{6}\dfrac{h}{2\pi}$

Ans. (D)

Solution

Orbital angular momentum $(\vec{L}) = \sqrt{(\ell)(\ell+1)}\,\frac{h}{2\pi}$

Illustration 48*.

What are the possible set of quantum number for highest energy electron (in ground state) for chlorine atom.

	n	***ℓ***	***m***
(A)	2	0	0
(B)	2	1	–2
(C)	3	1	2
(D)	3	1	0

Ans. (D)

Solution

$(n+\ell)$ is maximum for [D]

Illustration 49.

The electrons identified by n & ℓ ;

(i) n = 4, ℓ = 1 (ii) n = 4, ℓ = 0 (iii) n = 3, ℓ = 2 (iv) n = 3, ℓ = 1

can be placed in order of increasing energy from lowest to highest as

(A) (iv) < (ii) < (iii) < (i) (B) (ii) < (iv) < (i)

(C) (i) < (iii) < (ii) < (iv) (D) (iii) < (i) < (iv) < (ii)

Ans. (A)

Solution

Apply Aufbau principle :

(i) The orbital with lowest value of (n + ℓ) have lowest energy.

(ii) If n + ℓ value for two orbitals are same, the orbital with lower value of n is having lower energy.

for (i) n + ℓ = 5
(ii) n + ℓ = 4
(iii) n + ℓ = 5
(iv) n + ℓ = 4

for (iii) and (iv) n is lower hence correct order is ***(iv) < (ii) < (iii) < (i).***

Illustration 50*.

A compound of vanadium has magnetic moment of 1.73 BM. Work out the electronic configuration of vanadium ion in the compound.

Solution

Vanadium belongs to 3d series with Z = 23. The magnetic moment of 3d series metal is given by spin only formula.

$\mu = \sqrt{n(n+2)}$ BM (BM = Bohr's magneton)

$\because$ $\sqrt{1.73} = \sqrt{3}$

$\Rightarrow$ n(n+2) = 3 $\Rightarrow$ n = 1

$\Rightarrow$ Magnetic moment correspond to one unpaired electron.

$\Rightarrow$ Electronic configuration of vanadium atom $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$.

For one unpaired electron 4 electron must be removed in which first 2 electron are lost from 4s orbital (outermost).

Electronic configuration of V^{+4}

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^1$

* * * * *

ANSWERS

BEGINNER'S BOX-1

1.	(A)	**2.**	(C)	**3.**	(A)	**4.**	(D)	**5.**	(B)
6.	(C)	**7.**	(B)						

8. (A) → (R) & (T), (P), (S) (B) → (Q) & (U), (S), (P) (C) → (U) , (Q)
(D) → (Q) & (U), (S) , (P) (E) → (U), (Q) (F) → (U), (Q)

BEGINNER'S BOX-2

1. (i) 0.2 g-molecule CH_4 (ii) 5 g-molecule N_2
(iii) 0.83 g-molecule of O_3 (iv) 0.0002 g-molecule of H_2
(v) 0.5 g-molecule of an ideal gas (vi) 0.0002 g-molecule of SO_3
(vii) 0.5 g-molecule of C_2H_6 (viii) 0.005 g-molecule of He

2. 6.023×10^{25} protons

3. 2.43 gm

4. No. of molecules = 5 N_A No. of atoms = $15N_A$.

5. 280 gm of Si

6. 3.01×10^{21} molecules of H_2O

7. 6.023×10^{23} atom Na, 6.023×10^{23} atom Cl, 18.06×10^{23} atom O

8. 0.75 mole, 4.52×10^{23} molecule P_4, 18.04×10^{23} atom P.

9. 0.25 mol

10. (a) 23g (b) 71 g (c) 64 g

11. 68

12. (D)

13. (D)

14. (C)

15. (C)

BEGINNER'S BOX-3

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

BEGINNER'S BOX-4

Quantum Numbers

1.	(D)	**2.**	(D)	**3.**	(B)	**4.**	(C)	**5.**	(D)
6.	(C)	**7.**	(B)						

Electronic Configuration and Miscellaneous

8.	(D)	**9.**	(D)	**10.**	(D)	**11.**	(C)	**12.**	(A)
13.	(A)	**14.**	(C)						

15. (a) $0 \times (\pm 1/2) = 0$
(b) $0 \times (\pm 1/2) = 0$
(c) $1 \times (\pm 1/2) = \pm 1/2$
(d) $3 \times (\pm 1/2) = \pm 3/2$
(e) $5 \times (\pm 1/2) = \pm 5/2$

16. (C)

EXERCISE – 1 MCQ (SINGLE CHOICE CORRECT)

1. Which of the following expressions is correct (n = no. of moles of the gas, N_A = Avogadro constant, m = mass of 1 molecule of the gas, N = no. of molecules of the gas) ?
(A) $n = mN_A$ (B) $m = N_A$ (C) $N = nN_A$ (D) $m = n/N_A$

2. The maximum number of molecules is present in–
(A) 15 L of H_2 gas at STP (B) 5 L of N_2 gas at STP
(C) 0.5 L of H_2 gas (D) 10 L of O_2 gas

3. In which of the following pairs do 1 g of each have an equal number of molecules :
(A) N_2O and CO (B) N_2 and C_3O_2 (C) N_2 and CO (D) N_2O and C_2O

4. A quantity of aluminium has a mass of 54.0 g. What is the mass of the same number of magnesium atoms ?
(At. wt. Al = 27, Mg = 24)
(A) 12.1 g (B) 23.3 g (C) 48 g (D) 97.2 g

5. Which of the following samples contains the largest number of atoms ?
(A) 1 g of Ni(s) (B) 1 g of Ca(s) (C) 1 g of N_2(g) (D) 1 g of Br(s)

6. If the percentage of water of crystallization in $MgSO_4.x\,H_2O$ is 13%. What is the value of x :
(A) 1 (B) 4 (C) 5 (D) 7

7. A pure gas that is 14.3% hydrogen and 85.7% carbon by mass has a density of 2.5 g L^{-1} at 0°C and 1 atm pressure. What is the molecular formula of the gas :
(A) CH_2 (B) C_2H_4 (C) C_4H_8 (D) C_6H_{12}

8. One atomic mass unit in kilogram is
(A) $1/N_A$ (B) $12/N_A$ (C) $1/1000\,N_A$ (D) $1000/N_A$

9. The mass of 1 mole of protons ($m_p = 1.672 \times 10^{-27}$ kg) is :
(A) 1.800×10^{-3} kg (B) 1.008×10^{-4} kg (C) 1.080×10^{-3} kg (D) 1.007×10^{-3} kg

10. 2 isotopes of an element are present in 1 : 2 ratio of number, having mass number M and (M + 0.5) respectively. The mean mass number of element will be
(A) 3M + 1 (B) 1.5 M + 0.5 (C) 0.5 M + 0.5 (D) M + 1/3

11. From 2 mg calcium, 1.2×10^{19} atoms are removed. The number of g-atoms of calcium left is
(A) 5×10^{-5} (B) 2×10^{-5} (C) 3×10^{-5} (D) 5×10^{-6}

12. The number of electron in 3.1 mg NO_3^- is -
(A) 32 (B) 1.6×10^{-3} (C) 9.6×10^{20} (D) 9.6×10^{23}

13. The number of neutrons in 0.45 g water, assuming that all the hydrogen atoms are H^1 atoms and all the oxygen atoms are O^{16} atoms, is
(A) 8 (B) 0.2 (C) 1.2×10^{23} (D) 4.8×10^{24}

14. A gaseous mixture contains CO_2 (g) and N_2O (g) in a 2 : 5 ratio by mass. The ratio of the number of molecules of CO_2 (g) and N_2O (g) is
(A) 5 : 2 (B) 2 : 5 (C) 1 : 2 (D) 5 : 4

15. 1.61 gm of $Na_2SO_4.10H_2O$ contains same number of oxygen atoms as present in
(A) 0.98 gm H_2SO_4 (B) 0.08 gm SO_3 (C) 1.78 gm $H_2S_2O_7$ (D) 0.05 gm $CaCO_3$

16. Which of the following contain largest number of carbon atoms?
(A) 15 gm ethane, C_2H_6 (B) 40.2 gm sodium oxalate, $Na_2C_2O_4$
(C) 72 gm glucose, $C_6H_{12}O_6$ (D) 35 gm pentene, C_5H_{10}

17. If the mass of proton is doubled and that of neutron is halved, the molecular weight of CO_2, consisting only C^{12} and O^{16} atoms, will
(A) not change (B) increase by 25% (C) decrease by 25% (D) increase by 50%

18. The number of g-molecules of oxygen in 6.02×10^{24} CO molecules is
(A) 1 g-molecule (B) 0.5 g-molecule (C) 5 g-molecule (D) 10 g-molecule

19. Which of the following will occupy greater volume under the similar conditions of pressure and temperature?
(A) 6 gm oxygen (B) 0.98 gm hydrogen (C) 5.25 gm nitrogen (D) 1.32 gm helium

20. The volume of one mole of water at 277 K is 18 ml. One ml of water contains 20 drops. The number of molecules in one drop of water will be
(A) 1.07×10^{21} (B) 1.67×10^{21} (C) 2.67×10^{21} (D) 1.67×10^{20}

21. It is known that atom contain protons, neutrons and electrons. If the mass of neutron is assumed to half of its original value where as that of proton is assumed to be twice of its original value then the atomic mass of ${}^{14}_{6}C$ will be -
(A) same (B) 25% more (C) 14.28 % more (D) 28.5% less

22. 0.250 g of an element M, reacts with excess fluorine to produce 0.547 g of the hexafluoride MF_6. What is the element: [Cr = 52, Mo = 96, S = 32, Te = 127.6]
(A) Cr (B) Mo (C) S (D) Te

23. A 1000 gram sample of NaOH contains 3 moles of O atoms, what is the % purity of NaOH :
(A) 14% (B) 100% (C) 12% (D) 24%

24. The quantum numbers of four electrons (e1 to e4) are given below :-

	n	***ℓ***	***m***	***s***
e1	3	0	0	+1/2
e2	4	0	0	1/2
e3	3	2	2	–1/2
e4	3	1	–1	1/2

The correct order of decreasing energy of these electrons is :
(A) e4 > e3 > e2 > e1 (B) e2 > e3 > e4 > e1 (C) e3 > e2 > e4 > e1 (D) none of these

25. The correct set of quantum numbers for the unpaired electron of chlorine atom is

	n	***l***	***m***		***n***	***l***	***m***
(A)	2	1	0	(B)	2	1	1
(C)	3	1	1	(D)	3	0	0

26. Principal quantum number of an atom represents
(A) Size of the orbital (B) Spin angular momentum
(C) Orbital angular momentum (D) Space orientation of the orbital

27. The maximum number of electrons that can be accommodated in the Mth shell is

(A) 2 (B) 8 (C) 18 (D) 32

28. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon :-

(A) 3s (B) 2p (C) 2s (D) 1s

29. Correct set of four quantum numbers for valence electron of rubidium (Z = 37) is :-

(A) 5, 0, 0, $+\frac{1}{2}$ (B) 5, 1, 0, $+\frac{1}{2}$ (C) 5, 1, 1, $+\frac{1}{2}$ (D) 6, 0, 0, $+\frac{1}{2}$

30. The orbital diagram in which the Aufbau's principle is violated is :-

(A) 2s ↑↓ 2p$_x$ ↑↓ 2p$_y$ ↑ 2p$_z$ ↑ (B) 2s ↑ 2p$_x$ ↑↓ 2p$_y$ ↑ 2p$_z$ ↑ (C) 2s ↑↓ 2p$_x$ ↑ 2p$_y$ ↑ 2p$_z$ ↑ (D) 2s ↑↓ 2p$_x$ ↑↓ 2p$_y$ ↑↓ 2p$_z$ ↑

31. Which of the following sets of quantum numbers represent an impossible arrangement :-

	n	l	m	m_s		n	l	m	m_s
(A)	3	2	–2	$\frac{1}{2}$	(B)	4	0	0	$\frac{1}{2}$
(C)	3	2	–3	$\frac{1}{2}$	(D)	5	3	0	$\frac{1}{2}$

32. The explanation for the presence of three unpaired electrons in the nitrogen atom can be given by :-

(A) Pauli's exclusions principle (B) Hund's rule
(C) Aufbau's principle (D) Uncertainty principle

33. The electronic configuration of an element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$. This represents its :-

(A) Excited state (B) Ground state (C) Cationic form (D) None

34. Which of the following has maximum number of unpaired electron (atomic number of Fe 26) :-

(A) Fe (B) Fe (II) (C) Fe (III) (D) Fe (IV)

35. Which quantum number is not related with Schrodinger equation :-

(A) Principal (B) Azimuthal (C) Magnetic (D) Spin

36. Give the correct order of initials T (true) or F (false) for following statements :-

(I) If an ion has 2 electrons in K shell, 8 electrons in L shell and 6 electrons in M shell, then number of S electrons present in that element is 6.

(II) The maximum number of electrons in a subshell is given by $2n^2$

(III) If electron has magnetic quantam number –1, then it cannot be present in s-orbital.

(IV) Only one radial node is present in 3p orbital.

(A) TTFF (B) FTTF (C) TFTT (D) FFTF

EXERCISE – 2 MCQ (ONE OR MORE CHOICE CORRECT)

1. Same mass of glucose ($C_6H_{12}O_6$) and acetic acid (CH_3COOH) contain :
(A) Same number of carbon atoms
(B) Same number of Hydrogen atoms
(C) Same number of oxygen atoms
(D) All of above

2. Two flask of equal capacity contain NH_3 & SO_2 gases respectively, are kept under similar conditions of temperature & pressure. Select the correct option on the basis of above information:
(A) More moles are present in flask contain NH_3
(B) Flask of SO_2 has more mass
(C) Flask of NH_3 has more number of atoms.
(D) Both flask contain same number of molecules of NH_3 & SO_2 respectively

3. Which of the following contains the same number of molecules ?
(A) 1 g of O_2, 2 g of SO_2
(B) 1 g of CO_2, 1 g of N_2O
(C) 11.2 ml of O_2 at STP, 224 ml of He at 0.5 atm and 273 K
(D) 1 g of oxygen, 1 g of ozone

4. Select the correct statement(s) for $(NH_4)_3PO_4$.
(A) Ratio of number of oxygen atom to number of hydrogen atom is 1 : 3.
(B) Ratio of number of cation to number of anion is 3 : 1.
(C) Ratio of number of nitrogen atom to number of oxygen atom is 3 : 4.
(D) Total number of atoms in one mole of $(NH_4)_3PO_4$ is 20.

5. 1 mol of $^{24}_{12}Mg^{2+}$ ions contains :
(A) $12 \times 6.023 \times 10^{23}$ electrons
(B) $12 \times 6.023 \times 10^{23}$ protons
(C) $12 \times 6.023 \times 10^{23}$ neutrons
(D) $14 \times 6.023 \times 10^{23}$ protons

6. 8g O_2 has same number of molecules as that in :
(A) 14g CO
(B) 7 g CO
(C) 11 g CO_2
(D) 22 g CO_2

7. Which of the following statements(s) is/are correct for water ?
(A) H and O are in 2 : 1 atomic ratio
(B) H and O are in 2 : 1 weight ratio
(C) H and O are in 1 : 8 weight ratio
(D) H and O are in 1 : 16 weight ratio

8. 1 g atom of nitrogen represents
(A) 6.023×10^{23} N_2 molecules
(B) 22.4 *L* of N_2 at 1 atm and 273 K
(C) 11.2 *l* of N_2 at 1 atm and 273 K
(D) 14 g of N_2

9*. A sample of oxygen contains O^{16} & O^{18} isotopes only with percentage abundance respectively as 90% & 10%. Identify the correct option(s) :
(A) Average atomic mass of sample is 16.2.
(B) Average number of protons per atom is 8.
(C) Average number of neutrons per atom is 8.2.
(D) Molecular mass of oxygen gas which can be formed from the sample can vary from 32 to 36.

10. Which of the following will have same mass of the substance ?

(A) 11.2 litre of O_2 gas at NTP
(B) 44.8 litre of H_2 gas at NTP
(C) 22.4 litre of CH_4 gas at NTP
(D) 16 ml of H_2O at NTP

11. Which of the following sample/s must have molar mass greater than that of a mixture of CO & CO_2 ?

(A) Pure Ne
(B) Pure O_3
(C) Mixture of SO_2 & N_2O_5
(D) Mixture of SO_2 & F_2

12. Which of the following have equal no. of atoms ?

(A) 12 g $MgSO_4$
(B) 0.2 mole CO_2
(C) 5.6 L SO_2 at STP
(D) 24 g Ca

13. The number of d- electrons in Mn^{2+} is equal to that of

(A) p-electrons in N
(B) s-electron in Na
(C) d-electrons in Fe^{+3}
(D) p-electrons in O^{-2}

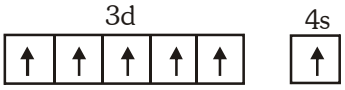
14. For $_{24}Cr$ which of the following statements is/are correct.

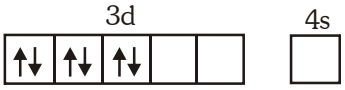
(A) Number of electrons with principle quantum number '3' are 13.
(B) Number of electrons with azimuthal quantum number '1' are 12.
(C) Number of electrons with magnetic quantum number '0' are 12.
(D) Number of minimum or maximum electrons with same spin quantum number are '9' or 15 respectively.

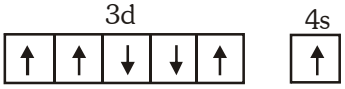
15. Which of the following energy level can not exist according to quantum theory ?

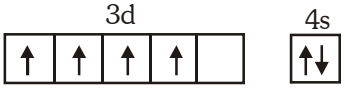
(A) 3f
(B) 5g
(C) 5h
(D) 6h

16. Which of the following configuration violates Hund's Rule ?

(A) 

(B) 

(C) 

(D) 

17. Choose the correct statement.

(A) d_{yz} orbital lies in the xz plane.
(B) p_z orbital lies along x–axis
(C) Lobes of $d_{x^2-y^2}$ orbital are at 90° with z–axis
(D) Lobes of d_{xy} orbital are at 90° with z-axis.

18. An element has mass number 23 and its unipositive ion has electronic configuration $1s^2 2s^2 2p^6$. Select the corect statement(s).

(A) It is isotonic with Mg^{24}.
(B) The ratio of n to ℓ for last electron in atom of above element is 2.
(C) Atom of the above element is isoelectronic with H_2O.
(D) Atom of the above element is paramagnetic.

Match the Column

19.

Column-I	***Column-II***
(A) 32 g each of O_2 and S	(p) 2 moles of Fe
(B) 2 gram-molecule of $K_3[Fe(CN)_6]$	(q) 3 moles of ozone molecule
(C) 144 g of oxygen atom	(r) one mole
(D) From 168 g of iron, 6.022×10^{23} atoms of iron are removed, the iron left	(s) 12 moles of carbon atoms

20. Match the following:

	Column I	***Column II***
(A)	Same number of unpaired electrons are present in	(p) Na^+, Mg^{2+}, F^-
(B)	Same number of electron in s & p subshells.	(q) F^-, Mg, O^{2-}
(C)	Same number of electrons with the $l = 1$	(r) Mg, Ne, O^{2-}
(D)	Same number of total electrons	(s) Li, Na, K

Comprehension Based Questions

Comprehension-1

9×10^{22} atoms of Ar and n moles of O_2 are kept in a vessel of capacity 5 L at 1 atm and 27°C. (Consider $N_A = 6 \times 10^{23}$) :

21. Find the mass of O_2 in vessel -

(A) 16 gm (B) 3.2 gm (C) 1.6 gm (D) 32 gm

22. If all the O_2 is converted to O_3 in vessel -

(A) moles of gas remain same
(B) molecules in vessel remain same
(C) pressure in vessel remain same
(D) total atoms in vessel remain same

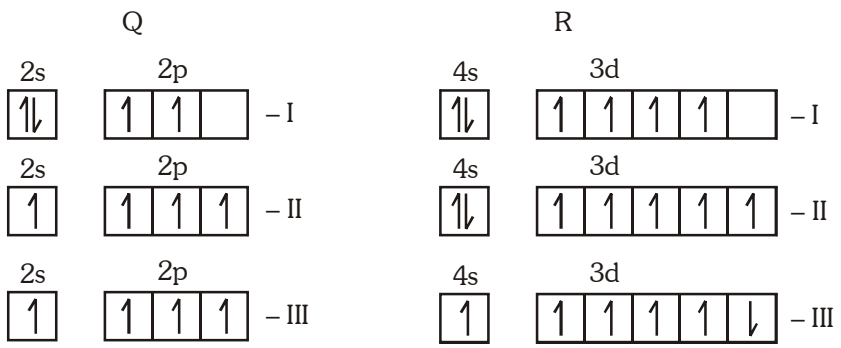
23. If 3×10^{22} molecules of O_2 are added in vessel. Find the new pressure in vessel at same temperature in vessel-

(A) 1.23 atm (B) 2.23 atm (C) 0.23 atm (D) None of the above

Comprehension-2

Electronic configuration of elements give an idea about various properties of elements and hence it is one of the basis for periodic classification of elements. An element prefers to stay in that configuration in which its energy is least. A substance is said to show "Paramagnetic properties" if it has unpaired electrons.

24. Which of the following options correctly mention the configuration which is most stable among Q and R.



(A) Q – I and R – I
(B) Q – I and R – II
(C) Q – II and R – I
(D) None of the above options

25. Which of the following is expected to be paramagnetic :

(A) Fe (B) Zn (C) Ne (D) Be

26. Specie having configuration same as ns^2np^4 where 'n' represents last shell is/are :

(A) ${}_{16}O^{32}$
(B) ${}_{34}Se^{79}$
(C) ${}_{9}F^{19}$
(D) Both ${}_{16}O^{32}$ and ${}_{34}Se^{79}$

EXERCISE – 3 SUBJECTIVE

1. Calculate the % by mass of 'H' in 1 ml of H_2O^{18} at 1 atm and 27°C.
(Express your answer as sum of all digits.)

2. Calculate the mass of urea (NH_2CONH_2) containing 1gm-atom H.
(Express your answer as sum of all digits.)

3. The average mass of one gold atom in a sample of naturally occuring gold is 3.2707×10^{-22} g. Use this to calculate the molar mass of gold.

4. A plant virus is found to consist of uniform symmetrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3/g. If the virus is considered to be a single particle, find its molecular weight.

5. A chemical commonly called "dioxin" has been very much in the news in the past few years. (It is the by product of herbicide manufacture and is thought to be quite toxic.) Its formula is $C_{12}H_4Cl_4O_2$. If you have a sample of dirt (28.3 g) that contains 1.0×10^{-4} % dioxin, how many moles of dioxin are in the dirt sample?

6. The action of bacteria on meat and fish produces a poisonous compound called cadaverine. As its name and origin imply, it stinks ! It is 58.77% C, 13.81 % H, and 27.42 % N. Its molar mass is 102 g/mol. Determine the molecular formula of cadaverine.

7. Given the following empirical formulae and molecular weight, compute the true molecular formulae :

	Empirical formula	***Molecular weight***
(a)	CH_2	84
(b)	CH_2O	150
(c)	HO	34
(d)	HgCl	472
(e)	HF	80

8. 1 mole of diatomic gas A_2 contain 32 and 36 moles of electrons and neutrons respectively. The representation of the element.

9. A sample of nitrogen contains 90% N^{14} and 10% N^{15} isotopes. The average number of neutron per atom is

10. If molecular weight of glucose-1-phosphate is 260 and its density is 1.5 g/ml. What is the average volume occupied by 1 molecule of this compound?

11. Find total no. of orbitals in nickel which have $|m| \le 1$ and at least one electron is present, where 'm' is magnetic quantum number.
(Given your ans. as sum digits for example. If your ans is 57 then 5 + 7 = 12 and 1 + 2 =3)

12. Calculate total number of orbitals having ***(n + ℓ) value = 8 and magnetic quantum number a non–zero*** quantity.

13. Maximum number of electrons in parallel spin in the group state of Chromium atom is:

14. If the magnetic quantum number for an electron is –3, the minimum value for its principal quantum number is :

EXERCISE – 4 RECAP OF AIEEE/JEE (MAIN)

1. The weight of 2.01×10^{23} molecules of CO is **[AIEEE-2002]**

(A) 9.3 g (B) 7.2 g (C) 1.2 g (D) 3 g

2. In an organic compound of molar mass 108 g mol^{-1} C, H and N atoms are present in 9 : 1 : 3.5 by weight. Molecular formula can be : **[AIEEE-2002]**

(A) $C_6H_8N_2$ (B) $C_7H_{10}N$ (C) $C_5H_6N_3$ (D) $C_4H_{18}N_3$

3. The number of d-electrons retained in Fe^{2+} (At. no. of Fe = 26) ion is : **[AIEEE-2003]**

(A) 6 (B) 3 (C) 4 (D) 5

4. 6.02×10^{21} molecules of urea are present in 100 ml of its solution. The concentration of urea solution is - **[AIEEE-2004]**

(A) 0.001 M (B) 0.01 M (C) 0.02 M (D) 0.1 M

5. Which of the following sets of quantum number is correct for an electron in 4f orbital ? **[AIEEE-2004]**

(A) $n = 3, l = 2, m = -2, s = +\frac{1}{2}$ (B) $n = 4, l = 4, m = -4, s = -\frac{1}{2}$

(C) $n = 4, l = 3, m = +1, s = +\frac{1}{2}$ (D) $n = 4, l = 3, m = +4, s = +\frac{1}{2}$

6. Consider the ground state of Cr atom (Z = 24). The numbers of electrons with the azimuthal quantum numbers, $l = 1$ and 2 are, respectively **[AIEEE-2004]**

(A) 16 and 5 (B) 12 and 5 (C) 16 and 4 (D) 12 and 4

7. Which one of the following sets of ions represents the collection of isoelectronic species ? **[AIEEE-2004]**

(A) Na^+, Mg^{2+}, Al^{3+}, Cl^- (B) Na^+, Ca^{2+}, Sc^{3+}, F^-

(C) K^+, Cl^-, Mg^{2+}, Sc^{3+} (D) K^+, Ca^{2+}, Sc^{3+}, Cl^-

8. In a multi-electron atom, which of the following orbitals described by the three quantum members will have the same energy in the absence of magnetic and electric fields ? **[AIEEE-2005]**

(a) $n = 1, l = 0, m = 0$ (b) $n = 2, l = 0, m = 0$ (c) $n = 2, l = 1, m = 1$ (d) $n = 3, l = 2, m = 1$

(e) $n = 3, l = 2, m = 0$

(A) (d) and (e) (B) (c) and (d) (C) (b) and (c) (D) (a) and (b)

9. Of the following sets which one does not contain isoelectronic species ? **[AIEEE-2005]**

(A) BO_3^{3-}, CO_3^{2-}, NO_3^- (B) SO_3^{2-}, CO_3^{2-}, NO_3^- (C) CN^-, N_2, C_2^{2-} (D) PO_4^{3-}, SO_4^{2-}, ClO_4^-

10. Which of the following statements in relation to the hydrogen atom is correct ? **[AIEEE-2005]**

(A) 3s, 3p and 3d orbitals all have the same energy

(B) 3s and 3p orbitals are of lower energy than 3d orbitals

(C) 3p orbital is lower in energy than 3d orbital

(D) 3s orbitals is lower in energy than 3p orbital

11. If we consider that 1/6, in place of 1/12, mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of the substance will :- ***[AIEEE-2005]***

(A) be a function of the molecular mass of the substance

(B) remain unchanged

(C) increase two fold

(D) decrease twice

12. How many moles of magnesium phosphate, $Mg_3(PO_4)_2$ will contain 0.25 mole of oxygen atoms? ***[AIEEE-2006]***

(A) 3.125×10^{-2} (B) 1.25×10^{-2} (C) 2.5×10^{-2} (D) 0.02

13. Which of the following sets of quantum numbers represents the highest energy of an atom ? ***[AIEEE-2007]***

(A) n = 3, l = 1, m =1, s = +½ (B) n = 3, l = 2, m =1, s = +½

(C) n = 4, l = 0, m =0, s = +½ (D) n = 3, l = 0, m =0, s = +½

14. Which one of the following constitutes a group of the isoelectronic species? ***[AIEEE-2008]***

(A) C_2^{2-}, O_2^-, CO, NO (B) $NO^+, C_2^{2-}, CN^-, N_2$ (C) $CN^-, N_2, O_2^{2-}, C_2^{2-}$ (D) N_2, O_2^-, NO^+, CO

15. If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established ?

(Given : Vapour pressure of H_2O at 300 K is 3170 Pa ; R = 8.314 $JK^{-1} mol^{-1}$) :- ***[AIEEE-2010]***

(A) 1.27×10^{-3} mol (B) 5.56×10^{-3} mol (C) 1.53×10^{-2} mol (D) 4.46×10^{-2} mol

16*. The increasing order of the ionic radii of the given isoelectronic species is :- ***[AIEEE-2012]***

(A) $K^+, S^{2-}, Ca^{2+}, Cl^-$ (B) $Cl^-, Ca^{2+}, K^+, S^{2-}$ (C) $S^{2-}, Cl^-, Ca^{2+}, K^+$ (D) $Ca^{2+}, K^+, Cl^-, S^{2-}$

17. The electrons identified by quantum numbers n and ℓ :- ***[AIEEE-2012]***

(a) n = 4 , ℓ = 1 (b) n = 4, ℓ = 0 (c) n = 3, ℓ = 2 (d) n = 3, ℓ = 1

Can be placed in order of increasing energy as

(A) (a) < (c) < (b) < (d) (B) (c) < (d) < (b) < (a) (C) (d) < (b) < (c) < (a) (D) (b) < (d) < (a) < (c)

18. A transition metal M forms a volatile chloride which has a vapour density of 94.8. If it contains 74.75% of chlorine the formula of the metal chloride will be ***[AIEEE 2012 (Online)]***

(A) MCl_2 (B) MCl_4 (C) MCl_5 (D) MCl_3

19. The ratio of number of oxygen atoms (O) in 16.0 g ozone (O_3), 28.0 g carbon monoxide (CO) and 16.0 g oxygen (O_2) is :-

(Atomic mass : C = 12, O = 16 and Avogadro's constant $N_A = 6.0 \times 10^{23}$ mol^{-1})***[AIEEE 2012 (Online)]***

(A) 3 : 1 : 1 (B) 1 : 1 : 2 (C) 3 : 1 : 2 (D) 1 : 1 : 1

20. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is ***[JEE(Main)-2013]***

(A) C_2H_4 (B) C_3H_4 (C) C_6H_5 (D) C_7H_8

21. The ratio of masses of oxygen and nitrogen in a particular gaseous mixture is 1 : 4. The ratio of number of their molecule is– ***[JEE Mains-2014]***

(A) 1 : 4 (B) 7 : 32 (C) 1 : 8 (D) 3 : 16

22*. The correct set of four quantum numbers for the valence electrons of rubidium atom (Z = 37) is: ***[JEE MAINS-2014]***

(A) 5, 0, 0 + $\frac{1}{2}$ (B) 5, 1, 0 + $\frac{1}{2}$ (C) 5, 1, 1 + $\frac{1}{2}$ (D) 5, 0, 1 + $\frac{1}{2}$

23. If the principal quantum number n = 6, the correct sequence of filling of electrons will be:- ***[JEE-MAIN, 2015]***

(A) ns→(n–1)d→(n–2)*f*→np (B) ns→np→(n–1)d→(n–2)*f*
(C) ns→(n–2)*f*→(n–1)d→np (D) ns→(n–2)*f*→np→(n–1)d

24. The total number of orbitals associated with the principal quantum number 5 is : ***[JEE-MAIN, 2016]***

(A) 25 (B) 5 (C) 20 (D) 10

25. The most abundant elements by mass in the body of a healthy human adult are : Oxygen (61.4%); Carbon (22.9%), Hydrogen (10.0%); and Nitrogen (2.6%). The weight which a 75 kg person would gain if all ^1H atoms are replaced by ^2H atoms is : ***[JEE MAINS-2017]***

(A) 10 kg (B) 15 kg (C) 37.5 kg (D) 7.5 kg

26. The group having isoelectronic species is : ***[JEE MAINS-2017]***

(A) O^-, F^-, Na^+, Mg^{2+} (B) O^{2-}, F^-, Na^+, Mg^{2+} (C) O^-, F^-, Na, Mg^+ (D) O^{2-}, F^-, Na, Mg^{2+}

27. An unknown chlorohydrocarbon has 3.55% of chlorine. If each molecule of the hydrocarbon has one chlorine atom only; chlorine atoms present in 1 g of chlorohydrocarbon are :
(Atomic wt. of Cl = 35.5 u; Avogadro constant = 6.023×10^{23} mol^{-1}) ***[JEE(Main)-2018]***

(A) 6.023×10^{21} (B) 6.023×10^{23} (C) 6.023×10^{20} (D) 6.023×10^{9}

28. An organic compound is estimated through Dumus method and was found to evolve 6 moles of $C0_2$. 4 moles of H_20 and 1 mole of nitrogen gas. The formula of the compound is: ***[JEE-MAIN-2019]***

(A) $C_{12}H_8N$ (B) $C_{12}H_8N_2$ (C) C_6H_8N (D) $C_6H_8N_2$

29. The quantum number of four electrons are given below - ***[JEE-MAIN-2019]***

I. n = 4, l = 2, m_l = –2, m_s = – ½ II. n = 3, l = 2, m_l = 1, m_s = + ½
III. n = 4, l = 1, m_l = 0, m_s = + ½ IV. n = 3, l = 1, m_l = 1, m_s = – ½
The correct order of their increasing energies will be -

(A) IV < III < II < I (B) IV < II < III < I (C) I < II < III < IV (D) I < III < II < IV

30. The percentage composition of carbon by mole in methane is : ***[JEE-MAIN-2019]***

(A) 80% (B) 25% (C) 75% (D) 20%

31. 5 moles of AB_2 weigh 125×10^{-3} kg and 10 moles of A_2B_2 weigh 300×10^{-3} kg. The molar mass of A(M_A) and molar mass of B(M_B) in kg mol^{-1} are : ***[JEE-MAIN-2019]***

(A) $M_A = 50 \times 10^{-3}$ and $M_B = 25 \times 10^{-3}$ (B) $M_A = 25 \times 10^{-3}$ and $M_B = 50 \times 10^{-3}$
(C) $M_A = 5 \times 10^{-3}$ and $M_B = 10 \times 10^{-3}$ (D) $M_A = 10 \times 10^{-3}$ and $M_B = 5 \times 10^{-3}$

32. 25 g of an unknown hydrocarbon upon burning produces 88 g of CO_2 and 9 g of H_2O. This unknown hydrocarbon contains. ***[JEE-MAIN-2019]***

(A) 20g of carbon and 5 g of hydrogen (B) 24g of carbon and 1 g of hydrogen
(C) 18g of carbon and 7 g of hydrogen (D) 22g of carbon and 3 g of hydrogen

33. The isoelectronic set of ions is : ***[JEE-MAIN-2019]***

(A) N^{3-}, Li^+, Mg^{2+} and O^{2-} (B) Li^+, Na^+, O^{2-} and F^- (C) F^-, Li^+, Na^+ and Mg^{2+} (D) N^{3-}, O^{2-}, F^- and Na^+

EXERCISE – 5 RECAP OF IIT-JEE/JEE (ADVANCED)

1. How many moles of e– weight one Kg : ***[JEE '2002 (Scr), 1]***

(A) 6.023×10^{23} (B) $\frac{1}{9.108} \times 10^{31}$ (C) $\frac{6.023}{9.108} \times 10^{54}$ (D) $\frac{1}{9.108 \times 6.023} \times 10^{8}$

2. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe, ^{57}Fe are 5%, 90% and 5% respectively, the atomic mass of Fe is : ***[JEE 2009]***

(A) 55.85 u (B) 55.95 u (C) 55.75 u (D) 56.05 u

3. A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titre value is : ***[JEE 2010]***

4. The maximum number of electrons that can have principal quantum number, n=3, and spin quantum number, $m_s = -1/2$, is ***[JEE 2011]***

5. In an atom, the total number of electrons having quantum numbers n = 4 $|m_l| = 1$ and $m_s = -\frac{1}{2}$ is ***[JEE 2014]***

ANSWERS

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	C	A	C	C	C	A	C	C	D	D	C	C	C	B	C
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	D	B	C	B	B	C	B	C	C	C	A	C	D	A	B
Que.	31	32	33	34	35	36									
Ans.	C	B	B	C	D	C									

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	ABCD	BCD	ABC	ABC	BC	BC	AC	CD	ABCD	ACD	BC	ABD	BC	ABCD	AC
Que.	16	17	18												
Ans.	BC	CD	AD												

- ***Match the Column***

  19. (A) - (r), (B) - (ps), (C) - (q), (D) - (p)

  20. (A) - (pqrs), (B) - (p), (C) - (pqr), (D) - (p)

- ***Comprehension Based Questions***

  Comprehension 1 : **21.** (C) **22.** (D) **23.** (A)

  Comprehension-2 : **24.** (B) **25.** (A) **26.** (D)

EXERCISE-3

1. (1) **2.** (6) **3.** (196.9)

4. 7.09×10^{7} **5.** 8.8×10^{-8} mol **6.** $C_5H_{14}N_2$

7. (a) C_6H_{12} (b) $C_5H_{10}O_5$ (c) H_2O_2 (d) Hg_2Cl_2 (e) H_4F_4

8. ${}_{16}A^{34}$ **9.** 7.10 **10.** 29×10^{-23} ml

11. (4) **12.** (12) **13.** (15) **14.** (4)

EXERCISE-4

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

EXERCISE-5

1. (D) **2.** (B) **3.** 3 **4.** 9 **5.** 6

PERIODIC TABLE

Recap of Early Classes

In the previous chapter, we introduced the concept of orbitals giving some insight about the structure of the atom. Based on the concepts developed in the previous chapter, especially quantum numbers, we will study about the arrangement of different elements in the periodic table, we will also discuss about general trends of chemical and physical properties of elements.

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PERIODIC TABLE

0.1 INTRODUCTION

The arrangement of all the known elements according to their properties in such a way that the elements of similar properties are grouped together in a tabular form is called periodic table.

2.0 DEVELOPMENT OF PERIODIC TABLE

(A) LAVOISIER CLASSIFICATION OF ELEMENTS

At first Lavoisier classified the elements into two categories.

(i) Metal (ii) Non-metal

Note : This classification cannot categories the metalloid variety.

(B) DOBEREINER'S TRIAD RULE [1817]

(i) He made groups of three elements having similar chemical properties called TRIAD.

(ii) In Dobereiner triad, atomic weight of middle element is nearly equal to the average atomic weight of first and third element.

e.g.

Cl	Br	I	
35.5	$\boxed{80.0}$	127	$\frac{35.5+127}{2} = 81.25$

Ca	Sr	Ba	
40	$\boxed{87.5}$	137	$\frac{40+137}{2} = 88.5$

Li	Na	K	
7	$\boxed{23}$	39	At. wt of Na $= \frac{7+39}{2} = 23$

(iii) Other examples – (K, Rb, Cs), (P, As, Sb), (S, Se, Te), (H, F, Cl), (Sc, Y, La)

(C) NEWLAND'S OCTAVE RULE [1865]

(i) He arranged the elements in the increasing order of their atomic mass and observed that properties of every 8th element was similar to the 1st one, like in the case of musical vowels notation.

Sa	Re	Ga	Ma	Pa	Dha	Ni	Sa
1	2	3	4	5	6	7	8

(ii) At that time inert gases were not known.

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

(iii) The properties of Li are similar to 8th element i.e. Na, Be are similar to Mg and so on.

Drawbacks or Limitations :

(a) This rule is valid only upto Ca. because after Ca due to filling of d-orbitals there is difference of 18 elements instead of 8 element.

(b) After the discovery of inert gas this law had to be dropped out.

(c) He failed in the case of heavier metals as Fe has been placed along with O and S.

(D) LOTHER MEYER'S CURVE [1869]

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

(ii) The following observations can be made from the curve –

(a) Most electropositive elements i.e. alkali metals (Li, Na, K, Rb, Cs etc.) occupy the peak portions of the curve.

(b) Less electropositive i.e. alkaline earth metals (Be, Mg, Ca, Sr, Ba) occupy the descending portions of the curve.

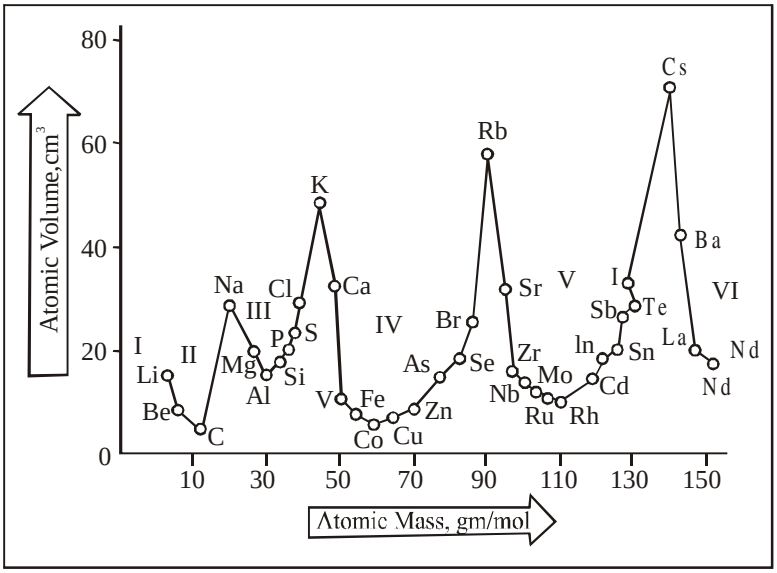
(c) Metalloids (B, Si, As, Te, At etc.) and transition metals occupy bottom part of the curve.

(d) Most electronegative i.e. halogens (F, Cl, Br, I) occupy the ascending portion of the curve.

Note : Elements having similar properties occupy similar portions of the curve.

Conclusion :

On the basis of this curve, Lother Meyer proposed that the physical properties of the elements are periodic function of their atomic weight and this became the basis of Mendeleev's periodic table.



(E) MENDELEEV'S PERIODIC TABLE [1869]

(i) Mendeleev's periodic law – The physical and chemical properties of elements are the periodic function of their atomic weight

(ii) 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 systamatic 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.

(e) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.

(f) Each group upto VIIth 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 VIIIth group consists of 9 elements in three rows.

(h) The elements belonging to same group exhibit similar properties.

(iii) 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.

$$\boxed{\text{Atomic Weight} = \text{Valency} \times \text{Equivalent weight.}}$$

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 × 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.

(iv) 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 weight of isotopes differs, they should have been placed in different position in Mendeleev's periodic table. But there was no such place for isotopes in Mendeleev's table.

(c) Anomalous pairs of elements – There were some pair of elements which did not follow the increasing order of atomic wts.

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

$$\begin{pmatrix} \text{Ar} & \text{K} \\ 39.9 & 39.1 \end{pmatrix} \qquad \begin{pmatrix} \text{Te} & \text{I} \\ 127.5 & 127 \end{pmatrix}$$

in modified mendeleev P.T.

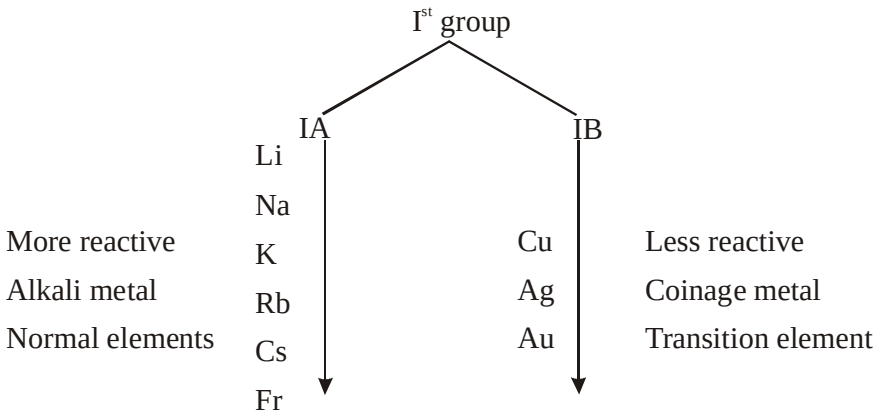
$$\begin{pmatrix} \text{Co} & \text{Ni} \\ 58.9 & 58.6 \end{pmatrix} \qquad \begin{pmatrix} \text{Th} & \text{Pa} \\ 232 & 231 \end{pmatrix}$$

(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	Au
VIII	IB

(e) Unlike elements were placed in same group.



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

2.5 Modern periodic table (Modified mendeleef Periodic Table)

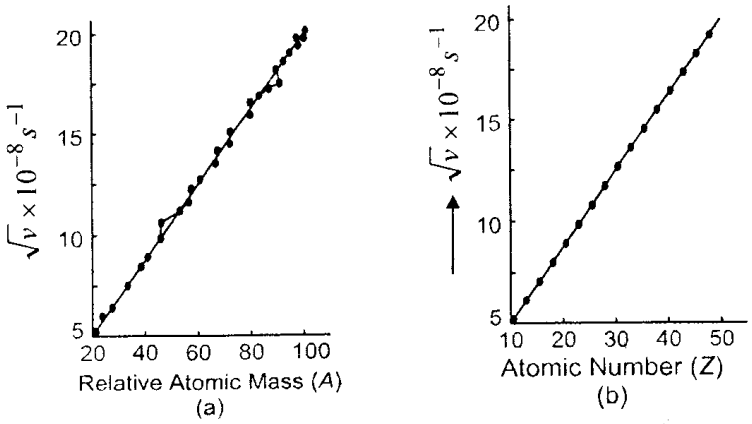
SL AL

(a) It was proposed by Moseley.

(b) Modern periodic table is based on atomic number.

(c) Moseley did an experiment in which he bombarded high speed electron on different metal surfaces and obtained X-rays.

He found out that frequency of X-rays, varies with atomic number as shown in the graph.



Moseley's Experiment

From this observation he established a mathematical expression

$\sqrt{\nu} = a(Z-b)$

Where, ν is the frequency of x-ray

a is the proportionality constant

b is constant (series constant)

Z is integer (Atomic number)

(d) ***Modern periodic law :*** The physical & chemical properties of elements are the periodic function of their atomic number.

- **Characteristics of modern periodic table**

(a) 9 vertical columns called groups.

(b) I^{st} to VIII group + 0 group of inert gases.

(c) Inert gases were introduced in periodic table by Ramsay.

(d) 7 horizontal series called periods.

2.6 Long form / Present form of Modern periodic table

SL AL

(It is also called as 'Bohr, Bury & Rang, Werner Periodic Table)

(a) It is based on the Bohr-Bury electronic configuration concept and atomic number.

(b) This model is proposed by Rang & Werner

(c) 7 periods and 18 vertical columns (groups)

(d) According to I. U. P. A. C. 18 vertical columns are named as I^{st} to 18th group.

(e) Elements belonging to same group having same number of electrons in the outermost shell so their properties are similar.

Extended or Long Form of the Periodic Table

s-Block Elements ⟷ | d-Block Elements ⟷ | p-Block Elements ⟷

Metals | Non metals | Metalloids

Period ↓ / Group →	IA (1)	IIA (2)	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIII (8)	VIII (9)	VIII (10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	0 (18)
1	1 H 1.0079 Hydrogen																	2 He 4.0026 Helium
2	3 Li 6.940 Lithium	4 Be 9.0122 Beryllium											5 B 10.811 Boron	6 C 12.011 Carbon	7 N 14.007 Nitrogen	8 O 15.999 Oxygen	9 F 18.998 Fluonne	10 Ne 20.180 Neon
3	11 Na 22.990 Sodium	12 Mg 24.305 Magnesium											13 Al 26.982 Aluminium	14 Si 28.086 Silicon	15 P 30.974 Phosporus	16 S 32.066 Sulphur	17 Cl 35.453 Chlorine	18 Ar 39.948 Argon
4	19 K 39.098 Potassium	20 Ca 40.078 Calcium	21 Sc 44.956 Scandium	22 Ti 47.867 Titanium	23 V 50.941 Vanadium	24 Cr 51.996 Chrominum	25 Mn 54.938 Manganese	26 Fe 55.847 Iron	27 Co 58.933 Cobolt	28 Ni 58.693 Nickel	29 Cu 63.546 Copper	30 Zn 65.39 Zinc	31 Ga 62.723 Gallium	32 Ge 72.61 Germanium	33 As 74.922 Arsenic	34 Se 78.96 Selenium	35 Br 79.904 Bromine	36 Kr 83.80 Krypton
5	37 Rb 85.468 Rubidium	38 Sr 87.62 Strontium	39 Y 88.906 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.906 Niobium	42 Mo 95.94 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.91 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.87 Silver	48 Cd 112.41 Cadmium	49 In 114.82 Indium	50 Sn 118.71 Tin	51 Sb 121.76 Antimony	52 Te 127.60 Tellurium	53 I 126.90 Iodine	54 Xe 131.29 Xenon
6	55 Cs 132.91 Cesium	56 Ba 137.33 Barium	57 La* 138.91 Lanthanum	72 Hf 178.49 Hafnium	73 Ta 180.95 Tantalum	74 W 183.84 Tungsten	75 Re 186.21 Rhenium	76 Os 190.23 Osmium	77 Ir 192.22 Iridium	78 Pt 195.08 Platinum	79 Au 196.97 Gold	80 Hg 200.59 Mercury	81 Tl 204.38 Thallium	82 Pb 207.2 Lead	83 Bi 208.98 Bismuth	84 Po 210 Polonium	85 At 210 Astatine	86 Rn 222 Radon
7	87 Fr 223 Francium	88 Ra 226 Radium	89 Ac** 227 Actinium	104 Rf 267 Rutherfordium	105 Db 268 Dubnium	106 Sg 269 Seaborgium	107 Bh 270 Bohrium	108 Hs 270 Hassium	109 Mt 278 Meitnerium	110 Ds 281 Darmstadtium	111 Rg 282 Roentgenium	112 Cn 285 Copernicium	113 Nh 286 Nihonium	114 Fl 289 Flerovium	115 Mc 290 Moscovium	116 Lv 293 Livermorium	117 Ts 294 Tennessine	118 Og 294 Oganesson

f-Block Elements ⟷

6	*Lanthanide Series	58 Ce 140.12 Cerium	59 Pr 140.91 Praseodymium	60 Nd 144.24 Neodymium	61 Pm 145 Promethium	62 Sm 150.36 Samarium	63 Eu 151.96 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.93 Terbium	66 Dy 162.50 Dyspro-	67 Ho 164.93 Holmium	68 Er 167.26 Erbium	69 Tm 168.93 Thulium	70 Yb 173.07 Ytterbium	71 Lu 174.97 Lutetium
7	**Actinide Series	90 Th 232.04 Thorium	91 Pa 231.04 Protactinium	92 U 238.03 Uranium	93 Np 237 Neptunium	94 Pu 244 Plutonium	95 Am 243 Americium	96 Cm 247 Curium	97 Bk 247 Berkelium	98 Cf 251 Califonium	99 Es 252 Einsteinium	100 Fm 257 Fermium	101 Md 258 Mendelevium	102 No 259 Nobelium	103 Lr 262 Lawrencium

IUPAC designations of groups of elements are given in brackets

- **Description of periods**

Period	*n*	*Sub shell*	*No. of elements*	*Element*	*Name of Period*
1.	1	1s	2	$_1H$, $_2He$	Shortest
2.	2	2s, 2p	8	$_3Li$ – $_{10}Ne$	Short
3.	3	3s, 3p	8	$_{11}Na$ – $_{18}Ar$	Short
4.	4	4s, 3d, 4p	18	$_{19}K$ – $_{36}Kr$	Long
5.	5	5s, 4d, 5p	18	$_{37}Rb$ – $_{54}Xe$	Long
6.	6	6s, 4f, 5d, 6p	32	$_{55}Cs$ – $_{86}Rn$	Longest
7.	7	7s, 5f, 6d,	26	$_{87}Fr$ – $_{118}Og$	Longest

3.0 NOMENCLATURE OF ELEMENTS

SL

(a) IUPAC gave names to elements above atomic number 100 as follows –

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

(b) In all the elements, suffix is – ium. ***Ex.***

Atomic No.	*IUPAC Name*	*Symbol*	*IUPAC Official Name*	*IUPAC Symbol*
101	Un nil unium	Unu	Mendelevium	Md
102	Un nil bium	Unb	Nobelium	No
103	Un nil trium	Unt	Lawrencium	Lr
104	Un nil quadium	Unq	Rutherfordium	Rf
105	Un nil pentium	Unp	Dubnium	Db
106	Un nil hexium	Unh	Seaborgium	Sg
107	Un nil septium	Uns	Bohrium	Bh
108	Un nil octium	Uno	Hassnium	Hs
109	Un nil ennium	Une	Meitnerium	Mt
110	Un un nilium	Uun	Darmstadtium	Ds

4.0 CLASSIFICATION OF ELEMENTS

SL AL

4.1 s-Block Elements

SL AL

(a) The elements of the periodic table in which the last electron enters in s-orbital, are called s-block elements.

(b) s-orbital can accommodate a maximum of two electrons.

(c) Their general formulae are ns^1 and ns^2 respectively, where n = (1 to 7)

(d) IA group elements are known as alkali metals because they react with water to form alkali. II A group elements are known as alkaline earth metals because their oxides react with water to form alkali and these are found in the soil or earth.

(e) Total number of s-block elements are 14.

(f) $_{87}Fr$ and $_{88}Ra$ are radioactive elements while H and He are gaseous elements.

(g) Cs and Fr are liquid elements belonging to s-block.

4.2 p-Block Elements

SL AL

(a) The elements of the periodic table in which the last electron gets filled up in the p-orbital, called p-block elements.

(b) p-orbital can accommodate a maximum of six electrons. Therefore, p-block elements are divided into six groups which are III A, IV A, V A, VI A, VII A and zero group.

(c) The general formula of p-block elements is $ns^2 p^{1-6}$ (where n = 2 to 6)

(d) The zero group elements having general formula ns^2p^6 are inert, because their energy levels are fully filled.

(e) The total number of p-block elements in the periodic table is 30 (excluding He).

(f) There are nine gaseous elements (Ne, Ar, Kr, Xe, Rn, F_2, Cl_2, O_2 and N_2) belonging to p-block. Gallium (Ga) and bromine (Br) are liquids.

(g) The step-like thick lines drawn in the periodic table in the p-block divides elements into metals, nonmetals and metalloids.

4.3 d-Block Elements

SL AL

(a) The elements of the periodic table in which the last electron gets filled up in the d-orbital, called d-block elements.

(b) The d-block elements are placed in the groups named III B, IV B, V B, VI B, VII B, VIII, I B and II B.

(c) In d-block elements the electron gets filled up in the d-orbital of the penultimate shell.

(d) d-block elements lie between s & p block elements.

(e) The general formula of these elements is $(n–1)s^{0–2}$, p^6, d^{1-10} ns^{1-2} where n = 4 to 7.

(f) All of these elements are metals.

(g) Out of all the d-block elements, mercury is the only liquid element.

4.4 f-Block Elements

SL AL

(a) The element of the periodic table in which the last electron gets filled up in the f-orbital, called f-block elements.

(b) The f-block elements are from atomic number 58 to 71 and from 90 to 103.

(c) The lanthanides occur in nature in low abundance and therefore, these are called rare earth elements.

(d) There are 28 f-block elements in the periodic table.

(e) The elements from atomic number 58 to 71 are called lanthanides because they come after lanthanum (57). The elements from 90 to 103 are called actinides because they come after actinium (89).

(f) All the actinide elements are radioactive.

(g) All the elements after atomic number 92 (i.e. U^{92}) are transuranic elements.

(h) The general formula of these elements is $(n–2)\ s^2\ p^6\ d^{10}\ f^{(1-14)}\ (n–1)\ s^2 p^6 d^{0-1} ns^2$ where n = 6 & 7.

5.0 TYPE OF ELEMENTS

SL AL

Using electronic configuration as the criteria, we generally recognize four general type of elements; the inert gas elements, the representative elements, the transition elements, and the inner transition elements. The classification of the elements into these groups is dependent on the extent to which the s, p, d and f orbitals are filled.

5.1 Inert Gases

SL AL

(a) s and p orbitals of the outer most shell of these elements are completely filled. The outermost electronic configuration is ns^2np^6.

(b) Helium is also inert gas but its electronic configuration is $1s^2$

5.2 Representative or Normal Elements

SL AL

(a) Outermost shell of these elements is incomplete. The number of electrons in the outermost shell is less than eight.

(b) Inner shell are complete.

(c) s-and p-block elements except inert gases are called normal or representative elements.

5.3 Transition Elements

SL AL

(a) Last two shells of these elements namely outermost and penultimate shells are incomplete.

(b) The last shell contains one or two electrons and the penultimate shell may contain more than eight or up to eighteen electrons.

(c) Their outermost electronic configuration is similar to d-block elements i.e. $(n-1)\ d^{1-10}\ ns^{1-2}$.

(d) According to definition of transition elements, those elements which have partly filled d-orbitals in neutral state or in any stable oxidation state are called transition elements. According to this definition Zn, Cd and Hg (IIB group) are d-block elements but not transition elements because these elements have d^{10} configuration in neutral as well as in stable +2 oxidation state.

(e) Because of the extra stability which is associated with empty, half-filled, and fully filled subshells, there are some apparent anomalies in electronic arrangements in the transition series. This empirical rule is illustrated by the chromium and copper configuration in the first d series of elements:

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3d	1	2	3	5	5	6	7	8	10	10
4s	2	2	2	1	2	2	2	2	1	2

5.4 Inner Transition Elements

(a) In these elements last three shells i.e. outermost, penultimate and prepenultimate shells are incomplete.

(b) These are related to IIIB i.e. group 3.

(c) The last shell contains two electrons. Penultimate shell may contain eight or nine electrons and pre-penultimate shell contains more than 18, up to 32 electrons.

(d) Their outemost electronic configuration is similar to f-block element i.e. $(n-2)f^{1-14}\ (n-1)s^2\ (n-1)p^6\ (n-1)d^{0-1}ns^2$

Metals, Non-metals & Metalloids : Despite of classifying elements into s, p, d and f-blocks another broad classification of elements based on their properties. The elements can be broadly classified into

(a) ***Metals :*** Majority of the elements in periodic table are metals and appears on the left side of the periodic table.

Properties:

(i) These are usually solid at room temperature [exception - mercury]

(ii) They have high melting and boiling point [exception Gallium & Cesium have very low melting point (303 K and 302 K respectively)]

(iii) They are good conductor of heat and electricity.

(iv) They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires)

(b) ***Non-Metals:*** These are placed at the top right hand side of periodic table. As we move horizontally along a period, the property of elements changes from metallic (on left) to non-metallic (on the right).

Properties :

(i) These are usually solids or gases at room temperature.

(ii) They have low melting point and boiling point (exception : Boron, Carbon).

(iii) Most Non-metallic solids are brittle and are neither malleable nor ductile.

(c) ***Metalloids (Semi-metals):*** Properties of these elements shows the characteristics of both metals and non-metals. Silicon (Si), Germanium(Ge), Arsenic(As), Antimony(Sb) and Tellurium(Te) are metalloids.

6.0 PREDICTING ATOMIC NUMBER OF SUCCESIVE MEMBER IN A GROUP OR FAMILY

SL AL

6.1 Magic Numbers

(a) Knowing the atomic number of the first member of a group, we can write the atomic number of the subsequent elements by adding given magic number

Ex. Group	1	2	3	4, 5, 6, 7, 8, 9	10, 11, 12,	13, 14,	15, 16, 17	18
	IA	IIA	IIIB			IIIA	IVA VA VIA VIIA	'0'gp.
PERIOD I +	2	–						8
II+	8	8					8	8
III+	8	8					18	18
IV+	18	18	18		18		18	18
V+	18	18	18		32		32	32
VI+	32	32	32		32		–	–
VII								

(b) In group IA – Atomic number of H is 1 and atomic number of other element will be as follows –

Magic number $\underbrace{H_1\ 1+2=3}_{2}$ $\underbrace{Li\ 3+8=11}_{8}$ $\underbrace{Na\ 11+8=19}_{8}$ $\underbrace{K\ 19+18=37}_{18}$ $\underbrace{Rb\ 37+18=55}_{18}$ Cs

6.2 Determination of period, block and group of an element

SL AL

(a) ***Period number:*** The period no. of the element can be predicted from the principal quantum no. (n) of the valence shell.

(b) ***Block number:*** Last electron enter in which orbital is knows as block no. .

(c) ***Group number:*** It is predicted from the number of electrons in the valence shell and penultimate shell.

Example :

S.No.	***Electronic Configuration***	***Period number***	***Block number***	***Prediction of Group***	***Group number***
1.	$[Ar]4s^2 3d^{10}4p^6, 5s^1$	5	s	No. of ns e^-	1
2.	$[Kr]\ 5s^2, 4d^{10}\ 5p^2$	5	p	ns e^- + 10 + np e^-	2+10+2 =14
3.	$[Rn]\ 7s^2, 6d^4\ 5f^{14}$	7	d	ns e^-+ (n–1)d e^-	2+4 =6
4.	$[Xe]\ 6s^2, 5d^1, 4f^{12}$	6	f	—	3/III B

BEGINNER'S BOX–1

Development of Periodic Table/Modern Periodic Table

1. The atom having the valence shell electronic configuration $4s^2\ 4p^2$ would be in:-

(A) Group II A and period 3 (B) Group II B and period 4

(C) Group IV A and period 4 (D) Group IV A and period 3

2*. The electronic configuration of transition elements is exhibited by :-

(A) $ns^{0-2}(n-1)d^{1-10}$ (B) $ns^2\ (n-1)\ d^{10}$ (C) $(n-1)d^{10}s^2$ (D) ns^2np^5

3. Configuration of Br^- is : $[Ar]\ 3d^{10}\ 4s^2 4p^6$. The electronic configuration of Br^{+2} would be identical with the element

(A) Se (B) As (C) Ga (D) Ge

4. $4d^3 5s^2$ configuration belongs to which group :-

(A) IIA (B) IIB (C) V B (D) III B

5. Which of the following match is correct :-

(A) Base of mendeleef periodic table - Number of protons

(B) Doberenier's triad - Na, K, Rb

(C) Newland's octave rule is obeyed by Li, F, Cl

(D) Lother meyer curve plotted between - Atomic number V/S Atomic weight

6. True statement is :-

(A) All the transuranic elements are synthetic elements

(B) Elements of third group are called bridge elements

(C) Element of $1s^2$ configuration is placed in IIA group

(D) Electronic configuration of elements of a group is same

7*. Which of the following electronic configurations in the outermost shell is characteristic of alkali metals:

(A) $(n-1)\ s^2p^6\ ns^2p^1$ (B) $(n-1)\ s^2p^6d^{10}\ ns^1$ (C) $(n-1)\ s^2p^6\ ns^1$ (D) $ns^2np^6\ (n-1)d^{10}$

8. The chemistry of lithium is very similar to that of magnesium even though they are placed in different groups. Its reason is :-

(A) Both are found together in nature (B) Both have nearly the same size

(C) Both have similar electronic configurations (D) The ratio of their charge to size is nearly the same

9. Which of the following statement is false :-

(A) Elements of ns^2np^6 electronic configuration lies in 1st to 6th period

(B) Typical elements lies in 3rd period

(C) The seventh period will accommodate thirty two elements

(D) Boron and silicon are diagonally related

10. In the third period Na to Cl seven element is/are called:-

(A) Lanthanides (B) Typical elements (C) Halogen elements (D) Metalloids

11. Both metals and non-metals are found among.....elements in the periodic table :-

(A) p-block (B) d-block (C) Transition (D) Inner transition

12. In the plot of the first ionization energy against atomic number the peaks are occupied by :-

(A) Inert gases (B) Alkali metals (C) Halogens (D) Transition elements

7.0 PERIODICITY

SL

(a) The regular gradation in properties from top to bottom in a group and from left to right in a period is called periodicity in properties.

(b) In a period, the ultimate orbit remain same, but the number of e^- gradually increases.

(c) In a group, the number of e^- in the ultimate orbit remains same, but the values of n increases.

7.1 Causes of periodicity

SL

(a) The cause of periodicity in properties is due to the same outermost shell electronic configuration coming at regular intervals.

(b) In the periodic table, elements with similar properties occur at intervals of 2, 8, 8, 18, 18 and 32. These numbers are called as magic numbers.

7.2 Periodic Properties

SL

Valency : It is defined as the combining capacity of the elements. The word valency is derived from an Italian word "Valentia" which means combining capacity.

Old concept

Given by : ***Frankland***

Valency with respect to Hydrogen : Valency of H = 1

It is defined as the number of hydrogen atoms attached with a particular element.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	H–Cl
Valency	1	2	3	4	3	2	1

Note : Valency w.r.t. H across the period increases upto 4 and then again decreases to 1.

Valency with respect to oxygen : Valency of 'O' = 2

It is defined as twice the number of oxygen atoms attached with a particular atom.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Valency	1	2	3	4	5	6	7

☞ ***Note :***

Valency with respect to oxygen increases from 1 to 7 across the period. Valency w.r.t. 'O' is equal to the group number.

New concept

This concept is based on the electronic configuration. According to this concept valency for IA to IVA group elements is equal to number of valence shell e^- and from VA to zero group, it is –

[8– (number of valence e^-)].

Valency = No. of valence e^- Valency = (8– no. of valence e^-)

	IA	IIA	IIIA	IVA	VA	VIA	VII	0
	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Valence shell e^-	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3	2	1	0

☞ ***Note :***

All the elements of a group have same valencies because they have same number of valence shell electrons.

8.0 SCREENING EFFECT (S) AND EFFECTIVE NUCLEAR CHARGE (Z_{EFF})

AL

(a) Valence shell e^- suffer force of attraction due to nucleus and force of repulsion due to inner shell electrons.

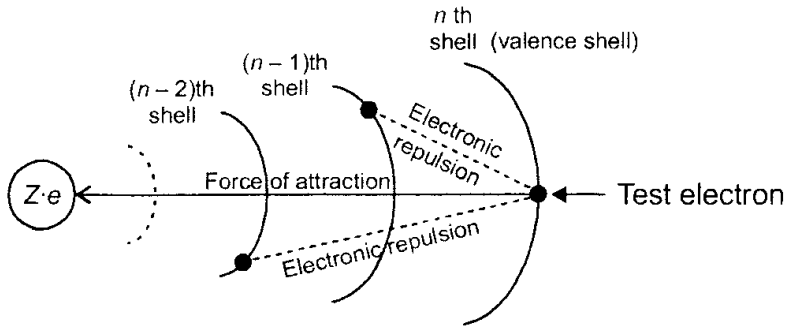
(b) The decrease in force of attraction on valence e^- due to inner shell e^- is called screening effect or shielding effect.(i.e. total repulsive force is called shielding effect.)

(c) 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 Zeff.)

(d) There is a reduction in nuclear charge due to screening effect. Reduced nuclear charge is called effective nuclear charge.

(e) If nuclear charge = Z, then effective nuclear charge = Z – σ (Where σ (Sigma) = Screening constant)

So, Zeff = (Z – σ)



CALCULATION OF σ (using slater's rule)

To calculate the shielding constant **(σ)** for an electron in ns or np orbital :

(a) Write the electronic configuration of the element in the following order and groupings :
(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p), etc.

<u>For s and p electrons :</u>

(b) Electrons in any group to the right of the (ns, np) group contribute nothing to the shielding constant.
(n-shell no. of the electron for which σ is calculated)

(c) All of the other electrons in the (ns, np) group, shield the concern electron to an extent of 0.35 each. (Except for the 1s orbital for which value is 0.30).

(d) All electrons in the (n – 1) shell shield to an extent of 0.85 each.

(e) All electrons (n – 2) or lower group shield completely ; that is, their contribution is 1.00 each.

<u>For d and f electrons :</u>

(f) Electrons in any group to the right of the nd or nf group contribute nothing to the shielding constant.

(g) All the other electrons in the nd or nf group, shield the valence electron to an extent of 0.35 each.

(h) All electrons in groups lying to the left of the nd or nf group contribute 1.00.

(Effective Nuclear charge of elements of second period)

Element	***Electronic Configaration***	***Z***	***σ of ns & np electron***	***σ (n–1) orbital***	***Total Screeing Constant***	***Effective nuclear charge***
			(a)	***(b)***	***(a + b)***	***Z*=Z – σ***
$_3Li$	$1s^2\,2s^1$	3	–	0.85× 2=1.70	1.70	1.30
$_4Be$	$1s^2, 2s^2$	4	1× 0.35=0.35	0.85× 2=1.70	2.05	1.95
$_5B$	$1s^2,2s^2,2p^1$	5	2× 0.35=0.70	0.85× 2=1.70	2.40	2.60
$_6C$	$1s^2,2s^2,2p^2$	6	3× 0.35=1.05	0.85× 2=1.70	2.75	3.25
$_7N$	$1s^2,2s^2,2p^3$	7	4× 0.35=1.40	0.85× 2=1.70	3.10	3.90
$_8O$	$1s^2,2s^2,2p^4$	8	5× 0.35=1.75	0.85× 2=1.70	3.45	4.55
$_9F$	$1s^2,2s^2,2p^5$	9	6× 0.35=2.10	0.85× 2=1.70	3.80	5.20

8.1 Periodic variation

AL

(a) From left to right in a period Zeff increases

(i) That is why in a period Zeff increases by 0.65 and hence atomic size decreases considerably.

(ii) In transition series Z increase by + 1 but screening effect increases by 0.85 So Zeff is 0.15 (1– 0.85 = 0.15) [Because e^- enters in (n – 1) orbit which has value of $\sigma = 0.85$]

In transition series Zeff increases very less amount, by 0.15 from left to right and hence atomic size remains almost constant.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zeff	3.00	3.15	3.30	3.45	3.60	3.75	3.90	4.05	3.70	4.35

(b) From top to bottom in a group Zeff remain constant

Element	Li	Na	K	Rb	Cs	Fr
Zeff	1.30	2.20	2.20	2.20	2.20	2.20

9.0 ATOMIC RADIUS

SL AL

The average distance of valence shell e^- from nucleus is called atomic radius. It is very difficult to measure the atomic radius because –

(i) The isolation of single atom is very difficult.

(ii) There is no well defined boundary for the atom. (The probability of finding the e^- is 0 only at infinity).

So, the more accurate definition of atomic radius is –

Half the inter-nuclear distance(d) between two atoms in a homoatomic molecule is known as atomic radius.

This inter-nuclear distance is also known as bond length.Inter-nuclear distance depends upon the type of bond by which two atoms combine.

9.1 Types of Atomic Radius

SL AL

Based on the chemical bonds, atomic radius is divided into four categories –

1. Covalent radius 2. Ionic radius 3. Metallic radius 4. Vander waal radius

(1) ***Covalent radius :*** One half of the distance between the nuclei (internuclear distance) of two covalently bonded atoms in homodiatomic molecule is called the covalent radius of that atom. The covalent bond must be single covalent bond. The covalent radius (r_A) of atom A in a molecule A_2 may be given as:

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

i.e. the distance between nuclei of two single covalently bonded atoms in a homodiatomic molecule is equal to the sum of covalent radii of both the atoms

$$d_{A-A} = r_A + r_A$$

In a heterodiatomic molecule AB where the electronegativity of atoms A and B are different, the experimental values of internuclear distance d_{A-B} is less than the theoretical values ($r_A + r_B$).

☞ ***Note :*** *According to Schomaker and stevenson –*

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

Where Δ_x is the difference of electronegativities of the atoms A and B.

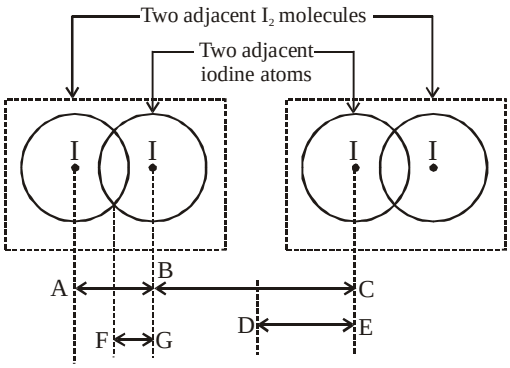
(2) *Metallic Radius :* Metal atoms are assumed to be closely packed spheres in the metallic crystal. These metal atom spheres are considered to touch one another in the crystal. One half of the internuclear distance between the two closest metal atoms in the metallic crystal is called metallic radius.

Metallic > Covalent radius

For example – Metallic radius and covalent radius of potassium are 2.3 Å and 2.03 Å respectively.

(3) *Van Der Wall's Radius or Collision radius :* The molecules of non metal atoms are generally gases. On cooling, the gaseous state changes to solid state. In the solid state, the non metallic elements usually exist as aggregations of molecules are held together by van der wall forces. ***One half of the distance between the nuclei of two adjacent atoms belonging to two neighbouring molecules of a compound in the solid state is called van der walls radius.***

It may also be defined as half of the inter nuclear distance of two non bonded neighbouring atoms of two adjacent molecules.



AB = Covalent inter-nuclear distance = 2.66Å.

FG = AB/2 = 2.66/2 = 1.33Å = covalent radius

BC = VanderWaals inter-nuclear distance = 4.30Å.

DE = BC/2 = 4.30/2 = 2.15Å = VanderWaal radius of iodine atom.

Van der wall's radius > Metallic radius > Covalent radius

The vander walls radius and covalent radius of chlorine atom are 1.80 Å and 0.99 Å respectively

(4) *Ionic Radius :* A neutral atom changes to a cation by the loss of one or more electrons and to an anion by the gain of one or more electrons. The magnitude of charge on cation and anion is equal to the number of electrons lost or gained respectively. The ionic radii of the ions present in an ionic crystal may be calculated from the inter molecular distance between the two ions.

(a) Radius of Cation :

Radius of cation is smaller than that of corresponding atom.

Reasons :

(i) During the formation of cation either one shell is removed or

(ii) After removing an electron effective nuclear charge increase.

(b) Radius of an Anion

Radius of an anion is invariably bigger than that of the corresponding atom.

Reasons :

(i) The effective nuclear charge decrease in the formation of anion. Thus the electrostatic force of attraction between the nucleus and the outer electrons decreases as the size of the anion increases.

(ii) Interelectronic repulsion increases.

9.2 Factors affecting atomic radius

SL AL

(a) Z_{eff} increases, atomic radius decreases — Li > Be > B > C > N > O > F

(b) Number of shell(n) increases, atomic radius increases — Li < Na < K < Rb < Cs

(c) Screening effect increases, atomic radius increases.

(d) Magnitude of –ve charge increases, atomic radius increases — $O < O^- < O^{-2}$

(e) Magnitude of +ve charge increases, atomic radius decreases — $Mn > Mn^{+2} > Mn^{+3} > Mn^{+4}$

(f) Bond order increases, atomic radius decreases — >N— N< > —N=N— >N≡N

9.3 Periodic Trend

SL AL

(a) ***For normal elements:***

(i) Across a period : It decreases from left to right in a period as $Z_{eff.}$ increases.

Ex. Ne > Li > Be > B > C > N > O > F

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

Ex. Li < Na < K < Rb < Cs

☞ ***Note :***

In III A group size of Al and Ga is nearly same

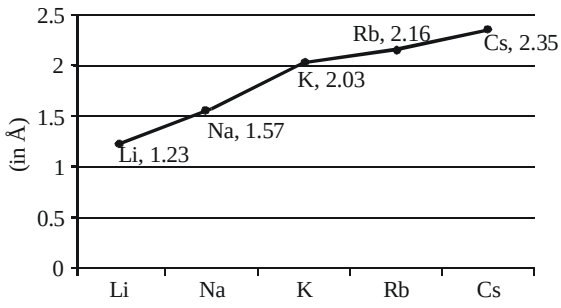
$_{13}Al$: (Ne), $3s^2$, $3p^1$

$_{31}Ga$: (Ar) $4s^2$, $3d^{10}$, $4p^1$

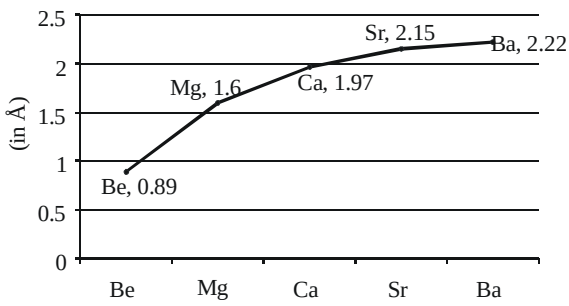
In boron family size of Al and Ga is nearly same. As we move down the group from Al to Ga 18 e^- increases, out of which 10 e^- goes to d orbitals, which have poor shielding. Due to which outer electrons in Ga are attracted more by nucleus as a result of which, size of Al and Ga becomes nearly same. Contraction in size due to poor shilding of 'd' electrons is known as ***transition contraction.***

ATOMIC RADIUS

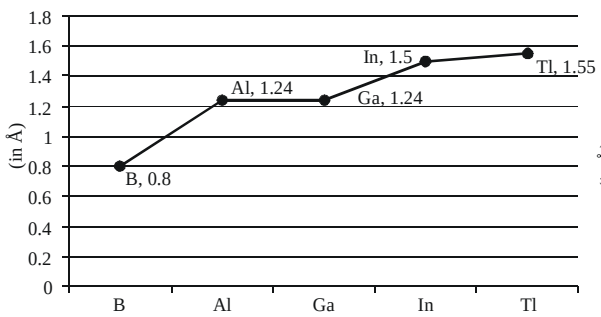
ALKALI METALS



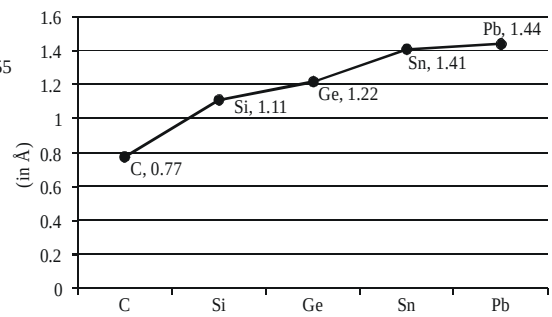
ALKALINE EARTH METALS



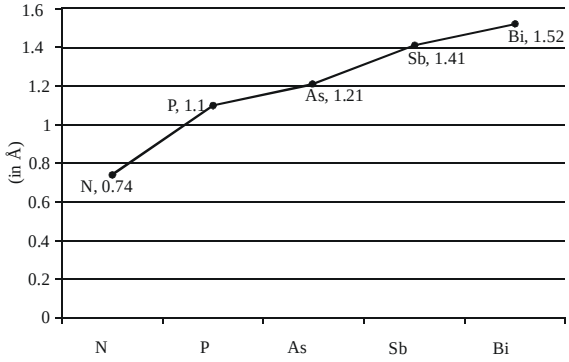
GROUP III-A



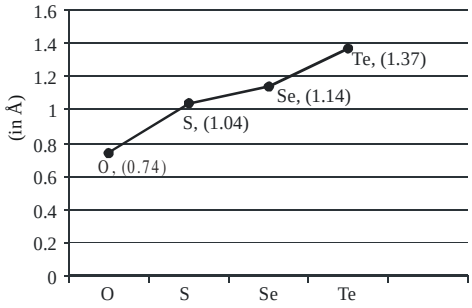
CARBON FAMILY



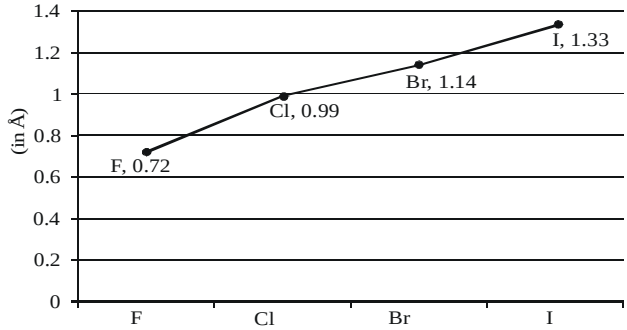
NITROGEN FAMILY (PNICOGENS)



OXYGENFAMILY(CHALCOGENS)



HALOGENS



(b) *For inert gases :*

In respective period, the atomic radius of inert gas is largest, because for inert gas VanderWaal's radius is defined. The VanderWaal's radius of inert gases also increases on moving from top to bottom in the group.

(c) *For transition elements :*

There are three series of transition elements:-

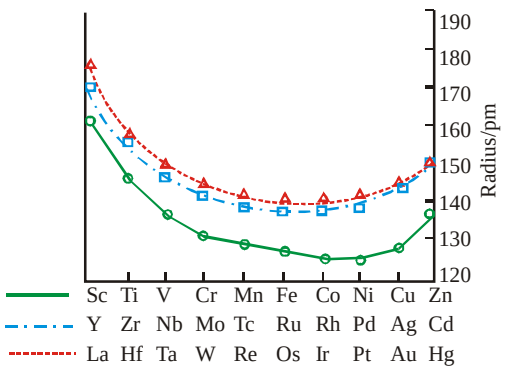
First transition series or 3d series – Sc (21) to Zn (30)

Second transition series or 4d series – Y (39) to Cd (48)

Third transition series or 5d series – La (57), Hf (72) to Hg (80)

From left to right in a period : In the first transition series the atomic radii slightly decreases from Sc to Mn because effect of effective nuclear charge is more prominent than the shielding effect. After that it remains almost the same because both the effects balance each other. The atomic size from Cu to Zn slightly increases because shielding effect is more prominent than effective nuclear charge due to d^{10} configuration of Cu and Zn. The atomic radii of the elements of 3d transition series are as under:

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius (pm)	162	147	134	127	126	126	124	124	124	138



Trends in atomic radii of transition elements

In a group :

(i) The atomic radius of elements increases on moving down the first transition series (3d) to second transition series (4d). This is due to the increases in number of shells with the increase in atomic number.

(ii) The atomic radii of second (4d) and third (5d) transition series in a group is almost same except Y(39) and La(57)

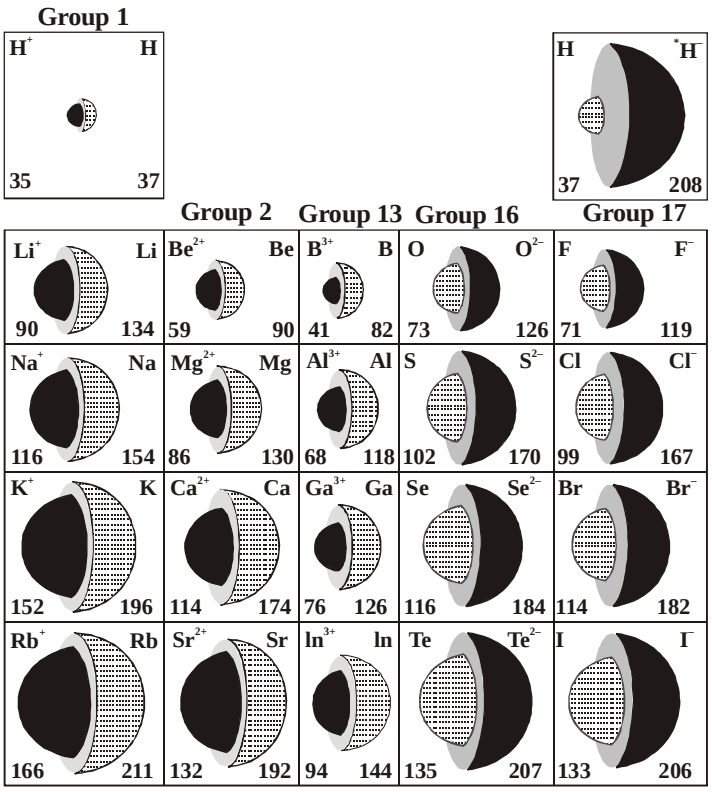
In third transition series, there are fourteen lanthanides in between La(57) of III B and Hf (72) of IVB groups, so the atomic radius of Hf (72) decreases much due to lanthanide contraction* in lanthanides. The difference in the nuclear charge in the elements of a group in first and second transition series is +18 units while this difference in second and third transition series is +32 units except Y(39) $\rightarrow$ La(57). Due to the increase of +32 units in the nuclear charge there is a sizeable decrease in the atomic radius which balances the increase in size due to the increase in number of shells.

So, in a group moving from 5th period to 6th period in transition series, the atomic radii of the elements remain almost the same except IIIB. The difference is about $0.02A^0$.

(d) ***For inner transition elements :*** As we move along the lanthanide series, there is a decrease in atomic as well as ionic radius. The decrease in size is regular in ions but not so regular in atoms. This is called lanthanide contraction*.

☞ ***Note :***

****Cause of Lanthanide contraction:*** *In the lanthanide elements, filling on (n-2) f orbitals takes place, while simultaneously the nuclear charge increases. The electrons in the (n-2) f orbitals shield the ns electrons, which largely determine the size, from the increase in nuclear charge almost completely [σ(per electron) = 1.00]. As a result of this, there is only a small decrease in the atomic radius from one element to another. But there are 14 elements in series, there is a total contraction of 13 pm across the series from La (Z = 57) to Lu (Z = 71). This is known as* ***lanthanide contraction,*** *because of which the atoms of elements (Hf to Hg) following Lu are unusually smaller than they would be if the lanthanides had not been built up before them. Lanthanide contraction almost exactly cancels out the effect of the last shell added in the sixth period and therefore, the transition elements of 4d and 5d series have almost the same atomic radii.*



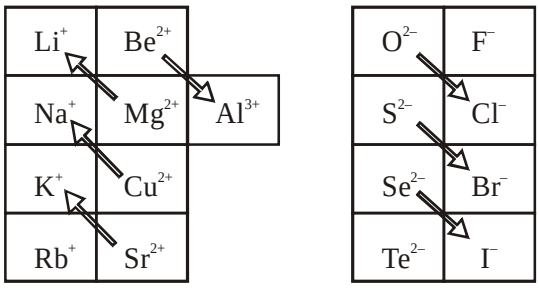
Sizes of atoms and their ions in pm

☞ ***Note :***

(i) *Size of free H^- ion is 208pm where as in LiH and NaH it is 130pm and 137pm.*

(ii) *The above values may vary with co–ordination number.*

(iii) *In the direction of arrow(⟹) ionic size increases.*



10.0 IONISATION POTENTIAL OR IONISATION ENERGY OR IONISATION ENTHALPY

SL AL

Ionisation Energy : Minimum amount of energy required, to remove an electron from outer most shell of an isolated gaseous atom, is known as ionisation energy.

If it is expressed in electron volts (eV) it is termed as ionisation potential.

A quantitative measure of the tendency of an element to lose electron is given by its ***Ionization Enthalpy.*** It represents the minimum energy required to remove one mole of electrons from one mole of isolated gaseous species in its ground state. In other words, the first ionization enthalpy for an element X is the enthalpy change (ΔH) for the reaction depicted in equation.

(Isolated $\rightarrow$ Without any bonding with other atom)

$X(g) \rightarrow X^+(g) + e.$

The ionization enthalpy is expressed in units of kJ/mol.

Successive Ionisation Energy

(a) For an atom M, successive ionisation energies are as follows -

$M + E_1 \longrightarrow M^+ + e^-$ $\quad E_1 = I^{st}$ Ionisation Potential

$M^+ + E_2 \longrightarrow M^{+2} + e^-$ $\quad E_2 = II^{nd}$ Ionisation Potential

$M^{+2} + E_3 \longrightarrow M^{+3} + e^-$ $\quad E_3 = III^{rd}$ Ionisation Potential

I^{st} Ionisation Potential $<$ IInd Ionisation Potential $<$ IIIrd Ionisation Potential

(b) Electron can not be removed from solid state of an atom, it has to convert in gaseous form, Energy required for conversion from solid state to gaseous state is called Sublimation energy.

(c) Ionisation Potential is always an endothermic process ($\Delta H = +ve$)

(d) It is measured in eV/atom (electron volt/atom) or Kcal/mole or KJ/mole

10.1 Factors affecting ionisation energy

SL AL

(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 e^- 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) ***Screening effect :*** Higher is the screening effect on the outer most electrons causes less attraction from the nucleus and can be easily removed, which is leading to the lower value of Ionisation Potential

$$\text{Ionisation Potential} \propto \frac{1}{\text{Screening effect}}$$

(d) ***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^- in comparision to p,d & f.

Ex. Be B

$1s^2, 2s^2$ $1s^2, 2s^2 2p^1$

Ionisation Potential Be > B

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

(e) ***Stability of half filled and fully filled orbitals :***

(i) Half filled p^3,d^5, f^7 or fully filled s^2, p^6, d^{10}, f^{14} are more stable than others so it requires more energy.

Ex. ***N*** ***O***

$1s^2, 2s^2 2p^3$ $1s^2, 2s^2 2p^4$ I^{st} Ionisation Potential order is O < N

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

I^{st} 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).

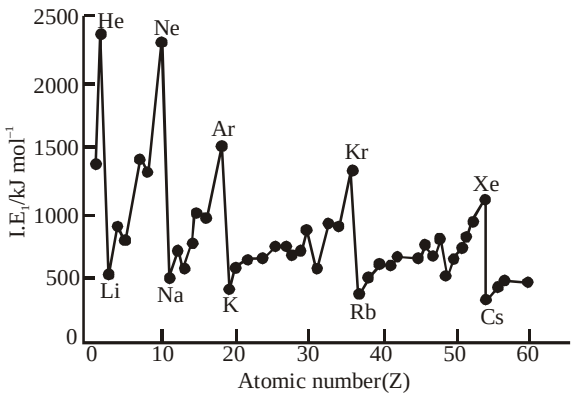
IInd ionisation potential order Mg^+ < Al^+ < Na^+

(2,8,1) (2,8,2) (2,8)

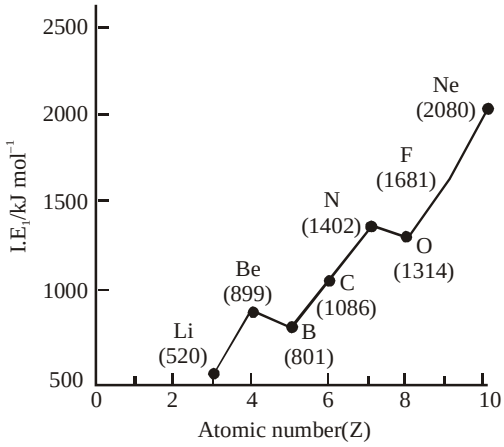
10.2 Periodic Trend

SL AL

(a) ***Variation in a period among the representative elements:*** Ionisation energies generally increases along the period because on moving left to right in a period the effective nuclear charge increases while the corresponding principal quantum number remain same.



Variation of first ionization energy (I.E$_1$) with atomic number for elements with Z = 1 to 60



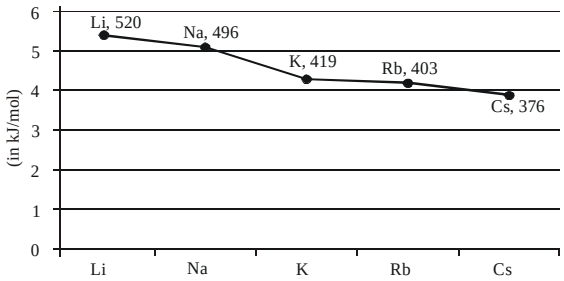
First ionization energy (I.E$_1$) of elements of the second period as a funciton of atomic number(Z)

(b) ***Variation in a group among the representative elements :*** The ionisation energy generally, decreases on moving from top to bottom because the size increases due to the increase of the principal quantum number. On the other hand the effective nuclear charge Z_{eff} for the outermost electron remains almost the same along the group.

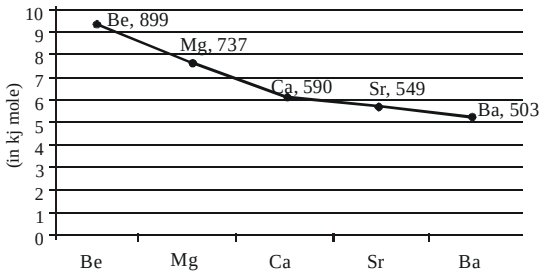
(c) ***Variation in a period among the transition elements :*** As the atomic number increases the effective nuclear charge also increases. Hence the I.P. increases, but this increase is not regular.

(d) ***Variation in a group among the transition elements :*** In a group on moving from first to second transition series, the values of I.P. decreases because atomic size increases. On moving from second to third transition series the value of I.P. some what increases.

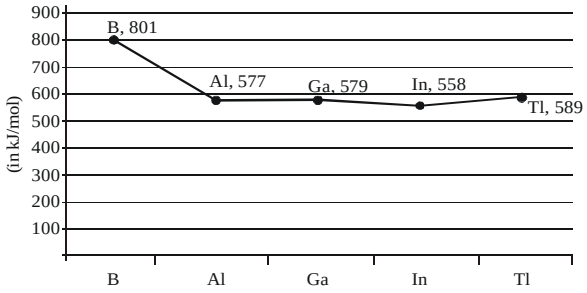
ALKALI METALS



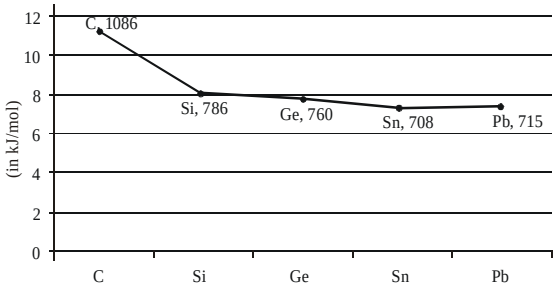
ALKALINE EARTH METALS



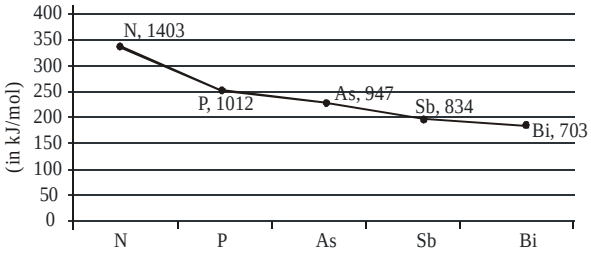
BORON FAMILY



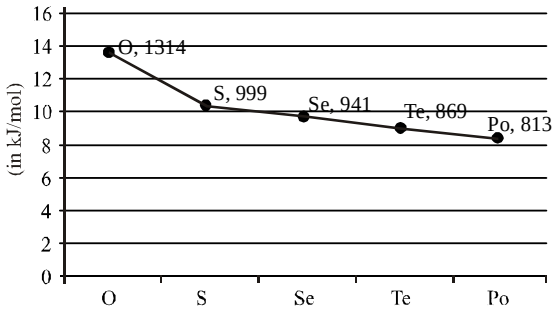
CARBON FAMILY



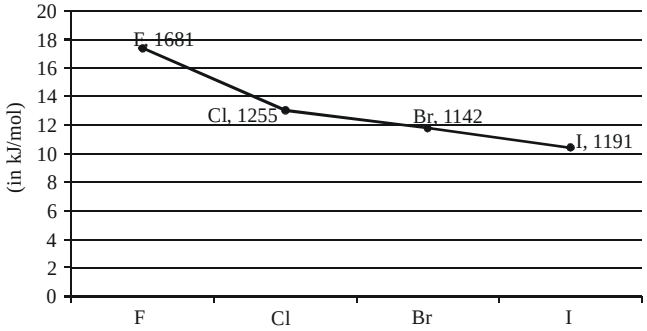
NITROGEN FAMILY (PNICOGENS)



CHALCOGENS



HALOGENS



Exception:

(a) In a period, the ionization energy of ***IIA group*** elements is more than the element of IIIA because the penetration power of s-orbital is more. The value of ionization energy of Be($1s^2 2s^2$) is more than B($1s^2 2s^2 2p^1$) because the penetration power of 2s-electrons of Be is more than the 2p electron of B

(b) In a period, the ionization energy of ***VA group*** elements is more than the elements of VIA because the half filled p^3 configuration of VA elements is comparatively of higher stability. VIA group elements (p^4) have the tendency to acquire comparatively more stable (p^3) configuration by the loss of one electron. Ionization energy

$N(1s^2 2s^2 2p^1_x p_y^1 p_z^1) > O(1s^2 2s^2 2p^2_x p_y^1 p_z^1)$

and P > S ; As > Se

(c) ***In group IIIA*** the ionization potential of Al(13) is nearly equal to the ionization potential of Ga(31) due to transition contraction.

(d) ***In group IVA*** the values of I.P. of Tl(81) and Pb(82) of sixth period is more than that I.P. values of 'In' (49) and Sn(50) of same groups in period fifth. This is because of the electrons are filled in 4f-orbitals for Tl(81) and Pb(82) which do not completely shield the outer electrons. Thus increase in +32 units in nuclear charge results in the increase of ionization potential values.

(e) On moving from ***second to third transition series*** the value of I.P. some what increases except IIIB group [Y(39) $\rightarrow$ La(57)]. This is because of 14 electrons are filled in 4f-orbitals of lanthanides which do not shield the 5d electrons effectively. Thus the increase in +32 units in nuclear charge results in the increase of I.P., on moving from left to right this effect decreases and becomes negligible in the later part.

☞ ***Note :***

(i) Helium (He) has the highest ionisation energy (IE_1) among all the elements and Caesium (Cs) has the least (IE_1) value.

(ii) Ionisation potential of inert gases is very high due to most stable s^2p^6 electronic configuration.

Element	He	Ne	Ar	Kr	Xe	Rn
IE_1(eV)	24.5	21.6	15.8	14.0	12.1	10.7

(iii) For isoelectronic species I.P. increases with positive charge and decreases with negative charge.

e.g. $Al^{+3} > Mg^{+2} > Na^+ > F^- > O^{-2} > N^{-3}$

10.3 Application of ionisation energy

(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) Reducing nature in gaseous phase

(c) Stability of oxidation states

(d) Prediction of group of element with the help of successive ionisation energies

BEGINNER'S BOX–2

Atomic Radius and Ionisation Energy

1*. From the given set of species, point out the species from each set having least atomic radius:-

(a) O^{-2}, F^-, Na^+ (b) Ni, Cu, Zn (c) Li, Be, Mg (d) He, Li^+, H^-

correct answer is -

(A) O^{-2},Cu, Li, H^- (B) Na^+ Ni, Be, Li^+ (C) F^-, Zn, Mg, He (D) Na^+, Cu, Be, He

2. K^+, Ar, Ca^{2+} and S^{2-} contains -

(A) Same electronic configuration and atomic volume

(B) Different electronic configuration but same IP.

(C) Same electronic configuration but different atomic volume

(D) None

3*. The IE_1, IE_2, IE_3, IE_4 and IE_5 of an element are 7.1, 14.3, 34.5, 46.8, 162.2 eV respectively. The element is likely to be:-

(A) Na (B) Si (C) F (D) Ca

4. The X – X bond length is 1.00 Å and C – C bond length is 1.54 Å. If electronegativities of 'X' and 'C' are 3.0 and 2.0 respectively, the C – X bond length is likely to be :-

(A) 1.27 Å (B) 1.18 Å (C) 1.08 Å (D) 1.28 Å

5. A neutral atom (Ar) is converted to (Ar^{+3}) by the following process

$$Ar \xrightarrow[-e]{E_1} Ar^+ \xrightarrow[-e]{E_2} Ar^{+2} \xrightarrow[-e]{E_3} Ar^{+3}$$

The correct order of E_1, E_2 and E_3 energies is:-

(A) $E_1 < E_2 < E_3$ (B) $E_1 > E_2 > E_3$ (C) $E_1 = E_2 = E_3$ (D) $E_1 > E_2 < E_3$

6. In which of the following the energy change corresponds to first ionisation potential :-

(A) $X_{(g)} \rightarrow X^+_{(g)} + e$ (B) $2X_{(g)} \rightarrow 2X^+_{(g)} + 2e$ (C) $X_{(s)} \rightarrow X^+_{(g)} + e$ (D) $X_{(aq)} \rightarrow X^+_{(aq)} + e$

7. In the ions P^{3-}, S^{2-} and Cl^- the increasing order of size is:-

(A) Cl^-, S^{2-}, P^{3-} (B) P^{3-}, S^{2-}, Cl^- (C) S^{2-}, Cl^-, P^{3-} (D) S^{2-}, P^{3-}, Cl^-

8. Which of the following order of atomic/ionic radius is not correct :–

(A) $I^- > I > I^+$ (B) $Mg^{+2} > Na^+ > F^-$ (C) $P^{+5} < P^{+3}$ (D) Li > Be > B

9*. Correct orders of I^{st} Ionisation Potential are :-

(a) Li < B < Be < C (b) O < N < F (c) Be < N < Ne

(A) a, b (B) b, c (C) a, c (D) a, b, c

10*. Mg forms Mg(II) because of :-

(A) The oxidation state of Mg is + 2

(B) Difference between $I.E_1$ and $I.E_2$ is large

(C) There are only two electrons in the outermost energy level of Mg

(D) Difference between $I.E_1$ and $I.E_2$ is small & IE_2 & IE_3 is large

11 Sucessive ionisation energies of an element 'X' are given below (in K. Cal)

IP_1	IP_2	IP_3	IP_4
165	195	556	595

Electronic configuration of the element 'X' is:-

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

11.0 ELECTRON AFFINITY

SL AL

(a) The amount of energy released when an electron is added to the outermost shell of one mole of an isolated gaseous atom in its lower energy state.

(b) When one mole of electrons is added to one mole of isolated gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the ***Electron Gain Enthalpy*** (ΔH_{EG}).

Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by :

$$X(g) + e^- \longrightarrow X^-(g)$$

(c) It is also the measure of tightness by which given electron is binded by the gaseous atom.

(d) The positive value of the electron affinity indicates that the process, i.e. $X_{(g)} + e^- \rightarrow X^-_{(g)}$, is exothermic and the negative value indicates the process to be an endothermic one. Thus the convention accepted in defining the electron affinity apparently contradicts the established convention in the thermodynamics.

Thus, $F_{(g)} + e^- \rightarrow F^-_{(g)}$, $\Delta H = -328$ kJ mol^{-1}, and EA = 328 kJ mol^{-1} and

$N_{(g)} + e^- \rightarrow N^-_{(g)}$, $\Delta H = +31$ kJ mol^{-1}, and EA = –31 kJ mol^{-1}

(e) ***Successive Electron affinities :*** Electron affinity just defined is actually first electron affinity since it corresponds to the addition of one electron only. In the process of adding further electron, the second electron will be added to gaseous anion against the electrostatic repulsion between the electron being added and the gaseous anion. Energy instead of being released is supplied for the addition of an electron to an anion. The sum of EA_1 and EA_2 is positive(energy required).

$$A(g) + e^- \longrightarrow A^-(g) + EA_1$$

$$A^-(g) + e^- + EA_2 \longrightarrow A^{2-}(g)$$

EA_1 is energy released (generally) $\therefore \Delta H_{EG_1} = -Ve$ (generally)

EA_2 is energy required (always) $\therefore \Delta H_{EG_2} = +Ve$ (always)

$(EA_1 + EA_2)$ is energy required (always) $\therefore \Delta H_{EG_1} + \Delta H_{EG_2} > 0$

☞ ***Note :***

For isolated gaseous atom.

(i) *Except* ΔH_{EG_1} all other electron gain enthalpies i.e. $\Delta H_{EG_2}, \Delta H_{EG_3} \ldots\ldots \Delta H_{EG_n}$ *are positive*

(ii) $|\Delta H_{EG_1}| < |\Delta H_{EG_2}|$

For Example :

First electron gain enthalpy:

$O(g) + e^- \longrightarrow O^-(g)$; ..... (i) $\Delta H_{eg_1} = -141$ kJ mol^{-1} (Energy is released)

Second electron gain enthalpy:

$O^-(g) + e^-(g) \longrightarrow O^{2-}(g)$; .....(ii) $\Delta H_{eg_2} = +780$ kJ mol^{-1} (Energy is absorbed)

$O(g) + 2e^- \longrightarrow O^{2-}(g)$ ..... (i) + (ii) $\Delta H = \Delta H_{EG_1} + \Delta H_{EG_2} = -141 + 780 = 639$ kJ/mol

11.1 Factors affecting electron affinity

SL AL

(A) Atomic size $\quad$ Electron Affinity $\propto \dfrac{1}{\text{Atomic size}}$

(B) Screening effect $\quad$ Electron Affinity $\propto \dfrac{1}{\text{Screening effect}}$

(C) Effective nuclear charge (Z_{eff}) Electron Affinity $\propto$ Zeff

(D) ***Stability of completely filled or half filled orbitals***

Electron affinity of filled or half filled orbital is very less or zero.

Ex. (i) Elements (He, Ne, Ar , ...), $\quad$ Electron Affinity = Zero ($\Delta egH = +$ ve)

(ii) Elements (Be, Mg, Ca, ...), $\quad$ Electron Affinity = $\simeq$ Zero ($\Delta egH = +$ ve)

(iii) Elements (N, P, As, ...), $\quad$ Electron Affinity = Very less

11.2 Periodic variation of electron affinity

SL AL

(a) ***In a period :*** The effective nuclear charge increases and the size decreases with the increase of atomic number in a period. This is why, the electron affinity in general increases in a period. In fact, it reaches the climax for the Group VII A (i.e. halogens) elements.

Electron affinities (kJ mol^{-1})

IA	IIA	IIIA	IVA	VA	VIA	VIIA	Noble gas
Li 59.8	Be –60	B 27	C 122	N –31	O 141	F 328	Ne –90
Na 53	Mg –60	Al 44	Si 134	P 72	S 200	Cl 349	Ar 0
		Ga 29	Ge 120	As 77	Se 195	Br 324	

(b) ***In a group :*** For the representative elements, in moving down in a group generally the electron affinity falls down with the increases of atomic number because the effective nuclear charge Zeff at periphery per electron remain almost same but the size gradually increases due to addition of new shell.

Exceptions

(a) Electron affinity values of nitrogen and phosphorous (VA) are lesser than the electron affinity values of carbon and silicon respectively. It is due to the comparatively stable half filled configuration (np^3) of nitrogen and phosphorus and the tendency to acquire the stable np^3 configuration by the gain of one electron in carbon and silicon (np^2).

(b) The theoretical value of the electron affinity of zero group i.e. inert gas elements is zero due to stable s^2p^6 configuration.

(c) F < Cl, O < S, N < P, B < Al. Here it is interesting to note that the electron affinity sequence is in the opposite order as is expected from the size sequence. To explain the observed sequence of electron affinity, we are to consider the other factors. Though the electrostatic attractive pull towards the nucleus favours the 2nd period elements more compared to the corresponding 3rd period elements, the added electron creates an unfavourable effect, i.e. electron-electron repulsion, which is more for the 2nd period elements because of their smaller sizes. This repulsive force is not so large in the 3rd period elements because of their larger size.

12.0 ELECTRONEGATIVITY (EN)

(a) A qualitative measure of the ability of an atom in a ***chemical compound*** to attract shared electrons towards itself is called ***electronegativity***. Unlike ionization enthalpy and electron gain enthalpy, it is not a measureable quantity. However, a number of numerical scales of electronegativity of elements viz., Pauling scale, Mulliken scale, Allred-Rochow scale have been developed.

(b) Electronegativity and Electron affinity both have tendency to attract electrons but electron affinity is for isolated atoms. Where as electronegativity is for bonded atoms.

(c) A polar covalent or ionic bond of A – B may be broken as

(i) $A - B \longrightarrow A^- : + B^+$ (Electronegativity A > Electronegativity B)

or ***(ii)*** $A - B \longrightarrow A^+ + :B^-$ (Electronegativity A < Electronegativity B)

depending on their tendency to attract bonded electron.

(d) There is no unit of electronegativity because it is a relative value

(e) Electronegativity is property of a bonded atom not an isolated gaseous atom so no energy will be liberated or absorbed.

Pauling's Scale : Pauling related the resonance energy (Δ_{AB}) of a molecule AB with the electronegativities of the atoms A and B. If X_A and X_B are the electronegativities of atoms A and B respectively then,

$X_A \sim X_B = 0.208\sqrt{\Delta_{A-B}}$ Δ in kcal/mol

$X_A \sim X_B = 0.102\sqrt{\Delta_{A-B}}$ Δ in kJ/mol

$\Delta_{AB} = E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}$

Pauling assumed the electronegativity value of hydrogen,2.1 and calculated the electronegativity values of other elements from this value.

Note: Electronegativity of F > Cl but Electron affinity of Cl > F

Electronegativity of Some Elements (on Paulling's Scale)

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9					

In **Pauling's Scale,** elements having almost same electronegativity are-

C ≃ S ≃ I ≃ 2.5
N = Cl = 3.0
P = H = 2.1
Cs= Fr = 0.7
Be= Al = 1.5

Mulliken's Scale: *According to Mulliken, the electronegativity of an element is the average value of its ionisation potential and electron affinity.*

$$\text{Electro-negativity} = \frac{\text{Electron affinity} + \text{Ionisation potential}}{2}$$

When both are expressed in electron volt,

Mulliken's values of EN are about 2.8 times the values of Pauling's scale.

i.e. $X_P = \frac{X_M}{2.8}$ (where X_P and X_M are in ev)

$X_P = 0.336$

Allred Rochow's Scale : The electronegativity of an element is measured by the electrostatic force of attraction between the electron present on the circumference of outermost shell and the atomic nucleus. If the distance between the circumference of outermost shell & the neucleus is r and the effective nuclear charge Z_{eff} then –

Electron-negativity $= \frac{0.359 Z_{eff}}{r^2} + 0.744 \Rightarrow Z_{eff} = Z - \sigma$

Z = The number of proton present in the nucleus.

σ = Shielding constant.

r = Covalent radius of atom (in Å)

12.1 Difference between electronegavity and Electron Affinity

SL AL

S.No.	Electronegativity	Electron Affinity
1.	Tendency of an atom in a molecule to attract the bonded electrons	Energy released when an electron is added to neutral isolated gaseous atom
2.	Relative value of an atom	Absolute value of an atom
3.	It regularly changed in a period or group	It does not changes regularly
5.	It has no unit	It is measured in eV/atom or KJ mol^{-1} or K cal $mole^{-1}$

☞ ***Note :***

Small atoms are normally having more electronegativity than larger atoms.

12.2 Factors Affecting electronegativity

SL AL

(a) Charge on atom : The cation will be more electronegative than parent atom. As the +ve charge on the cation increases electronegativity increases E.N. of $Fe^{+3} > Fe^{+2}$

The anion will be less electronegative then atom. As the –ve charge on the anion increases electronegatively decreases $O^{2-} < O^{-} < O$

(b) Effect of Substitution : The electronegativity of an atom depends upon the nature of substituent attached to that atom. For example - Carbon atom in CF_3I acquires greater positive charge than in CH_3I. Hence C atom in CF_3I is more electronegative than in CH_3I.

(c) Ionization energy and electron affinity : Higher the ionization energy and electron affinity of an atom, greater will be the its electronegativity.

(d) Hybridisation state : s-electrons are more penetrated (on attracted) than p-electron towards the nucleus. So, as the s-character in hybrid orbital increases, electronegativity increases.

For example:

CH_4	sp^3	25% s-character
C_2H_4	sp^2	33% s-character
C_2H_2	sp	50% s-character

The electronegativity of carbon atom increases as we move from CH_4 to C_2H_2.

(e) ***Atomic Radius & Ionic Radius :*** As the atomic radius and ionic radius increases the electronegativity value decreases

(f) ***Effective Nuclear Charge :*** The electronegativity value increases as the effective nuclear charge on the atomic nucleus increases.

12.3 Periodic Variation

SL AL

(a) ***In a period :*** In moving from left to right in a period, the size gradually contracts and the effective nuclear charge increases. This is why, the electronegativity gradually increases with the increase of atomic number in a period up to the group VIIA elements.

(b) ***In a group :*** In the representative elements, in moving down in a group, the size increase while Zeff per electron at the periphery remains almost constant. This is why, the electronegativity generally falls in a group with the increase of atomic number.

Exceptions

(a) In '***0' group*** – Electronegativity is always zero, because inert gas do not form molecule.

(b) 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.

(c) In group of IIB elements (Zn, Cd, Hg) value of electronegativity increases down the group, because of lanthanide contraction

(d) In IIIA group, value of electronegativity increases down the group, because of transition contraction Electronegativity of Ga > Electronegativity of Al

☞ ***Note :***

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

Electronegativity of F > Cl but Electron affinity of Cl > F

12.4 Application of electronegativity

SL AL

(a) ***Metallic and non metallic nature***

Low electronegativity $\longrightarrow$ Metals High electronegativity $\longrightarrow$ 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 Δ EN = difference in electronegativities of bonded atoms

☞ ***Note :***

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

(c) ***Acidic strength of hydrides***

$NH_3 < H_2O < HF$

In a perticular period acidic strength of hydride is depends on electronegativity of M in M – H bond. Higher the electronegativity of M greater the acidic strength of hydride.

(d) ***Nature of bonds :***

(i) According to Hanny & Smith formula

Ionic % = $16\,(X_A - X_B) + 3.5\,(X_A - X_B)^2$

Here X_A = Electronegativity of A

Here X_B = Electronegativity of B

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

(ii) According to Gallis

$X_A - X_B \geq 1.7$ Ionic

$X_A - X_B \leq 1.7$ Covalent

If $X_A = X_B$; then A – B will be non polar.

Ex. H—H, F—F

If $X_A > X_B$ and difference of electronegativities is small then

$A^{\delta-}$ —— $B^{\delta+}$ bond will be polar covalent

(e) 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

Ex.	NaOH	ClOH
X_A	0.9	3.0
Nature	Basic	Acidic

(iii) If $X_A - X_0 \geq X_0 - X_H$ then AO bond will be more polar and will break up as

$A — OH \longrightarrow A^+ + OH^-$ It shows basic nature

(iv) If $X_A - X_O \leq X_O - X_H$

$A — O — H \longrightarrow H^+ + AO^-$ It shows Acidic nature

Ex. ***In NaOH***

$X_O - X_{Na}$ (2.6) > $X_O - X_H$ (1.4) So hydroxide is basic

In ClOH

$X_O - X_{Cl}$ (0.5) < $X_O - X_H$ (1.4) So hydroxide is acidic

(f) Nature of oxides : Consider an oxide AO

(i) Along a period acidic nature of oxide increases.

(ii) Down the group basic nature of oxide increases

(iii) Non metal form acidic oxide and metal form basic oxides.

Na_2O MgO Al_2O_3 SiO_2 P_4O_{10} SO_3 Cl_2O_7

$\longleftrightarrow$

$X_A - X_O > 2.3$	$X_A - X_O = 2.3$	$X_A - X_O < 2.3$
Basic	Amphoteric	Acidic

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

$NO_2 > ZnO > K_2O$

$\longrightarrow$

acidic character decreases

☞ ***Note :***

Oxide of Al, Ga, Zn, Sn, As(III), Sb(III), Cr(III), Mn(IV), Pb, Be are amphoteric.. *CO, H_2O, NO, N_2O are neutral oxides.*

Acidic strength of oxide and oxyacid $\propto$ Electronegativity

B_2O_3 CO_2 N_2O_5

$\longrightarrow$

EN increase, acidic nature increasse.

$SO_3 > SeO_3 > TeO_3$ $HNO_3 > H_2CO_3 > H_3BO_3$ $HClO_4 > HBrO_4 > HIO_4$

$H_2SO_4 > H_2SeO_4 > H_2TeO_4$ $H_3PO_4 > H_3AsO_4 > H_3SbO_4$ $N_2O_5 > P_2O_5 > As_2O_5$

$H_2SO_3 > H_2SeO_3 > H_2TeO_3$ HOF > HOCl > HOBr > HOI $N_2O_3 > P_2O_3 > As_2O_3 > Sb_2O_3$

Acidic properties increases with increasing oxidation state of an element when centrel atom is same.

- Increassing Acidic order $\overset{+3}{N_2O_3} < \overset{+4}{NO_2} < \overset{+5}{N_2O_5}$ or $\overset{+3}{P_2O_3} < \overset{+5}{P_2O_5}$. (Increases with increase in oxidation number)
- $MnO < Mn_2O_3 < MnO_2 < MnO_3 < Mn_2O_7$
  (Basic Basic Amphoteric Acidic, Most acidic)
- Metal oxides in their higher oxidation state like V_2O_5, CrO_3, Mn_2O_7 are acidic.

Ex.

(i) $Sb_2O_5 > Sb_2O_3$ ***(ii)*** $HClO_4 > HClO_3 > HClO_2 > HClO$

(iii) $HNO_3 > HNO_2$ ***(iv)*** $SO_3 > SO_2$

(v) $N_2O_5 > N_2O_3$ ***(vi)*** $H_2SO_4 > H_2SO_3$

(h) Nomenclature of inorganic compounds

Prefix —— less electronegative element

Suffix —— More electronegative element

Ex. 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)

BEGINNER'S BOX–3

Electron Affinity and Electronegativity

1*. In which case the energy released is minimum:-

(A) $Cl \rightarrow Cl^-$ (B) $P \rightarrow P^-$ (C) $N \rightarrow N^-$ (D) $C \rightarrow C^-$

2. The electron affinity values for the halogens shows the following trend :–

(A) F < Cl > Br > I (B) F < Cl < Br < I (C) F > Cl > Br > I (D) F < Cl > Br < I

3. The process requiring the absorption of energy is.

(A) $F \rightarrow F^-$ (B) $Cl \rightarrow Cl^-$ (C) $O \rightarrow O^{2-}$ (D) $H \rightarrow H^-$

4. Correct order of electronegativity of N, P, C and Si is :–

(A) N < P < C < Si (B) N > C > Si > P (C) N = P > C = Si (D) N > C > P > Si

5. In the formation of a chloride ion, from an isolated gaseous chlorine atom, 3.8 eV energy is released, which would be equal to :-

(A) Electron affinity of Cl^- (B) Ionisation potential of Cl

(C) Electronegativity of Cl (D) Ionisation potential of Cl^-

6*. Electron addition would be easier in :-

(A) O (B) O^+ (C) O^- (D) O^{+2}

7. In the process $Cl_{(g)} + e^- \xrightarrow{\Delta H} Cl^-(g)$, ΔH is

(A) Positive (B) Negative (C) Zero (D) None

8. Second electron affinity of an element is :–
(A) Always exothermic
(B) Endothermic for few elements
(C) Exothermic for few elements
(D) Always endothermic

9*. If the ionisation potential is IP, electron affinity is EA and electronegativity is x then which of the following relation is correct :-
(A) 2X – EA – IP = 0
(B) 2EA – X – IP = 0
(C) 2IP – X – EA = 0
(D) All of the above

10. The properties which are common to the elements belonging to groups 1 and 17 of periodic tables are-
(A) Electropositive character increases down the group
(B) Reactivity decreases from top to bottom
(C) Atomic radii increases as atomic number increases
(D) Electronegativity decreases on moving down a group

11. Be and Mg have zero value of electron affinity, because :–
(A) Be and Mg have [He] $2s^2$ and [Ne]$3s^2$ configuration respectively.
(B) 2s and 3s orbitals are filled to their capacity
(C) Be and Mg are unable to accept electron.
(D) All the above are correct.

12. The maximum energy will be released in the following process :-
(A) $B + e^- \longrightarrow B^-$
(B) $C + e^- \longrightarrow C^-$
(C) $N + e^- \longrightarrow N^-$
(D) $O + e^- \longrightarrow O^-$

13. Which of the following represents a correct sequence of electronegativity values :-
(A) F > N > O > C
(B) F > N < O > C
(C) F > N > C > O
(D) F < N < O < C

14. The electronegativites of the following elements H, O, F, S and Cl increase in the order:–
(A) H < O < F < S < Cl
(B) S < H < Cl < O < F
(C) H < S < O < Cl < F
(D) H < S < Cl < O < F

13.0 DENSITY

AL

(a) In a group volume of an atom increases along with atomic weight but atomic weight increases more than atomic volume, So density increases in a group.

(b) Factors affecting density are
(i) Inner shell configuration
(ii) Atomic weight
(iii) Packing capacity
(iv) Chemical bond

13.1 Periodic variation

AL

(a) ***In period*** density first increases till maximum and then decreases. (s-block to d-block increases, d-block to p-block decreases)

(b) ***In group*** from top to bottom density increases regularly

Ex. In VIIA group – F and Cl are gases (Low density)
Br is liquid (density 3.19 g/cm^{-3})
I is solid (density 4.94 g/cm^{-3})

From s-block to p-block packing capacity and strength of bond increases.

Exceptions

(a) The density of sodium and magnesium is greater than K and Ca respectively. This can be explained by inner shell configuration.

In K, $3d^0$ orbital is vacant, 3rd orbit has the capacity to hold $18e^-$ but it has only $8e^-$. Due to empty orbitals atomic volumes increases and so density decreases

(b) Li is the lightest metal known.

(c) Highest density of solid metal Ir (22.63 gm/cc) and Os (22.6 gm/cc) and liquid metal Hg(13.6 gm/cc)

Order of density of elements

Li < K < Na < Rb < Cs	Sc < Y < La	Hg < Au < Os < Ir	Cr < Fe < Cu
Ca < Mg < Be < Sr < Ba	Ti < Zr << Hf	Sc < Zn < Fe < Hg	Fe < Cu < Pb
He < Ar < Kr < Rn	Zn < Cd < Hg		Fe < Hg < Au

14.0 MISCELLANEOUS PROPERTIES

14.1 Lattice Energy

AL

The lattice energy of an ionic compound is the energy required to separate 1 mole of solid ionic substance completely into gaseous ions.

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \quad \text{Lattice energy} = +788\ kJ\ mol^{-1}$$

Lattice energies are large and positive because of attraction between positive and negative ions.

14.2 Hydration Energy

AL

It is the energy released when 1 mol of gaseous ions are hydrated in water. It is directly proportional to nuclear charge and inversely proportional to size. It always decreases down the group.

General trends

(a) ***Hydration energy*** decreases along a group.

(b) ***Lattice energy*** decreases along a group.

1. Periodicity of hydra acids :

(a) Acidic character of hydra acid increases from left to right in a period.

(b) Acidic character of hydra acid increases from top to bottom in a group.

2. Periodicity of oxy acids :

(a) Acidic character of oxy acid increases from left to right in a period.

(b) Acidic character of oxy acid decreases from top to bottom in a group.

3. Periodicity of nature of oxide :

(a) On moving from left to right in a period acidic nature of oxide generally increases.

e.g. $CO_2 < P_2O_5 < SO_3 < Cl_2O_7$

(b) On moving from top to bottom in a group acidic nature of oxide generally decreases.

14.3 Diagonal relationship: [Abnormal behaviour of second period elements]

AL

Elements of 2nd periods resembles with elements of 3rd periods which are diagonally placed due to nearly same ionic potentials values of their respective cations. This is called diagonal relationship. e.g.

$$\begin{array}{ccc} Li & Be & B \\ \searrow & \searrow & \searrow \\ Mg & Al & Si \end{array}$$

(i) Lithium resembles with Mg

(a) Li forms covalent compound like Mg but rest of the alkali metal form ionic compounds

(b) Lithium has tendency to form normal oxide like Mg but rest have tendency to form higher oxides like peroxide & superoxide.

(c) Lithium salts like carbonate, nitrate, hydroxides, sulphates etc. on heating changes to oxide whereas rest of the alkali metal salts are thermally stable.

(d) Lithium form oxide & nitride like Mg when burn in air whereas rest form only oxide.

(ii) Be resembles with Al

(a) Both forms covalent compounds.

(b) Oxides & hydroxide of both are amphoteric

(c) Oxides of both form transparent glassy beads used as precious stone.

(d) Halides of both like $BeCl_2$, $AlCl_3$ are electron deficient & act as Lewis acid.

(iii) Boron resembles with silicon

(a) Oxide of both B_2O_3 & SiO_2 are acidic.

(b) Both are non-metal & displaces H_2 gas from NaOH

(c) Halides of both fumes in air because on hydrolysis they form HX.

BEGINNER'S BOX–4

Miscellaneous

1. Set of elements having one electron in their valence shell are :-

(A) Cl, Br, I (B) Na, Mg, Al (C) B, Al, Ga (D) K, Rb, Cs

2. The electronic configuration of two neutral elements A and B are

A = $1s^2\ 2s^2\ 2p^6\ 3s^1$ and B = $1s^2\ 2s^2\ 2p^5$

(A) $A^+ B^-$ (B) $A^- B^+$ (C) A – B (D) $A^{2+} (B^-)_2$

3. In the periodic table, the metallic character of element :

(A) Decreases from left to right across a period and on descending a group

(B) Decreases from left to right across a period and increases on descending a group

(C) Increases from left to right across a period and on descending a group

(D) Increases from left to right across a period and decreases on descending a group

4. Fluorine is the most reactive among all the halogens, because of it's :

(A) small size (B) low dissociation energy of F - F bond

(C) large size (D) high dissociation energy of F - F bond

5. Which order is wrong :-

(A) Electronegativity – P < N < O < F (B) I^{st} ionisation potential – B < Be < O < N

(C) Basic property – MgO > CaO > FeO > Fe_2O_3 (D) Reactivity – Be < Li < K < Cs

6*. Atomic radii of alkali metals (M) follow the order Li < Na < K < Rb but ionic radii in aqueous solution follow the reverse order $Li^+ > Na^+ > K^+ > Rb^+$. The reason of the reverse order is :

(A) Increase in the ionisation energy (B) Decrease in the metallic bond character

(C) Increase in the electropositive character (D) Decrease in the amount of hydration

7*. The ground state electronic configurations of the elements, U, V, W, X and Y (these symbols do not have any chemical significance) are as follows :

U $1s^2 2s^2 2p^3$ V $1s^2 2s^2 2p^6 3s^1$

W $1s^2 2s^2 2p^6 3s^2 3p^2$ X $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

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

Determine which sequence of elements satisfy the following statements :

(i) Element forms a carbonate which is not decomposed by heating

(ii) Element is most likely to form coloured ionic compounds

(iii) Element has largest atomic radius

(iv) Element forms only acidic oxide

(A) V W Y U (B) V X Y W (C) V W Y X (D) V X W U

8. Diagonal relationships are shown by :

(A) Be and Al (B) Li and Mg (C) Mg and Al (D) B and P

GOLDEN KEY POINTS

- 2nd period elements (Li, Be, B) Shows diagonal relationship with 3rd period elements (Mg, Al, Si) so (Li, Be, B) are called Bridge elements. Because of same ionic potential value they shows similarity in properties.

  (Ionic potential = Charge/Radius)

  Li → Na, Be → Mg, B → Al, Al → Si

- 3rd period elements (Na, Mg, Al, Si, P, S, Cl) are called typical elements because they represent the properties of other element of their respective group.
- Atomic number of last inert gas element is 86.
- Number of Gaseous elements – 11 (H, N, O, F, Cl + Noble gases)

  Number of Liquid elements – 6 (Cs, Fr, Ga, Hg, Br, Uub)

  Bromine is the only non-metal which exists in liquid form.

  Number of Solid elements – 95 (if discovered elements are 112)
- 2nd period contains maximum number of gaseous elements. They are 4 ***(N, O, F, Ne)***

- ***ISOELECTRONIC SERIES***

  A series of atoms, ions and molecules in which each species contains same number of electrons but different nuclear charge is called isoelectronic series.

	N^{3-}	O^{2-}	F^-	Ne	Na^+	Mg^{2+}
Number of e^-	10	10	10	10	10	10
Number of p	7	8	9	10	11	12

(a) Number of electrons is same.

(b) Number of protons is increasing.

(c) So the effective nuclear charge is increasing and atomic size is decreasing. In an isoelectronic series atomic size decreases with the increase of charge.

Some of the examples of isoelectronic series are as under.

(i) S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+}

(ii) SO_2, NO_3^-, CO_3^{2-}

(iii) N_2, CO, CN^-

(iv) NH_3, H_3O^+

SOME WORKED OUT EXAMPLES

Illustration 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?

Solution.

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

Illustration 2*.

An element X with Z = 112 has been recently discovered. What is the electronic configuration of the element? To which group and period will it belong?

Solution.

(a) The electronic configuration of element X is $[Rn]^{86} 5f^{14} 6d^{10} 7s^2$

(b) It belongs to d-block as last electron enters in d subshell.

(c) As number of electrons in (n – 1)d subshell and valence shell is equal to twelve i.e. 10 + 2. So it belongs to group 12.

(d) ***It belongs to period 7 of the periodic table as principal quantum number of valence shell is 7 (i.e., $7s^2$)***

Illustration 3*.

What is the effective nuclear charge at the periphery of nitrogen atom when an extra electron is added during the formation of an anion. Compare the value of Z_{eff} when the atom is ionized to N^+.

Solution.

Ground state electron configuration of N(Z = 7) = $1s^2 2s^2 2p^3$

Electron configuration of N^- = $(1s^2)(2s^2 2p^4)$

Shielding constant for the last 2p electron,

$\sigma = [(5 \times 0.35) + (2 \times 0.85)] = 3.45$

So $Z_{eff} = Z - \sigma = 7 - 3.45 = 3.55$

Electron configuration of N^+ = $(1s^2)(2s^2 2p^2)$

Shielding constant for the last 2p electron,

$\sigma = [(3 \times 0.35) + (2 \times 0.85)] = 2.75$

So Z_{eff} for last electron on N^+ = 7 – 2.75 = 4.25

Illustration 4.

X – X bond length is 1.00 Å and C – C bond length is 1.54 Å. If electronegativities of X and C are 3.0 and 2.0 respectively, then C – X bond length is likely to be? (using ***Stevenson & Schomaker*** formula).

Solution.

$r_{C-X} = r_C + r_X - 0.09\,\Delta x$

$= \frac{1.00}{2} + \frac{1.54}{2} - 0.09$ [$\Delta x = 1$]

= 1.27 – 0.09 ;

Ans. C – X bond length = 1.18 Å.

Illustration 5.

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+}

Solution.

(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 smalller 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 removed successively. So the correct order is P^{5+}, P^{4+}, P^{3+}

Illustration 6.

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

Solution.

Mg^{2+} and O^{2-} both are isoelectronic i.e., have same number of electrons. But Z_{eff} in Mg^{2+} is greater than that in O^{2-} ion.

Illustration 7.

I.E. of one H atom is 2.18×10^{-18} J. The I.E. of H atom in kJ $mole^{-1}$ is-

(A) 1505 kJ $mole^{-1}$ (B) 1310 kJ $mole^{-1}$ (C) 1608 kJ $mole^{-1}$ (D) None

Ans. (B)

Solution.

$$\text{I.E.} = \frac{2.18\times10^{-18}\,\text{J}}{1\,\text{atom}}\times\frac{6.02\times10^{23}\,\text{atom}}{\text{mole}} = 1.31 \times 10^{6}\ \text{J mole}^{-1} = 1310\ \text{kJ mole}^{-1}$$

Illustration 8.

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

Solution.

(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.

Illustration 9.

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}].

Solution.

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

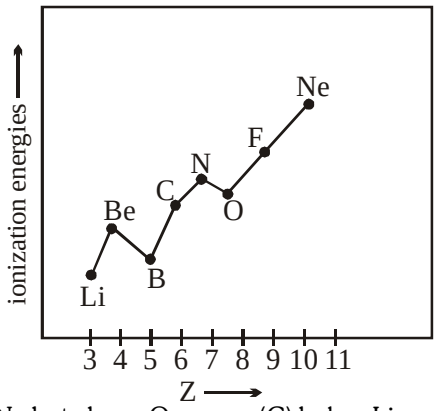
$= IE_I + IE_{II} = 22.681$ eV $= 2188.6$ kJ mol^{-1}.

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

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

Illustration 10*.

Following graph shows variation of ionization energies with atomic number in second period (Li–Ne). Value of ionization energies of Na(11) will be –



(A) above Ne (B) below Ne but above O (C) below Li (D) between N and O

Ans. (C)

Solution.

Na is 3rd period element and is larger than Li. Thus the outer most electron is loosely bounded with nucleus and removal of electron is easier. So option (C) is correct.

Illustration 11.

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

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

Ans. ***(ABD)***

Illustration 12.

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

Solution.

Order of increasing negative electron gain enthalpy is N < P < O < S.

Illustration 13.

Why do halogens have high electron gain enthalpies ?

Solution.

The valence shell electronic configuration of halogens is $ns^2\ np^5$ and thus they acquire the stable noble gas configuration $ns^2\ np^6$ on addition of e^-, because of this they have strong tendency to accept an additional electron and hence have high electron gain enthalpies.

Illustration 14.

Which will have the maximum value of electron affinity O^x, O^y, O^z [x, y and z respectively are 0, –1 and –2]

(A) O^x
(B) O^y
(C) O^z
(D) All have equal

Ans. ***(A)***

Solution.

Being neutral atom oxygen will have higher electron affinity as there is electrostatic repulsion between additional electron and negative ion in case of O^- and O^{2-}. So option (A) is correct.

Illustration 15.

The amount of energy when million atoms of iodine are completely converted into I^- ions in the vapour state according to the equation, $I(g) + e^-(g) \rightarrow I^-(g)$ is 5.0×10^{-13} J.

Calculate the electron gain enthalpy of iodine in terms of kJ mol^{-1} and eV per atom.

Solution.

The electron gain enthalpy of iodine is equal to the energy released when 1 mole of iodine atoms in vapour state are converted into I^- ions.

$$= \frac{5.0 \times 10^{-13} \times 6.023 \times 10^{23}}{10^6} = -30.1 \times 10^4 \text{ J} = -301 \text{ kJ}$$

Electron gain enthalpy of iodine in eV per atom $= \dfrac{-301}{96.5} = -3.12.$

Illustration 16.

Account for the large decrease in electron affinity between Li and Be despite the increase in nuclear charge.

Solution.

The electronic configurations of Li and Be are $[He]2s^1$ and $[He]\ 2s^2$, respectively. The additional electron enters in the 2s orbital of Li but in the 2p orbital of be and hence is much less tightly bound. In fact, the nuclear charge is so well shielded in Be that electron gain is endothermic.

Illustration 17.

The electronegativities of F and H are 4.0 and 2.1 respectively. The percent ionic character in H and F bond is-

(A) 43
(B) 34
(C) 94
(D) 39

Ans. ***(A)***

Solution.

% Ionic haracter $= 16\ (4.0 - 2.1) + 3.5\ (4.0 - 2.1)^2 = 43$

Illustration 18.

Which of the following order is correct for acidic property -

(A) $SiH_4 > PH_3 > H_2S$ (B) $(SiH_4 = PH_3 = H_2S)$

(C) $PH_3 > SiH_4 > H_2S$ (D) $SiH_4 < PH_3 < H_2S$

Ans. (D)

Solution.

The acidic character of hydrides increase in a period from left to right and also increases when we move down in a group from top to bottom.

Illustration 19*.

Calculate the electronegativity of carbon from the following data:

$E_{H-H} = 104.2$ kcal mol^{-1}, $E_{C-C} = 83.1$ kcal mol^{-1}

$E_{C-H} = 98.8$ kcal mol^{-1}, $X_H = 2.1$

Solution.

Let the electronegativity of carbon be X_C, applying Pauling equaiton,

$X_C - X_H = 0.208\,[E_{C-H} - (E_{C-C} \times E_{H-H})^{1/2}]^{1/2}$

$x_C - 2.1 = 0.208\,[98.8 - (83.1 \times 104.2)^{1/2}]^{1/2}$

$\Rightarrow x_C = 2.5$

Illustration 20.

Arrange the following in decreasing basic nature

LiOH, NaOH, KOH, CsOH

Solution.

The basic nature of hydroxides and oxides of IA elements increases on descending the group with increase in size of cation as CsOH > RbOH > KOH > NaOH > LiOH.

ANSWERS

BEGINNER'S BOX-1

1.	(C)	**2.**	(A)	**3.**	(B)	**4.**	(C)	**5.**	(C)
6.	(A)	**7.**	(C)	**8.**	(B)	**9.**	(A)	**10.**	(B)
11.	(A)	**12.**	(A)						

BEGINNER'S BOX-2

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

BEGINNER'S BOX-3

1.	(C)	**2.**	(A)	**3.**	(C)	**4.**	(D)	**5.**	(D)
6.	(D)	**7.**	(B)	**8.**	(D)	**9.**	(A)	**10.**	(ACD)
11.	(D)	**12.**	(D)	**13.**	(B)	**14.**	(D)		

BEGINNER'S BOX-4

1.	(D)	**2.**	(A)	**3.**	(B)	**4.**	(B)	**5.**	(C)
6.	(D)	**7.**	(B)	**8.**	(AB)				

EXERCISE – 1 MCQ (SINGLE CHOICE CORRECT)

1. If the ionic radii of K^+ and F^- are about 1.34 Å each, then the expected values of atomic radii of K and F should be respectively :
(A) 2.31 and 1.34 Å (B) 2.31 and 0.64 Å (C) 0.64 and 2.31 Å (D) 1.34 and 1.34 Å

2. The best reason to account for the general tendency of atomic diameters to decrease as the atomic numbers increase within a period of the periodic table is the fact that
(A) Outer electrons repel inner electrons
(B) Closer packing among the nuclear particles is achieved
(C) The number of neutrons increases
(D) The increasing nuclear charge exerts a greater attractive force on the electrons

3. The second ionisation potentials in electron volts of oxygen and fluorine atoms are respectively given by :-
(A) 35.1, 38.3 (B) 38.3, 38.3 (C) 38.3, 35.1 (D) 35.1, 35.1

4. In which of the following pairs, the ionisation energy of the first species is less than that of the second :-
(A) O^-, O^{2-} (B) S, P (C) N, P (D) Be^+, Be

5. IP_1 and IP_2 of Mg are 178 and 348 K. cal mol^{-1}. The enthalpy required for the reaction
$Mg_{(g)} \rightarrow Mg_{(g)}^{2+} + 2e^-$ is :-
(A) + 170 K.cal (B) + 526 K.cal (C) - 170 K.cal (D) - 526 K.cal

6. The energy needed to remove one electron from unipositive ion is abbreviated as :-
(A) I^{st} I.P. (B) 3rd I.P. (C) 2nd I.P. (D) 1st E.A.

7. 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) $M^{2+}_{(g)} \rightarrow M^{3+}_{(g)}$

8. Out of Na^+, Mg^{+2}, O^{-2} and N^{-3}, the pair of species showing minimum and maximum IP would be.
(A) Na^+, Mg^{+2} (B) Mg^{+2}, N^{-3} (C) N^{-3}, Mg^{+2} (D) O^{-2}, N^{-3}

9. The correct order of electron affinity is :-
(A) Be < B < C < N (B) Be < N < B < C
(C) N < Be < C < B (D) N < C < B < Be

10. Process $Na^+ \xrightarrow{I} Na_{(g)} \xrightarrow{II} Na_{(s)}$
(A) In (I) energy released, (II) energy absorbed (B) In both (I) and (II) energy is absorbed
(C) In both (I) and (II) energy is released (D) In (I) energy absorbed, (II) energy released

11. $O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)}$ ΔHeg = 744.7 KJ/mole. The positive value of ΔHeg is due to :-
(A) Energy is released to add on 1 e^- to O^{-1}
(B) Energy is required to add on 1 e^- to O^{-1} & is much more than energy released when $1e^-$ is added to$O_{(g)}$.
(C) Energy is needed to add on $1e^-$ to O
(D) None of the above is correct

12*. In boron atom screening is due to :-
(A) Electrons of K shell only (B) All the electrons of K and L shell
(C) Two electrons of 1s and 2s each (D) Only by electrons of L shell

13. The electron affinity of fluorine is less than that of chlorine because :-
(A) The incoming electron enters the 3p orbital in fluorine
(B) The incoming electron enters the 2p orbitals in fluorine and 3p orbital in chlorine
(C) The electron density in fluorine is higher
(D) Fluorine has lower ionisation potential than chlorine

14. Which ionisation potential (IP) in the following equations involves the greatest ammount of energy:-
(A) $K^+ \rightarrow K^{+2} + e^-$ (B) $Li^+ \rightarrow Li^{+2} + e^-$ (C) $Fe \rightarrow Fe^+ + e^-$ (D) $Ca^+ \rightarrow Ca^{+2} + e^-$

15. The correct electron affinity order of N, O, S, Cl is:-
(A) O < N < Cl < S (B) Cl > O > S > N (C) N < O < S < Cl (D) N = Cl > O = S

16. Decreasing order of size of ions is :-
(A) $Br^- > S^{-2} > Cl^- > N^{-3}$ (B) $N^{3-} > S^{-2} > Cl^- > Br^-$
(C) $Br^- > Cl^- > S^{-2} > N^{-3}$ (D) $N^{-3} > Cl^- > S^{-2} > Br^-$

17. In which case the maximum energy is needed in the formation of monopositive gaseous ion :
(A) 1 mole of Li atoms (B) 1 mole of Na atoms
(C) 1 mole of Cs atoms (D) 1 mole of Be atoms

18. Correct order of ionic size of elements :-
(A) $Mn^{+7} > Mn^{+6} > Mn^{+4}$ (B) $C^+ > C > C^-$
(C) $Fe^{+3} > Fe^{+2} > Fe$ (D) All are incorrect

19. Triad - I [N^{3-} , O^{2-} , Na^+]
Triad - II [N^+ , C^+ , O^+]
Choose the species of lowest IP from triad–I and highest IP from triad–II respectively
(A) N^{3-} , O^+ (B) Na^+ , C^+ (C) N^{3-} , N^+ (D) O^{2-}, C^+

20. The correct values of ionization energies (in kJ mol^{-1}) of Be, Ne, He and N respectively are
(A) 899, 2080, 1403, 2372 (B) 2080, 899, 1403, 2372
(C) 899, 2080, 2372, 1403 (D) 899, 1403, 2080, 2372

21. Which of the following processes involve absorption of energy :-
(A) S (g) + e^- $\rightarrow$ S^- (g) (B) O^- (g) + e^- $\rightarrow$ O^{2-} (g)
(C) Cl (g) + e^- $\rightarrow$ Cl^- (g) (D) O (g) + e^- $\rightarrow$ O^- (g)

22. The corret values of ionization energies (in KJ $mole^{-1}$) of Si, P, Cl and S respectively are
(A) 786, 1012, 999, 1256 (B) 1012, 786, 999, 1256
(C) 786, 1012, 1256, 999 (D) 786, 999, 1012, 1256

23*. Which of the following sequence is correct for decreasing order of ionic radius :–
(A) Se^{-2}, I^-, Br^-, O^{-2}, F^- (B) I^-, Se^{-2}, O^{-2}, Br^-, F^-
(C) Se^{-2}, I^-, Br^-, F^-, O^{-2} (D) I^-, Se^{-2}, Br^-, O^{-2}, F^-

24. Which of the following orders for electron affinity is /are correct :–
(a) S > O < Se (b) Cl > F (c) S > O (d) O > S
(e) N > P (f) C > N
(A) a, b, c, e (B) a, b, c, f (C) b, c, d, e (D) b, c, f

25. The electronic configuration of some neutral atoms are given below :–
(1) $1s^2\ 2s^1$ (2) $1s^2\ 2s^2\ 2p^3$ (3) $1s^2\ 2s^2\ 2p^4$ (4) $1s^2\ 2s^2\ 2p^6\ 3s^1$
In which of these electronic configuration would you expect to have highest :–
(i) IE_1 (ii) IE_2
(A) 3, 1 (B) 2, 1 (C) 3, 2 (D) 2, 4

26. Which of the following pairs has elements containing same number of electrons in outer most orbit

(A) Sc, Cu (B) Na, Ca (C) Pb, Sb (D) As, Bi

27. Increasing order of metallic characteristic of C, Sb, As, Bi, Si is shown by :

(A) C, Si, As, Sb, Bi (B) C, Si, Bi, Sb, As

(C) C, Si, Sb, Bi, As (D) C, Si, As, Bi, Sb

28*. In which of the following arrangements the order is not according to the property indicated against it ?

(A) $Al^{3+} < Mg^{2+} < Na^{+} < F^{-}$ - increasing ionic size

(B) B < C < N < O - increasing first ionization potential

(C) I < Br < F < Cl - increasing electron gain ethalpy (with negative sign)

(D) Li < Na < K < Rb - increasing metallic radius

29. Lanthanoid contraction is caused due to :

(A) the same effective nuclear charge from Ce to Lu

(B) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge

(C) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge

(D) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge

30*. Consider the following chages :

(1) $M(s) \longrightarrow M(g)$ (2) $M(s) \longrightarrow M^{2+}(g) + 2e^{-}$

(3) $M(g) \longrightarrow M^{+}(g) + e^{-}$ (4) $M^{+}(g) \longrightarrow M^{2+}(g) + e^{-}$

(5) $M(g) \longrightarrow M^{2+}(g) + 2e^{-}$

The second ionization energy of M could be calculated from the energy values associated with :

(A) 1 + 3 + 4 (B) 2 – 1 + 3 (C) 1 + 5 (D) 5 – 3

EXERCISE – 2 MCQ (ONE OR MORE CHOICE CORRECT)

1*. Which are correct match :-
(A) O < C < S < Se — Atomic size
(B) Na < Al < Mg < Si — I^{st} I.P
(C) MgO < SrO < Cs_2O < K_2O — Basic character
(D) P_4O_{10} > SO_3 > Cl_2O_7 - Acidic character

2. Which are correct match :-
(A) O > F > N > C — IInd I.P.
(B) S^{-2} > Cl^- > K^+ > Ca^{+2} — Ionic radius
(C) N > C > P > Si — E. N.
(D) F > Na > Ne — I^{st} I.P.

3. Which of the following statement is/are not correct:-
(A) I.P. increases down the group
(B) IP of s–block elements is less than corresponding d– block elements
(C) If ΔIP > 16 eV higher oxidation state is more stable
(D) IP of halogen elements is maximum in their respective period

4. Out of the following statements which is/are correct :-
(A) H is an element of minimum atomic radius
(B) He is an element of highest I.P.
(C) Cl is an element of highest EA
(D) Li is an element of lowest I.P.

5. AB is predominantly ionic as A^+ B^- if :-
(A) $(IP)_A$ < $(IP)_B$
(B) $(EA)_A$ < $(EA)_B$
(C) $(EN)_A$ < $(EN)_B$
(D) Size of A < size of B

6. The number of which subatomic particle is same in case of chlorine atom and chloride ion :
(A) Electron
(B) Proton
(C) Neutrons
(D) All of the above

7. Which of the following show amphoteric behaviour :
(A) $Zn(OH)_2$
(B) BeO
(C) Al_2O_3
(D) $Pb(OH)_2$

8. Fluorine is stronger oxidizing agent than chlorine in aqueous solution. This can be attributed to the property:
(A) Heat of dissociation
(B) Electron affinity
(C) Ionization potential
(D) Heat of hydration

9. Electron affinify of the elements or ions shown correct :
(A) S > O^-
(B) O > S^-
(C) O^- > S^-
(D) N^- > S

10*. Select equations having endothermic step :
(A) $S^-(g) \longrightarrow S^{2-}(g)$
(B) $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$
(C) $N(g) \longrightarrow N^-(g)$
(D) $Al^{2+}(g) \longrightarrow Al^{3+}(g)$

11. Consider the following ionization steps :
$M(g) \longrightarrow M^+(g) + e^-$; ΔH = 100 eV
$M(g) \longrightarrow M^{2+}(g) + 2e^-$; ΔH = 250 eV
select correct statement(s) :
(A) $I.E._1$ of M(g) is 100 eV
(B) $I.E._1$ of M^+ (g) is 150 eV
(C) $I.E._2$ of M(g) is 250 eV
(D) $I.E._2$ of M (g) is 150 eV

12. Which of the following statements are correct :
(A) F is the most electronegative and Cs is the most electropositive element.
(B) The electronegativity of halogens decreases from F to I
(C) The electron affinity of Cl is higher than that of F though their electronegativities are in the reverse order
(D) The electron affinity of noble gases is almost zero.

13. Zinc does not show the variable valency as elements of d-block, because :
(A) This is soft metal
(B) d-orbital is full
(C) Its melting point is low
(D) Volatile Metal

14*. The incorrect order of ionization energies of F^-, Cl^-, F and Cl is:
(A) Cl < F < Cl^- < F^-
(B) Cl^- < F^- < Cl < F
(C) F^- < Cl^- < Cl < F
(D) Cl^- < Cl < F^- < F

Match the Column

15. Match Column–I (atomic number of elements) withColumn–II (position of element in periodic table) and select the correct answer using the codes given below :

Column-I	***Column-II***
(A) 19	(p) p-block
(B) 22	(q) f-block
(C) 32	(r) d-block
(D) 64	(s) s-block

16. Match Column–I (Elements) withColumn–II (configuration of elements) and select the correct answer using the codes given below :

Column-I	***Column-II***
(A) The third alkali metal	(p) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
(B) The second transition element	(q) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$
(C) The fourth noble gas element	(r) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
(D) The second halogen element	(s) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

17.

Column-I	***Column-II***
(A) Metalloid	(p) Selenium
(B) Radioactive	(q) Silver
(C) Transition	(r) Arsenic
(D) Chalcogen	(s) Uranium

Comprehension Based Questions

Comprehension-1

Ionization energies of five elements in kcal/mol are given below :

Atom	***I***	***II***	***III***
P	300	549	920
Q	99	734	1100
R	118	1091	1652
S	176	347	1848
T	497	947	1500

18*. Which element is a noble gas ?
(A) P (B) T (C) R (D) S

19*. Which element form stable unipositive ion :
(A) P (B) Q (C) R (D) S

20*. The element having most stable oxidation state +2 is :
(A) Q (B) R (C) S (D) T

21*. Which is a non-metal (excluding noble gas) :
(A) P (B) Q (C) R (D) S

22*. If Q reacts with fluorine and oxygen, the molecular formula of fluoride and oxide will be respectively :
(A) QF_3, Q_2O_3 (B) QF, Q_2O (C) QF_2, QO (D) None of these

23*. Which of the following pair represents elements of same group :
(A) Q, R (B) P, Q (C) P, S (D) Q, S

Comprehension-2

Four elements P,Q,R & S have ground state electronic configuration as :

P → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ Q → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

R → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$ S → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^1$

24*. Which of the following option represent the correct order of true (T) and False (F) Statement:
I. size of P< size of Q II. size of R < size of S
III. size of P < size of R (appreciable difference) IV. size of Q < size of S (appreciable difference)
(A) TTTT (B) TTTF (C) FFTT (D) TTFF

25*. Order of IE_1 values among the following is :
(A) P > R > S > Q (B) P < R < S < Q (C) R > S > P > Q (D) P > S > R > Q

EXERCISE – 3 SUBJECTIVE

1. Can an element with atomic number 126, if discovered, be accommodated in the present long from of periodic table ?

2*. Third period of the periodic table contains 8 and not18 elements. Justify.

3. If scientist succeed in obtaining element with atomic number 114, which well known element would you expect it to resemble ?

4*. Ist and 2nd IE of few elements have been given below –

	IE_1 (KJ/mole)	IE_2 (KJ/mole)
(A)	520	7300
(B)	1680	3380
(C)	2370	5250
(D)	900	1760

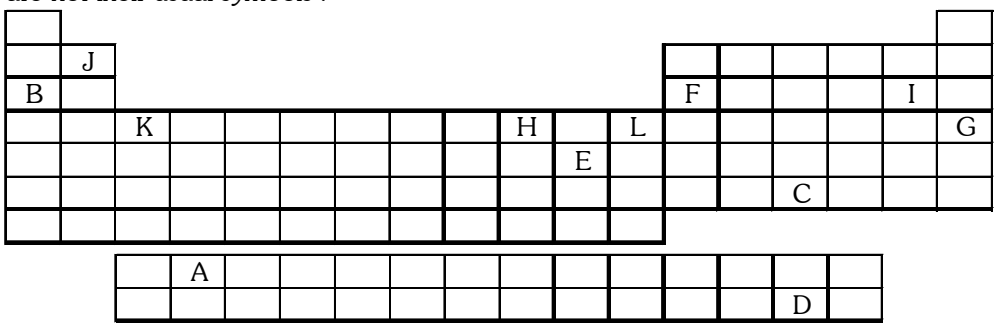
[Assuming each of the following has one unique answer identify.]

(i) Which is reactive metal ?
(ii) Which is reactive non metal ?
(iii) Which is inert gas ?
(iv) A metal that form a stable binary halide of formulae AX_2 (X = Halogen)

5. Among the elements B, Al, C and Si,
(a) which has the highest first ionization enthalpy?
(b) which has the most negative electron gain enthalpy ?
(c) which has the largest atomic radius ?
(d) which has the most metallic character ?

6. Which of the elements Na, Mg, Si and P would have the greatest difference between the first and second ionization enthalpies. Briefly explain your answer.

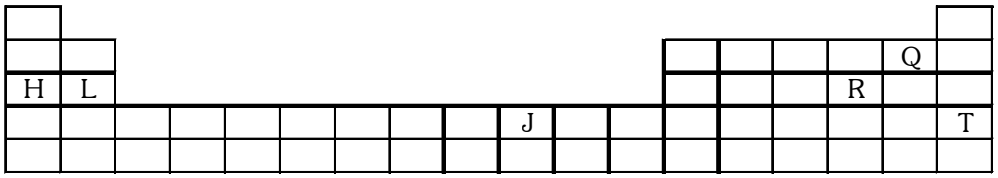
7*. The diagram below shows part of the skeleton of the periodic table in which element are indicated by letters which are not their usual symbols :



Answer the following on the basis of periodic table :

(I) Alkali metal(s)
(II) An elements with the outer configuration of d^8s^2
(III) Lanthanoids
(IV) Representative elements(s)
(V) Elements with incomplete f-subshell
(VI) Halogen(s)
(VII) s-block element(s)
(VIII) Transition element (s)
(IX) Noble gase (s)
(X) Non-transition element (s) which is of d–block.

8. The diagram below shows part of the skeleton of the periodic table in which element are indicated by letter which are not their usual symbols :



Answer the following on the basis of modern periodic table

(I) Element having greatest ionic character in its compound with non-metals

(II) Metal cation which is coloured in its aqueous solution

(III) Element (s) of which carbonate salt is/are water soluble

(IV) Which element is monoatomic gas at room temperature

9.* The ionisation potentials of atoms A and B are 400 and 300 kcal mol^{-1} respectively. The electron affinities of these atoms are 80.0 and 85.0 kcal mol^{-1} respectively. Identify which of the atoms has higher electronegativity.

10. ***(a)*** 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)

(b) Compare the following giving reasons

Acidic nature of oxides : CaO, CO, CO_2, N_2O_5, SO_3

11*. With the help of EN values [EN_A = 1.8, EN_B = 2.6, EN_C = 1.6, EN_D = 2.8] answer the following questions for the compounds

HAO, HBO, HCO, HDO

(a) Compounds whose aqueous solution is acidic and order of their acidic strength

(b) Compounds whose aqueous solution is basic and order of their basic strength

(c) Comment on the chances of being coloured on the basis of percent ionic character for the compounds CD & AB.

12. Arrange the following ions in increasing order of their radius ?

V^{+5}, K^+ , S^{2-} , Mn^{+7}, Ca^{+2}, Cl^-, P^{3-}

13. Out of Li^+, Be^{+2} and B^{+3} ions, which has the smallest ionic radius and why ?

14*. A student reported the radii of Cu, Cu^+ and Cu^{2+} as 122 pm, 96 pm and 72 pm. Do you agree with the reported values. Justify the answer. Explain why ?

15. The first ionisation energy of beryllium is greater than that of lithium but reverse is true for the second ionisation energy.

EXERCISE – 4 RECAP OF AIEEE/JEE (MAIN)

1. According to the Modern Periodic law of elements, the variation in properties of elements is related to their:- **[AIEEE-2003]**
(A) Nuclear masses (B) Atomic numbers
(C) Nuclear neutron-proton number ratio (D) Atomic masses

2*. The reduction in atomic size with increase in atomic number is a characteristic of elements of :- **[AIEEE-2003]**
(A) d-block (B) f-block (C) Radioactive series (D) High atomic masses

3. Which of the following groupings represent a collection of isoelectronic species ? **[AIEEE-2003]**
(At. no. Cs = 55, Br = 35)
(A) N^{3-}, F^-, Na^+ (B) Be, Al^{3+}, Cl^- (C) Ca^{2+}, Cs^+, Br (D) Na^+, Ca^{2+}, Mg^{2+}

4*. The atomic numbers of vanadium, (V), chromium (Cr), manganese (Mn) and iron (Fe) are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionization enthalpy ?
(A) Cr (B) Mn (C) Fe (D) V **[AIEEE-2003]**

5. Which one of the following sets of ions represents the collection of isoelectronic species ? **[AIEEE-2004]**
(A) K^+, Cl^-, Mg^{2+}, Sc^{3+} (B) Na^+, Ca^{2+}, Sc^{3+}, F^- (C) K^+, Ca^{2+}, Sc^{3+}, Cl^- (D) Na^+, Mg^{2+}, Al^{3+}, Cl^-

6. Which of the following ions has the highest value of ionic radius ? **[AIEEE-2004]**
(A) O^{2-} (B) B^{3+} (C) Li^+ (D) F^-

7*. Among Al_2O_3, SiO_2, P_2O_3 and SO_2, the correct order of acid strength is :- **[AIEEE-2004]**
(A) $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$ (B) $SiO_2 < SO_2 < Al_2O_3 < P_2O_3$
(C) $SO_2 < P_2O_3 < SiO_2 < Al_2O_3$ (D) $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$

8. The formation of the oxide ion $O^{2-}(g)$ requires first an exothermic and then an endothermic step as shown below **[AIEEE-2004]**
$O(g) + e^- = O^-(g)$, $\Delta H° = -142$ kJ mol^{-1}
$O^-(g) + e^- = O^{2-}(g)$, $\Delta H° = 844$ kJ mol^{-1}
This is because :-
(A) O^- ion will tend to resist the addition of another electron
(B) Oxygen has high electron affinity
(C) Oxygen is more electronegative
(D) O^- ion has comparitively larger size than oxygen atom

9. In which of the following arrangements the order is NOT according to the property indicated against it ? **[AIEEE-2005]**
(A) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ – increasing ionic size
(B) B < C < N < O - increasing first ionization enthalpy
(C) I < Br < F < Cl - increasing electron gain enthalpy (with negative sign)
(D) Li < Na < K < Rb - increasing metallic radius

10*. Which of the following oxides is amphoteric in character ? **[AIEEE-2005]**
(A) SnO_2 (B) SiO_2 (C) CO_2 (D) CaO

11. Pick out the isoelectronic structure from the following : **[AIEEE-2005]**

I. $^{+}CH_3$ II. H_3O^{+} III. NH_3 IV. CH_3^{-}

(A) I and II (B) III and IV (C) I and III (D) II, III and IV

12*. The lanthanide contraction is responsible for the fact that **[AIEEE-2005]**

(A) Zr and Y have about the same radius (B) Zr and Nb have similar oxidation state

(C) Zr and Hf have about the same radius (D) Zr and Zn have the same oxidation state

13. Which of the following factors may be regarded as the main cause of lanthanide contraction ? **[AIEEE-2005]**

(A) poor shielding of one of 4f electron by another in the subshell

(B) effective shielding of one of 4f electrons by another in the subshell

(C) poorer shielding of 5d electrons by 4f electrons

(D) greater shielding of 5d electrons by 4f electrons

14. The increasing order of the first ionization enthalpies of the elements B, P, S and F (lowest first) is :- **[AIEEE-2006]**

(A) F < S < P < B (B) P < S < B < F (C) B < P < S < F (D) B < S < P < F

15. Which one of the following sets of ions represents a collection of isoelectronic species ? **[AIEEE-2006]**

(A)N^{3-},O^{2-}, F^{-}, S^{2-} (B) LI^{+},Na^{+},Mg^{+2}, Ca^{+2} (C)K^{+},Cl^{-}, Ca^{+2}, Sc^{+3} (D) Ba^{+2},Sr^{+2}, K^{+2}, Ca^{+2}

16*. 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 ? **[AIEEE-2006]**

(A) In both the alkali metals and the halogens the chemical reactivity decreases with increase in atomic number down the group

(B) Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens

(C) In alkali metals the reactivity increases but in the halogen it decreases with increase in atomic number down the group

(D) The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group

17. The set representing the correct order of ionic radius is :- **[AIEEE- 2009]**

(A) $Li^{+} > Na^{+} > Mg^{2+} > Be^{2+}$ (B) $Mg^{2+} > Be^{2+} > Li^{+} > Na^{+}$

(C) $Li^{+} > Be^{2+} > Na^{+} > Mg^{2+}$ (D) $Na^{+} > Li^{+} > Mg^{2+} > Be^{2+}$

18. The correct sequence which shows decreasing order of the ionic radii of the elements is :- **[AIEEE- 2010]**

(A) $O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$ (B) $Al^{3+} > Mg^{2+} > Na^{+} > F^{-} > O^{2-}$

(C) $Na^{+} > Mg^{2+} > Al^{3+} > O^{2-} > F^{-}$ (D) $Na^{+} > F^{-} > Mg^{2+} > O^{2-} > Al^{3+}$

19. Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides? **[AIEEE- 2011]**

(A) $Na_2O < K_2O < MgO < Al_2O_3$ (B) $K_2O < Na_2O < Al_2O_3 < MgO$

(C) $Al_2O_3 < MgO < Na_2O < K_2O$ (D) $MgO < K_2O < Al_2O_3 < Na_2O$

20. The outer electron configuration of Gd (Atomic No. : 64) is :- **[AIEEE- 2011]**

(A) $4f^4\ 5d^4\ 6s^2$ (B) $4f^7\ 5d^1\ 6s^2$ (C) $4f^3\ 5d^5\ 6s^2$ (D) $4f^8\ 5d^0\ 6s^2$

21. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I, having atomic number 9, 17, 35 and 53 respectively, is :- ***[AIEEE- 2011]***

(A) I > Br > Cl > F (B) F > Cl > Br > I (C) Cl > F > Br > I (D) Br > Cl > I > F

22. The increasing order of the ionic radii of the given isoelectronic species is :- ***[AIEEE- 2012]***

(A) K^+, S^{2-}, Ca^{2+} , Cl^- (B) Cl^-, Ca^{2+}, K^+, S^{2-} (C) S^{2-}, Cl^-, Ca^{2+}, K^+ (D) Ca^{2+}, K^+, Cl^-, S^{2-}

23. The ionic radii (in Å) of N^{3-}, O^{2-} and F^- are respectively : ***[JEE MAINS - 2015]***

(A) 1.36, 1.40 and 1.71 (B) 1.36, 1.71 and 1.40 (C) 1.71, 1.40 and 1.36 (D) 1.71, 1.36 and 1.40

24. Which one has the highest boiling point ? ***[JEE MAINS - 2015]***

(A) He (B) Ne (C) Kr (D) Xe

25*. Which of the following atoms has the highest first ionization energy ? ***[JEE MAINS - 2016]***

(A) Rb (B) Na (C) K (D) Sc

26. The non-metal that does not exhibit positive oxidation state is : ***[JEE-MAIN-2016]***

(A) Oxygen (B) Fluorine (C) Iodine (D) Chlorine

27. The electronic configuration with the highest ionization enthalpy is:- ***[JEE-MAIN 2017]***

(A) [Ar] $3d^{10}4s^2 4p^3$ (B) [Ne] $3s^2 3p^1$ (C) [Ne] $3s^2 3p^2$ (D) [Ne] $3s^2 3p^3$

28. Consider the following ionization enthalpies of two elements 'A' and 'B' : ***[JEE-MAIN 2017]***

Element	Ionization enthalpy (kJ/mol)		
	1st	2nd	3rd
A	899	1757	14847
B	737	1450	7731

Which of the following statements is correct ?

(A) Both A and B belong to group-2 where A comes below B

(B) Both A and B belong to group-1 where A comes below B

(C) Both A and B belong to group-1 where B comes below A

(D) Both A and B belong to group-2 where B comes below A

29. In the following reactions, ZnO is respectively acting as a/an : ***[JEE-MAIN 2017]***

(a) $ZnO + Na_2O \rightarrow Na_2ZnO_2$ (b) $ZnO + CO_2 \rightarrow ZnCO_3$

(A) base and acid (B) base and base (C) acid and acid (D) acid and base

30. The group having isoelectronic species is :- ***[JEE-MAIN 2017]***

(A) O^{2-} , F^-, Na^+ , Mg^{2+} (B) O^- , F^-, Na , Mg^+ (C) O^{2-} , F^-, Na , Mg^{2+} (D) O^- , F^-, Na^+ , Mg^{2+}

31. When the first electron gain enthalpy ($A_{eg}H$) of oxygen is –141 kJ/mol, its second electron gain enthalpy is **[JEE-MAIN-2019]**

(A) almost the same as that of the first (B) negative, but less negative than the first

(C) a positive value (D) a more negative value than the first

32. In general, the properties that decrease and increase down a group in the periodic table, respectively, are
(A) electronegativity and electron gain enthalpy. **[JEE-MAIN-2019]**
(B) electronegativity and atomic radius.
(C) atomic radius and electronegativity.
(D) electron gain enthalpy and electronegativity.

33. The 71st electron of an element X with an atomic number of 71 enters into the orbital :**[JEE-MAIN-2019]**
(A) 4f (B) 6p (C) 6s (D) 5d

34. The correct option with respect to the Pauling electronegativity values of the elements is **[JEE-MAIN-2019]**
(A) Ga < Ge (B) Si < Al (C) P > S (D) Te > Se

35. The correct order of the atomic radii of C, Cs, Al and S is : **[JEE-MAIN-2019]**
(A) S < C < Al < Cs (B) S < C < Cs < Al (C) C < S < Cs < Al (D) C < S < Al < Cs

36. The element with Z = 120 (not yet discovered) will be an/a : **[JEE-MAIN-2019]**
(A) transition metal (B) inner-transition metal
(C) alkaline earth metal (D) alkali metal

37. The IUPAC symbol for the element with atomic number 119 would be :
(A) unh (B) uun (C) une (D) uue

38. The element having greatest difference between its first and second ionization energies, is :
(A) Ca (B) K (C) Ba (D) Sc

39. The group number, number of valence electrons, and valency of an element with atomic number 15, respectively, are
(A) 16, 5 and 2 (B) 16, 6 and 3 (C) 15, 5 and 3 (D) 15, 6 and 2

40. In comparison to boron, berylium has :
(A) lesser nuclear charge and greater first ionisation enthalpy
(B) lesser nuclear charge and lesser first ionisation enthalpy
(C) greater nuclear charge and greater first ionisation enthalpy
(D) greater nuclear charge and lesser first ionisation enthalpy

41. The pair that has similar atomic radii is :
(A) Sc and Ni (B) Ti and Hf (C) Mo and W (D) Mn and Re

42. The size of the iso-electronic species Cl^-, Ar and Ca^{2+} is affected by -
(A) Principal quantum number of valence shell
(B) Nuclear charge
(C) Azimuthal qunatum number of valence shell
(D) Electron-electron interaction in the outer orbitals

EXERCISE – 5 RECAP OF IIT-JEE/JEE (ADVANCED)

1. ***Assertion***: F atom has a less negative electron gain enthalpy than Cl atom. ***[JEE 2000]***

Reason: Additional electron is repelled more efficiently by 3p electron in Cl atom than by 2p electron in F atom.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

2. The correct order of radii is: ***[JEE 2000]***

(A) N < Be < B (B) $F^- < O^{2-} < N^{3-}$ (C) Na < Li < K (D) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

3. The IE_1 of Be is greater than that of B.[***T/F***] ***[JEE 2001]***

4. The set representing correct order of IP_1 is ***[JEE 2001]***

(A) K > Na > Li (B) Be > Mg > Ca (C) B > C > N (D) Fe > Si > C

5. Which ion is most difficult to form from its atom. ***[JEE 2002]***

(A) Li^- (B) Be^- (C) B^- (D) C^-

6*. The maximum number of electrons that can have principal quantum number n=3, and spin quantum number, $m_s = -1/2$, is ***[JEE 2011]***

7*. The increasing order of atomic radii of the following Group 13 elements is ***[JEE 2016]***

(A) Al < Ga < In < Tl (B) Ga < Al < In < Tl (C) Al < In < Ga < Tl (D) Al < Ga < Tl < In

8. The option(s) with only amphoteric oxides is (are): ***[JEE 2017]***

(A) Cr_2O_3, CrO, SnO, PbO (B) NO, B_2O_3, PbO, SnO_2

(C) Cr_2O_3, BeO, SnO, SnO_2 (D) ZnO, Al_2O_3, PbO, PbO_2

ANSWERS

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	D	C	B	B	C	D	C	B	C	B	C	C	B	C
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	A	D	D	A	C	B	C	D	B	B	D	A	B	B	D

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	AB	ABC	ACD	ABC	ABC	BC	ABCD	AD	AB	ACD
Que.	11	12	13	14						
Ans.	ABD	ABCD	B	ABD						

- ***Match the Column***

15. (A) - s (B) - r (C) - p (D) - q **16.** (A) - s (B) - r (C) - q (D) - p

17. (A) - r (B)- s (C) - q (D) - p

- ***Comprehension Based Questions***

Comprehension 1 : **18.** (B) **19.** (BC) **20.** (C)

21. (A) **22.** (B) **23.** (A)

Comprehension 2 : **24.** (B) **25.** (A)

EXERCISE-3

1. No. because there no provision for filling of g-block element in periodic table.

2. The no. of elements in a period is equal to the no. of orbitals filled in 2nd period–2s and 2p orbitals are filled so 8 elements are filled.

3. 14th group, carbon family

4. (i) Most reactive metal will be an alkali metal of 1st group with its $IE_2 >> IE_1$. Thus most reactive metal is (a).

(ii) Most reactive non-metal will be a halogen of 17th group. Its IE_1 will be quite high. Thus most reactive non metal is (b).

(iii) A noble gas will have very, very high IE_1. Thus (c) is a noble gas.

(iv) A metal that forms a stable binary halide will be an alkaline earth metal of 2nd group. Its IE_2 will not be much higher than IE_1. Thus (d) is such a metal that forms a stable binary halide of formula AX_2.

5. (a) C (b) Si (c) Al (d) Al

6. Na, becuase during IP_2 electron is removed from stable octet configuration ($ns^2 np^6$).

7. (i) B, (ii) H, (iii) A, (iv) B, C, F, J, I, (v) A, (vi) I (vii) B, J (viii) E, H, K (ix) G (x) L

8. (i) H, (ii) J, (iii) H (iv) T

9. EN on Mulliken scale = $\frac{\text{I.E.(eV)} + \text{E.A.(eV)}}{2}$

10. (a) 5.919 Å (b) $CaO < CO < CO_2 < N_2O_5 < SO_3$

11. (a) Acidic - HBO, HDO acidic strength - HDO > HBO
(b) Basic - HAO, HCO Basic strength - HCO > HAO
(c) % Ionic character = $16\ |X_A - X_B| + 3.5\ (X_A - X_B)^2$
for CD = 16 (1.2) + 3.5 (1.2)2 = 24.24 %
∴ Colourless.

12. $Mn^{+7} < V^{+5} < Ca^{+2} < K^{+} < Cl^{-} < S^{2-} < P^{3-}$

13. B^{+3} due to more z_{eff}.

14. Cu, Cu^{+} and Cu^{2+} have same number of protons but different number of electrons. In moving from Cu to Cu^{+} to Cu^{2+}, the number of electrons decreases thus effective nucelar charge and force of attraction between the nucleus and valence elecron increases and hence size decreases. Thus the correct order is
Cu (0.122 nm) > Cu^{+} (0.096 nm)> Cu^{+2} (0.072 nm).

15. The electronic configuration of Li and Be are $1s^2\ 2s^1$ and $1s^2\ 2s^2$ respectively.
Since in beryllium 2s orbital is complete while in lithium it is incomplete, it requires more energy to pull out an electron from beryllium than from lithium. Moreever beryllium has higher nuclear charge.
After removal of one electron, Li^{+} and Be^{+} ions have electronic configuration $1s^2$ and $1s^2\ 2s^1$ respectively. Now it will be easier to remove $2s^1$ electron rather than $1s^2$. Thus IE_2 of Li higher.

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	B	A	A	C	A	D	A	B	A	D	C	C	D	C
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	C	D	A	C	B	C	D	C	D	D	B	D	D	D	A

EXERCISE-5

1. (C) **2.** (B) **3.** True **4.** (B) **5.** (B)
6. (9) **7.** (B) **8.** (CD)

STOICHIOMETRY & CONCENTRATION TERMS

Recap of Early Classes

In the previous chapters, we studied about the electronic configuration & how it affects properties of elements. Some of these properties give an idea of why elements combine. The chapter aims to introduce various such theories required for bond formation. The theory of chemical bond is not perfect. Scientists are constantly discovering new compounds, orderly arranging the facts about them, trying to explain with the existing knowledge, organising to modify the earlier views or evolve theories for explaining the newly observed facts.

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1.0 STOICHIOMETRY

1.1 Significance of stoichiometric coefficients
1.2 Limiting Reagent (L.R.)
1.3 Problems based on mixture
1.4 Percentage yield
1.5 Percentage purity
1.6 Problems related with Sequential reaction
1.7 Problem related with Parallel reaction
1.8 PRINCIPLE OF ATOM CONSERVATION (POAC)

2.0 SOLUTIONS

3.0 CONCENTRATION TERMS :

3.1 Mass percentage
3.2 Mass-volume percentage (W/V %)
3.3 Volume Percent :
3.4 Mole %
3.5 Mole Fraction (X)
3.6 Molarity (M)
3.7 Molality (m)
3.8 Parts per million (ppm) :

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CONTENTS

THEORY

1. Comprehensive theory covering all concepts & subtopics for ***excellence*** in both ***school level*** as well as ***competitive exams***.

   Symbols used for categorization

   SL ⇒ Topics required for ***school level*** preparations.

   AL ⇒ Topics required for ***Advance level*** preparations useful for competitive exams.

2. ***Golden Key Points :*** Important points/formulaes or concepts summarized at the end to have a ***quick revision*** of the topic.

3. ***Illustrations : Subtopic based solved questions*** to get comfortable in problem solving. [Students should go through these after the topic is dealt]

4. ***Solved examples :*** A collection of ***miscellaneous solved question*** based on different concepts from the chapter at the end to be referred before exercise solving.

5. ***Beginner Boxes :*** Collection of ***elementary sub–topic*** based questions to be attempted on completion of each subtopic.

EXERCISE

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STOICHIOMETRY

1.0 STOICHIOMETRY

Stoichiometry is the calculation of amounts of reactants and products involved in a reaction. Stoichiometric calculations require a balanced chemical equation of the reaction.

- Remember a balanced chemical equation is one which contains an equal number of atoms of each element on both sides of equation.

1.1 SIGNIFICANCE OF STOICHIOMETRIC COEFFICIENTS :

Stoichiometric coefficients of chemical equation tells us about the ratio in which moles of reactants react and moles of products form.

Ex.	$2H_2(g)$ +	$O_2(g)$	$\longrightarrow$ $2\,H_2O\,(g)$
1st interpretation	2 moles	1 mole	2 moles
2nd interpretation	$2\,N_A$ molecules	N_A molecules	$2\,N_A$ molecules
3rd interpretation	2 molecules	1 molecules	2 molecules

Illustration 1. What mass of CaO is formed by heating 50 g $CaCO_3$ in air ?

Sol. $CaCO_3\,(s) \longrightarrow CaO\,(s) + CO_2\,(g)$

50 gm

$= \frac{50}{100}$ mol

$= \frac{1}{2}$ mol $\qquad \frac{1}{2}$ mol

$= \frac{1}{2} \times 56 = 28$ gm

Illustration 2. If 1 mole of ethanol (C_2H_5OH) completely burns to form carbon dioxide and water, mass of carbon dioxide formed is about

Sol. $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

1 $\qquad$ 3 $\qquad$ 2 $\qquad$ 2

2 mole of CO_2 are formed = 88g

Illustration 3. What volume of CO_2 at 0°C and 1 atm is formed by heating 200 g $CaCO_3$?

Sol. $CaCO_3\,(s) \longrightarrow CaO(s) + CO_2\,(g)$

200 gm

$= \frac{200}{100}$ mol $\qquad$ = 2 mol $\qquad$ 2 mol

Volume of gas at 0°C and 1 atm = No. of moles × 22.4 L = 2 × 22.4 = 44.8 L.

1.2 LIMITING REAGENT (L.R.) :

(i) The reactant which is completely consumed when a reaction goes to completion is called Limiting Reactant or Limiting reagent.

(ii) The reactant whose Stoichiometric amount is least, is limiting reactant.

Where ; Stoichiometric amount = $\frac{\text{Given moles of reactant}}{\text{Stoichiometric coefficient of reactant in balance Reaction}}$

(iii) For calculation of moles of product, LR should be used. When amounts of two or more than two reactants are given :

	aA +	bB $\longrightarrow$	cC +	dD
Initial reacting mixture	n_A mol	n_B mol		
Stoichiometric amount	$\frac{n_A}{a}$	$\frac{n_B}{b}$		

If $\frac{n_A}{a} < \frac{n_B}{b}$ $\Rightarrow$ A is limiting reagent.

If $\frac{n_A}{n_B} = \frac{a}{b}$ then reaction occurs to completion & no reactant is left at the end.

If $\frac{n_A}{a} > \frac{n_B}{b}$ $\Rightarrow$ B is limiting reagent.

Illustration 4. ***28 gm Lithium is mixed with 48 gm O_2 to reacts according to the following reaction.***

$$4Li + O_2 \longrightarrow 2Li_2O$$

The mass of Li_2O formed is

Sol. $4Li + O_2 \longrightarrow 2Li_2O$

moles taken $\frac{28}{7}$ $\frac{48}{32}$

$= 4$ $= 1.5$

$\frac{\text{moles taken}}{\text{stoich.coeff.}}$ $\frac{4}{4} = 1$ $\frac{1.5}{1} = 1.5$

(L.R.)

Moles of Li_2O formed $= \frac{2}{4} \times 4 = 2$

Mass of Li_2O formed $= 2 \times 30 = 60$ gm

Illustration 5. ***Calculate the mass of sucrose $C_{12}H_{22}O_{11}$ (s) produced by mixing 78 g of C(s), 11 g of H_2(g) & 67.2 litre of O_2 (g) at 0°C and 1 atm according to given reaction (unbalanced) ?***

Sol. $12C(s) + 11\,H_2(g) + \frac{11}{2}O_2 \rightarrow C_{12}H_{22}O_{11}(s)$

Moles taken $\frac{78}{12}$ $\frac{11}{2}$ $\frac{67.2}{22.4}$

$= 6.5$ $= 5.5$ $= 3$

$\frac{\text{moles taken}}{\text{stoich.coeff.}}$ $\frac{6.5}{12}$ $\frac{5.5}{11}$ $\frac{3}{5.5}$

$= 0.54$ $= 0.5$ $= 0.545$

(L.R.)

$\therefore$ Moles of $C_{12}H_{22}O_{11}$ formed $= \frac{5.5}{11} = 0.5$

Mass of sucrose obtained $= 0.5 \times 342 = 171$ grams.

1.3 PROBLEMS BASED ON MIXTURE :

The composition of any mixture may be determined by reacting the mixture with some substance, by which either one or more component of mixture may react.

Illustration 6. ***1.5 gm mixture of SiO_2 and Fe_2O_3 on very strong heating leave a residue weighting 1.46 gm. The reaction responsible for loss of weight is***

$$Fe_2O_3\,(s) \rightarrow Fe_3O_4\,(s) + O_2(g)$$

What is the percentage by mass of Fe_2O_3 in original sample.

Sol. $3Fe_2O_3\,(s) \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$

3×160 $\qquad$ $\frac{1}{2} \times 32$

$= 480$ gm $\rightarrow$ $\qquad$ $= 16$ gm

loss of 16 gm $\rightarrow$ 480 gm Fe_2O_3

loss of 0.04 gm $\rightarrow 0.04 \times \frac{480}{16} = 1.2$ gm Fe_2O_3

% by mass $= \frac{1.2}{1.5} \times 100 = 80\%$

1.4 PERCENTAGE YIELD :

In general, when a reaction is carried out in the laboratory we do not obtain actually the theoretical amount of the product. The amount of the product that is actually obtained is called the actual yield. Knowing the actual yield and theorectical yield the percentage yield can be calculate as :

$$\boxed{\%\text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100}$$

The percentage yield of any product is always equal to the percentage extent of that reaction.

Illustration 7. ***Aluminium reacts with sulphur to form aluminium sulphide. If 5.4 gm of Aluminium reacts with 12.8gm sulphure gives 12gm of aluminium sulphides, then the percent yield of the reaction is-***

Sol $\qquad 2Al + 3S \longrightarrow Al_2S_3$

Mole taken $\quad \frac{5.4}{27}$ gm $\qquad \frac{12.8}{32}$ gm

$= 0.2 \qquad = 0.4$

$\frac{\text{moles taken}}{\text{stoich. coeff.}} \quad \frac{0.2}{2} \qquad \frac{0.4}{3}$

$= 0.1 \qquad = 0.133$

(L.R.)

moles of Al_2S_3 formed $= \frac{1}{2} \times 0.2 = 0.1$

mass $= 0.1 \times 150 = 15$ gm

% yield $= \frac{\text{actual yield}}{\text{theoritical yield}} \times 100 = \frac{12}{15} \times 100 = 80\,\%$

1.5 PERCENTAGE PURITY :

The percentage of a specified compound or element in an impure sample may be given as

$$\% \text{ purity} = \frac{\text{Actual mass of compound}}{\text{Total mass of sample}} \times 100$$

If impurity is unknown, it is always considered as inert (unreactive) material.

Illustration 8. A chalk sample exactly requires 17.52 gram HCl for complete reaction with all $CaCO_3$ present in it. If the chalk sample is 72% pure, the mass of sample taken is

Sol. $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$

Moles of HCl = $\frac{17.52}{36.5}$

Moles of $CaCO_3$ = $\frac{1}{2} \times \frac{17.52}{36.5}$

Weight of $CaCO_3$ required = $\frac{1}{2} \times \frac{17.52}{36.5} \times 100$

Mass of sample taken :

$= \frac{1}{2} \times \frac{17.52}{36.5} \times \frac{100 \times 100}{72}$

= 33.33 gm

1.6 PROBLEMS RELATED WITH SEQUENTIAL REACTION :

When one of products formed in previous reaction is consumed in the next one.

Illustration 9. How many grams H_2SO_4 can be obtained from 1320 gm PbS as per reaction sequence ?

$$2PbS + O_2 \longrightarrow 2PbO + 2SO_2$$

$$3SO_2 + 2HNO_3 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO$$

[At. mass : Pb = 208, S = 32]

Sol. Moles of PbS = $\frac{1320}{240}$

= 5.5 mol

Moles of SO_2 = 5.5 mol = moles of H_2SO_4

Mass of H_2SO_4 = 5.5 × 98

= 539 gm

[When amount of only one reactant is given generally other is assumed in excess.]

1.7 PROBLEM RELATED WITH PARALLEL REACTION :

When same two reactants form two or more products by independent reactions.

Illustration 10. ***Carbon reacts with oxygen forming carbon monoxide and/or carbon dioxide depending an availablity of oxygen. Find moles of each product obtained when 160 gm oxygen reacts with (a) 12 g carbon (b) 120 g carbon (c) 72 g carbon.***

Sol. ***(a)*** $C + \frac{1}{2}O_2 \longrightarrow CO$ [initially use a reaction using lesser amount of oxygen]

t = 0	1mol	5mol		
t =∞	0	5–0.5	=	1mol
	(LR)	4.5mol		

Since CO & O_2 are left CO_2 is formed.

$CO + \frac{1}{2}O_2 \longrightarrow CO_2$

t = 0	1mol	4.5mol	0
t = ∞	0	4 mol	1 mol

At end 1 mole CO_2 & no CO present

(b) $C + \frac{1}{2}O_2 \longrightarrow CO$

t = 0	10mol	5mol	0
t =∞	0	0	10mol

At end only 10 mol CO present.

(c) $C + \frac{1}{2}O_2 \longrightarrow CO$

t = 0	6mol	5mol	0
t =∞	0	2mol	6mol
	[LR]		

$CO + \frac{1}{2}O_2 \longrightarrow CO_2$

t = 0	6mol	2mol	0
t =∞	2mol	0 [LR]	4 mol

At end [2mol CO + 4mol CO_2] left.

Illustration 11. 25.4 gm of iodine and 14.2 gm of chlorine are made to react completely to yield mixture of ICl and ICl_3. Ratio of moles of ICl & ICl_3 formed is (Atomic mass : I = 127, Cl = 35.5)

Sol.

$I_2 + Cl_2 \longrightarrow ICl + ICl_3$

0.1mol 0.2 mol x mol y mol

⇒ 0.2=x+y ⇒ x=0.1

0.4=x+3y ⇒ y=0.1

Ans. 1 : 1

1.8 PRINCIPLE OF ATOM CONSERVATION (POAC)

POAC is nothing but the conservation of atoms of reactants and products involved in a chemical reaction. And if atoms are conserved, moles of atoms shall also be conserved. The principle is fruitful for the students when they don't get the idea of balanced chemical equation in the problem using POAC we do not need to balance a reaction and we can even add two or more reactions. This principle can be understood by the following example.

Consider the decomposition of $KClO_3$ (s) → KCl (s) + O_2 (g) (unbalanced chemical reaction)

Apply the principle of atom conservation (POAC) for K atoms.

or moles of K atoms in $KClO_3$ = moles of K atoms in KCl

Now, since 1 molecule of $KClO_3$ contains 1 atom of K
Thus, moles of K atoms in $KClO_3$ = 1 × moles of $KClO_3$
and moles of K atoms in KCl = 1 × moles of KCl

$\therefore$ moles of $KClO_3$ = moles of KCl or $\dfrac{\text{wt. of } KClO_3 \text{ in g}}{\text{mol. wt. of } KClO_3} = \dfrac{\text{wt. of KCl in g}}{\text{mol. wt. of KCl}}$

- The above equation gives the mass-mass relationship between $KClO_3$ and KCl which is important in stoichiometric calculations. Again, applying the principle of atom conservation for O atoms,
moles of O in $KClO_3$ = 3 × moles of $KClO_3$
moles of O in O_2 = 2 × moles of O_2
$\therefore$ 3 × moles of $KClO_3$ = 2 × moles of O_2

or $3 \times \dfrac{\text{wt. of } KClO_3}{\text{mol. wt. of } KClO_3} = 2 \times \dfrac{\text{vol. of } O_2 \text{ at 1atm and 0°C}}{\text{Molar vol. (22.4 lt)}}$

- The above equations thus gives the mass-volume relationship of reactants and products.

Illustration 12. ***Calcium phosphide Ca_3P_2 formed by reacting magnesium with excess calcium orthophosphate $Ca_3(PO_4)_2$, was hydrolysed by excess water. The evolved phosphine PH_3 was burnt in air to yield phosphrous pentoxide (P_2O_5). How many gram of magnesium metaphosphate would be obtain if 192 gram Mg were used (Atomic weight of Mg = 24, P = 31)***

$$Ca_3(PO_4)_2 + Mg \longrightarrow Ca_3P_2 + MgO$$

$$Ca_3P_2 + H_2O \longrightarrow Ca(OH)_2 + PH_3$$

$$PH_3 + O_2 \longrightarrow P_2O_5 + H_2O$$

$$MgO + P_2O_5 \longrightarrow Mg(PO_3)_2$$

magnesium metaphosphate.

Sol. POAC on Mg

$$1 \times n_{Mg} = 1 \times n_{Mg(PO_3)_2}$$

$$\frac{192}{24} = n_{Mg(PO_3)_2}$$

$$W_{Mg(PO_3)_2} = \frac{192}{24} \times 182\text{gm}$$

$$= 1456 \text{ gm.}$$

Illustration 13. ***27.6 g K_2CO_3 was treated by a series of reagents so as to convert all of its carbon to $K_2Zn_3[Fe(CN)_6]_2$. Calculate the weight of the product. [mol. wt. of K_2CO_3 = 138 and mol. wt. of $K_2Zn_3[Fe(CN)_6]_2$ = 698]***

Sol. Here we have no knowledge about series of chemical reactions but we know about initial reactant and final product, accordingly.

$$K_2CO_3 \xrightarrow[\text{Steps}]{\text{Several}} K_2Zn_3[Fe(CN)_6]_2$$

Since C atoms are conserved, applying POAC for C atoms,
moles of C in K_2CO_3 = moles of C in $K_2Zn_3[Fe(CN)_6]_2$
1 × moles of K_2CO_3 = 12 × moles of $K_2Zn_3[Fe(CN)_6]_2$
($\because$ 1 mole of K_2CO_3 contains 1 moles of C)

$$\frac{\text{wt. of } K_2CO_3}{\text{mol. wt. of } K_2CO_3} = 12 \times \frac{\text{wt. of the product}}{\text{mol. wt. of product}}$$

wt. of $K_2Zn_3[Fe(CN)_6]_2$ = $\dfrac{27.6}{138} \times \dfrac{698}{12}$ ***= 11.6 g***

BEGINNER'S BOX–1

1. 50 g of $CaCO_3$ is allowed to react with 70 g of H_3PO_4. Calculate :
(i) amount of $Ca_3(PO_4)_2$ formed (ii) amount of unreacted reagent

2. N_2H_4, Hydrazine a rocket fuel can be produced according to the following reaction :
$ClNH_2 + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl$
When 1000 g $ClNH_2$ is reacted with excess of NH_3, 473 g N_2H_4 is produced. What is the % yield of the reaction.

3. Carbon disulphide 'CS_2', can be made from by product SO_2. The overall reaction is
$5C + 2SO_2 \longrightarrow CS_2 + 4CO$
How much CS_2 can be produced from 450 kg of waste SO_2 with excess of coke if the SO_2 conversion is 82%.

4. XeF_6 fluorinates I_2 to IF_7 and liberates Xenon (g). 210 mmol of XeF_6 can yield a maximum of __ mmol of IF_7:
(A) 420 (B) 180 (C) 210 (D) 245

5. When 100 g of ethylene polymerises entirely to polyethene, the weight of polyethene formed as per the equation $nCH_2 = CH_2 \rightarrow (CH_2 - CH_2)n$ is :
(A) (n/2)g (B) 100g (C) (100/n)g (D) 100n g

6*. A 10 gram sample of natural gas containing CH_4 and C_2H_4 was burnt in excess of oxygen to give 29.0 grams of CO_2 and some water. How many grams of water are formed :
(A) 9.42 g (B) 18.81 g (C) 11.42 g (D) 15.31 g

7*. 50 g of ZnS are strongly heated in air to effect partial oxidation and the resultant mass weighed 44 g. What is the ratio of ZnO to ZnS in the resultant mixture :
(A) 13.5 : 30.5 (B) 27 : 12.58 (C) 27 : 15.31 (D) 30.52 :13.48

8. The % loss in weight after heating a pure sample of potassium chlorate (M. wt. 122.5) will be :
(A) 12.25 (B) 24.50 (C) 39.17 (D) 49.0

9*. Iodobenzene (C_6H_5I) is prepared from aniline ($C_6H_5NH_2$) in a two step process as shown below
$C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2{}^+Cl^- + 2H_2O$
$C_6H_5N_2{}^+Cl^- + KI \rightarrow C_6H_5I + N_2 + KCl$
In an actual preparation 9.30 g of aniline was converted to 16.32 g of iodobenzene. The percentage yield of iodobenzene is :
(A) 8 % (B) 50 % (C) 75 % (D) 80 %

10. How many grams of urea on heating yield 10^{22} molecules of biuret by the reaction :
$2\ CO\ (NH_2)_2 \longrightarrow H_2N - CO - NH - CO - NH_2 + NH_3$?
(A) 1.495 (B) 0.995 (C) 1.99 (D) 1.753

CONCENTRATION TERMS

2.0 SOLUTIONS

A solution is a homogenous mixture of two or more pure substances whose composition may be altered within certain limits. Though the solution is homogenous in nature, yet it retains the properties of its constituents. Generally solution is composed of two components, solute and solvent. Such type of solution is known as binary solutions.

Solvent is that component in solution whose physical state is the same as that of the resulting solution while other component is called as solute. If the physical state of both component is same, than the component in excess is known as solvent and other one is called as solute. Each component in a binary solution can be in any physical state such as liquid, solid and gaseous state.

Table 2.1: Types of Solutions

Type of Solutions	Solute	Solvent	Common Example
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

3.0 CONCENTRATION TERMS :

The concentration of a solution is the amount of solute dissolved in a known amount of the solvent or solution. Solution can be described as dilute or concentrated solution as per their concentration. A dilute solution has a very small quantity of solute while concentrated solution has a large quantity of solute in solution. Various concentration terms are as follows.

3.1 Mass percentage :

It may be defined as the number of parts of mass of solute per hundred parts by mass of solution.

$$\textbf{\% by mass}\left(\frac{w}{W}\right): = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$$

[X % by mass means 100 gm solution contains X gm solute ; $\therefore$ (100 – X) gm solvent]

3.2 Mass-volume percentage (W/V %) :

It may be defined as the mass of solute present in 100 cm^3 of solution. For example, If 100 cm^3 of solution contains 5 g of sodium hydroxide, than the mass-volume percentage will be 5% solution.

$$\% \left(\frac{w}{V}\right) = \frac{\text{wt. of solute}}{\text{volume of solution}} \times 100 \text{ [for liq. solution]}$$

[X % $\left(\frac{w}{V}\right)$ means 100 ml solution contains X gm solute]

3.3 Volume Percent :

It can be represented as % v/v or % volume and used to prepare such solutions in which both components are in liquids state. It is the number of parts of by volume of solute per hundred parts by volume of solution. Therefore,

$$\% \left(\frac{v}{V}\right) = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$$

3.4 Mole % $= \frac{\text{Moles of solute}}{\text{Total moles}} \times 100$

- For gases ***% by volume*** is same as ***mole %***

3.5 Mole Fraction (X) :

Mole fraction may be defined as the ratio of number of moles of one component to the total number of moles of all the components (solute and solvent) present in solution. It is denoted by letter X and the sum of all mole fractions in a solution always equals one.

$$\text{Mole fraction (X)} = \frac{\text{Moles of solute}}{\text{Total moles}}$$

Mole fraction does not depend upon temperature and can be extended to solutions having more than two components.

3.6 Molarity (M) :

Molarity is most common unit for concentration of solution. It is defined as the number of moles of solute present in one litre or one dm^3 of the solution or millimol of solute present in one mL of solution.

$$\text{Molarity (M)} = \frac{\text{Mole of solute}}{\text{volume of solution in litre}}$$

3.7 Molality (m) : The number of gram mole of the solute present in 1000 g of the solvent is known as molality of solution. It represented by letter 'm'.

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

The unit of molality is mol/kg and it does not effect by temperature.

3.8 Parts per million (ppm) : The very low concentration of solute in solution can be expressed in ppm. It is the numbers of parts by mass of solute per million parts by mass of the solution.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solvent}} \times 10^6$$

$$\cong \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

◆ Get yourselves very much confortable in their inter conversion. It is very handy.

Concentration Type	Mathematical Formula	Concept
Percentage by mass	$\%\left(\frac{w}{w}\right)=\frac{\text{Mass of solute}\times 100}{\text{Mass of solution}}$	Mass of solute present in 100 gm of solution.
Volume percentage	$\%\left(\frac{v}{v}\right)=\frac{\text{Volume of solute}\times 100}{\text{Volume of solution}}$	Volume of solute present in 100 cm^3 of solution.
Mass-volume percentage	$\%\left(\frac{w}{v}\right)=\frac{\text{Mass of solute}\times 100}{\text{Volume of solution}}$	Mass of solute present in 100 cm^3 of solution.
Parts per million	$\text{ppm}=\frac{\text{Mass of solute}\times 10^6}{\text{Mass of solution}}$	Parts by mass of solute per million parts by mass of the solution
Mole fraction	$X_A=\frac{\text{Mole of A}}{\text{Mole of A}+\text{Mole of B}+\text{Mole of C}+....}$ $X_B=\frac{\text{Mole of B}}{\text{Mole of A}+\text{Mole of B}+\text{Mole of C}+....}$	Ratio of number of moles of one component to the total number of moles.
Molarity	$M=\frac{\text{Mole of solute}}{\text{Volume of solution (in L)}}$	Moles of solute in one litre of solution.
Molality	$m=\frac{\text{Mass of solute}\times 1000}{\text{Molar mass of solute}\times\text{Mass of solvent(g)}}$	Moles of solute in one kg of solvent

Illustration 14. ***Calculate the mole fractions of the components of the solution composed by 92 g glycerol and 90 g water ? (M (water) = 18 ; M (glycerol) = 92)***

Ans. Moles of water = 90 g / 18 g = 5 mol water

Moles of glycerol = 92 g / 92 g = 1 mol glycerol

Total moles in solution = 5 + 1 = 6 mol

Mole fraction of water = 5 mol / 6 mol = 0.833

Mole fraction of glycerol = 1 mol / 6 mol = 0.167

Illustration 15. ***What will be the Molarity of solution when water is added to 10 g $CaCO_3$ to make 100 mL of solution?***

Ans. Mol of $CaCO_3$ = 10 / 100 = 0.1

Molarity = Mole of solute / Volume of solution (L) = 0.10 mol / 0.10 L

Therefore ; Molarity of given solution = 1.0 M

Illustration 16. ***Calculate the molality of a solution containing 20 g of sodium hydroxide (NaOH) in 250 g of water?***

Ans. Moles of sodium hydroxide = 20 / 40 = 0.5 mol NaOH

250 gm = 0.25 kg of water

Hence molality of solution = Mole of solute / Mass of solvent (kg) = 0.5 mol / 0.25 kg

or Molality(m) = 2.0 m

Illustration 17. ***Calculate the grams of copper sulphate ($CuSO_4$) needed to prepare 250.0 mL of 1.00 M $CuSO_4$?***

Ans. Moles of $CuSO_4$ = M × V = $1 \times \frac{250}{1000}$

Molar mass of copper sulphate = 159.6 g/mol

Hence Mass of copper sulphate (gm) = Moles of $CuSO_4$ × Molar mass of copper sulphate.

$$= 1 \times \frac{250}{1000} \times 159.6 \text{ g/mol}$$

= 39.9 gm of Copper sulphate

Illustration 18. ***How many grams of H_2SO_4 are present in 500 ml of 0.2M H_2SO_4 solution ?***

Ans. $M = \frac{\text{moles}}{\text{vol.}}$

$\Rightarrow$ moles of H_2SO_4 = M × V

$$= 0.2 \times \frac{500}{1000} L$$

= 0.1

Mass of H_2SO_4 = 0.1 × 98 = 9.8 g

Illustration 19. ***Calculate the ppm of mercury in water in given sample contain 30 mg of Hg in 500 ml of solution.***

Ans. Parts per million = $\frac{\text{Mass of solute} \times 10^6}{\text{Mass of solution}}$

Mass of Hg = 30 mg

Mass of water = 500/1 = 500g = 50×10^4 mg

(density = mass / volume ; density of water 1 g / ml) $w = \frac{v}{d}$

Therefore, ppm of mercury = $\frac{30 \times 10^6}{50 \times 10^4}$ = 60 ppm of mercury

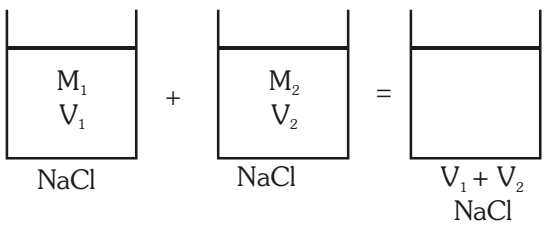
---

4. ***MIXING OF SOLUTIONS :***

It is based on law of conservation of moles.

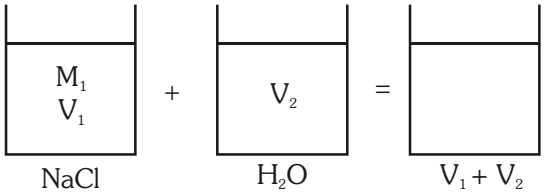
(i) ***Two solutions having same solute***

Final molarity = $\frac{\text{Total moles}}{\text{Total volume}} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$



(ii) ***Dilution Effect :*** When a solution is diluted, the moles of solute do not change but molarity changes while on taking out a small volume of solution from a larger volume, the molarity of solution do not change but moles change proportionately.

$$\text{Final molarity} = \frac{M_1V_1}{V_1 + V_2}$$



n-fold or n-times dilution

$\Rightarrow$ ***Final volume = $V_1 + V_2 = n(V_1)$***

Illustration 20. ***50 ml 0.2 M H_2SO_4 is mixed with 50 ml 0.3M H_2SO_4. Find molarity of final solution.***

Ans. $$M_f = \frac{\text{Total moles of } H_2SO_4}{\text{Total volume}} = \frac{50 \times 0.2 \times 10^{-3} + 50 \times 10^{-3} \times 0.3}{(50+50) \times 10^{-3}}$$

$$= \boxed{0.25\,M}$$

Illustration 21. ***Find final molarity in each case :***

Ans. ***(i)*** 500 ml 0.1 M HCl + 500 ml 0.2M HCl

$$M_f = \frac{500 \times 0.1 + 500 \times 0.2}{500 + 500} = \boxed{0.15\,M}$$

(ii) 50 ml 0.1M HCl + 150 ml 0.3MHCl + 300 ml H_2O

$$M_f = \frac{50 \times 0.1 + 150 \times 0.3}{50 + 150 + 300} = \frac{50}{500} = 0.1\ M$$

(iii) 4.9g H_2SO_4 + 250 ml H_2O + 250 ml 0.1 M H_2SO_4

$$M_f = \frac{\frac{4.9}{98} + \frac{250}{1000} \times 0.1}{\left(\frac{250+250}{1000}\right)} = \frac{50+25}{500} = \boxed{0.15\,M}$$

Illustration 22. ***How much water should be added to 2M HCl solution to form 1 litre of 0.5 M HCl?***

Ans. Let V be initial volume

Then mol of HCl = constant

$2 \times V = 1 \times 0.5$

$\Rightarrow$ V = 0.25 L

Volume of water added = 1 – 0.25 = 0.75 L

Illustration 23. ***Find number of Na^+ & PO_4^{-3} ions in 250 ml of 0.2M Na_3PO_4 solution.***

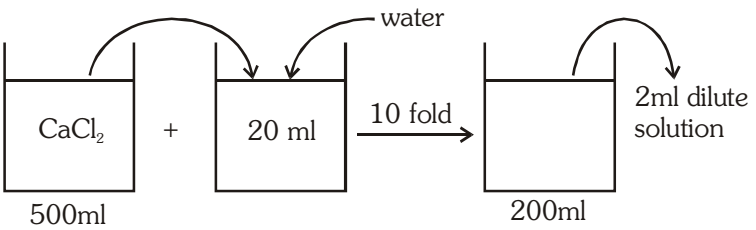
Ans. Na_3PO_4 + aq. $\longrightarrow$ $3Na^+(aq)$ + $PO_4^{-3}(aq)$ [Ionic compound when added to water ionize completely].

50 millimoles (m.m.) 150 mm 50 mm

No. of Na^+ ions = $150 \times 10^{-3} \times N_A$; No. of PO_4^{-3} ions = $50 \times 10^{-3} \times N_A$

Illustration 24. ***1.11g $CaCl_2$ is added to water forming 500 ml of solution. 20 ml of this solution is taken and diluted 10 folds. Find moles of Cl^- ions in 2 ml of diluted solution.***

Ans. $\frac{1.11}{111} = 0.01$ mol $CaCl_2$



Moles of $CaCl_2$ in 20ml solution $= \frac{0.01}{500} \times 20 = \frac{0.01}{25}$

In 200 ml solution moles of $CaCl_2 = \frac{0.01}{25}$ [Note : Dilution does not change moles of solute]

In 2 ml of dilute solution moles of $CaCl_2 = \frac{\frac{0.01}{25}}{200} \times 2 = \frac{0.01}{2500} = 8 \times 10^{-6}$

$\therefore$ moles of $Cl^- = 2 \times 8 \times 10^{-6} = 1.6 \times 10^{-5}$

Illustration 25. ***What volumes of 1M & 2M H_2SO_4 solution are required to produce 2L of 1.75M H_2SO_4 solution?***

Ans. Let XL be vol. of 1M solution.

$\therefore$ (2 – X)L is vol. of 2M solution.

Moles of $H_2SO_4 = 2 \times 1.75 = 1(X) + (2 - X)2$

$3.5 = 4 - X$; $X = 0.5$ L

i.e. 0.5L of 1M & 1.5 L of 2M solution required.

Illustration 26. ***80g NaOH was added to 2L water. Find molality of solution if density of water = 1g/mL***

Ans. $m = \frac{\text{moles of NaOH}}{\text{mass of } H_2O} \times 1000 = \frac{80/40}{2 \times 1000} \times 1000 = \boxed{1\text{ molal}}$

Illustration 27. ***A 100g NaOH solution has 20g NaOH. Find molality.***

Ans. $m = \frac{20/40}{100 - 20} \times 1000$

$= \frac{500}{80} = \boxed{6.25\text{ mol/kg}}$

Illustration 28. ***Find molality of aqueous solution of CH_3COOH whose molarity is 2M and density d = 1.2 g/mL.***

Hint : $\boxed{\mathbf{m = \frac{M}{d - MM_S} \times 1000}}$

where d = density in gL^{-1} , M = Molarity, m = molality, M_S = molar mass of solute.

Ans. $m = \frac{2}{1200 - 2 \times 60} \times 1000 = \boxed{1.85\text{ m}}$

Illustration 29. ***A solution is made by mixing 300 ml 1.5M $Al_2(SO_4)_3$ + 300 ml 2M $CaSO_4$ + 400 ml 3.5M $CaCl_2$***

Find final molarity of (1) SO_4^{-2}, (2) Ca^{2+}, (3) Cl^-. [Assume complete dissociation of these compounds].

Ans. (1) $[SO_4^{-2}]_f = \dfrac{\text{Total moles}}{\text{Total volume}} = \dfrac{300\times1.5\times10^{-3}\times3+300\times2\times10^{-3}}{(300+300+400)\times10^{-3}} = 1.95M$

(2) $[Ca^{+2}]_f = \dfrac{300\times2+400\times3.5}{1000} = 2M$

(3) $[Cl^-]_f = \dfrac{400\times3.5\times2}{1000} = 2.8M$

Illustration 30. ***A solution has 80% $\frac{w}{w}$ NaOH with density $2gL^{-1}$. Find (a) Molarity (b) Molality of solution.***

Ans. Let V_{lit} be vol. of solution

Mass of solute = (d × V) × $\dfrac{\left(\%\frac{w}{w}\right)}{100} = 2 \times V \times \dfrac{80}{100} = 1.6V$

(a) $M = \dfrac{1.6V/40}{V} = \boxed{0.04M}$ (b) $m = \dfrac{1.6V/40}{2V-1.6V} \times 1000 = \boxed{100\,mol\,kg^{-1}}$

Illustration 31. ***4.450 g 100 per cent sulphuric acid was added to 82.20 g water and the density of the solution was found to be 1.029 g/cc at 25°C and 1 atm pressure. Calculate (a) the weight percent, (b) the mole fraction , (c) the mole percent, (d) the molality , (e) the molarity of sulphuric acid in the solution under these conditions.***

Ans. Sulphuric acid = 4.450 g , Water = 82.20 g ⇒ Wt. of solution = 86.65 g

∴ Density of solution = 1.029 g/cc.

(a) Weight percent $= \dfrac{\text{wt. of solute}}{\text{wt. of solution}}\times100 = \dfrac{4.450}{86.65}\times100 = 5.14$

(b) Mole fraction :

Mole of solute $= \dfrac{\text{wt. of solute}}{\text{mol wt. of solute}} = \dfrac{4.45}{98} = 0.0454$

Mole of solvent $= \dfrac{82.20}{18} = 4.566$

Total moles in solution = 0.0454 + 4.566 = 4.6114

Mole fraction of solute $= \frac{0.0454}{4.6114} = 0.0098$

(c) Mole percent $= \frac{\text{moles of solute}}{\text{Total moles in solution}} \times 100$

= mole fraction of solute × 100 = 0.0098 × 100 = 0.98

(d) Molality $= \frac{\text{moles of solute}}{\text{mass of solvent (in gm)}} \times 1000$

$= \frac{0.0454 \times 1000}{82.2} = 0.552$

(e) Molarity $= \frac{\text{moles of solute}}{\text{litre of solution}}$

Volume of solution $= \frac{\text{Mass}}{\text{Density}} = \frac{86.65}{1.029}$ ml

$= \frac{86.65}{1.029 \times 1000}$ litre

Molarity $= \frac{0.0454}{\frac{86.54}{1.029 \times 1000}} = \frac{0.0454 \times 1000 \times 1.029}{86.65} = 0.539$

Illustration 32. ***A solution of KCl has a density of 1.69 g mL^{-1} and is 67% by weight. Find the density of the solution if it is diluted so that the percentage by weight of KCl in the diluted solution is 30%.***

Ans. Let the volume of the KCl solution be 100 mL,

Weight of KCl solution = 100 × 1.69 = 169 g

100 g of solution contains = 67 g of KCl

169 g of solution $= \frac{67}{100} \times 169 = 113.23$g

Lex x mL of H_2O be added.

New volume of solution = (100 + x) mL

New weight of solution = (169 + x) g

(Since x mL of H_2O = x g of H_2O, $d_{H_2O} = 1$)

New percentage of the solution = 30%

$$\% \text{ by weight} = \frac{\text{weight of solute} \times 100}{\text{weight of solution}}$$

$$30 = \frac{113.23}{(169 + x)} \times 100$$

x = 208.43 mL = 208.43 g

$$\text{New density} = \frac{\text{New weight of solution}}{\text{New volume of solution}}$$

$$= \frac{(169 + x)}{(100 + x)}$$

$$\frac{(169 + 208.43)}{(100 + 208.43)} = \frac{377.43}{308.43}$$

$\therefore$ d = 1.224

BEGINNER'S BOX–2

Concentration terms

1*. Calculate the percent of BaO in 29.0 g of a mixture of BaO and CaO which just reacts with 100.8 mL of 6.00 M HCl.

$$BaO + 2HCl \rightarrow BaCl_2 + H_2O$$
$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

2. Calculate the amount of 95% pure Na_2CO_3 required to prepare 5 litre of 0.5 M solution.

3. Calculate the molality of a sulphuric acid solution of specific gravity 1.2 containing 27% H_2SO_4 by weight.

4. Calculate the molarity of the following solutions :
(a) 4g of caustic soda is dissolved in 200 mL of the solution.
(b) 5.3 g of anhydrous sodium carbonate is dissolved in 100 mL of solution.
(c) 0.365 g of pure HCl gas is dissolved in 50 mL of solution.

5. A mixture of ethanol and water contains 54 % water by mass. Calculate the mole fraction of alcohol in this solution.

6. A 15 mL sample of 0.20 M $MgCl_2$ is added to 45 mL of 0.40 M $AlCl_3$, What is the molarity of Cl^-ions in the final solution:
(A) 1.0 M (B) 0.60 M (C) 0.35 M (D) 0.30 M

7. Mole fraction of ethanol in ethanol and water mixture is 0.25. Hence percentage concentration of ethanol by weight of mixture is :
(A) 25% (B) 75% (C) 46% (D) 54%

8. How many moles of Na^+ ions are in 20 mL of 0.40 M Na_3PO_4 :
(A) 0.0080 (B) 0.024 (C) 0.050 (D) 0.20

9*. The molality of a 1 L solution with x % H_2SO_4 is 9. The weight of solvent present in the solution is 910 grams. The value of x is :
(A) 90 (B) 80.3 (C) 30.38 (D) 46.87

10. The molarity of the solution containing 2.8% mass-volume solution of KOH/(Given atomic mass of K = 39) is :
(A) 0.1 M (B) 0.5 M (C) 0.2 M (D) 1 M

11. 500 mL of a glucose solution contains 6.02×10^{22} molecules. The concentration of the solution is :
(A) 0.1 M (B) 1.0 M (C) 0.2 M (D) 2.0 M

12. A solution containing 12.0% sodium hydroxide by mass has a density of 1.131 g/mL. What volume of this solution contains 5.00 mol of NaOH :
(A) 0.0240 L (B) 1.67 L (C) 1.47 L (D) 1.00 L

13. An aqueous solution of concentrated hydrobromic acid contains 48% HBr by mass. If the density of the solution is 1.50 g / mL, what is its concentration :
(A) 11.4 mol/L (B) 8.9 mol/L (C) 5.9 mol/L (D) 18.5 mol/L

ANSWERS

BEGINNER'S BOX-1

1. (i) 51.66 g (ii) 37.31g ***2.*** 76.12% ***3.***219.09 kg
4. (B) ***5.***(B) ***6.***(B) ***7.***(D) ***8.***(C) ***9.***(D)
10.(C)

BEGINNER'S BOX-2

1. 65..65% ***2.***278.94 g ***3.*** 3.8 ***4.***(a) 0.5M, (b) 0.5M, (c) 0.2M
5.0.25 ***6.***(A) ***7.***(C) ***8.***(B) ***9.***(D) ***10.***(B)
11.(C) ***12.***(C) ***13.***(B)

EXERCISE – 1 MCQ (SINGLE CHOICE CORRECT)

1. 0.250 g of an element M, reacts with excess fluorine to produce 0.547 g of the hexafluoride MF_6. What is the element: [Cr = 52, Mo = 96, S = 32, Te = 127.6]
(A) Cr (B) Mo (C) S (D) Te

2. A 1000 gram sample of NaOH contains 3 moles of O atoms, what is the % purity of NaOH :
(A) 14% (B) 100% (C) 12% (D) 24%

3. Out of Molarity (M), Molality (m), Formality (F) and Mole fraction (x), those independent of temperature are:
(A) M,m (B) F,x (C) m,x (D) M,x

4. Mole fraction of A in H_2O is 0.2. The molality of A in H_2O is :
(A) 13.8 (B) 15.5 (C) 14.5 (D) 16.8

5. The molality of a sulphuric acid solution is 0.2 mol/kg. Calculate the total weight of the solution :
(A) 1000 g (B) 1098.6 g (C) 980.4 g (D) 1019.6 g

6. What volume of a 0.8 M solution contains 100 millimoles of the solute :
(A) 100 mL (B) 125 mL (C) 500 mL (D) 62.5 mL

7. What is the molality m, of methanol in a solution prepared by dissolving 160 g of methanol, CH_3OH, in 200.0 g of water :
(A) 1.0 m (B) 5.0 m (C) 10.0 m (D) 25.0 m

8. If 1 g of HCl and 1 g of MnO_2 heated together the maximum weight of Cl_2 gas evolved will be :
[$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$] :
(A) 2 g (B) 0.975 g (C) 0.486 g (D) 0.972 g

9. Molarity of H_2SO_4 is 18 M. Its density is 1.8 g/cm^3, hence molality is :
(A) 18 (B) 100 (C) 36(D) 500

10. If 1.5 moles of oxygen combine with Al to form Al_2O_3, the weight of Al used in the reaction is (Al = 27):
(A) 27 g (B) 54 g (C) 40.5 g (D) 81 g

11. The density of 2.45 M aqueous methanol (CH_3OH) is 0.976 g/mL. What is the molality of the solution (CH_3OH = 32) ?
(A) 27.3 m (B) 0.273 m (C) 7.23 m (D) 2.73 m

12. Equal volumes of 10% (v/v) of HCl is mixed with 10% (v/v) NaOH solution. If density of pure NaOH is 1.5 times that of pure HCl then the resultant solution be ?
(A) basic (B) neutral (C) acidic (D) can't be predicted.

13. How many litres of oxygen at 1atm & 273K will be required to burn completely 2.2 g of propane (C_3H_8)
(A) 11.2 L (B) 22.4 L (C) 5.6 L (D) 44.8 L

14. Volume of CO_2 obtained at STP by the complete decomposition of 9.85 g $BaCO_3$ is
(At. wt of Ba = 137)
(A) 2.24 lit (B) 1.12 lit (C) 1.135 lit (D) 2.27 lit

15. The drain cleaner, ***Drainex*** contains small bits of aluminium (At. Wt. = 27) which reacts with caustic soda to produce dihydrogen. What is the volume (in ml) of dihydrogen at 27°C and 1.013 bar that is produced when 0.27 gm of aluminium reacts :
$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$
(A) 0.3694 (B) 369.4 (C) 246.3 (D) 540.4

16. Volume of O_2 obtained at 2 atm & 546K, by the complete decomposition of 8.5 g $NaNO_3$ is

$2NaNO_3 \rightarrow 2NaNO_2 + O_2$

(A) 2.24 lit (B) 1.12 lit (C) 0.84 lit (D) 0.56 lit

17. Maximum mass of sucrose $C_{12}H_{22}O_{11}$ produced by mixing 84 gm of carbon, 12 gm of hydrogen and 56 lit. O_2 at 1 atm & 273 K according to given reaction, is

$C(s) + H_2(g) + O_2(g)$ ¾® $C_{12}H_{22}O_{11}(s)$

(A) 138.5 (B) 155.5 (C) 172.5 (D) 199.5

18. The mass of P_4O_{10} produced if 440 gm of P_4S_3 is mixed with 384 gm of O_2 is

$P_4S_3 + O_2$ ¾® $P_4O_{10} + SO_2$

(A) 568 gm (B) 426 gm (C) 284 gm (D) 396 gm

19. The mass of Mg_3N_2 produced if 48 gm of Mg metal is reacted with 34 gm NH_3 gas is

$$Mg + NH_3 \longrightarrow Mg_3N_2 + H_2$$

(A) $\frac{200}{3}$ gm (B) $\frac{100}{3}$ gm (C) $\frac{400}{3}$ gm (D) $\frac{150}{3}$ gm

20. An ideal gaseous mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 28 litre at 1atm, 0°C. The mixture reacts completely with 128 gm O_2 to produce CO_2 and H_2O. Mole fraction of C_2H_6 in the mixture is–

(A) 0.6 (B) 0.4 (C) 0.5 (D) 0.8

21. 280 g of a mixture containing CH_4 and C_2H_6 in 5 : 2 molar ratio is burnt in presence of excess of oxygen. Calculate total moles of CO_2 produced.

(A) 9 (B) 18 (C) 7 (D) 12

22. Mixture of $MgCO_3$ & $NaHCO_3$ on strong heating gives CO_2 & H_2O in 3 : 1 mole ratio. The weight % of $NaHCO_3$ present in the mixture is:

(A) 30% (B) 80% (C) 40% (D) 50%

23. One commercial system removes SO_2 emission from smoke at 95°C by the following set of reactions-

$SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(g)$

$SO_2Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$

$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$

Assuming the process to be 95% efficient. How many moles of $CaSO_4$ may be produced from 128g SO_2. [Ca = 40, S- 32, O-16]

(A) 1.9 moles (B) 2 mol (C) 3.8 mol (D) 0.95 mol

24. Equal masses of $KClO_3$ undergoes different reaction in two different container :

(i) $2KClO_3 \rightarrow 2KCl + 3O_2$

(ii) $4KClO_3 \rightarrow KCl + 3KClO_4$

Mass ratio of the KCl produced in respective reaction is x : 1. Value of '***x***' will be.

(A) 4 (B) 2 (C) 0.25 (D) 3

25. If 18 g of glucose is present in 1000 g of solvent, the solution is said to be :

(A) 1 molar (B) 0.1 molar (C) 0.5 molar (D) 0.1 molal

26. A molal solution is one that contains one mole of a solute in

(A) 1000 g of the solvent (B) one litre of the solution

(C) one litre of the solvent (D) 22.4 litres of the solution

27. The mole fraction of oxygen in a mixture of 7g of nitrogen and 8g of oxygen is :

(A) $\frac{8}{15}$ (B) 0.5 (C) 0.25 (D) 1.0

28. The molarity of 98% by wt. H_2SO_4 (d = 1.8 g/ml) is

(A) 6 M (B) 18 M (C) 10 M (D) 4 M

29. For preparing 0.1 M solution of H_2SO_4 in one litre, we need H_2SO_4 :

(A) 0.98 g (B) 4.9 g (C) 49.0 g (D) 9.8 g

30. 1000 g aqueous solution of $Ca(NO_3)_2$ contains 10 g of calcium nitrate. Concentration of the solution is :

(A) 10 ppm (B) 100 ppm (C) 1000 ppm (D) 10,000 ppm

31. How much volume of 3.0 M H_2SO_4 is required for the preparation of 1.0 litre of 1.0 M solution?

(A) 300 ml (B) 320 ml (C) 333.3 ml (D) 350.0 ml

32. Equal weight of NaCl and KCl are dissolved separately in equal volumes of solutions. Molarity of the solutions will be –

(A) Equal (B) Greater for NaCl (C) Greater for KCl (D) Uncomparable.

33. How much water should be added to 200 cc of semimolar solution of NaOH to make it exactly decimolar :-

(A) 1000 cc (B) 400 cc (C) 800 cc (D) 600 cc

34. 100 ml of 0.3 M HCl solution is mixed with 200 ml of 0.3 M H_2SO_4 solution. What is the molarity of H^+ in resultant solution ?

(A) 0.9 (B) 0.6 (C) 0.4 (D) 0.5

35. Molality of 20% (w/w) aq.glucose solution is :

(A) $\frac{25}{18}$ m (B) $\frac{10}{9}$ m (C) $\frac{25}{9}$ m (D) $\frac{5}{18}$ m

36. Molarity of liquid HCl, if density is 1.17 g/cc. :

(A) 36.5 M (B) 18.25 M (C) 32.05 M (D) 42.10 M

37. The molarity of a solution made by mixing 50 ml of conc. H_2SO_4 (18 M) with 50 ml of water, is:

(A) 36 M (B) 18 M (C) 9 M (D) 6M

38. Molarity and Molality of a solute (M. wt = 50) in aqueous solution is 9 and 18 respectively. What is the density of solution.

(A) 1 g/cc (B) 0.95 g/cc (C) 1.05 g/cc (D) 0.662 g/cc

39. The relationship between mole fraction (X_A) of the solute & molality 'm' of its solution in ammonia would be

(A) $\frac{55.56(X_A)}{1-X_A} = m$ (B) $\frac{58.82(X_A)}{1-X_A} = m$

(C) $\frac{58.82(1-X_A)}{X_A} = m$ (D) $\frac{55.56(1-X_A)}{X_A} = m$

40. 3.0 molal NaOH solution has a density of 1.12 g/mL. The molarity of the solution is-

(A) 2.97 (B) 3 (C) 3.05 (D) 3.5

EXERCISE – 2 MCQ (ONE OR MORE CHOICE CORRECT)

ONE OR MORE THAN ONE CORRECT:

1. 12 g of Mg was burnt in a closed vessel containing 32 g oxygen. Which of the following is /are correct.
(A) 2 gm of Mg will be left unburnt.
(B) 0.75 gm-molecule of O_2 will be left unreacted.
(C) 20 gm of MgO will be formed.
(D) The mixture at the end will weight 44 g.

2. 50 gm of $CaCO_3$ is allowed to react with 68.6 gm of H_3PO_4 then select the correct option(s)-

$$3CaCO_3 + 2H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 3H_2O + 3CO_2$$

(A) 51.67 gm salt is formed
(B) Amount of unreacted reagent = 35.93 gm
(C) $n_{CO_2} = 0.5$ moles
(D) 0.7 mole CO_2 is evolved

3. The molar concentration of HCl (aq.) is 10^{-5} M. Which of the following statements are correct.
($d_{solution}$ = 1 gm /cc)
(A) The mole fraction of HCl $\cong 1.8 \times 10^{-7}$
(B) The concentration of HCl in ppm is 3.65 ppm
(C) The molality of HCl solution is approximately 10^{-5} m
(D) The (w/v)% of solution is 3.65×10^{-5} %

4. Solutions containing 23 g HCOOH is/are :
(A) 46 g of 70% $\left(\frac{w}{v}\right)$ HCOOH ($d_{solution}$ = 1.40 g/mL)
(B) 50 g of 10 M HCOOH ($d_{solution}$ = 1 g/mL)
(C) 50 g of 25% $\left(\frac{w}{w}\right)$ HCOOH
(D) 46 g of 5 M HCOOH ($d_{solution}$ = 1 g/mL)

5. Solution(s) containing 40 gm NaOH is/are
(A) 50 gm of 80% (w/w) NaOH
(B) 50 gm of 80% (w/v) NaOH [$d_{soln.}$ = 1.2 gm/ml]
(C) 50 gm of 20 M NaOH [$d_{soln.}$ = 1 gm/ml]
(D) 50 gm of 5m NaOH

6. The ***incorrect*** statement(s) regarding 2M $MgCl_2$ aqueous solution is/are ($d_{solution}$ = 1.09 gm/ml)
(A) Molality of Cl^- is ***4.44 m***
(B) Mole fraction of $MgCl_2$ is exactly ***0.035***
(C) The conc. of $MgCl_2$ is ***19% w/v***
(D) The conc. of $MgCl_2$ is ***19×10^4 ppm***

7. Solution(s) containing 30 gm CH_3COOH is / are
(A) 50 gm of 70% (w/v) CH_3COOH [$d_{sol.}$ = 1.4 gm/ml]
(B) 50 gm of 10 M CH_3COOH [$d_{sol.}$ = 1 gm / ml]
(C) 50 gm of 60% (w/w) CH_3COOH
(D) 50 gm of 10 m CH_3COOH

8. $A + B \rightarrow A_3B_2$ (unbalanced)
$A_3B_2 + C \rightarrow A_3B_2C_2$ (unbalanced)
Above two reactions are carried out by taking 3 moles each of A and B and one mole of C. Then which option is/are correct ?
(A) 1 mole of $A_3B_2C_2$ is formed.
(B) 1/2 mole of $A_3B_2C_2$ is formed.
(C) 1/2 mole of A_3B_2 is formed.
(D) 1/2 mole of A_3B_2 is left finally.

9. If 27 g of Carbon is mixed with 88 g of Oxygen and is allowed to burn to produce CO_2 , then :
(A) Oxygen is the limiting reagent.
(B) Volume of CO_2 gas produced at NTP is 50.4 L.
(C) C and O combine in mass ratio 3 : 8.
(D) Volume of unreacted O_2 at STP is 11.2 L.

10. 100 ml of 0.06 M $Ca(NO_3)_2$ is added to 50 ml of 0.06 M $Na_2C_2O_4$. Select the correct option (s) :
(A) After the reaction is complete 0.003 moles of calcium oxalate will get precipitated.
(B) After the reaction is complete 0.003 M of Ca^{2+} will remain in excess.
(C) $Na_2C_2O_4$ is limiting reagent.
(D) $Ca(NO_3)_2$ is excess reagent.

11. If 100 ml of 1M H_2SO_4 solution is mixed with 100 ml of 98%(w/w) H_2SO_4 solution (d = 0.1 gm/ml) then:
(A) concentration of solution remains same
(B) volume of solution become 200 ml.
(C) mass of H_2SO_4 in the solution is 98 gm.
(D) mass of H_2SO_4 in the solution is 19.6 gm.

12*. A sample of a mixture of $CaCl_2$ and NaCl weighing 4.44 gm was treated to precipitate all the Ca as $CaCO_3$, which was then heated and quantitatively converted to 1.12g of CaO. Calculate the % of $CaCl_2$ in the mixture. (At . wt. : Ca = 40, Na = 23, Cl = 35.5)
(A) Mixture contains 50% NaCl.
(B) Mixture contains 60% $CaCl_2$.
(C) Mass of $CaCl_2$ is 2.22 g.
(D) Mass of $CaCl_2$ is 1.11 g.

13. 3 moles of the gas C_2H_6 is mixed with 60 gm of this gas and 2.4×10^{24} molecules of the gas is removed. The left over gas is combusted in the presence of excess oxygen, then :
($N_A = 6 \times 10^{23}$) (Density of water = 1gm/ml)
(A) 2 Moles of C_2H_6 left for combustion.
(B) Volume of CO_2 at S.T.P. produced after combustion 44.8 litre.
(C) Volume of liquid water produced is 54 ml.
(D) None of these

Match the Column

14.

	Column-I		***Column-II (mass of product)***
(A)	$2H_2 + O_2 \longrightarrow 2H_2O$ 1g 1g	(p)	1.028 g
(B)	$3H_2 + N_2 \longrightarrow 2NH_3$ 1g 1g	(q)	1.333 g
(C)	$H_2 + Cl_2 \longrightarrow 2HCl$ 1g 1g	(r)	1.125 g
(D)	$2H_2 + C \longrightarrow CH_4$ 1g 1g	(s)	1.214 g

15.

	Column-I (Concentration of aqueous solution)		***Column-II (Density of given solutions is 1.2 g/ml)***
(A)	2M NaOH solution (P)		16gm solute in 240gm solution
(B)	$8\%\left(\frac{w}{V}\right)$ KOH solution	(Q)	60gm solute in 240 gm solution
(C)	$25\%\left(\frac{w}{W}\right)$ $CaCO_3$ solution	(R)	8gm solute in 100 ml solution
(D)	$X_{C_3H_7OH} = \frac{1}{11}$	(S)	30 gm solute in 100 ml solution
		(T)	1 mole solute in 400 gm solution

Comprehension Based Questions

Comprehension-1

NaBr, used to produce AgBr for use in photography can be self prepared as follows :

$Fe + Br_2 \longrightarrow FeBr_2$ .....(i)

$FeBr_2 + Br_2 \longrightarrow Fe_3Br_8$ .....(ii) (not balanced)

$Fe_3Br_8 + Na_2CO_3 \longrightarrow NaBr + CO_2 + Fe_3O_4$ .....(iii) (not balanced)

How much Fe in kg is consumed to produce 2.06×10^3 kg NaBr .....(iv)

16. Mass of iron required to produce 2.06×10^3 kg NaBr

(A) 420 g (B) 420 kg (C) 4.2×10^5 kg (D) 4.2×10^8 g

17. If the yield of (ii) is 60% & (iii) reaction is 70% then mass of iron required to produce 2.06×10^3 kg NaBr.

(A) 10^5 kg (B) 10^5 g (C) 10^3 kg (D) none

18. If yield of (iii) reaction is 90% then mole of CO_2 formed when 2.06×10^3 g NaBr is formed.

(A) 20 (B) 10 (C) 40 (D) none

Comprehension 2:

2 litre of 9.8 % w/w H_2SO_4 (d = 1.5 gm/ml) solution is mixed with 3 litre of 1 M KOH solution.

19. The number of moles H_2SO_4 added are

(A) 1 (B) 2 (C) 3 (D) 0.5

20. The concentration of H^+ if solution is acidic or concentration of OH^- if solution is basic in the final solution is

(A) 0 (B) $\frac{3}{10}$ (C) $\frac{3}{5}$ (D) $\frac{2}{5}$

EXERCISE – 3 SUBJECTIVE

1. Calculate the molarity of the following solutions :

(a) 4g of caustic soda is dissolved in 200 mL of the solution.

(b) 5.3 g of anhydrous sodium carbonate is dissolved in 100 mL of solution.

(c) 0.365 g of pure HCl gas is dissolved in 50 mL of solution.

2. How many gm of HCl is needed for complete reaction with 43.5 gm MnO_2 ? (Mn = 55)

$$HCl + MnO_2 \rightarrow MnCl_2 + H_2O + Cl_2$$

3. Carbon reacts with chlorine to form CCl_4. 36 gm of carbon was mixed with 142 g of Cl_2. Calculate mass of CCl_4 produced and the remaining mass of reactant.

4. Potassium superoxide, KO_2, is used in rebreathing gas masks to generate oxygen :

$$KO_2(s) + H_2O(l) \rightarrow KOH\ (s) + O_2\ (g)$$

If a reaction vessel contains 0.158 mol KO_2 and 0.10 mol H_2O, how many moles of O_2 can be produced ?

5. Sulphuric acid is produced when sulphur dioxide reacts with oxygen and water in the presence of a catalyst : $2SO_2(g) + O_2\ (g) + 2\ H_2O(l) \rightarrow 2\ H_2SO_4$. If 5.6 mol of SO_2 reacts with 4.8 mol of O_2 and a large excess of water, what is the maximum number of moles of H_2SO_4 that can be obtained ?

6. Determine the percentage composition (by mass) of a mixture of anhydrous sodium carbonate and sodium bicarbonate from the following data:

wt. of the mixture taken = 2g Loss in weight on heating = 0.124 gm.

7. Calculate the percent loss in weight after complete decomposition of a pure sample of potassium chlorate.

$$KClO_3(s) \rightarrow KCl(s) + O_2(g)$$

8. A sample of calcium carbonate is 80% pure, 25 gm of this sample is treated with excess of HCl.How much volume of CO_2 will be obtained at 1 atm & 273 K?

9. $Br_2(l)$ reacts with $Cl_2(g)$ to form BrCl and $BrCl_3$, simultaneously. How many moles of $Cl_2(g)$ reacts completely with 3 moles of $Br_2(l)$ to form BrCl and $BrCl_3$ in 5 : 1 molar ratio.

10. Sulphur trioxide may be prepared by the following two reactions :

$$S_8 + 8O_2(g) \rightarrow 8SO_2(g)$$

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

How many grams of SO_3 will be produced from 1 mol of S_8?

11. A 7.0 M solution of KOH in water contains 28% by mass of KOH. What is density of solutionin gm/ml ?

12. 1200gm aqueous solution contains 200gm calcium bromide ($CaBr_2$). Calculate molality of solution.

13. Find out the volume of 98% w/w H_2SO_4 (density = 1.8 gm/ ml), must be diluted to prepare 12.6 litres of 2.0 M sulphuric acid solution.

14. 500 ml of 2 M NaCl solution was mixed with 200 ml of 2 M NaCl solution. Calculate the molarity of NaCl in final solution.

15. Calculate the amount of the water "in ml"which must be added to a given solution of concentration of 40 mg silver nitrate per ml, to yield a solution of concentration of 16 mg silver nitrate per ml ?

16. 100 mL, 3%(w/v) NaOH solution is mixed with 100 ml, 9%(w/v) NaOH solution. The molarity of final solution is-

17. A chemist wants to prepare diborane by the reaction

$6\ LiH + 8\ BF_3 \longrightarrow 6\ Li\ BF_4 + B_2H_6$

If the starts with 2.0 moles each of LiH & BF_3. How many moles B_2H_6 can be prepared.

18. One gram of an alloy of aluminium and magnesium when heated with excess of dil. HCl forms magnesium chloride, aluminium chloride and hydrogen. The evolved hydrogen collected over mercury at 0°C has a volume of 1.2 litres at 0.92 atm pressure. Calculate the composition of the alloy.

19*. A 10 g sample of a mixture of calcium chloride and sodium chloride is treated with Na_2CO_3 to precipitate calcium as calcium carbonate. This $CaCO_3$ is heated to convert all the calcium to CaO and the final mass of CaO is 1.62 g. Calculate % by mass of NaCl in the original mixture.

20. By the reaction of carbon and oxygen, a mixture of CO and CO_2 is obtained. What is the composition of the mixture by mass obtained when 20 grams of O_2 reacts with 12 grams of carbon ?

EXERCISE – 4 RECAP OF AIEEE/JEE (MAIN)

1. In the reaction **[AIEEE-2007]**
$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 6Cl^{-}_{(aq)} + 3H_2(g)$.
(A) 6L $HCl_{(aq)}$ is consumed for every 3L $H_2(g)$ produced
(B) 33.6 L $H_{2(g)}$ is produced regardless of temperature and pressure for every mole Al that reacts
(C) 67.2 L $H_{2(g)}$ at STP is produced for every mole Al that reacts
(D) 11.2 L $H_{2(g)}$ at STP is produced for every mole $HCl_{(aq)}$ consumed

2. Which one of the following constitutes a group of the isoelectronic species? **[AIEEE-2008]**
(A) C_2^{2-}, O_2^-, CO, NO (B) $NO^+, C_2^{2-}, CN^-, N_2$ (C) $CN^-, N_2, O_2^{2-}, C_2^{2-}$ (D) N_2, O_2^-, NO^+, CO

3. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH, is supplied. What is the mole fraction of methyl alcohol in the solution ? **[AIEEE-2011]**
(A) 0.086 (B) 0.050 (C) 0.100 (D) 0.190

4. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is :- **[AIEEE-2012]**
(A) 2.05 M (B) 0.50 M (C) 1.78 M (D) 1.02 M

5. The concentrated sulphuric acid that is peddled commercially is 95% H_2SO_4 by weight. If the density of this commerical acid is 1.834 g cm^{-3}, the molarity of this solution is :- **[JEE-(Main)-2012]**
(A) 17.8 M (B) 15.7 M (C) 10.5 M (D) 12.0 M

6. 10 mL of 2(M) NaOH solution is added to 200 mL of 0.5 (M) of NaOH solution. What is the final concentration ? **[JEE(Main-online)-2013]**
(A) 0.57 M (B) 5.7 M (C) 11.4 M (D) 1.14 M

7. The density of 3M solution of sodium chloride is 1.252 g mL^{-1}. The molality of the solution will be (molar mass, NaCl = 58.5 g mol^{-1}) **[JEE(Main-online)-2013]**
(A) 2.18 m (B) 3.00 m (C) 2.60 m (D) 2.79 m

8. The amount of $BaS0_4$ formed upon mixing 100 mL of 20.8% $BaCl_2$ solution with 50 mL of 9.8% H_2SO_4 solution will be : **[JEE(Main-online)-2014]**
(Ba = l37, Cl = 35.5, S=32, H = l and O = 16)
(A) 33.2 g (B) 11.65 g (C) 23.3 g (D) 30.6 g

9. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralizaton. The percentage of nitrogen in the compound is : **[JEE(Main-online)-2014]**
(A) 3% (B) 5% (C) 6% (D) 10%

10. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is : (Atomic mass Ag = 108; Br = 80) **[JEE(Main)-2015]**
(A) 48 (B) 60 (C) 24 (D) 36

11. 1 gram of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2. the molar mass of M_2CO_3 in g mol^{-1} is :- **[JEE(Main)-2017]**
(A) 1186 (B) 84.3 (C) 118.6 (D) 11.86

12. The ratio of mass percent of C and H of an organic compound ($C_XH_YO_Z$) is 6 : 1. If one molecule of the above compound ($C_XH_YO_Z$) contains half as much oxygen as required to burn one molecule of compound C_XH_Y completely to CO_2 and H_2O. The empirical formula of compound $C_XH_YO_Z$ is ***[JEE(Main)-2018 (offline)]***

(A) C_2H_4O (B) $C_3H_4O_2$ (C) $C_2H_4O_3$ (D) $C_3H_6O_3$

13. For per gram of reactant, the maximum quantity of N_2 gas is produced in which of the following thermal decomposition reactions ? ***[JEE(Main)-2018 (online)]***

(Given : Atomic wt. – Cr = 52u, Ba = 137u)

(A) $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$ (B) $Ba(N_3)_2(s) \rightarrow Ba(s) + 3N_2(g)$

(C) $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + 4H_2O(g)$ (D) $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

14. An unknown chlorohydrocarbon has 3.55% of chlorine. If each molecule of the hydrocarbon has one chlorine atom only; chlorine atoms present in 1 g of chlorohydrocarbon are :

(Atomic wt. of Cl = 35.5 u; Avogadro constant = 6.023×10^{23} mol^{-1}) ***[JEE(Main)-2018 (online)]***

(A) 6.023×10^{21} (B) 6.023×10^{23} (C) 6.023×10^{20} (D) 6.023×10^{9}

15. A solution of sodium sulfate contains 92 g of Na^+ ions per kilogram of water. The molality of Na^+ ions in that solution in mol kg^{-1} is : ***[JEE(Main)-2019]***

(A) 16 (B) 8 (C) 4 (D) 12

16. The amount of sugar ($C_{12}H_{22}O_n$) required to prepare 2 L of its 0.1 M aqueous solution is :

[JEE-MAIN-10-01-2019-Evening]

(A) 68.4 g (B) 17.1 g (C) 34.2 g (4)136.8 g

17. A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 ml of CO_2 at T = 298.15 K and p = 1 bar. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet ? [Molar mass of $NaHCO_3$ = 84 g moH]

[JEE-MAIN-11-01-2019-Morning]

(A) 16.8 (B) 8.4 (C) 0.84 (D) 33.6

18. 8g of NaOH is dissolved in 18g of H_20. Mole fraction of NaOH in solution and molality (in mol kg^{-1}) of the solutions respectively are: ***[JEE-MAIN-12-01-2019-Evening]***

(A) 0.167, 11.11 (B) 0.2, 22.20 (C) 0.2, 11.11 (D) 0.167,22.20

19. For the following reaction, the mass of water produced from 445 g of $C_{57}H_{110}O_6$ is :

$2C_{57}H_{110}O_6(s) + 163O_2(g) \rightarrow 114CO_2(g) + 110\ H_2O(A)$ ***[JEE-MAIN-09-01-2019-Evening]***

(A) 495 g (B) 490 g (C) 890 g (D) 445 g

20. 0.27 g of a long chain fatty acid was dissolved in 100 cm^3 of hexane. 10 mL of this solution was added dropwise to the surface of water in a round watch glass. Hexane evaporates and a monolayer is formed. The distance from edge to centre of the watch glass is 10 cm. What is the height of the monolayer?

[Density of fatty acid = 0.9 g cm^{-3}, π = 3]

(A) 10^{-8} m (B) 10^{-6} m (C) 10^{-4} m (D) 10^{-2} m

21. For a reaction,
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$;
identify dihydrogen (H_2) as a limiting reagent in the following reaction mixtures.
(A) 14g of N_2 + 4g of H_2
(B) 28g of N_2 + 6g of H_2
(C) 56g of N_2 + 10g of H_2
(D) 35g of N_2 + 8g of H_2

22. At 300 K and 1 atmospheric pressure, 10 mL of a hydrocarbon required 55 mL of O_2 for complete combustion and 40 mL of CO_2 is formed. The formula of the hydrocarbon is :
(A) C_4H_8
(B) C_4H_7Cl
(C) C_4H_{10}
(D) C_4H_6

23. The minimum amount of $O_2(g)$ consumed per gram of reactant is for the reaction :
(Given atomic mass : Fe = 56, O = 16, Mg = 24, P = 31, C = 12, H = 1)
(A) $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$
(B) $P_4(s) + 5\ O_2(g) \rightarrow P_4O_{10}(s)$
(C) $4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ FeO_3(s)$
(D) $2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$

24. 25 g of an unknown hydrocarbon upon burning produces 88 g of CO_2 and 9 g of H_2O. This unknown hydrocarbon contains.
(A) 20g of carbon and 5 g of hydrogen
(B) 24g of carbon and 1 g of hydrogen
(C) 18g of carbon and 7 g of hydrogen
(D) 22g of carbon and 3 g of hydrogen

EXERCISE – 5 RECAP OF IIT-JEE/JEE (ADVANCED)

1. Calculate the molarity of pure water using its density to be 1000 kg m^{-3}. **[JEE'2003]**

2. Calculate the amount of Calcium oxide required when it reacts with 852 g of P_4O_{10}. ***[JEE 2005]***

$6CaO + P_4O_{10} \longrightarrow 2\ Ca_3(PO_4)_2$ [Ca = 40, P = 31]

3. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is

(A) 1.78 M (B) 2.00 M (C) 2.05 M (D) 2.22 M ***[JEE 2011]***

4*. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g ml^{-1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is ***[JEE 2014]***

5. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $NiCl_2.6H_2O$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952g of $NiCl_2.6H_2O$ are used in the preparation, the combined weight (in grams) of gypsum and the nickel-ammonia coordination compound thus produced is___. ***[JEE 2018]***

(Atomic weights in g mol^{-1}: H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59)

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4.2H_2O + 2NH_3$$

$$NiCl_2 \cdot 6H_2O + 6NH_3 \rightarrow [Ni(NH_3)_6]Cl_2 + 6H_2O$$

6. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnance such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of O_2 consumed is _____ .

(Atomic weights in g mol^{-1} : O = 16, S = 32, Pb = 207) ***[JEE 2018]***

$PbS + O_2 \longrightarrow Pb + SO_2$

7. The mole fraction of urea in an aqueous urea solution containing 900 g of water is 0.05. If the density of the solution is 1.2 g cm^{-3}, the molarity of urea solution is ___

(Given data : Molar masses of urea and water are 60 g mol^{-1} and 18 g mol^{-1}, respectively)

[JEE 2019]

ANSWERS

EXERCISE-1

Que.	22	23	24	25	26	27	28	29	30	10	11	12	13	14	15
Ans.	B	C	C	A	D	B	D	C	D	B	D	A	C	C	B
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	B	B	N	A	B	B	D	A	A	D	A	B	B	D	D
Que.	31	32	33	34	35	36	37	38	39	40					
Ans.	C	B	C	D	A	C	C	B	B	B					

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13
Ans.	BCD	ABC	ACD	AB	AC	BD	BC	BD	BCD	ACD	ABD	AC	BC

- ***Match the Column***

  14. (A) $\rightarrow$ r ; (B) $\rightarrow$ s ; (C) $\rightarrow$ p ; (D) $\rightarrow$ q

  15. (A) $\rightarrow$ P, R ; (B) $\rightarrow$ P, R ; (C) $\rightarrow$ Q, S, T ; (D) $\rightarrow$ S, Q

- ***Comprehension Based Questions***

  Comprehension 1 : **16.** (B) **17.** (C) **18.** (B)

  Comprehension 1 : **19.** (C) **20.** (C)

EXERCISE-3

1. (a) 0.5 M, (b) 0.5 M, (c) 0.2 M **2.** 73 gm **3.** 154 gm, 24 gm

4. 0.1185 **5.** 5.6 **6.** $NaHCO_3$ = 16.8 %; Na_2CO_3 = 83.2 %

7. 39.18% **8.** 4.48 litre **9.** 4 **10.** 640

11. 1.4 **12.** 1 **13.** 1.4 litre **14.** 2 M

15. 1.5 ml **16.** 1.5 **17.** 0.250 **18.** Al = 0.546 gm Mg = 0.454 g

19*. 67.9% **20.** CO : CO_2 = 21 : 11

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	D	B	A	A	A	A	D	B	D	C	B	C	D	C	D
Que.	16	17	18	19	20	21	22	23	24						
Ans.	A	A	A	A	B	C	D	C	B						

EXERCISE-5

1. 55.5 mol L^{-1} **2.** 1008 g **3.** C **4.** (8)

5. 2992 **6.** 6.47 **7.** (2.80 or 3.05)

IMPORTANT NOTES

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IMPORTANT NOTES

CHEMICAL BONDING

Recap of Early Classes

In the previous chapters, we studied about the electronic configuration & how it affects properties of elements. Some of these properties give an idea of why elements combine. The chapter aims to introduce various such theories required for bond formation. The theory of chemical bond is not perfect. Scientists are constantly discovering new compounds, orderly arranging the facts about them, trying to explain with the existing knowledge, organising to modify the earlier views or evolve theories for explaining the newly observed facts.

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- 1.2 Cause of chemical combination

2.0 CLASSIFICATION OF BONDS

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EXERCISE-1

EXERCISE-2

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CONTENTS

THEORY

1. Comprehensive theory covering all concepts & subtopics for ***excellence*** in both ***school level*** as well as ***competitive exams***.

   Symbols used for categorization

   SL ⇒ Topics required for ***school level*** preparations.

   AL ⇒ Topics required for ***Advance level*** preparations useful for competitive exams.

2. ***Golden Key Points :*** Important points/formulaes or concepts summarized at the end to have a ***quick revision*** of the topic.

3. ***Illustrations : Subtopic based solved questions*** to get comfortable in problem solving. [Students should go through these after the topic is dealt]

4. ***Solved examples :*** A collection of ***miscellaneous solved question*** based on different concepts from the chapter at the end to be referred before exercise solving.

5. ***Beginner Boxes :*** Collection of ***elementary sub–topic*** based questions to be attempted on completion of each subtopic.

EXERCISE

EXERCISE-1
EXERCISE-2
EXERCISE-3
EXERCISE-4
EXERCISE-5

CHEMICAL BONDING

1.0 INTRODUCTION

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.

1.1 Chemical Bond

SL AL

(a) A force that acts between two or more atoms to hold them together as a stable molecule.

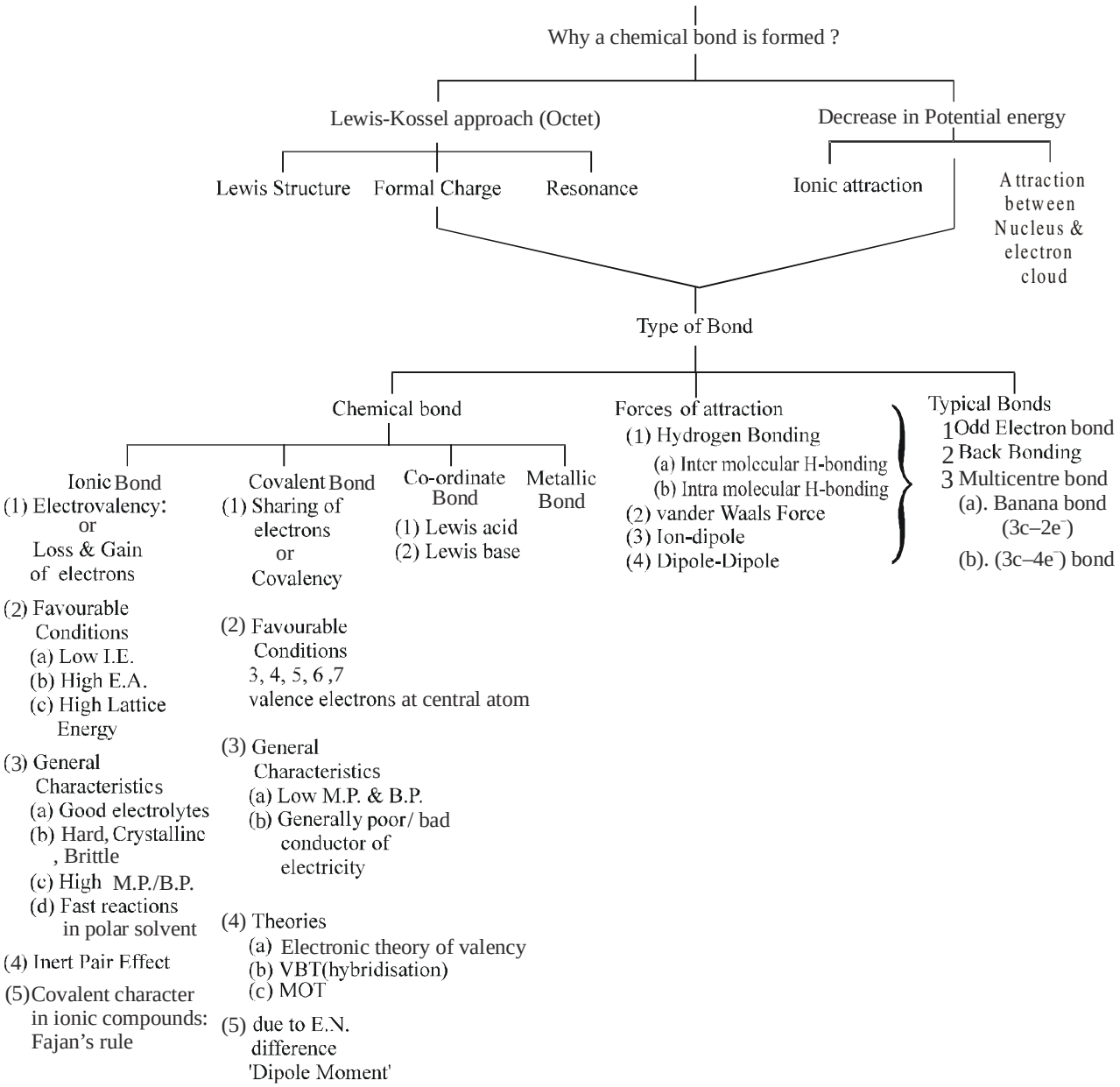
(b) It is union of two or more atoms involving redistribution of e^- among them.

(c) This process is accompanied by decrease in energy.

(d) Decrease in energy α Strength of the bond.

(e) A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms. Therefore molecules are more stable than atoms.

FLOWCHART TO CHEMICAL BONDING



1.2 Cause of chemical combination

SL AL

Tendency to acquire minimum energy

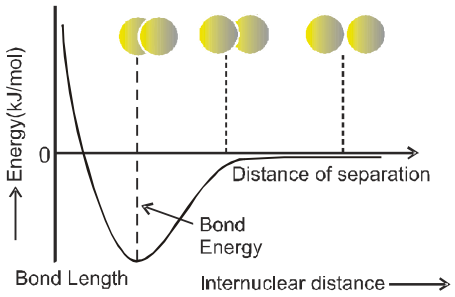
(a) When two atoms approaches to each other-
Nucleus of one atom attracts the electron of another atom.

(b) Two nuclei and electron of both the atoms repells each other.

(c) If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.

(d) So Attraction α 1/energy α Stability.

(e) Bond formation is an exothermic process.



Potential Energy diagram

- **Octet rule**

Octet rule was given by Lewis & Kossel.

Atoms Combines to complete an octet of electrons in their outer most orbit. Complete orbital represents to get most stable state. Hence all atoms have a tendency to acquire octet (s^2p^6) configuration in their outermost orbit.

The octet may be complete in following manner:

Complete transfer of electrons from one atom to another.

Ex. NaCl, $CaCl_2$ & MgO etc. (Ionic Bond)

Sharing of electrons between atoms.

(a) Sharing of equal number of electron between two atoms.
Ex. Cl_2, N_2, O_2 etc., (Covalent bond)

(b) Sharing of electron pair given by only one atom
Ex. $[NH_3 \rightarrow H^+]$ & $NH_3 \rightarrow BF_3$ (Co-ordinate Bond)

Exceptions of octet rule

(i) Transition metal ions

Cr^{3+}	Mn^{2+}	Fe^{2+}
$[Ar]3d^3$	$[Ar]3d^5$	$[Ar]3d^6$
[2, 8, 11]	[2, 8, 13]	[2, 8, 14]

(ii) Pseudo inert gas configuration [$s^2p^6d^{10}$]

Zn^{2+}	Cd^{2+}
$[Ar]3d^{10}$	$[Kr]4d^{10}$

(iii) Contraction of octet (incomplete octet)

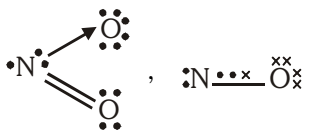
$\underline{Be}F_2$	$\underline{B}F_3$	$\underline{Al}Cl_3$	$\underline{B}Cl_3$
(4e)	(6e)	(6e)	(6e)

(iv) Expansion of Octet (due to empty d-orbitals)

PCl_5	SF_6	ClF_3	ICl_5	IF_7
↓	↓	↓	↓	↓
(10e)	(12e)	(10e)	(12e)	(14e)

(v) Odd electron species

Ex. NO, NO_2, ClO_2 etc.



(vi) Compounds of Noble gases

Noble gases which have already completed their octets (or douplet in case of He.) should not form compounds. However, their compouinds like XeF_2, XeF_6 & KrF_2 etc., have been actually prepared.

2.0 CLASSIFICATION OF BONDS

SL AL

ATTRACTIVE FORCES

- STRONG BOND
  - Ionic bond
  - Covalent bond
  - Co-ordinate bond
  - Metallic bond
- WEAK INTERACTION
  - Hydrogen bond
  - Vander waal's Interaction

3.0 ELECTROVALENT OR IONIC BOND

SL AL

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

(b) Electro possitive atom loses electron (group IA to IIIA)

(c) Electro negative atom gains electron (group VA to VIIA)

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

(e) Total number of electron lose or gained is called electrovalency.

Ex. :

(i)

$$\underset{2,\,8,\,2}{Mg} + \underset{2,\,6}{O} \longrightarrow Mg^{+2} + O^{-2}$$

$2e^-$

electrovalency of Mg = 2
electrovalency of O = 2

(ii)

$$\underset{2,8,8,2}{Ca} + \underset{2,8,7}{Cl} \longrightarrow Ca^{+2} + 2Cl^-$$

One e^-

$$\underset{2,8,7}{Cl}$$

One e^-

electrovalency of Ca = 2
electrovalency of Cl = 1

(iii)

$$\underset{2,\,8,\,8,2}{Ca} + \underset{2,\,6}{O} \longrightarrow Ca^{+2} + O^{-2}$$

$2e^-$

electrovalency of Ca = 2
electrovalency of O = 2

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

(g) A definite three dimensional structure is formed called crystal lattice.

(h) Ionic compound do not have molecular formula. It has only empirical formula.

Ex. : NaCl is empirical formula of sodium chloride

3.1 Varibable Electrovalency

SL AL

While some metal show a single electrovalency some show variable electrovalency. 's' block metals show single valency where as 'd' and 'p' block metals show variable valencies because of following factor.

Inert Pair Effect : In p-block elements the stability of the lower oxidation state increases on descending the group. Because increased effective nuclear charge holds ns electrons tightly due to poor shielding effect of inner d & f orbitals and thereby, restrict their (ns electrons) participation in bonding only np electrons take part in bond formation. As a result of this, +1 oxidation state of Tl is more stable than it's +3 oxidation state. Pb shows +2 stable oxidation state and Bi shows +3 stable oxidation state.

For example :

Group 13	***Group 14***
B III	C IV
Al III	Si IV
Ga III, I	Ge IV, II
In III, I	Sn IV, II
Tl III, I	Pb IV, II

Order of stability : $Tl^{+1} > In^{+1} > Ga^{+1}$ (due to inert pair effect)

Order of stability : $Pb^{+2} > Sn^{+2} > Ge^{+2}$ (due to inert pair effect)

Instability of the Core : Various ions in 'd' block do not attain inert gas configuration & hence they have unstable core. Also since there is comparatively moderate difference in successive ionization energy therefore they can exist in multiple valancies.

Illustrations

Illustration 1*. $PbCl_4$ is stable at room temperature, $PbBr_4$ does exist but unstable at room temperature whereas PbI_4 doesn't exist.

Solution. Due to inert pair effect Pb(IV) is less stable than Pb(II). Hence it is very good oxidant.

$Pb(IV) + 2e^- \longrightarrow Pb(II)$

Reducing abilities of halides follows the sequence

$I^- > Br^- > Cl^-$

$Pb(IV) + 4Cl^- \longrightarrow PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$

$Pb(IV) + 4Br^- \longrightarrow PbBr_4 \longrightarrow PbBr_2 + Br_2$

$Pb(IV) + 4I^- \longrightarrow \cancel{PbI_4} \longrightarrow PbI_2 + I_2$

So we can say, simultaneous co-existence of Pb(IV) and I^- is not possible, hence PbI_4 does not exist.

3.2 Formation of ionic compound - Born Haber Cycle

SL AL

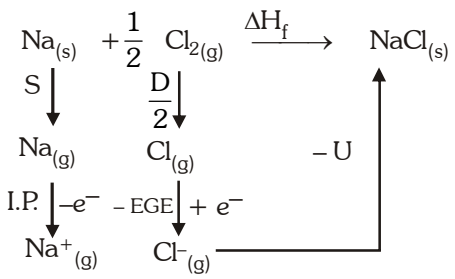
(a) When elements react to form compounds, ΔG (the free energy of formation) is negative. For a reaction to proceed spontaneously, the free energy of the products must to lower than that of the reactants. [To be dealt in thermodynamics]

(b) Usually the energy changes are measured as enthalpy values ΔH, and ΔG is related to ΔH by the equation

$$\Delta G = \Delta H - T\Delta S$$

(c) A whole series of energy changes is involved when one starts from the elements and finishes with an ionic crystal. These changes are shown in the Born-Haber cycle.

Formation of NaCl (s) involves



thus $S + I.P. + \frac{D}{2} - EGE - U = \Delta H_f$

here S = heat of sublimation of Na(s)
I.P. = ionisation potential of Na(g)
D = bond dissociation energy of Cl_2
EGE = electron gain enthalpy of Cl(g)
U = lattice energy
ΔH_f = enthalpy heat of formation of NaCl(s)

If lattice is $MgX_2(s)$ then

$$S + (IP_1 + IP_2) + D - 2EGE - U = \Delta H_f$$

where $(IP_1 + IP_2)$ = total ionisation energy to form $Mg^{2+}_{(g)}$ from $Mg_{(g)}$.

3.3 Factors favouring Ionic Bonding

SL AL

(a) ***Ionisation energy :*** 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 Ionization energy → Greater tendency to form cation.

Ex. $Na^+ > Mg^{+2} > Al^{+3}$
$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ } Cation formation tendency

(b) ***Electron affinity :*** Amount of energy released when an electron is added to an isolated gaseous atom to form –ve ion (anion) energy released.
Higher electron affinity → Greater tendency to form anion
Ex. $Cl^- > F^- > Br^- > I^-$
$F^- > O^{-2} > N^{-3}$

(c) ***Lattice energy -*** (Energy released) : The energy released in the formation of 1g mole electrovalent compound from isolated gaseous ions is called lattice energy (U) of that compound.
Higher lattice energy → Greater will be the stability or strength of ionic compound.

- **Factors affecting lattice energy**

(i) Magnitude of charge → $U \propto z^+ z^-$ (Ionic charge)
Lattice energy α Magnitude of charge

NaCl	$MaCl_2$	$AlCl_3$
Na^+	Mg^{+2}	Al^{+3}

⟶
– Charge on cation increases.
– Size of cation decreases.
– Lattice energy increases

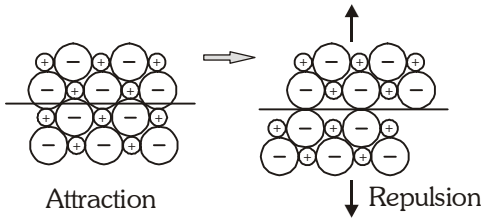
(ii) Size of Cation :- Lattice energy $\propto \frac{1}{r^+ + r^-}$

LiCl NaCl KCl RbCl CsCl
⟶
– Size of cation increasing
– Size of anion is constant
– Lattice energy decreases.

3.4 Properties of Ionic Compound

SL AL

(a) ***Physical state*** – Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction. Brittleness → {Same charged ions comes nearer. So they repell each other}



(b) ***Isomorphism*** – Different ionic compounds, having same configuration/geometry of ions are isomorphs of each other and phenomenon is known as isomorphism

Ex. NaF, MgO, $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$. All alums $M_2'SO_4 \cdot M_2''(SO_4)_3 \cdot 24H_2O$.

(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.

(i) In solid state - No free ions - Bad conductor of electricity.

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

Conductivity order : Solid state < fused state < Aqueous solution

(d) ***Solubility of salts :*** Solubility of compound is defined as the molar concentration of saturated solution at given temperature. Saturated solution is that solution in which no more solute can be dissolved at the given temperature.

3.5 Factor affecting solubility

AL

(a) ***Dielectric constant of solvent*** – The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant. It is represented by ε.

(i) Water has maximum dielectric constant ($\varepsilon = 80$)

(CH_3OH $\varepsilon = 35$) , (Acetone $\varepsilon = 21$)

(C_2H_5OH $\varepsilon = 27$) , (Ether $\varepsilon = 4.1$)

(Benzene $\varepsilon = 2.3$)

$H_2O > CH_3OH > CH_3CH_2OH > CH_3COCH_3 > CH_3OCH_3 > C_6H_6$

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

☞ ***Note :***

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

(b) ***Lattice energy and Hydration energy*** –

$$MX(s) \longrightarrow M^+(aq) + X^-(aq) \quad \Delta G^\circ < O$$

$$\downarrow +U$$

$$M^+(g), X^-(g) \xrightarrow{-\Delta H_{hydration}} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

For the solubility of ionic compounds in water, it is necessary that ΔG° must be negative.

Favourable conditions for solubility of ionic compound in water is

$$\Delta H_{hydration} > \Delta H_{Lattice\text{-}energy}$$

$$LE \propto \frac{1}{r^+ + r^-}, \quad HE \propto \frac{1}{r^+} + \frac{1}{r^-}$$

If lattice energy decreases, solubility increases

If hydration energy decreases, solubility decreases

In s-block moving down the group, solubility of most of the salts decreases because hydration energy decreases more rapidly as compared to lattice energy.

☞ ***Note :***

Order of Solubility :

(1) *In Sulphates of alkaline earth metals solubility decreases down the group*
$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

(2) *In Chlorides of alkaline earth metals solubility decreases down the group*
$BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

(3) *In Hydroxides of alkali metals solubility increases down the group*
$LiOH < NaOH < KOH < RbOH < CsOH$

(4) *In Hydroxides of alkaline earth metals solubility increases down the group*
$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

(5) *In Carbonates of alkali metals solubility increases down the group*
$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

(6) *In HCO_3^- of alkaline earth metals solubility increases down the group*
$Be(HCO_3)_2 < Mg(HCO_3)_2 < Ca(HCO_3)_2 < Sr(HCO_3)_2 < Ba(HCO_3)_2$

(7) *In F^- of alkali metals solutbility increases down the group*
$LiF < NaF < KF < RbF < CsF$

(8) *In F^- of alkaline earth metals*
$BaF_2 > BeF_2 > SrF_2 > CaF_2 > MgF_2$

(9) *In Oxides of alkaline earth metals solubility increases down the group.*
$BeO < MgO < CaO < SrO < BaO$

(10) *BeX_2 is highly solubile in water due to the formation of the soluble complex.*

$$BeX_2 + 4H_2O \underset{K_f > K_b}{\rightleftharpoons} [Be(H_2O)_4]^{+2} + 2X^-_{(aq)}$$

4.0 TRANSITION FROM IONIC TO COVALENT BOND – FAJANS' RULE

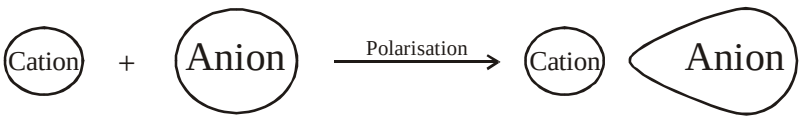
SL AL

Just as a covalent bond may have partial ionic character an ionic bond may also show a certain degree of covalent character. When two oppositely charged ions aproach each other closely, the cation would attract the electrons in the outer shell of the anion and simultaneously repel its nucleus. This produces distortion or polarization of the anion, which is accompanied by some sharing of electrons between the ions, i.e., the bond acquires a certain covalent character.

Terms used in polarisation in ionic compounds.

Polarisation Power :

The ability of cation to polarise a nearby anion is called Polarisation power of cation.



Polarised anion

Polarisation power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi \text{ (phi)} = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

Polarizability :

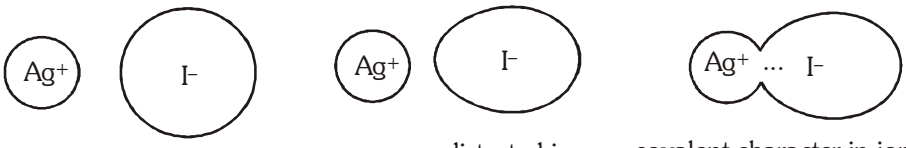
(i) It is the ability of anion to get polarised by the cation.

(ii) Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.

(iii) Increase in polarisation increases covalent character.

(iv) Magnitude of polarisation depends upon a number of factors, suggested by Fajan and are known as Fajan's rule.

The formation of a covalent bond between two ions may be illustrated with reference to formation of Agl.



separate ions distorted ion covalent character in ionic bond

4.1 Factors influencing ion – Deformation or increasing covalent character

SL AL

(i) ***Large charge on the ions –*** The greater the charge on the cation, the more strongly will it attract the electrons of the anion. For example, Al^{3+} can distort Cl^- ion more than Na^+ ion. So aluminium chloride is a covalent compound whereas NaCl, AlF_3, AgF are ionic.

(ii) ***Small cation and large anion –*** For a small cation, the electrostatic force with which its nucleus will attract the anion will be more. Moreover a large anion cannot hold the electrons in its outermost shell, especially when they are attracted by a neighbouring cation. Hence there will be increased covalent charcter with a small cation and a large anion, as in AgI.

(iii) ***Cation with a pseudo-inert gas type of electronic configuration –*** A cation with a 18 electron in outermost shell such as Ag^+ ([Kr] $4d^{10}$) polarizes anions more strongly than a cation with a 8 electron arrangement as in K^+. The 'd' electrons in Ag^+ do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in K^+. Thus AgI is more covalent than KI, although Ag^+ and K^+ ions are nearly of the same size. Cuprous and mercurous salts are covalent.

4.2 Application of the concept of polarisation

AL

(a) ***To determine covalent and ionic character of molecule***

$$\phi \propto \frac{\text{Covalent character}}{\text{Ionic character}}$$

From left (larger size) to right (smaller size) in a period ϕ increases so covalent character increases.

Na^+, Mg^{++} Al^{+++} Si^{++++}

$\longrightarrow$

- charge increases
- size decreases ϕ increases
- Covalent character increases with particular anion

From top to bottom in a group ϕ decreases so covalent, character decreases.

Li^+

Na^+ - Size increases (charge is fix)

K^+ - ϕ decreases

Rb^+ - Hence covalent character decreases with particular anion

Cs^+

(b) ***To determine nature of oxide***

$\sqrt{\phi} < 2.2$ (Basic oxides)

$\sqrt{\phi} = 2.2$ to 3.2 (Amphoteric oxides)

Neutral oxides doesn't react with acid & base eg. H_2O, CO etc.

Amphoteric oxides (Al_2O_3 etc.) reacts with acid & base

$\sqrt{\phi} > 3.2$ (Acidic oxide)

Ex. Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O

$\longrightarrow$

– $\sqrt{\phi}$ decreases

– Basic character increases

(c) ***To determine conductivity of metal halides (MX)***

If $\sqrt{\phi} < 2.2$ MX - ionic nature

If $\sqrt{\phi} > 2.2$ MX - covalent nature

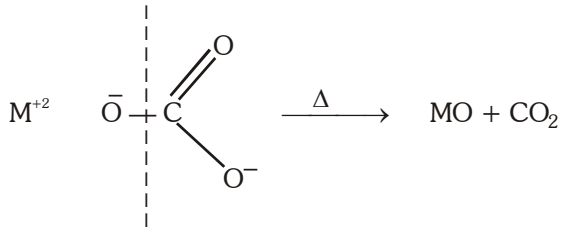
(d) ***Formation of complex compounds***

Smaller the cation, more will be the tendency of forming complex compounds.
High value of ϕ shows tendency of forming complex compounds.
If ϕ is low $\rightarrow$ No or less tendency of forming complex compounds.

- s-block metals (larger size) doesn't have the tendency to form complex compounds.
  Exceptions - Li, Be, Mg (small size)
- d-block metals have the tendency to form complex compounds (small in size, high charge).

(e) ***To determine thermal stability of metal carbonates***

Stability $\alpha \frac{1}{\phi}$ (Covalent nature)



More smaller the size of metal cation, its polarisation capacity increases - strength of M—O bond increases and C—O bond decreases. So thermal stability of carbonates decreases.

$$CO_3^{-2} \xrightarrow{\Delta} O^{-2} + CO_2$$

From top to bottom thermal stability of carbonates increases (as size of cation increases)
(Ionic character increases or covalent character decreases)

$BeCO_3$
$MgCO_3$ – size of cation increases
$CaCO_3$ – ϕ decreases (covalent character decreases)
$SrCO_3$ – Thermal stability increases
$BaCO_3$

(f) Colour density $\propto \phi$ (Covalent character)

To explain colour of compounds

More the covalent character, more will be the colour intensity.

Ex.

AgCl	AgBr	AgI
(White)	(Light yellow	(Dark yellow)
SnO_2	SnS_2	
(White)	(Yellow)	

(g) ***To explain diagonal relationship :***

Since the value of ϕ for Be^{2+} is almost of the same order as that of diagonally situated Al^{3+}. Hence have many similar properties. Similarly value of ϕ for Li^+ is equal to Mg^{+2}, so have diagonal relationship.

BEGINNER'S BOX–1

Chemical bond formation and Ionic bond

1. An electrovalent bond or ionic bond is formed between :-
(A) Two electronegative atoms
(B) Two metals
(C) Electropositive and electronegative atoms
(D) Two electropositive atoms

2. Most favourable conditions for electrovalent bonding are :-
(A) Low ionisation potential of one atom and high electron affinity of the other atom
(B) High electron affinity and high ionisation potential of both the atoms
(C) Low electron affinity and low ionisation potential of both the atoms
(D) High ionisation potential of one atom and low electron affinity of the other atom

3. The electronegativity of cesium is 0.7 and that of fluorine is 4.0. The bond formed between the two is
(A) Covalent (B) Electrovalent/ionic (C) Coordinate (D) Metallic

4. Electrovalent bond or ionic bond is formed by :-
(A) Sharing of electrons (B) Donaton of electrons (C) Transfer of electrons (D) None of these

5. Element X is strongly electropositive and Y is strongly electronegative. Both are univalent. The compound formed would be :
(A) $X^+ Y^-$ (B) X – Y (C) $X^- Y^+$ (D) $X \rightarrow Y$

6. Element A has 3 electrons in the outermost orbit and element B has 6 electrons in the outermost orbit. The formula of the compound formed between A and B would be :-
(A) A_2B_3 (B) A_2B_6 (C) A_2B (D) A_3B_2

7. Compound of a metal 'M' is M_2O_3, The formula of its nitride will be:-
(A) M_3N (B) MN (C) M_3N_2 (D) M_2N_3

8. 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) $SrCl_2 > BeCl_2 > CaCl_2 > Mg\ Cl_2$

9*. Which of the compound is least soluble in water
(A) AgF (B) AgCl (C) AgBr (D) AgI

10*. Which pair in the following has maximum and minimum ionic character respectively :
(A) LiCl, RbCl (B) RbCl, $BeCl_2$ (C) $BeCl_2$, RbCl (D) AgCl, RbCl

11. The M.P. of $SnCl_4$ is less than that of $SnCl_2$, the suitable reason for the observed fact is
(A) There is more charge on Sn^{+4} (B) The size of Sn^{+4} is small
(C) Ionic potential (ϕ) of Sn^{+4} is high (D) The shape of $SnCl_4$ is tetrahedral

12. 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

13. The combination of atoms occur because they want
(A) To decrease number of electrons in the outer most orbit
(B) To attain an inert gas configuration
(C) To increase number of electrons in the outer most orbit
(D) To attain 18 electrons in the outermost orbit

14. 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

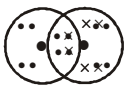
5.0 COVALENT BOND

SL AL

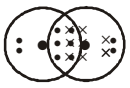
(a) A covalent bond is formed by the mutual sharing of electrons between two atoms of same electronegativity to complete their octet.(Except H which completes its duplet)

H – H

H_2 molecule



O O



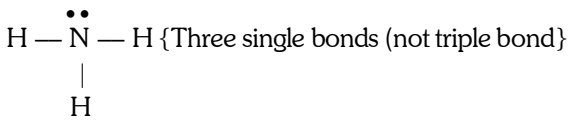
N N

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

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

No. of electrons shared between two atoms	***Bonded Electron pair***	***Bond.***
2	1	Single bond (–)
4	2	Double bond (=)
6	3	Triple bond (≡)

Ex.



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

5.1 Characteristic of Covalent Compound

SL AL

(i) ***Physical state:-*** Covalent compounds are found in all the three states - Gas, Solid & Liquid.
Separate molecules – In gaseous state
Associate molecules – In liquid & solid state
(Due to strong vander waal's force and hydrogen bonding among the molecules.)
As the size of molecule increases physical state changes -

eg. $\xrightarrow[\text{gas}]{F_2, Cl_2} \xrightarrow[\text{liquid}]{Br_2} \xrightarrow[\text{solid}]{I_2}$

(ii) ***Covalent solid :*** Those solids in which atoms are linked together by covalent bonds, forms inifinite three dimensional giant structure.
e.g. Diamond, Graphite, AlN, SiC, SiO_2 etc.
Molecular solid : Discrete (separate) molecules are formed by covalent bonds and then the molecules associated due to intermolecular force of attraction. (Vander waal force)
eg. Solid I_2, dry ice (Solid CO_2) etc.

(iii) ***Conductivity : -*** Mostly covalent compounds are bad conductor of electricity. But few polar covalent compounds due to self ionisation can conduct electricity.e.g. H_2O, liq. NH_3 etc.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

Free ions are formed which can conduct electricity.
Exceptions:- Graphite, HCl in water.

(iv) ***Solubility:-*** Non polar compound are soluble in non polar solvents. Non polar compounds forms Vander waal bond with non polar solvent molecules.

(v) ***Isomerism : -*** Covalent bond is rigid and directional, so it shows isomerism.
eg. Organic compounds.

(vi) ***Reaction:-*** Reaction between covalent compounds are slow. Because it involves breaking of existing bonds and formation of new bonds.

5.2 Co-ordinate bond

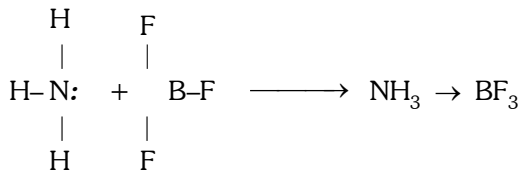
SL AL

(a) It is a covalent bond in which the shared electron pair come from one atom is called coordinate bond.

(b) Necessary conditions for the formation of co-ordinate bond are -
(i) Octet of donor atom should be complete and should have atleast one lone pair of electron.
(ii) Acceptor atom should have a defficiency of at least one pair of electron.

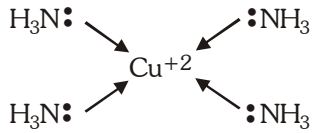
(c) Atom which provide electron pair for shairing is called donor.

(d) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond.

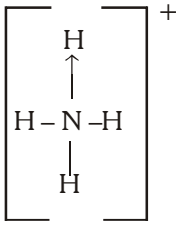


BF_3 is electron defficient compound.

Metal co-ordinate compounds - $[Cu(NH_3)_4]^{+2} \Rightarrow$

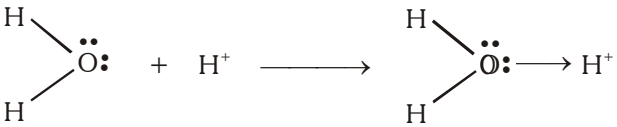


Ex. NH_4^+ ; $H_3N + H^+ \longrightarrow$



(Lowry-Bronsted acid)
(e^- acceptor)

H_3O^+ ;



N_2O ; $N \equiv N: \rightarrow O$

☞ ***Note :***

Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows -

NH_4Cl, $CuSO_4.5H_2O$, $K_4[Fe(CN)_6]$, KNC, KNO_3, *etc.*

5.3 Variable valency in covalent bonds

SL AL

(i) Variable valencies are shown by those elements which have empty orbitals in outermost shell.

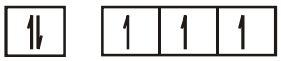
(ii) Lone pair electrons get excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.

(iii) The energy required for excitation of electrons is called promotion energy.

(iv) Promotion rule – Excitation of electrons in the same orbit.

Ex.

(a) Phosphorus → Ground state



3s 3p

Covalency 3 (PCl_3)

Phosphorus → Excited state

3s 3p 3d

Covalency – 5 (PCl_5)

(b) Sulphur → Ground state.

3s 3p 3d

Covalency - 2 (SF_2)

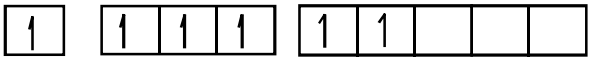
Sulphur → Excited state

Ist excited state

3s 3p 3d

Covalency - 4 (SF_4)

2nd excited state

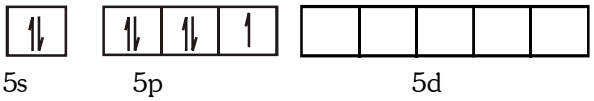


3s 3p 3d

Covalency - 6 (SF_6)

So variable covalency of S is 2, 4, & 6.

(c) Iodine has three lone pair of electrons

(Ground state) 

So it shows three excited states – Maximum number of unpaired electrons = 7
Variable Valencies are 1, 3, 5, 7

6.0 LEWIS DOT STRUCTURES OR LEWIS SYMBOLS

SL AL

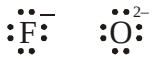
According to lewis in the formation of a molecule, only the outer most shell electrons take part in chemical combination & they are called valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. Lewis introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols or Lewis dot structure.

Lewis symbols for atoms and monoatomic ions :

Lewis symbol for second period elements are :

Number of dots around the symbol represents the number of valence electrons.

Lewis symbol for some anions are



How to draw the Lewis electron dot/Bond line structure of inorganic covalent compounds :

1. ***(i)*** First of all, identify the central atom in the given species. Central atom in a given molecule/ion is usually that atom which is least electronegative.

(ii) Hydrogen can't be central atom as its covalency is one.

(iii) Sometimes the central atom is that atom which is less in number.

(iv) Sometimes the central atom in the given molecule/ion can't be decided on the basis of electronegativity or number of atoms (less). In such cases, that atom is central atom which appears in central position of given formula of molecule/ion.

To make it more clear, central atoms in the following species are starred (*).

$\Rightarrow \overset{*}{C}H_4, \overset{*}{N}H_3, H_2\overset{*}{O}, \overset{*}{C}H_2Cl_2, \overset{*}{C}HF_3, H\overset{*}{P}O_3$

(Note-that electronegativity of H is less than that of central atom).

$\Rightarrow \overset{*}{C}O_2, \overset{*}{S}O_2, \overset{*}{S}O_3, \overset{*}{S}OCl_2, \overset{*}{P}SCl_3$

$\Rightarrow \overset{*}{O}Cl_2, \overset{*}{O}Br_2$ (Note that oxygen is more electronegative, but it is less in number)

$\Rightarrow (\overset{*}{S}CN)^-$, (order of apperance)

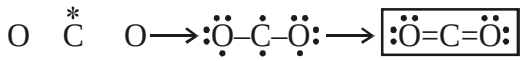
2. Surrounding atoms are the atoms which are directly bonded to central atom.

3. Arrange the surrounding atoms around the central atom and first form single bond between all surrounding atom with central atom.

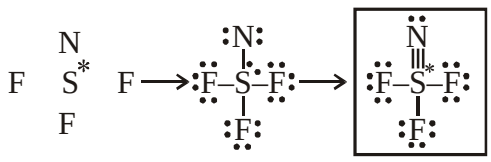
4. Always make sure that octet of all the surrounding atoms is complete. It is not achieved by forming single bond, then try to make the double bond or triple bond between central atom and surrounding atom, as required to complete the octet of surrounding atoms.

E.g.,

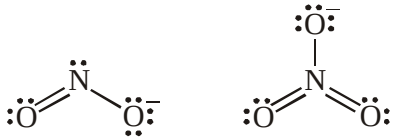
<u>CO_2</u>



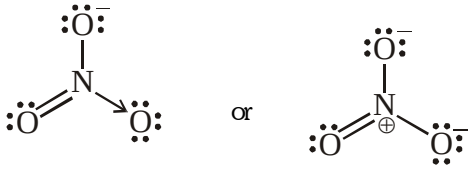
<u>SNF_3</u>



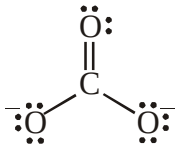
5. After the bond formation, represent the lone pair of electrons on central atom as well as on surrounding atoms.
6. Make sure that, in the structure you have made, the octet of the all surrounding atoms must be completed.
7. If the central atom belongs to second period, it can have $\leqslant$ 8 (max.) electrons i.e. $\leqslant$ 4 bonds, but never greater than 8 electrons (i.e. > 4 bonds).
8. However, if the central atom belongs to third or lower period it can have $\geqslant$ 8electrons.
9. At last verify the covalency of central atom.
10. ***Lewis Structure of ions :*** Distribute the negative charge on surrounding atom in such a way that octet of none of the surrounding atom is complete before the bond formation with central atom. If however, the octet of surrounding atom is complete by making it uninegatively charged (particularly in case of halogen which contain seven valence electron), then such surrounding atom will attach itself with central atom through a co-ordinate covalent bond.



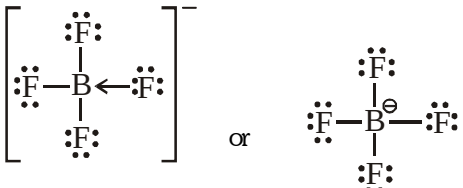
But the above structures of NO_3^- is incorrect as the central nitrogen belongs to second period, it can never form five covalent bond i.e., it can't have more than 8 electrons, so its actual structure is :



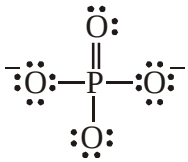
NO_3^-



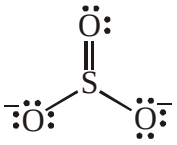
CO_3^{2-}



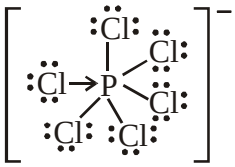
BF_4^-



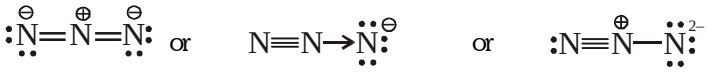
PO_4^{3-}



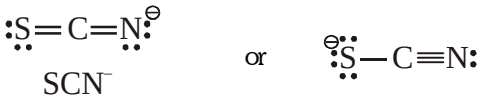
SO_3^{2-}



PCl_6^-



N_3^-



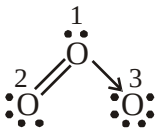
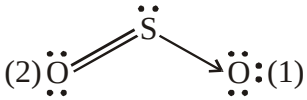
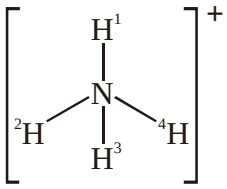
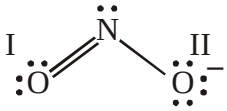
SCN^-

6.1 Formal Charge

SL

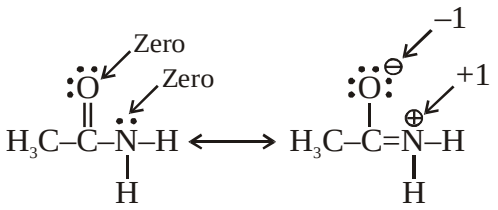
Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic 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	=	[Total number of valence electron in the free atom]	−	[Total number of non bonding (lone pair) electrons]	–½	[Total number of bonding(shared) electrons]

Molecule	***Structure***	***Formal Charge***
O_3		$O(1) = 6 - 2 - \frac{1}{2}(6) = +1$
		$O(2) = 6 - 4 - \frac{1}{2}(4) = 0$
		$O(3) = 6 - 6 - \frac{1}{2}(2) = -1$
SO_2		$S = 6 - 2 - \frac{1}{2} \times 6 = +1$
		$O(1) = 6 - 6 - \frac{1}{2} \times 2 = -1$
		$O(2) = 6 - 4 - \frac{1}{2} \times 4 = 0$
CO		$C = 4 - 2 - \frac{1}{2} \times 6 = -1$
		$O = 6 - 2 - \frac{1}{2} \times 6 = +1$
$CN^{\ominus}$		$C = 4 - 2 - \frac{1}{2} \times 6 = -1$
		$N = 5 - 2 - \frac{1}{2} \times 6 = 0$
NH_4^+		$N = 5 - 0 - \frac{1}{2}(8) = +1$
		On each $H = 1 - 0 - \frac{1}{2}(2) = 0$
NO_2^-		$N = 5 - 2 - \frac{1}{2}(6) = 0$
		$O(I) = 6 - 4 - \frac{1}{2}(4) = 0$
		$O(II) = 6 - 6 - \frac{1}{2}(2) = -1$

It should be kept in mind that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule/ion. ***Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.*** Generally the lowest energy structure is the one with the smallest formal charges on the atoms.

For example :



This structure is lower in energy

This structure is higher in energy

Formal charges are useful for helping decide which of the several possible Lewis structures is best.

1. A Lewis structure with small formal charges are preferable to large formal charges.
2. Lewis structure with negative formal charges on the more electronegative atom are preferable than Lewis structures with negative formal charges on the less electronegative atom.
3. Lewis structures with unlike charges close together are more likely than Lewis structure with opposite charges widely separated.
4. Lewis structures with like charges on adjacent atoms are very unlikely.

7.0 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

SL AL

Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. ***Sidwick and Powel 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 :

1. The shape of the molecule is determined by repulsion between all of the electron pairs present in the valence shell. (This is the same as the Sidgwick-Powell theory)

2. A lone pair of electrons takes up more space round the central atom than a bond pair, since the lone pair is attracted to one nucleus whilst the bond pair is shared by two nuclei. It follows that repulsion between two lone pairs is greater than repulsion between a lone pair and a bond pair, which is turn is greater than the repulsion between two bond pairs.
   Thus the presence of lone pairs on the central atom causes slight distortion of the bond angles from the ideal shape. If the angle between a lone pair, the central atom and a bond pair is increased, it follows that the actual bond angles between the atom must be decreased. lone pair (ℓp) - lone pair (ℓp) > lone pair (ℓp) - bond pair (bp) > bond pair (bp) -bond pair (bp)

3. The magnitude of repulsion between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.

4. Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond.

5. The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of p-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small.

8.0 WAVE MECHANICAL CONCEPT OF CO-VALENT BONDING

8.1 Modern Concept of Covalent Bond (VBT)

SL AL

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 (434.2 kJ mol^{-}, 74 pm) and F_2 (150.6 kJ mol^{-}, 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.

9.0 VALENCE BOND THEORY

SL AL

It 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 and the hybridization of atomic orbitals.

Formation of H_2 molecule :

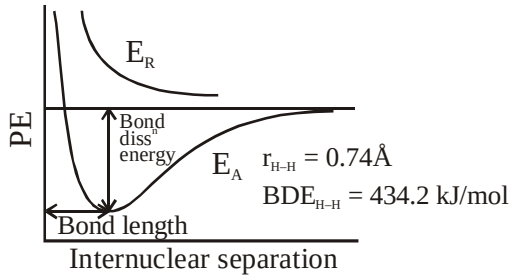
When two 'H'-atoms approaches towards each other for the formation of H_2 molecule. The following interactions takes place.

(i) e-e repulsion

(ii) e-p attraction

(iii) p-p repulsion

Experimentally, it has been found that the magnitude of attractive forces is more than the repulsive forces. As a result, when two atoms approach each other then potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy.



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.

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.

Bond Length : Internuclear distance at minimum potential energy is called bond length.

Bond Dissociation Energy : The amount of energy released when one mole of same type of bonds are formed is called B.D.E.

434.2 kJ/mol of energy is required to dissociate one mole of H_2 molecule.

$H_2(g) + 434.2 \text{ kJ mol}^{-} \rightarrow H(g) + H(g)$

10.0 ORBITAL OVERLAP CONCEPT

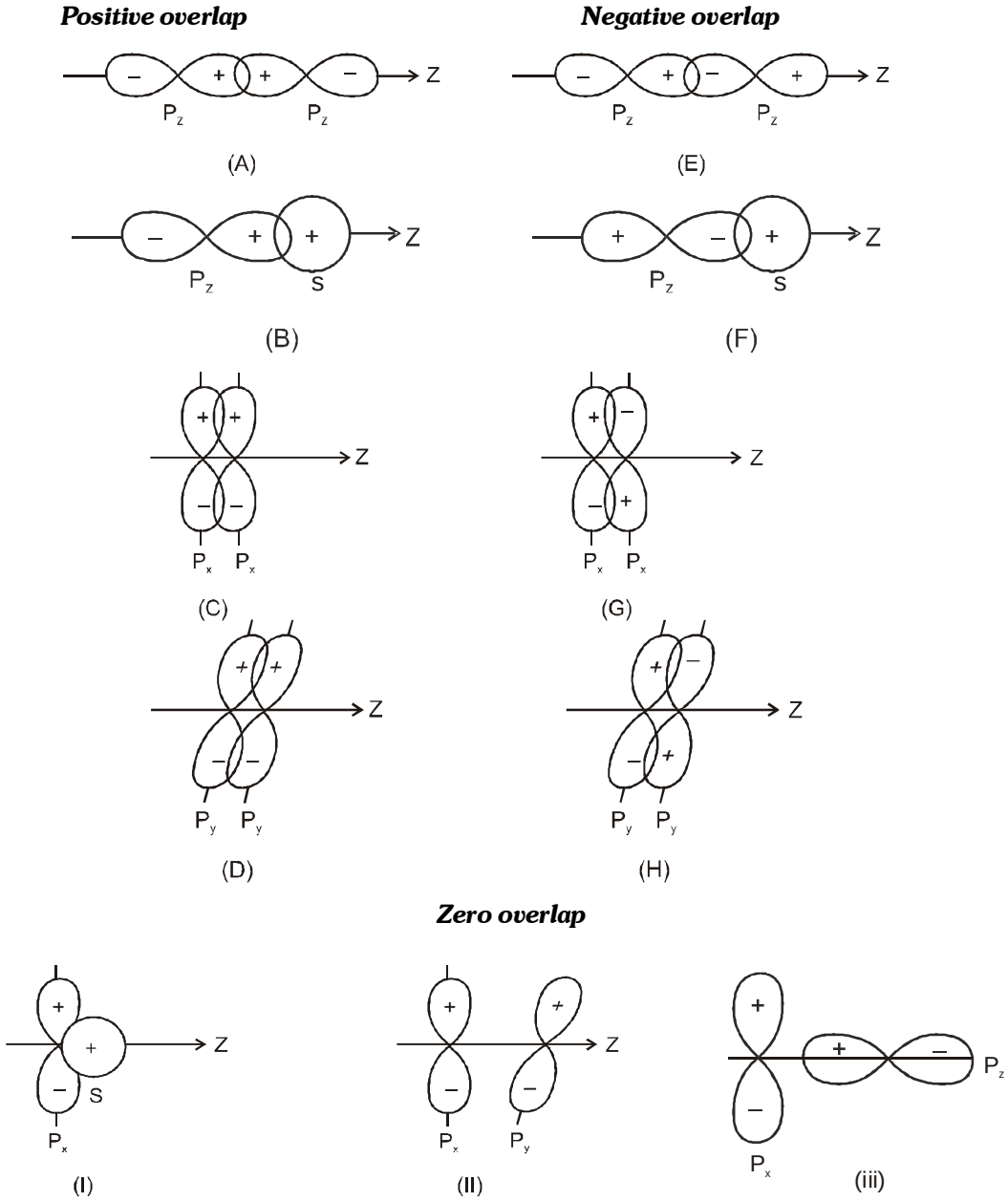
SL AL

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 or merging 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.

Directional Properties of Bonds : The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like CH_4, NH_3 and H_2O, etc. in terms of overlap and hybridisation of atomic orbitals.

Overlapping of Atomic Orbitals : When two atoms come closer 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 figures.

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.



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

10.1 Types of Overlapping and Nature of Covalent Bonds

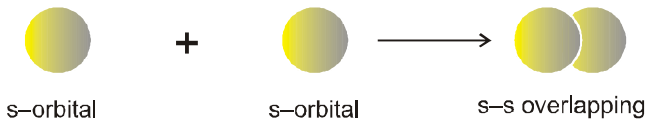
SL AL

The covalent bond may be classified into following types depending upon the types of overlapping :-

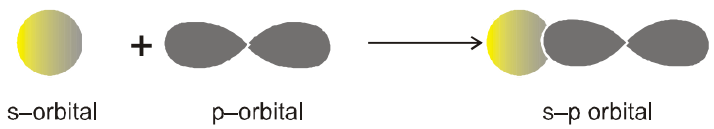
(i) sigma(σ) bond (ii) pi (π) bond (iii) delta(δ) bond

(i) Sigma (σ) bond : This type of covalent bond is formed by the end to end (head on or axial) overlap of bonding orbitals along the internuclear axis. 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 :

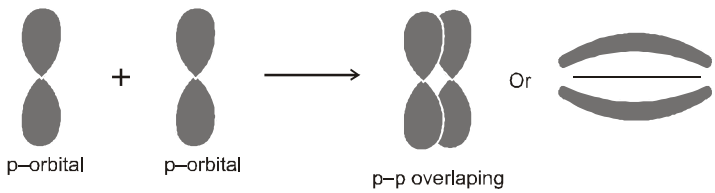


- s-p overlapping: This type of overlap occurs between half filled s-orbital of one atom and half filled p-orbital of another atom.

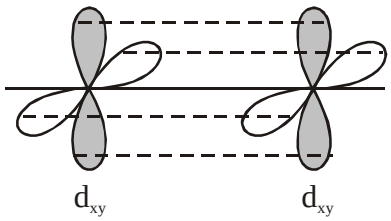


- p-p overlapping : This type of overlap takes place between half filled similar p-orbitals of the two approaching atoms.

(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.



(iii) delta (δ) ***bond :*** are the covalent bonds where four lobes of d-orbital of one atom overlap with four lobes of the similar d-orbital of other atom. Except d_{z^2} all d orbitals form δ bond.



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 where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

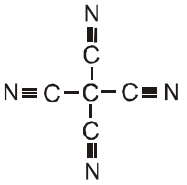
Difference between sigma and pi-bond

	Sigma-bond	***Pi-bond***
1.	A σ-bond is formed by the axial overlapping of atomic orbitals.	A π-bond is formed by the side ways overlapping of orbitals.
2.	σ-bond formation involves overlapping of s-s, s-p and p-p orbitals.	It involves overlapping of p-p orbitals.
3.	σ-bond is stronger because of larger extent of overlapping	π-bond is relatively weaker because of smaller extent of overlapping.
4.	The molecular orbital is symmetrical about internuclear axis and electron cloud is present on this axis	The molecular orbital is discontinuous and consists two electron clouds below and above the internuclear axis
5.	Free rotation exists around a σ-bond.	Free rotation does not exist around π-bonds.
6.	A sigma bond may exist either alone or or along with π-bonds.	A π-bond is always present along with a sigma-bond
7.	Hybridised orbitals or unhybridised orbitals are involved in σ-bond.	Hybridised orbitals are never involved in π-bond.

Illustrations

Illustration 2. What are the total number of σ & π bonds in tetracyanomethane.

Solution.



(in triple bond $\overset{\pi}{\underset{\pi}{\overset{\sigma}{=}}}$)

From the structure it is clear that it has 8σ and 8π bonds.

Advantages of VBT

- It explain various bond characteristics e.g., bond length, bond strength.
- It explains the quantitative relationship between the extent of overlapping and bond dissociation energy.
- This theory accounts for shape and nature of bonding of the molecule whose covalency is not according to the number of half-filled orbitals present in the ground state.
- This theory redefined the stability of molecules e.g. BF_3, $AlCl_3$, PCl_5, SF_6 etc which are exception to octet rule.

Disadvantages of VBT

- According to this theory three bond angle in CH_4 should be 90°, as these are formed by p–p overlapping, but actually it has four 109°28 angles. In NH_3 & H_2O, angle should be 90°. This is in disagreement with the actual bond angles of 107° & 104.5° in NH_3 & H_2O molecules respectively.
- In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3, H_2O etc. Pauling introduced the concept of hybridisation.

BEGINNER'S BOX–2

Covalent bond, Co–ordinate bond and Lewis dot structure

1. A covalent bond is possible between :-
(A) Similar atoms (B) Dissimilar atoms
(C) Similar and dissimilar atoms (D) Similar molecules

2. Which of the following statements is not true about covalent compounds :-
(A) They may exhibit space isomerism (B) They have low melting and boiling points
(C) They show ionic reactions (D) They show molecular reactions

3. In a triple bond there is sharing of :-
(A) 3 electrons (B) 4 electrons (C) Several electrons (D) 6 electrons

4. Which of the following bonds will have directional character
(A) Ionic bond (B) Metallic bond (C) Covalent bond (D) Both covalent & metallic

5*. The type of bond formed between two electronegative atoms would be
(A) Covalent (B) Ionic (C) Coordinate (D) All the above

6. Correct statement regarding this reaction : $BF_3 + NH_3 \longrightarrow [F_3B \leftarrow NH_3]$
(A) Hybridiration of N is changed (B) Hybridiration of B is changed
(C) NH_3 act as a Lewis base (D) (B) & (C) both

7. The correct statement for the reaction : $NH_3 + H^+ \rightarrow NH_4^+$:-
(A) Hybridisation state is changed (B) Bond angle increases
(C) NH_3 act as a Lewis acid (D) Regular geometry is changed

8. The bonds present in N_2O_5 are :
(A) Only ionic
(B) Covalent & coordinate
(C) Only covalent
(D) Covalent & ionic

9*. The pair of compounds which can form a co–ordinate bond is :-
(A) $(C_2H_5)_3B$ and $(CH_3)_3N$
(B) HCl and HBr
(C) BF_3 and NH_3
(D) (A) & (C) both

10. In which compound coordinate bond is present
(A) NH_3
(B) NH_4OH
(C) H_2O
(D) HCl

11. Which of the following statements regarding covalent bond is not true ?
(A) The electrons are shared between atoms
(B) The bond is non-directional
(C) The strength of the bond depends upon the extent of overlapping
(D) The bond formed may or may not be polar

11.0 HYBRIDISATION THEORY

SL AL

(a) It is introduced by pauling and slater, to explain equivalent nature of covalent bonds in a molecule.
Consider an example of Be compound :- $BeCl_2$
If it is formed without hybridisation then -

$$Cl \overset{p\text{-}s}{\text{——}} Be \overset{p\text{–}p}{\text{————}} Cl$$

both the Be–Cl bonds should have different parameters and p–p bond strength > s–p bond strength.
Practically bond strength and distance of both the Be–Cl bonds are same.
This problem may overcome if hybridisation of s and p-orbital occurs.

(b) ***Definition :*** Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals. and the phenomenon is called hybridisation.
Now after considering s–p hybridisation in $BeCl_2$

$$Cl \overset{p\text{–}sp}{\text{———}} Be \overset{sp\text{–}p}{\text{————}} Cl$$

bond strength of both the bonds will be equal.

11.1 Characteristic of Hybridisation

SL AL

(a) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridisation fully filled, half filled and empty orbitals may take part.
(b) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.
(c) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
(d) The number of hybrid orbitals on central atom of a molecule or ion = number of σ bonds + lone pair of electron.
(e) One element can represent many hybridisation state depending on experimental conditions
Ex. C showing sp, sp^2 and sp^3 hybridisation in its compounds.
(f) Hybrid orbitals are differentiated as sp, sp^2, sp^3 etc.
(g) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond.

11.2 Determination of hybridisation state

SL AL

Method (I)

Count the following pair of e^- arround the central atom :
(a) Count all pure σ bonded electron pairs (or σ bonds)
(b) Count all lone pair of electron
(c) Count all coordinate bond.
(d) Count all negative charge.

Method (II)

To predict hybridisation following formulae may be used :

No. of hybrid orbital = $\frac{1}{2}$ [Total number of valence e^- in the central atom + total number of monovalent atoms – charge on cation + charge on anion]

Ex. 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.

If such type of e^- pairs are –

two	–	sp	hybridisation
three	–	sp^2	hybridisation
four	–	sp^3	hybridisation
five	–	sp^3d	hybridisation
six	–	sp^3d^2	hybridisation
seven	–	sp^3d^3	hybridisation

11.3 Types of Hybridisation

SL AL

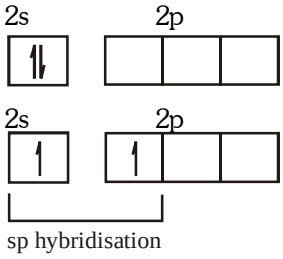
(i) sp hybridisation

(a) 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.

(b) These two sp hybrid orbitals are arranged in straight line & at bond angle 180°.

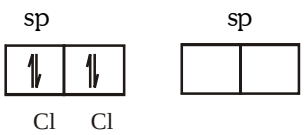
(c) s-character 50%

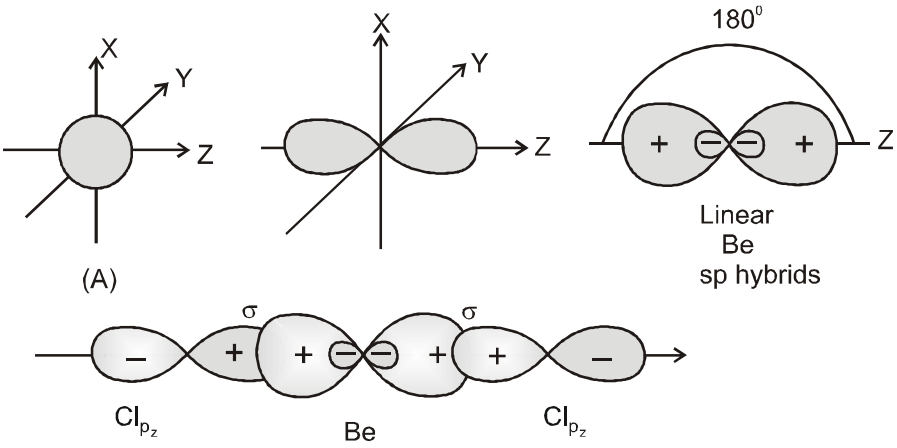
Ex. $BeCl_2$ Be (ground state)



Be (excited state)

Be atom share two electrons with Cl in $BeCl_2$,





(ii) sp^2 Hybridisation

(a) In this hybridisation one s & two p orbitals are mixed to give three new sp^2 hybrid orbitals which all are in same shape & equivalent energies.

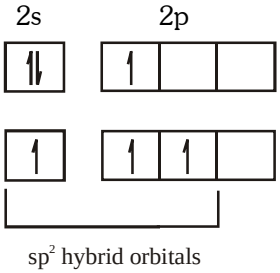
(b) These three sp^2 hybrid orbitals are at angle of 120° & give trigonal planar shape.

(c) s-character 33.33% in each orbital.

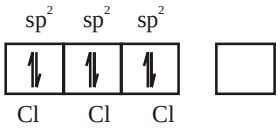
Ex. BCl_3

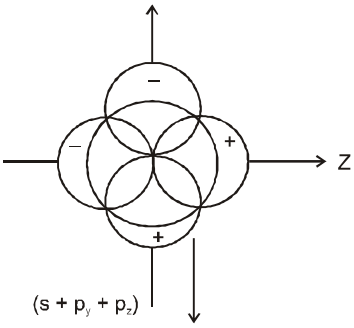
B (ground state)

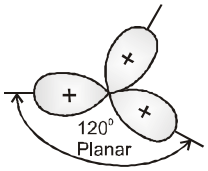
B (excited state)



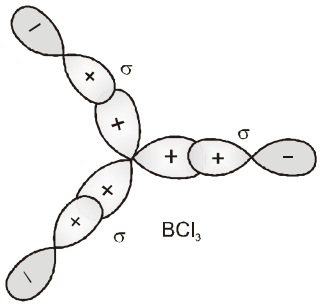
B atom share 3 electrons with 3 Cl atoms in BCl_3







sp^2 hybrids



(iii) sp^3 Hybridisation

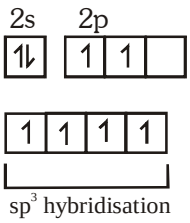
(a) In this hybridisation one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp^3 hybrid orbitals.

(b) The angle between these four hybrid orbitals will be 109° 28'

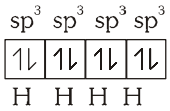
Ex. CH_4

C (ground state)

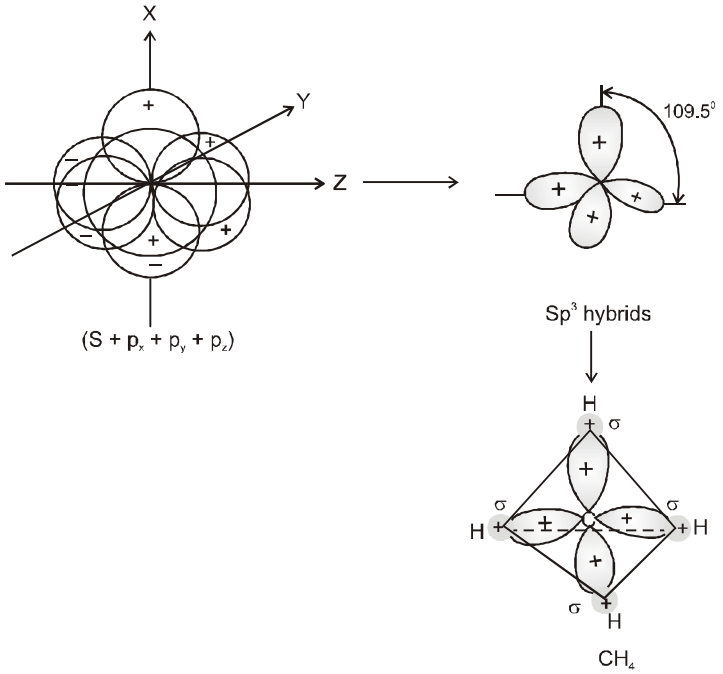
C (excited state)



C atom share four electrons with 4 hydrogen atoms



(c) The shape obtained from these hybrid orbitals would be tetrahedral.



(iv) sp^3d Hybridisation

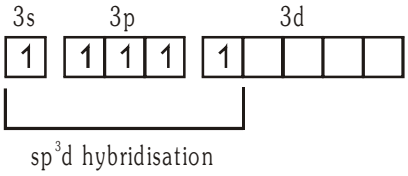
(a) In this hybridisation one s orbital, three p orbitals and one d orbital are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as sp^3d hybrid orbitals.

(b) Out of these five hybrid 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.

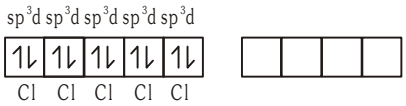
For example, PCl_5 showing sp^3d hybridisation

P (ground state)

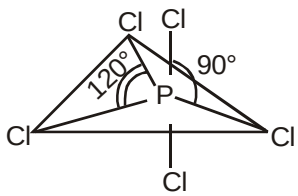
P* (excited state)



P atom share five *e* with Cl



(c) In this hybridisation dz^2 orbital is hybridised with s and p orbitals. In this way five sp^3d hybrid orbitals form five sigma bond with five Cl atoms and give a molecule of PCl_5, shape of this molecule is trigonal bipyramidal.



(d) Axial two P–Cl bonds are longer than equatorial three P–Cl bond due to repulsion between 3 equatorial b.p. of e^- and 2 axial b.p. of e^-

(v) sp^3d^2 ***Hybridisation***

(a) In this hybridisation, one s-orbital, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as sp^3d^2 hybrid orbitals.

(b) The shape of molecule obtained from above six hybrid orbitals will be symmetrical octahedral.

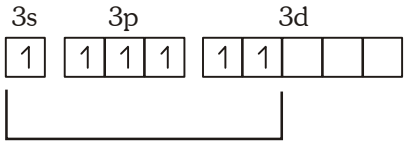
(c) The angle between all hybrid orbitals will be 90°.

Ex. SF_6, AlF_6^{-3}, PF_6^-, ICl_5, XeF_4, $XeOF_4$, ICl_4^-,

(d) Two 'd' orbital participates in the hybridisation are $dx^2–y^2$ and dz^2.

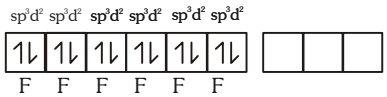
SF_6 S (ground state)

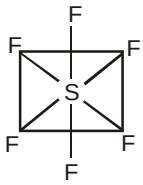
S (IInd excited state)



sp^3d^2 hybridisation

S (after hybridisation) share $6e^-$ with 6 F atoms





(vi) sp^3d^3 ***Hybridisation***

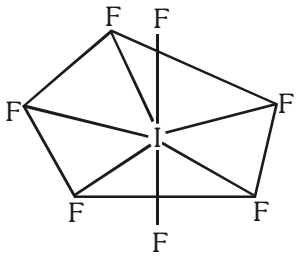
(a) In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp^3d^3 hybrid orbitals.

(b) In this hybridisation d-orbitals used are d_{xy}, $d_{x^2-y^2}$ & d_{z^2} orbitals.

(c) These seven sp^3d^3 orbitals are configurated in pentagonal bipyramidal shape.

(d) Five bond angles are of 72° & two bond angles of 90°.

(e) The following examples showing sp^3d^3 hybridisation –IF_7 & XeF_6.

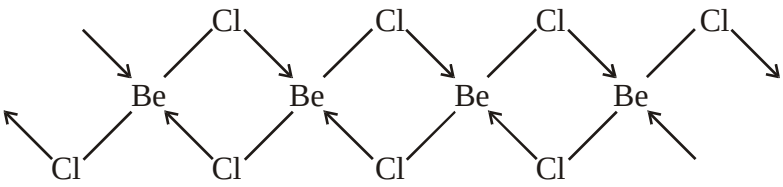


12.0 HYBRIDISATION IN SOLID STATE

AL

Hybridisation in Ionic solid species :

Species	***Cationic part***	***Anionic part***
PCl_5	PCl_4^+ (sp^3)	PCl_6^- (sp^3d^2)
PBr_5	PBr_4^+ (sp^3)	Br^-
XeF_6	XeF_5^+ (sp^3d^2)	F^-
N_2O_5	NO_2^+ (sp)	NO_3^- (sp^2)
I_2Cl_6 (liquid)	ICl_2^+ (sp^3)	ICl_4^- (sp^3d^2)
Cl_2O_6	ClO_2^+ (sp^2)	ClO_4^- (sp^3)
$(BeCl_2)_n$	$(BeCl_2)_n$ (sp^3)	



13.0 BENT'S RULE

AL

(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.

As s-orbital is more close to nucleus, the electron pair present in s-orbital will experience more attraction of the nucleus, i.e. stability of the system increases, therefore, a lone pair prefers to occupy that hybrid orbital which has greater percentage of s-character.

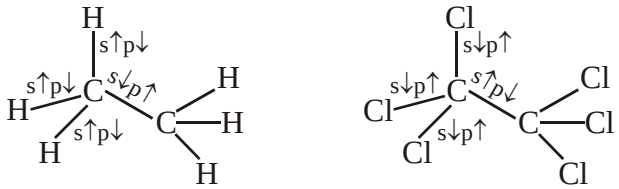
A more electronegative atom has tendency to attract the shared pair of electron towards itself, thus it will prefer to overlap with that hybrid orbital which has less percentage of s-character (i.e. relatively more distant from nucleus of central atom) because by doing so, it increases the stability of the system.

Illustrations

Illustration 3*. Compare C–C bond length in C_2H_6 and C_2Cl_6

Solution. In C_2H_6 and C_2Cl_6 both carbon atom are sp^3 hybrid and there is no lone pair of electron on central atom, but all the four sp^3 hybrid orbital around any of the carbon are non-equivalent.

In C_2H_6 molecule, to one of the C-atom three hydrogen atom (less electronegative) and one carbon atom (more electronegative than H) is attached. According to Bent rule, more electronegative carbon will overlap with that hybrid orbital has less character of s-character.

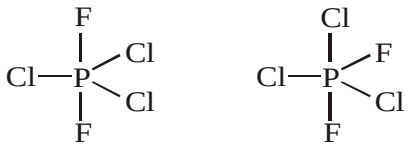


whereas in C_2Cl_6 molecule three Cl-atom (attached to any one of the carbon) will overlap with that hybrid orbital which has less s-character and the other (fourth atom attached with one carbon) being less electronegative will overlap with hybrid orbital which has more s-character. Due to more p-character in C–C bond, bond length in C_2H_6 is more than that in C_2Cl_6. Hence.

$$C–C_{(C_2H_6)} > C–C_{(C_2Cl_6)}$$

Illustration 4. Draw the geometry of PCl_3F_2

Solution.



Correct Structure Wrong Structure

Because highly electronegative atom occupy axial position (axial position has smaller percentage of s-character).

14.0 DRAGO GENERALISATION

AL

On the basis of experimental bond angles of certain molecules fulfilling the following three conditions,

(i) Belongs to third or lower period in periodic table

(ii) Contain atleast one lone pair of electron, and

(iii) Electronegativity of surrounding atom is $\leqslant 2.5$

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.

In such molecules bond angle is approximately 90°.

Group 15	***Bond angle***	***Group 16***	***Bond angle***
NH_3	107°48'	H_2O	104°28'
PH_3	93°36'	H_2S	92°
AsH_3	91°48'	H_2Se	91°
SbH_3	91°18'	H_2Te	90.5°

- Right order of bond angle.

  (a) $H_2O > H_2S > H_2Se > H_2Te$ (b) $NH_3 > PH_3 > AsH_3 > SbH_3$

BEGINNER'S BOX–3

Modern theory for covalent bond formation

1. A sp^3 hybrid orbital contains:-

(A) $\frac{3}{4}$ s- character (B) $\frac{1}{4}$ p - character (C) $\frac{3}{4}$ p - character (D) $\frac{1}{2}$ s - character

2. In the compound

$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H_2{-}\overset{4}{C}H_2{-}\overset{5}{C}{\equiv}\overset{6}{C}H$, the C_2—C_3 bond is formed by the overlapping of :-

(A) $sp - sp^2$ (B) $sp^3 - sp^3$ (C) $sp - sp^3$ (D) $sp^2 - sp^3$

3*. Which of the set of species have same hybridisation state but different shapes:-

(A) NO_2^+, NO_2 ,NO_2^- (B) ClO_4^-, SF_4, XeF_4 (C) NH_4^+, H_3O^+, OF_2 (D) SO_4^{2-}, PO_4^{3-},ClO_4^-

4. Which of the following elements can not exhibit sp^3d hybridisation state:-

(a) C (b) P (c) Cl (d) B

Correct answer is:-

(A) a, c (B) a, d (C) b, c (D) b, d

5*. In the protonation of NH_3 molecule, following statement is true:-

(A) A covalent bond is formed (B) Hydrogen bond is formed

(C) Hybridisation state of N is changed (D) Shape of NH_3 molecule is changed

6. The shape of sulphate ion is :–

(A) Hexagonal (B) Square planar

(C) Trigonal bipyramidal (D) Tetrahedral

7. In which following set of compound/ion has linear geometry:-

(A) CH_4, NH_4^+, BH_4^- (B) CO_3^{2-}, NO_3^-, BF_3 (C) NO_2^+, CO_2, N_3^- (D) $BeCl_2$, BCl_3, CH_4

8. Which of the molecule is trigonal bipyramidal

(A) BF_3 (B) CH_4 (C) PCl_5 (D) SF_6

9. The type of hybrid orbitals used by chlorine atom in ClO^-, ClO_2^- , ClO_3^- and ClO_4^- is/are :-

(A) sp, sp^2, sp^3 and sp^3d (B) sp and sp^3

(C) Only sp^3 (D) Only sp

10. Which of the following having a square planar structure is

(A) NH_4^+ (B) BF_4^- (C) XeF_4 (D) CCl_4

11*. The shape of I_3^- is

(A) Tetrahedral (B) Linear (C) T-shape (D) Trigonal

12. Which of the following will be octahedral ?

(A) SF_6 (B) BF_4^- (C) PCl_5 (D) XeF_6

13. Which of the following is not isostructural with $SiCl_4$?

(A) NH_4^+ (B) SCl_4 (C) SO_4^{2-} (D) PO_4^{3-}

15.0 BOND PARAMETERS

15.1 Bond length

SL AL

(i) The internuclear distance between the two single covalently bonded atoms is called bond length or bond distance.

(ii) If the electronegativities of both the atoms are equal, then the bond length is equal to the sum of the covalent radii of two bonded atoms. $d_{A-A} = r_A + r_A$

(iii) If the electronegativities of two bonded atoms differ, then the bond length is smaller than the sum of their covalent radii. $d_{A-B} < r_A + r_B$

- **Factors affecting bond length**

(i) ***Size of atoms:***

HI > HBr > HCl > HF

$H_2Te > H_2Se > H_2S > H_2O$

(ii) ***Hybridization state of the bonded atoms:*** If the s-character in hybridization state of the bonded atoms increases, the C–H bond distance decreases.

Ex. In C – C single bond.

$sp^3 - sp^3$ single bond length = 1.54 Å	$sp^3 - sp^2$ single bond length = 1.52 Å
$sp^2 - sp^2$ single bond length = 1.51 Å	$sp^3 - sp$ single bond length = 1.46 Å
$sp^2 - sp$ single bond length = 1.45 Å	sp – sp single bond length = 1.37 Å
Bond length decreases in the order	$sp^3 - sp^3 > sp^2 - sp^2 > sp - sp$

(iii) ***Resonance or delocalisation of electrons of the bond:*** Bond length between atoms are changed if a molecule shows resonance.

15.2 Bond angle

SL AL

The angle between two bonds is known as bond angle.

- **Factors affecting bond angle**

(i) ***Hybridisation state of central atom:*** Compounds having different hybridisation have diferent bond angle.

Ex.	BeH_2	BH_3	CH_4
Hybridisation	sp	sp^2	sp^3
Bond angle	180º	120º	109º28'

(ii) ***Lone pair of electron:*** If compounds have same hybridisation states then bond angle depends on lone pair of electron.

Ex.	CH_4	NH_3	H_2O
Hybridisation	sp^3	sp^3	sp^3
Lone pair e^-	zero	one	two
Bond angle	109º28'	107º	105º

The different in bond angle is explained on the basis of following repulaion sequence

The repulsion between

lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair

(iii) ***Electronegativity:*** When compounds having same hybridisation state of central atom and same number of lone pair of electrons, then bond angle depends on electronegativity.

Bond angle $\propto$ electronegativity

Ex. $H_2O > H_2S$

$NH_3 > PH_3$

E.N. of oxygen is more than sulphur therefore the bond angle in H_2O will be more than H_2S.

(iv) ***Size of terminal atoms:*** When size of terminal atoms increases, bond angle increases.

Ex. $OF_2 < Cl_2O < Br_2O$

$PF_3 < PCl_3 < PBr_3$

15.3 Bond Energy

SL AL

(i) The amount of energy required to break one mole of the bond and separate the bonded atoms in the gaseous state is known as the bond energy of that particular bond.

(ii) B.E. is expressed in KJ mol^{-1} (in SI units) or in Kcal mol^{-1}.

- **Factors afecting bond energy**

(a) ***Electronegativity difference of the bonded atoms :*** As the EN difference of the bonded atoms increases the bond energy increases because the ionic nature of the bond increases.

Ex. Bond strength of hydrogen halides decreases in the order

H – F > H – Cl > H – Br > H – I

(b) ***Bond Order*** Bond energy ∝ Bond order, therefore the increasing order of bond energy is

C – C < C = C < C ≡ C

(c) ***Hybridisation state of the bonded atoms :*** Bond energy ∝ s-character

Ex. $\underset{sp^3}{-C-H} < \underset{sp^2}{-C=H} < \underset{sp}{-C\equiv H}$

(d) ***Atomic size of bonded atoms :*** Atoms with small atomic radii form stronger bonds because the extent of overlapping of atomic orbitals is more

Ex. B.E. of halogens is of the order

Cl – Cl > Br – Br > I – I

because their atomic sizes are in the order Cl < Br < I.

(e) ***Extent of overlapping of atomic orbitals:*** A larger extent of overlapping of component atomic orbitals imparts great strength to the bond.

(f) ***Repulsion between the lone pairs of electrons of bonded atoms:***

$$\text{Bond energy} \propto \frac{1}{\text{No. of lone pair of electron on the bonded atoms}}$$

Ex. the bond energies of the following single bonds having zero, one, two and three lone pair of electrons are in the order.

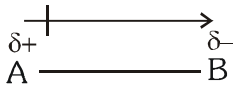
C – C > $\ddot{N}-\ddot{N}$ > $:\ddot{O}-\ddot{O}:$ > $:\ddot{\underset{..}{F}}-\ddot{\underset{..}{F}}:$

16.0 DIPOLE MOMENTS & MOLECULAR POLARITY

SL AL

(a) The degree of polarity of covalent bond is given by the dipole moment (μ), which is the product of charge (e) and the distance (d) between them. $\mu = e \times d$. 'e' is the order of magnitude of the electronic charge, i.e., about 10^{-10} esu and d is the distance between the atomic centres, i.e., about 10^{-8} cm.

(b) Hence dipole moments may be expected to have value around $10^{-10} \times 10^{-8} = 10^{-18}$ esu-cm. It is however, general particle to express dipole moments in ***Debye units*** (D), 1 D = 10^{-18} esu-cm.



Electronegativity of A < Electronegativity of B

If the charge is in SI units (Coulumbs) and d in metre, μ will be coulumb-metre (cm) unit.

1D = 3.336×10^{-30} C.m

(c) Any covalent bond which has a certain degree of polarity will have a coresponding dipole moment, though it does not follow that compound containing such bonds will have dipole moment,for the polarity of the molecule as a hole is the vector sum of the individual bond moment.

$$\mu_{resultant} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

(i) For example, CO_2 is a linear molecule, O = C = O, so that the dipole moments of the two C=O bonds cancel out.

(ii) The C → Cl bond has a definite polarity and a definite dipole moment but carbon tetrachloride has zero dipole moment becaue it is a tetrahedral molecule, and the resultant of the 4C – Cl bond moments is zero.

(iii) On the contrary CH_3Cl, CH_2Cl_2 and $CHCl_3$ have definite dipole moments.

☞ ***Note :***

(Order of dipole moment $CH_3Cl > CHCl_3 > CH_2Cl_2 > CCl_4 = CH_4$)

16.1 Application of Dipole Moment Measurements

SL AL

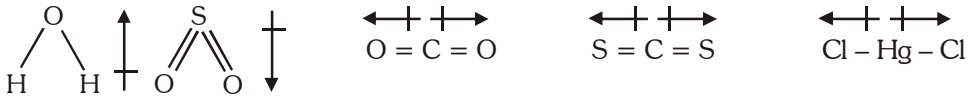
Dipole moment is a measure of the electrical dissymmetry (polarity) in the molecule and so its measurement provides valuable information concerning the shape of molecules. Conversely, when the symmetry of the molecules is known, dipole moment could be estimated.

(i) Inorganic substances:

(a) Monoatomic molecules such as He, Ne, etc., have zero dipole moment becaue they are symmetrical.

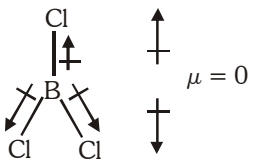
(b) Homodiatomic molecules such as H_2, Cl_2 and N_2 have no dipole moment; so these molecules are symmetrical.

(c) Triatomic molecules some of these molecules possess zero dipole moment so they have a symmetrical linear structure, ***Ex.*** CO_2, CS_2, $HgCl_2$. Others like water and sulphur dioxide have definite dipole moments. They are said to have angular or bent structures. (V-shaped)

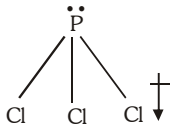


1.84 D 1.63 D 0 D 0 D 0 D

(d) Tetratomic molecules some molecules like BCl_3 have zero dipole moment. They are said to possess a flat and symmetrical (triangular) structure; other example are BF_3, BBr_3, CO_3^{2-}, and NO_3^-

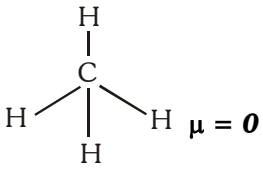


(e) PCl_3, $AsCl_3$, NH_3, PH_3, AsH_3, H_3O^+ have apreciable dipole moment. They possess trigonal pyramidal structure.



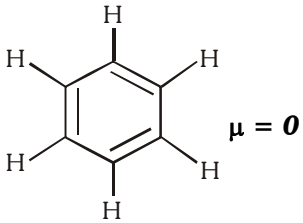
(ii) Organic substances

(a) Mathane and CCl_4 have zero dipole moment. So they possess symmetrical tetrahedral structures with C atom at the centre of the tetrahedron.



Methane

(b) Benzene has zero dipole moment. All the 6C and 6H atoms are assumed to be in the same plane (symmetrical hexagonal structure).

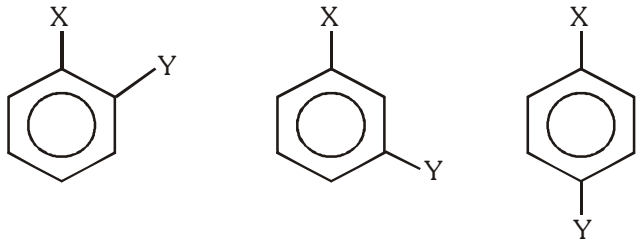


(c) Measurement of dipole moments will enable us to detect cis-and trans isomers of organic compounds (you will learn about cis-trans or geometrical isomerism later in the organic chemistry).

The trans-isomer, which is symmetrical, has zero dipole moment while the cis-isomer has a definite dipole moment.

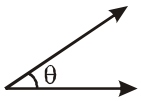
cis-dibromoethylene (μ = 1.4D) trans-dibromoethylene (μ = 0)

(d) The dipole moments of the aromatic compounds present a very good illustration of dipole moment. We know that when substituted benzene is treated with reagent different products (namely ortho, meta and para products) are formed. The dipole moments of these products are different since the orientation of the groups is different. Let us take an example to clarify it. Let us take three isomers. o-nitrophenol, m-nitrophenol and p-nitrophenol. We also have three other isomers, o-aminophenol, m-aminophenol and p-aminophenol. We want to arrange these isomers in the order of their dipole moments.



Ortho Meta Para

In those cases where X = Y, the para isomer becomes symmetrical and have zero dipole moment. In order to find their dipole moment, we need to know about the nature of the groups linked to the benzene ring. In nitro phenols, one group (OH) is electron pushing and the other (NO_2) is electron withdrawing while in aminophenols, both the groups (OH and NH_2) attached are electron pushing. So, depending on the nature of the groups attached, the isomers have different dipole moment.



$$\mu_{resultant} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1,\mu_2 \cos\theta}$$

16.2 Dipole moment and percentage ionic character

SL AL

The measured dipole moment of a substance may be used to calculate the percentage ionic character of a covalent bond in simple molecules.

1 unit charge = Magnitude of electronic charge = 4.8×10^{-10} e.s.u.

1 D = 1×10^{-18} e.s.u × cm.

$$\therefore \quad \% \text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Theoritical dipole moment}} \times 100$$

Theoritical dipole moment is confined when we assume that the bond is 100% ionic and it is broken into ions while observed dipole moment is with respect to fractional charges on the atoms of the bond.

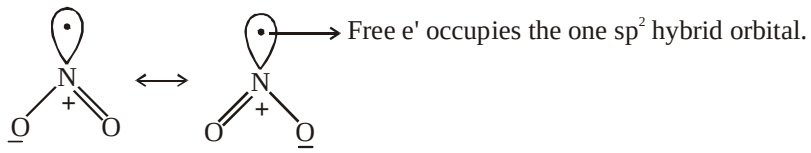
17.0 TYPICAL CONCEPTS IN BONDING

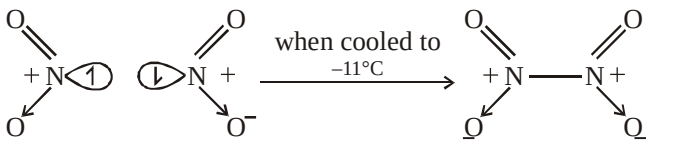
17.1 Odd Electronic Species

AL

(1) ***NO_2 :*** It is observed that the N–O bond length is in between single bond length and double bond length.

Structure of NO_2 :



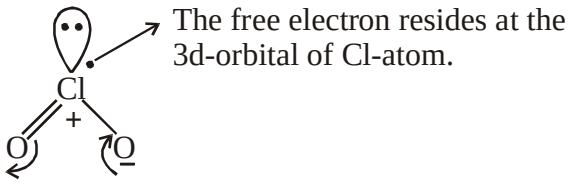


Paramagnetic (unpaired electron) Brown colour gas

Diamagnetic (no unpaired electron) white coloured solid

(2) ***ClO_2 :*** The Cl–O bond length is in between single bond & double bond length,

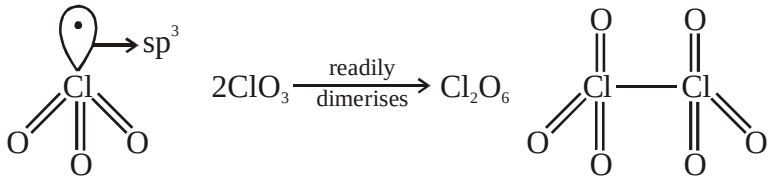
Structure :



Since the free electron is delocalised in d-orbital, it's dimear formation tendency is very less as compared to NO_2.

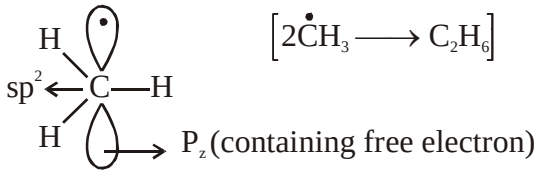
(3) ***ClO_3 :***
Bond angle = 119°
Hybridisation = sp^3
Shape = pyramidal

Structure :



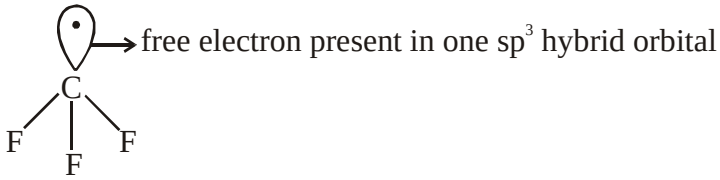
(4) $\dot{C}H_3$ ***:***
Bond angle = 120°
Hybridisation = sp^2
Shape = planer

Structure :



(5) $\dot{C}F_3$ ***:***
Bond angle = 109°28'
Hybridisation = sp^3
Shape = pyramidal

Structure :



Since the fluorine is more electronegative element which increases the p character in its attached orbital and finally accesses the sp^3 hybridisation hence it is pyramidal in shape.

17.2 Molecules that do not exist

AL

(i) SF_4, SF_6, PF_5 exists while. OF_4, OF_6, NF_5 do not exists
Reason :- Due to the non avalibility of vacant 2d-orbital, N and O atom cann't expand their octet.

(ii) ***(a)*** PI_5(vap) & SCl_6 do not exist
Reason :- Due to the steric crowding of the surrounding atoms.
(b) SCl_6 does not exists while $TeCl_6$ exists
Reason :- Size of Te > Size of S.

(iii) SF_6, PF_5, XeF_6, XeF_4, XeF_2 exists while SH_6, PH_5, XeH_6, XeH_4, XeH_2 do not exist
Reason :- F is more electronegative and causes ***d-orbital contration*** by which the required hybridisation is possible and H is less electronegative, cann't do so and the required hybirdisation is not possible, hence above compounds do not exist.

BEGINNER'S BOX–4

Comparison of bond parameters & Dipole moment

1. BeF_2 has zero dipole moment where as H_2O has a dipole moment because :-
(A) Water is linear
(B) H_2O is bent
(C) F is more electronegative than O
(D) Hydrogen bonding is present in H_2O

2. Which of the following molecule have zero dipole moment:-
(A) BF_3
(B) CH_2Cl_2
(C) NF_3
(D) SO_2

3*. The dipole moment of NH_3 is:-
(A) Less than dipole moment of NCl_3
(B) Higher than dipole moment of NCl_3
(C) Equal to the diple moment of NCl_3
(D) None of these

4. Which of the following species are polar :
(a) C_6H_6
(b) XeF_2
(c) SO_2
(d) SF_4
(e) SF_6
Correct answer is :-
(A) (b) and (d)
(B) (a), (b) and (e)
(C) (a) and (e)
(D) (c) and (d)

5. Which set of molecules is polar :-
(A) XeF_4, IF_7, SO_3
(B) PCl_5, C_6H_6, SF_6
(C) $SnCl_2$, SO_2, NO_2
(D) CO_2, CS_2, C_2H_6

6*. The correct order of dipole moment is :
(A) $CH_4 < NF_3 < NH_3 < H_2O$
(B) $NF_3 < CH_4 < NH_3 < H_2O$
(C) $NH_3 < NF_3 < CH_4 < H_2O$
(D) $H_2O < NH_3 < NF_3 < CH_4$

7. What conclusion can be drawn from the fact that BF_3 has no dipole moment but PF_3 does
(A) BF_3 is not symmetrical but PF_3 is symmetrical
(B) BF_3 molecule must be linear
(C) Atomic radius of P is larger than that of B
(D) BF_3 molecule must be planar triangular

8. Species having zero dipole moment :-
(A) XeF_4
(B) SO_2
(C) SF_4
(D) CH_2Cl_2

9. Higher is the bond order, greater is -
(A) Bond dissociation energy
(B) Covalent character
(C) Bond length
(D) Paramagnetism

18.0 MOLECULAR ORBITAL THEORY

SL AL

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

(i) Just as elctrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals. We know the names of atomic orbitals like s, p, d and f orbitals but the molecular orbitals will be having different names as well as different electronic distributions.

(ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

(iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclie depending upon the number of the atoms in the molecule. ***Thus an atomic orbital is monocentric while a molecular orbital is polycentric.***

(iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called ***bonding molecular orbital*** and ***anti-bonding molecular orbital*** are formed.

(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(vi) Just as the electron probability distribution around a nuclues in an atom is given by an atomic orbital , the electron probablity distribution around a group of nuclei in a molecule is given by molecular orbital.

(vii) The molecular orbitals like the atomic orbitals are filled in accordance with the ***Aufbau principle*** obeying the ***Pauli Exclusion principle*** and the ***Hund's Rule of Maximum Multiplicity***. But the filling order of these molecular orbitals is always ***experimentally decided***, there is no rule like (n + l) rule in case of atomic orbitals.

☞ ***Note :***

(In Valence Bond Theory we modify the pure orbitals of a single atom first - in hybridisation and then use these modified or hybridised orbitals to form the bonds while in Molecular orbital Theory orbitals of different atom are used to form new kind of orbitals called molecular orbitals).

18.1 Formation of Molecular Orbitals: Linear Combination of Atomic Orbitals(LCAO)

SL AL

In principle, Schrodinger equation can be written for any molecule. However, since it can not be solved exactly for any system containing more than one electron, molecular orbitals which are one electron wave functions for the molecules are difficult to obtain directly from the solution of the Schrodinger equation. This difficulty is overcome by resorting to an approximation method called the ***Linear Combination of Atomic Orbitals(LCAO) method to form molecular orbitals.***

Let us consider the application of the LCAO method to the homonuclear diatomic hydrogen molecule. The two hydrogen atoms in the H_2 molecule, fot the sake of converience may be labelled as A and B. Each hydrogen atom in ground state has one electron in the 1s orbital. These atomic orbitals may be represented by the wave functions Ψ_A and Ψ_B. Mathermatically the formation of molecular orbitals is described by the linear combination (addition or subtraction of the wave functions of the individual atomic orbitals) of Ψ_A and Ψ_B as shown below. $\Psi_{MO} = \Psi_A \pm \Psi_B$

Therefore, two molecular orbitals σ and σ* are formed

$$\sigma = \Psi_A + \Psi_B$$
$$\sigma^* = \Psi_A - \Psi_B$$

The molecular orbital σ formed by the addition of atomic orbitals is called the ***bonding molecular orbital*** and the molecular orbital σ* formed by the subtraction of atomic orbitals is called ***antibonding molecular orbital (Fig.)***

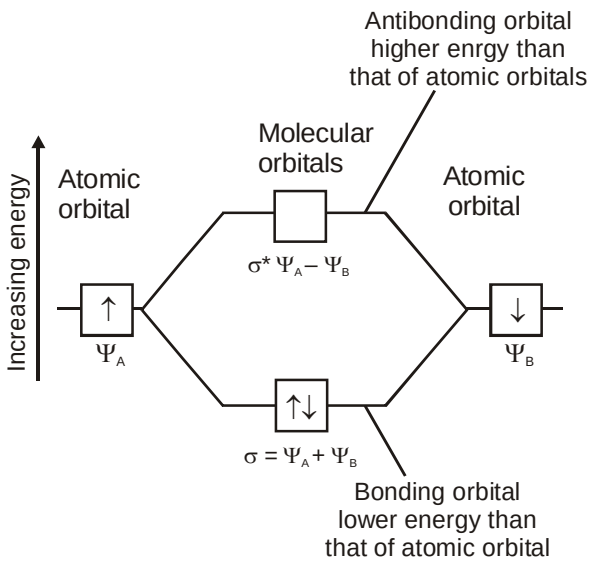


Fig. Formation of bodnding (σ) and antibonding (σ) molecular orbitals by the linear combination of atomic orbitals Ψ_A and Ψ_B centered on two atoms A and B respectively.*

Qualitatively, the formation of molecular orbitals can be understood in terms of the constrcutive or destructive interference of the electron waves of the combining atoms. In the formation of bonding melecular orbital, the two electron waves of the bonding atoms reinforce each other (constructive interference) while in th formation of antibonding molecular orbital, these electron waves cancel each other (destructive interference). The result is that in a bonding molecular orbital most of the electron density is located between the nuclei of the bonded atoms and hence the repulsion between the nuclei is very low while in an antibonding molecular orbital, most of the electron denstity is located away from the space between the nuclei, as a matter of fact there is a *nodal plane* (i.e., plane in which the electron density is zero) between the nuclei. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. A bonding molecular orbital is, therfore, always of lower energy than either of the atomic orbitals that have combined to form it. In contrast, electrons placed in the antibonding molecular orbital destabilize the molecule. The attraction between the electrons and the nuclei is less than the mutual repulsion of electrons in this orbital and this produces a net increase in enrgy. Consequently, the electrons placed in this molecular orbital tend to destabilise the molecule and that is why this orbital is said to be antibonding.

It needs to be pointed out that the energy of the antibonding orbital is raised above the energy of the atomic orbitals that have combined by an amount more than that by which the energy of the bonding orbital has been lowered. The total energy for two molecular orbitals however remains the same as that of the two orginal atomic orbitals.

18.2 Conditions for the combination of atomic orbitals

SL AL

The linear combination of atomic orbitals to from molecular orbitals takes place only if the following conditions are satisfied :

(i) ***The combining atomic orbitals must have the same or neraly the same energy.*** This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. It, therefore, means that only a limited number of combinations of atomic orbitals are possible.

(ii) ***The combining atomic orbitals must have the same symmetry about the molecular axis.*** By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of the other atom but not with the $2p_x$ or $2p_y$ orbitals because of their different symmetries.

(iii) ***The combining atomic orbitals must overlap to the maximum extent.*** Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

18.3 Types of molecular orbitals

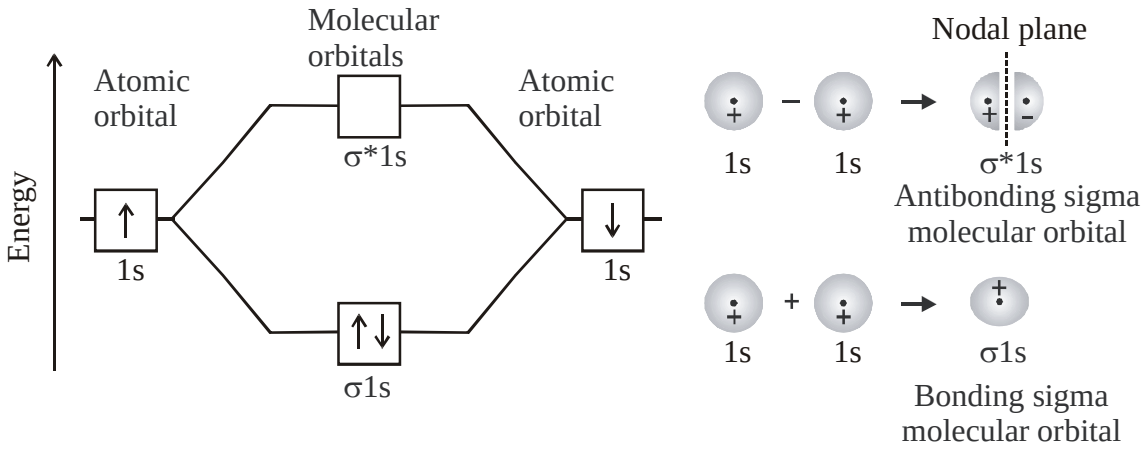
SL AL

Molcular orbitals of diatomic moelcules are designated as σ(sigma),π (pi), δ(delta), etc.

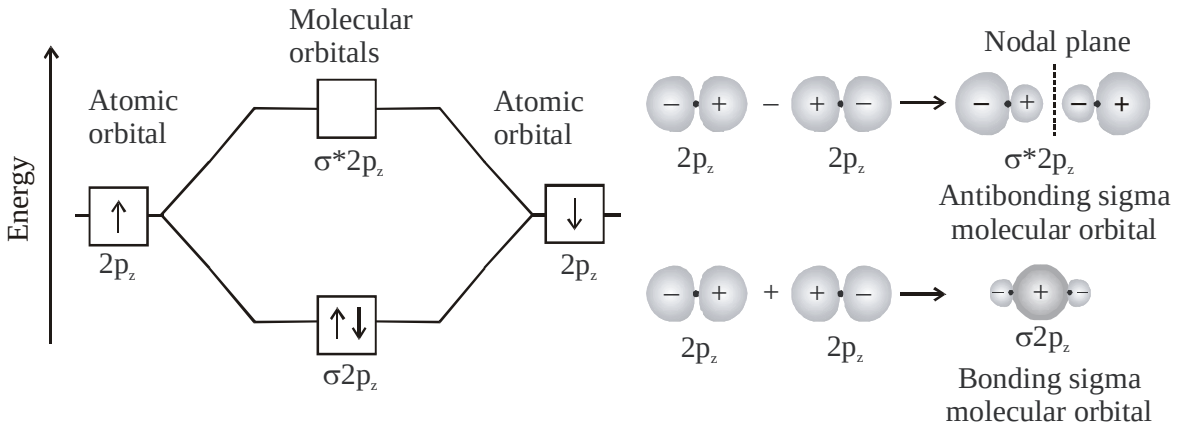
In this nomenclature, the ***sigma (σ) moleuclar orbitals are symmetrical around the bond-axis while pi (π) molecular orbitals are not symmetrical.*** For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbital's are of the σ type and are designated as σ 1s and σ*1s [Fig.(a)]. If internuclear axis is taken to be in the direction, it can be seen that a linear comination of $2p_z$ - orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma 2p_z$ and σ* 2pz. [Fig. (b)] Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitlas are not symmetrical around the bond axis because of the presence of positive lobes plane. Such molecular orbitals, are labelled as π and π* [Fig. (c)]. A π bonding MO has large electron density above and below the inter nuclear axis. The π* antibonding MO has a node between the nuclei.

δ-type of molecular orbitals are obtained by in involment of d-orbitals into bonding which is not required for us to study.

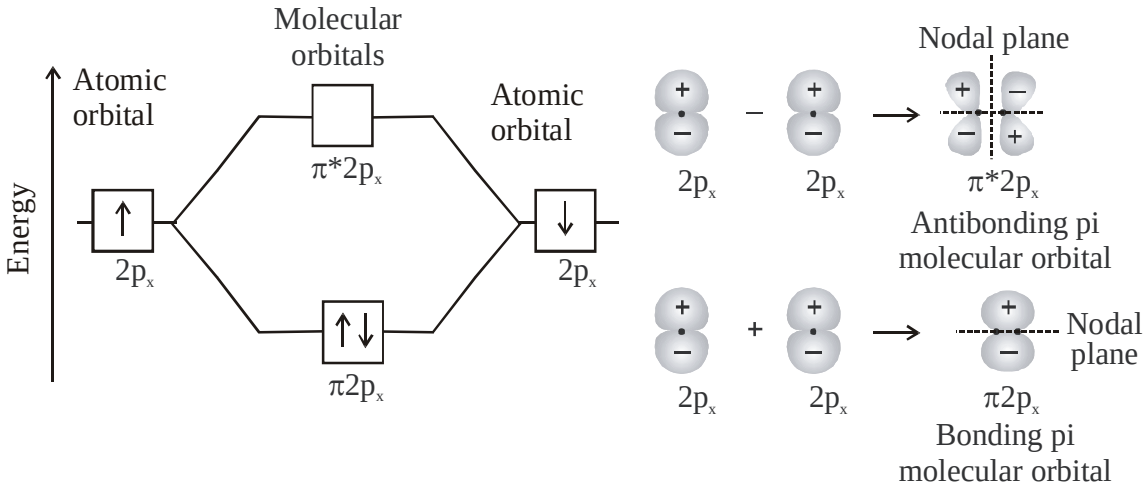
(a) s-s combination of orbitals



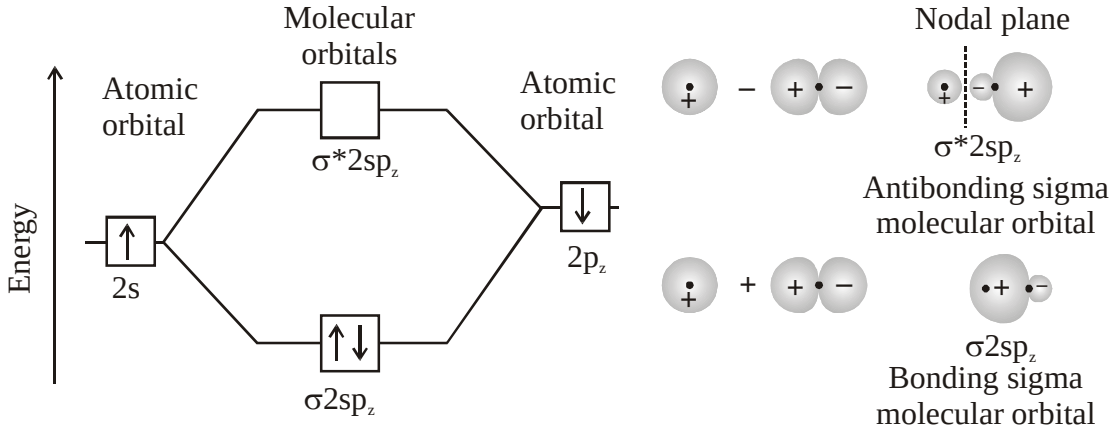
(b) p-p combination of orbitals (end to end overlap)



(c) p-p combination of orbitals (side by side overlap)

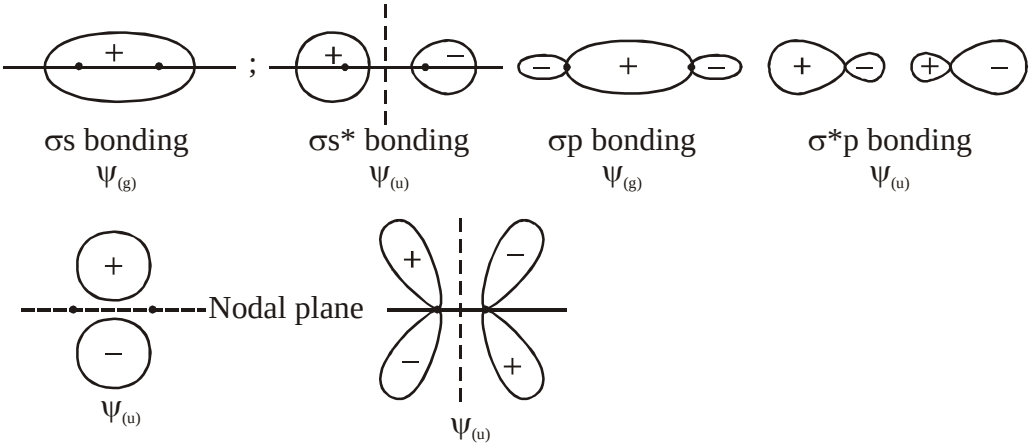


(d) s-p combination of orbitals



☞ ***Note :***

The molecular orbital wave functions are designated as $\psi_{(g)}$ & $\psi_{(u)}$; 'g' stands for gerade (even) and 'u' for ungerade (odd). 'g' & 'u' refers to symmetry of the orbital about its centre. For determining symmetry of the MO is to rotate the orbital about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remains the same, the orbital is gerade & if the sign changes, the orbital is ungerade.



18.4 Energy level diagram for molecular orbitals

SL AL

We have seen that 1s atomic orbitlas on two atoms from two molecular orbitals designated as σ1s and σ * 1s. In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals :

Antibonding MO's σ^*2s σ^*2p_z π^*2p_x π^*2p_y

Bonding MO's $\sigma2s$ $\sigma2p_z$ $\pi2p_x$ $\pi2p_y$

The energy levels of these molecular orbitals have been determined expermientally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below $\sigma1s < \sigma^*1s < \sigma2s < \sigma^*2s < \sigma2P_z < (\pi2px = \pi2py) < (\pi^*2px = \pi^*2py) < \sigma^*2p_z$.

However, this sequence of energy levels of moleuclar orbitals is not correct for the remaining molecules Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, C_2, N_2 etc. the increasing order of energies of various molecular orbitals is

$\sigma 1s < \sigma^* 1s < \sigma2s < \sigma^*2s < (\pi2P_x = \pi2p_y) < \sigma2p_z < (\pi^*2P_x = \pi^*2p_y) < \sigma^*2p_z$

The important characteristic feature of this order is that the ***energy of $\sigma2p_z$ moleuclar orbital is higher than that of $\pi2p_x$ and $\pi2p_y$ molecular orbitals.***

18.5 Electronic configuration and molecular behaviour

SL AL

The distribution of electrons among varous molecular orbitals is called the electronic configuration of the moelcule. From the electronic configuraiton of the molecule, it is possible to get important information about the molecule as discussed below.

(i) The molecule is stable if N_b is greater than N_a, and

(ii) The molecule is unstable if N_b is less than N_a In (i) more bonding orbitals are occupied and so the bonding influence is stroger and a stable molecule results. In (ii) the antibonding influence is strogner and therfore the moleucle is unstable.

N_b – number of e– in bonding molecular orbitals and N_a – number of e^- in antibonding Molecular orbitals.

- **Bond order**

Bond order (B.O.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding molecualr orbitals i.e.,

Bond order (b.o.) = ½ $(N_b - N_a)$

The rules discussed above regarding the stability of the moleuclar can be restated in terms of bond order as follows : A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable moelcule.

- **Nature of the bond**

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively as studied in the classical concept.

- **Bond-length**

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

- **Magnetic nature**

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 moleucle.

18.6 Bonding in some Homonuclear diatomic molecules

SL AL

In this section we shall discuss bonding in some homonuclear diatomic molecules.

(i) ***Hydrogen molecule (H_2) :*** It is formed by the combination of two hydrogen atoms. Each hydrogen atoms has one electron in 1s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in σ1s molecular orbital. So electronic configuration of hydrogen molecule is

$H_2 : (\sigma 1s)^2$

The bond order of H_2 molecule can be calculated as given below :

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol^{-1} and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

(ii) ***Helium molecule (He_2) :*** The electronic configuration of helium atoms is $1s^2$. Each helium atom contains 2 electrons, therefore, in He_2 molecule there would be 4 elctrons. These electrons will be accommodated in σ 1s and σ*1s molecular orbitals leading to electronic configuration :

$He_2 : (\sigma 1s)^2 (\sigma^* 1s)^2$

Bond order of He_2 is ½(2 – 2) = 0

He_2 molecule is therefore unstable and does not exist. Similarly, it can be shown that Be_2 moelcule $(\sigma 1s)^2$ $(\sigma^* 1s)^2$ $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ does not exist.

(iii) *Lithium molecule (Li_2) :* The electronic configuration of lithium is $1s^2, 2s^1$. There are six electrons is Li_2. The electrons in Li_2. The electronic confiugraiton of Li_2 molecule, therefore, is

$Li_2 : (\sigma 1s)^2 \ (\sigma^* 1s)^2 \ (\sigma 2s)^2$

The above configuration is also written as $KK(\sigma 2s)^2$ where KK represents the closed K shell structure $(\sigma 1s)^2 (\sigma^* 1s)^2$.

From the electronic configuration of Li_2 molecule it is clear that there are four electrons present in bonding molecular orbitals and two electrons present in antibonding moleuclar orbitals. Its bond order, therefore, is ½ (4 – 2) = 1. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

(iv) *Boron molecule (B_2) :* The electronic configuration of boron is $1s^2\ 2s^2\ 2p^1$. There are ten electrons in B_2. The electronic configuraiton of B_2 molecule, therefore, is

$B_2 : (\sigma 1s)^2 \ (\sigma^* 1s)^2 \ (\sigma 2s)^2 \ (\sigma^* s)^2 \ (\pi 2p^1_x = \pi 2p^1_y)$ or $KK\,(\sigma 2s)^2 \ (\sigma^* 2s)^2 \ (\pi 2p^1_x = \pi 2p^1_y)$

The bond order of B_2 is ½ (6 – 4) = 1 and B_2 should be paramagnetic.

(v) *Carbon molecule (C_2) :* The electronic configuration of carbons is $1s^2\ 2s^2\ 2p^2$. There are twelve electrons in C_2. The electronic configuraiton of C_2 molecule, therefore, is

$C_2 : (\sigma 1s)^2 \ (\sigma^* 1s)^2 \ (\sigma 2s)^2 \ (\sigma^* s)^2 \ (\pi 2p^2_x = \pi 2p^2_y)$ or $KK\,(\sigma 2s)^2 \ (\sigma^* 2s)^2 \ (\pi 2p^2_x = \pi 2p^2_y)$

The bond order of C_2 is ½ (8 – 4) = 2 = 2 and C_2 should be diamagnetic. Diamagnetic C_2 molecules have indeed been detected in vapour phase. It is important to note that double bond in C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond.

(vi) *Nitrogen molecule (N_2) :*

Electronic configuration : $(\sigma 1s)^2 \ (\sigma^* 1s)^2 \ (\sigma 2s)^2 \ (\sigma^* 2s)^2 \ (\pi 2p^2_x = \pi 2p^2_y)\,(\sigma 2p_z)^2$

or $KK\,(\sigma 2s)^2 \ (\sigma^* 2s)^2 \ (\pi 2p^2_x = \pi 2p^2_y)\,(\sigma 2p_z)^2$

B.O. of $N_2 = \frac{1}{2}(10 - 4) = 3$. one sigma and two π bonds.

(vii) *N_2^- :* Though $15e^-$ but derived from N_2, hence EC will be occording to N_2

Electronic configuration : $(\sigma 1s)^2 \ (\sigma^* 1s)^2 \ (\sigma 2s)^2 \ (\sigma^* 2s)^2 \ (\pi 2p^2_x = \pi 2p^2_y)\,(\sigma 2p_z)^2, (\pi^* 2px)^1$

or $KK\,(\sigma 2s)^2 \ (\sigma^* 2s)^2 \ (\pi 2p^2_x = \pi 2p^2_y)\,(\sigma 2p_z)^2, (\pi^* 2px)^1$

B.O. of $N_2^- = \frac{1}{2}(10 - 5) = 2.5$

(viii) *N_2^+ :* B.O. = 2.5, out of N_2^+ and N_2^-, N_2^- is less stable though both have equal bond order but N_2^- has greater number of antibonding electrons.

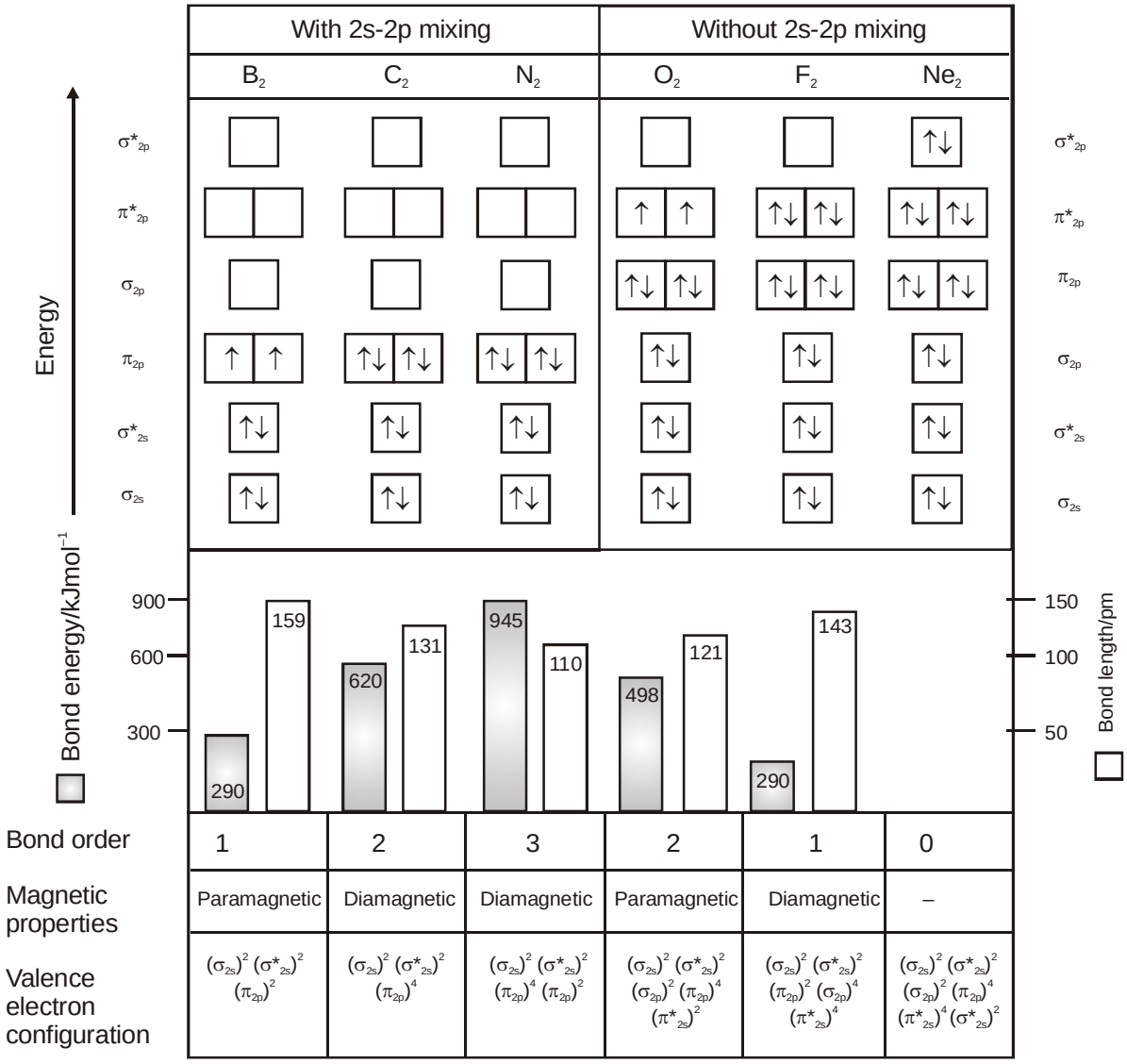


Fig. MO occupancy and molecular properties for B_2 through Ne_2.

(ix) Oxygen molecule (O_2) : The electronic configuration of oxygen atoms is $1s^2\ 2s^2\ 2p^4$. Each oxygen atom has 8 electrons, hence, in O_2 moleucle there are 16 electrons. The electronic configuration of O_2 molecule, therefore, is

$O_2 : (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p^2_x = \pi 2p^2_y)\ (\pi^* 2p_x^1 = \pi^* 2p^1_y)$ or

$$O_2 : \left[\begin{array}{l} KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2 \\ (\pi 2p_x^2 = \pi 2p_y^2), (\pi^* 2p_x^1 = \pi^* 2p_y^1) \end{array}\right]$$

From the electronic configuration of O_2 moleucle it is clear that ten electrons are present in bonding moleclar orbitals and six electrons are present in antibonding molcular orbitals. Its bond order, therefore, is

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 6] = 2$$

So in oxgyen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in π^*2p_x and π^*2p_y molecular orbitals, therefore, ***O_2 molecule should be paramagnetic, a prediction that corresponds to experimental observation.*** In this way, the theory successfully explains the paramagnetic nature of oxygen.

Similarly, the electronic configurations of other homonuclear diatomic molecules of the second row of the periodic table can be written. In Fig. are given the molecular orbital occupancy and molecular properties for B_2 through Ne_2. The sequence of MOs and their electron population are shown. The bond energy bond length, bond order, magnetic properties and valence electron configuraiton appear below the orbital diagrams.

(x) O_2^+ **:** B.O. = 2.5 paramagnetic.

(xi) O_2^- **:** B.O. = 1.5 paramagnetic.

(xii) O_2^{2-} **:** B.O. = 1 diamagnetic.

	O_2^{2-}	O_2^-	O_2	O_2^+	O_2^{2+}
No. of unpaired e⁻ s	0	1	2	1	0
B.O.	1.0	1.5	2.0	2.5	3.0

BEGINNER'S BOX–5

Molecular orbital theory

1. The number of antibonding electron pairs in O_2^{2-} molecular ion on the basis of molecular orbital theory is (At. no. O = 8) :
(A) 2 (B) 3 (C) 4 (D) 5

2. Which of the following option w.r.t. increasing bond order is correct ?
(A) $NO < C_2 < O_2^- < He_2^+$
(B) $C_2 < NO < He_2^+ < O_2^-$
(C) $He_2^+ < O_2^- < NO < C_2$
(D) $He_2^+ < O_2^- < C_2 < NO$

3. The ion that is isoelectronic with CO and having same bond order is :-
(A) CN^- (B) O_2^+ (C) O_2^- (D) N_2^+

4. Which of the following is paramagnetic:-
(A) O_2^- (B) CN^- (C) CO (D) NO^+

5. In the following which of the two are paramagnetic
(a) N_2 (b) CO (c) B_2 (d) NO_2
Correct answer is :-
(A) a and c (B) b and c (C) c and d (D) b and d

6*. Increasing order of bond length in NO, NO^+ and NO^- is :-
(A) $NO > NO^- > NO^+$
(B) $NO^+ < NO < NO^-$
(C) $NO < NO^+ < NO^-$
(D) $NO < NO^+ = NO^-$

7. In which of the following set, the value of bond order will be 2.5:-
(A) O_2^+, NO, NO^{+2}, CN
(B) CN, NO^{+2}, CN^-, F_2
(C) O_2^+, NO^{+2}, O_2^{2+}, CN^-
(D) O_2^{2-}, O_2^-, O_2^+ O_2

8. The paramagnetic property of oxygen is well explained by:-
(A) Molecular orbital theory
(B) Resonance theory
(C) Valence bond theory
(D) VSEPR theory

9. Which of the following has fractional bond order ?
(A) O_2^{2+} (B) O_2^{2-} (C) F_2^{2-} (D) H_2^-

10. The bond order of CO molecule on the basis of molecular orbital theory is
(A) Zero (B) 2 (C) 3 (D) 1

19.0 HYDROGEN BOND

SL AL

Nitrogen, oxygen and fluorine are the higly electronegative elements. When they are tied to a hydrogen atom to form covalent bond , the electrons of the covalent bond are tends towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other electronegative atom. This bond is i as hydrogen bond and is weaker than covalent bond. For example, in HF molcule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as depicted below :

$$--- H^{\delta+} - F^{\delta-} --- H^{\delta+} - F^{\delta-} --- H^{\delta+} - F^{\delta-}$$

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 (– – –) 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.

- **Cause of Formation of Hydrogen Bond**

When hydrogen is bonded to strongly electronegative element 'X'. the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge (+) while X' attain fractional negative charge (δ^-). This results in the formation of a polar molecule having electrostatic force of attraction which can be representes as :

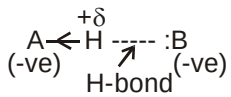
$$H^{\delta+} - X^{\delta-} - - - H^{\delta+} - X^{\delta-} - - - H^{\delta+} - F^{\delta-}$$

The magnitude of H – bonding depends on the physical state of the compound. It is maximum in the solid state and minimum in the gaseous state. Thus, the hydrogen bonds have strong Influence on the structure and properties of the compounds.

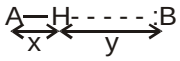
☞ ***Note :***

- *Energy of H-bond is usually low but there are examples in which H-bond energy is found to be nearly 220 kJ/mol (comparable to covalent bond) Therefore H-bond can be classified into 3 categories.*
  - ***(a)*** *Weak BE < 25 kJ/mol.*
  - ***(b)*** *Medium 25 – 35*
  - ***(c)*** *Strong > 35 kJ/mol ex : $K^+HF_2^-$ or $[HF_2^-]$ ion energy = 220 kJ/mol.*

- *H-bond is due to electrostatics attraction between the pole of H and ℓ.p. of e^- s on another –ve atom*



- *H-bonds are found to be much stronger with F-atoms but in case of other atoms the relative strength of H-bond will depend upon +δ charge of H(↑possiblity when atom A is more -ve) and availability of l.p. on B-atom. (B must be relatively less –ve)*

- 

(generally distance x < y)

  But in case of very strong H-bonding
  x = y,

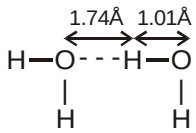
19.1 Types of H-Bonding

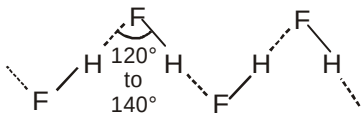
SL AL

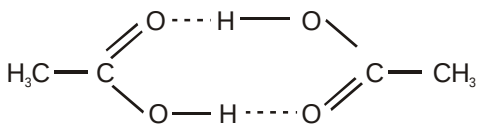
(A) Intermolecular

Ex. : H_2O, HF, R – OH, CH_3COOH / HCOOH, NH_3(R), R – NH_2,

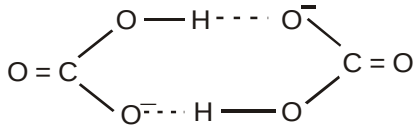
, HCN, H_3BO_3(s) etc.



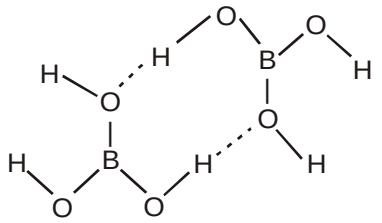




HCO_3^- in $KHCO_3$

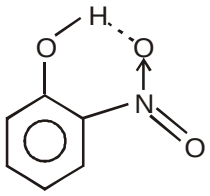


$H_3BO_3(s)$



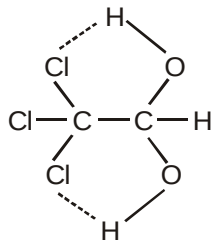
(B) Intramolecular :

(i) O-nitrophenol



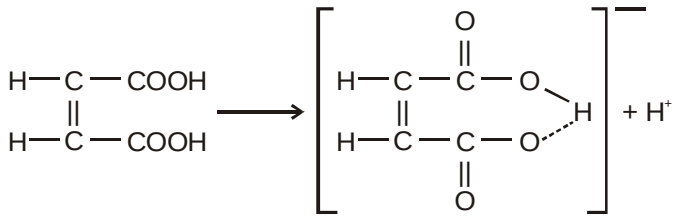
(ii) Chloral-hydrate $\longrightarrow$ $CCl_3CH(OH)_2$

CCl_3CHO (Chloral)

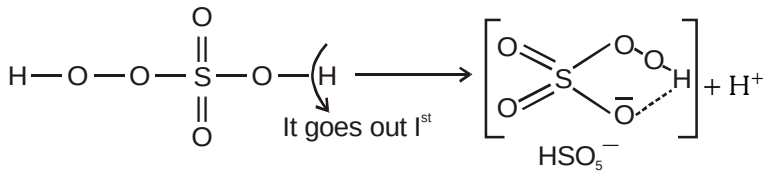


2 – OH groups are stabilised on the same C-atom.

(iii) Maleic Acid :

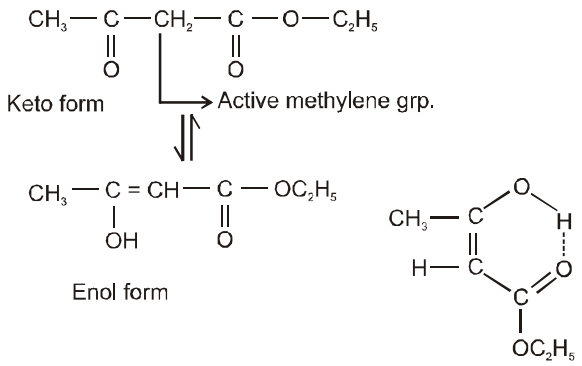


(iv) Anion of Caro's Acid :

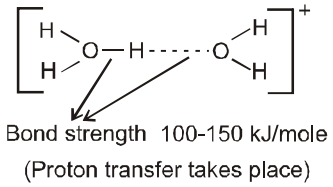


$K_2 << K_1$

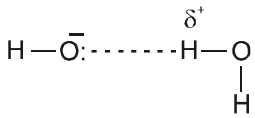
(v) Enolic form of Acetoacetic ester (AAE)



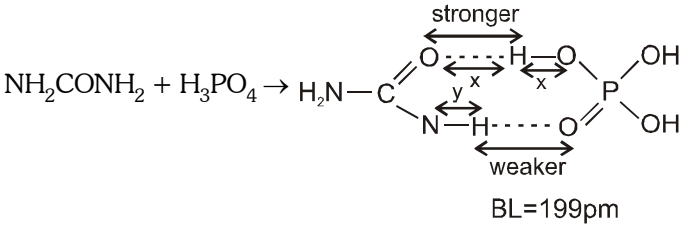
(vi) An interesting hydrate of Hydronium ion with the formula $H_3O^+(H_2O)_{20}$ in which H_2O molecules are hydrogen bonded. Some lower species like $H_5O_2^+$ have also been observed where the 2 water molecules are linked three H bonds.



Similarly $H_3O_2^-$ ions are also observed which is actually hydrate OH^- ion.



It is found urea and phosphoric Acid form H bond with each other



2 types of H–bond

B.L.OH $\Rightarrow$ x = 122 pm ; B.L. N–H $\Rightarrow$ y = 100 pm

19.2 Application of Hydrogen Bonding

AL

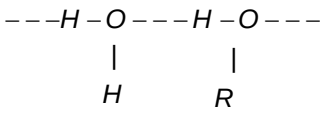
(i) H_2O is liquid but H_2S is gas

(ii) HF is liquid but HCl is gas.

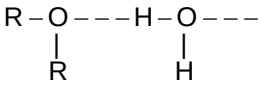
Due to intermolecular H bonding molecules undergo association (molecular assoication) due to which that substance become liquid or solid at room temperature.

$\therefore$ its B.pt $\uparrow$

(iii) C_2H_5OH is soluble in water but ether is much less soluble



Association is large



Association is very small

∴ solubility of ether is much less.
$C_2H_5OC_2H_5$ 8 gm/100gm H_2O
$CH_3CH_2CH_2CH_2OH$
Hydrocarbon chain ↑ ∴ solubility ↓

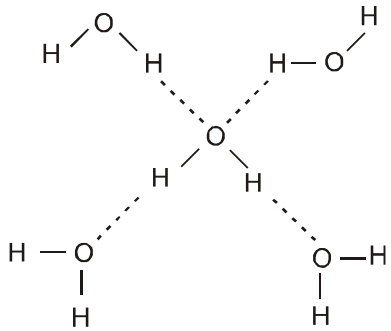
(iv) $HF_{(aq.)}$ is a weak acid
HF < HCl < HBr < HI

(v)

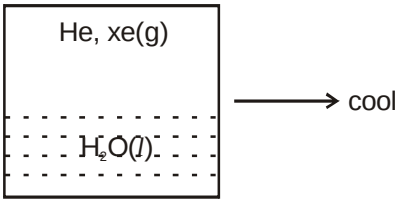
$E^{o}_{H^+/H_2} = 0$ $E^{o}_{D^+/D_2} = -0.01V$

D is more +ve than H
∴ It is capable of forming slightly more H bond than H thats why D_2O molecule are more associated and its B.pt is more than the B.pt of H_2O liq.

(vi) Ice floats on water
No. of water molecule attached to 1 H_2O molecule = 4
No. of H bonds in a molecule = 2
One H_2O is tetrahedrally bonded with $4H_2O$ molecules.
Intermolecular specing ↑ ∴ ρ^- of ice ↓
$D_2O(s)$
density of $D_2O(s)$ > density of $H_2O(l)$
∴ it sinks in $H_2O(l)$ but floats on $D_2O(l)$



☞ ***Note :***
Due to open structure, ice is capable of forming Clatherates. (cage like compounds)



Xe will be captured by ice.
Xe(g) because of its bigger atomic size is trapped in the cages formed by H_2O molecules in the structures of ice.
He cannot be trapped due to smaller size. Such compounds are called clatherates compounds.
(No chemical bonding)

(vii) Density of water max at 4°C

$$H_2O(s) \xrightarrow[\text{warm}]{\text{slightly}} H_2O\,(\ell)$$

density increases with increase in temperature upto 4°C.
In this temperature region some of the ice melts and hence some H_2O molecule go into the cages of remaining ice structure.
∴ V ↓ d ↑ becoming max at 4°C but beyond this temp thermal effects become dominating V ↑ ∴ d ↓

(viii) Water can extinguish the burning alcohol but not the burning petrol or a Hydrocarbon (in general).
$H_2O(l)$ + R–OH(l) → solution
(miscible)
$H_2O(l)$ + Petrol or hydrocarbon (l) → Not miscible
(No H bonding)
density of open chain HC < H_2O i.e. lighter than water. ∴ continue burning even in presence of H_2O

Illustrations

Illustration 5*. Which is a stronger base why?

(a) Trimethyl ammonium hydroxide $\left[(CH_3)_3NH\right]OH$

(b) Tetramethyl ammonium hydroxide $\left[N(CH_3)_4\right]^+OH^-$

Solution. ***(b)*** is more basic

$(CH_3)_3NH$: - - - - O – H

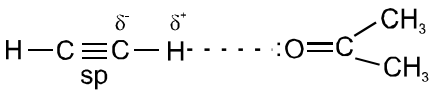
Due to intramolecular H bonding, release of OH^- ion become difficult $\therefore$ it is a weaker base.

Illustration 6. C_2H_2 is most soluble in

(A) H_2O (B) C_2H_5OH (C) CH_3COCH_3 (D) none or equally

Ans. ***(C)***

Solution. C_2H_2 is highly soluble in acetone due to H bonding



None of the above 2 has H-bonding individually.

But C_2H_2 is not soluble in water because water molecules already so much associated through H-bond that it is almost impossible for C_2H_2 molecules to break that association.

$\therefore$ it is not soluble in H_2O (*l*)

Illustration 7. Boiling point of o-nitrophenol is less than m-nitrophenol or p-nitrophenol and this compound is much less soluble in water than the remaining two. Explain.

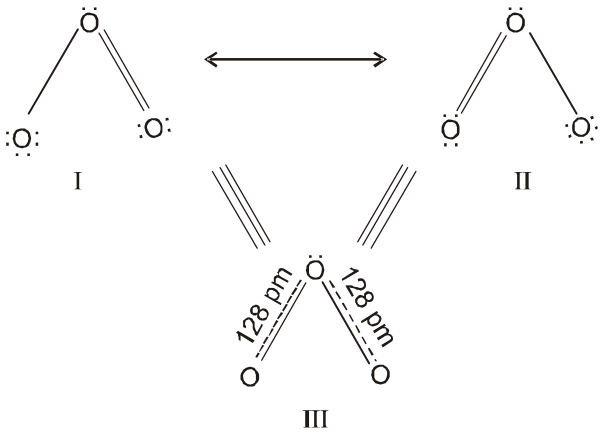
Solution. Due to intromalecular H-bonding in O –

Due to intermolecular H-bonding in m-p-

20.0 RESONANCE

SL AL

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 :***



Resonance in the O_3 molecule

(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

In both structures we have a O – O single bond and a O = O double bond. The normal O – O and O = 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.

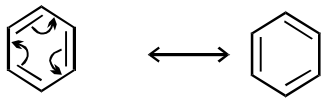
The concept of resonance was introduced to deal with the Type of difficulty experienced in the depiction of accurate structures of molecules like O_3 . According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding electrons are taken as the canonical structures of the hybrid 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.

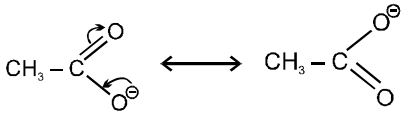
Some of the other examples of resonance structures are provided by the carbonate Ion and the carbon dioxide molecule.

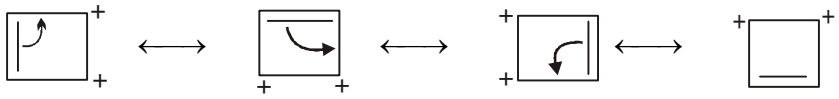
20.1 Definition

SL AL

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

(I) 

(II) 

(III) 

(IV) $CH_2 = CH - CH = \overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2$

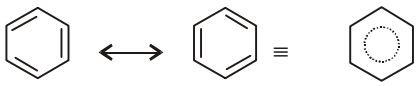
(V) $\overset{\ominus}{C}H_2 = CH - \overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = CH_2$

(VI) $CH_2 = CH - \overset{\bullet}{C}H_2 \longleftrightarrow \overset{\bullet}{C}H_2 - CH = CH_2$

20.2 Resonance Hybrid

SL AL

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.

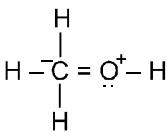


Resonance hybrid

20.3 Rules for Resonance

SL AL

(a) All the canonical forms (resonating structure) must have proper lewis structure. For instance none of them may have a carbon atom with five bonds.

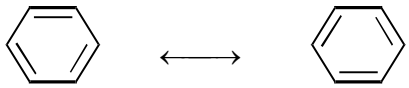


This is not a proper resonance structure for methanol because carbon has five bonds. Elements of the first major row of the periodic table cannot have more than eight electrons in their valence shell

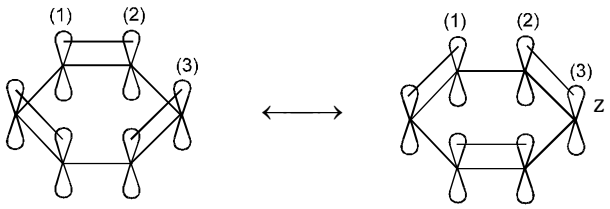
(b) The positions of the nuclei of the atoms must remain the same in all of the structures. Structures 3 is not a resonance structure of 1 or 2, for example, because in order to form it we would have to move a hydrogen atoms and this is not permitted :

$$\underbrace{\underset{1}{CH_3-\overset{+}{C}H-CH=CH_2} \longleftrightarrow \underset{2}{CH_3-CH=CH-\overset{+}{C}H_2}}_{\text{These are resonance structures}} \quad \underbrace{\underset{3}{\overset{+}{C}H_2-CH_2-CH=CH_2}}_{\text{This is not a proper resonance structure of 1 or 2 because a hydrogen atom has been moved.}}$$

(c) All atoms taking part in the resonance (π-electron resonance) must lie in a plane so that orbitals overlaping for resonance become parallel to each other.



i.e.



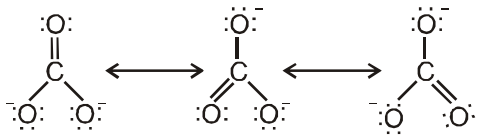
(d) The energy of actual molecule is lower than of any form. Therefore delocalisation is a stabilizing phenomenon.

(e) All canonical forms do not contribute equally to the true molecule. The more stable a structure is the greater contributor to its resonance hybrid. ***[To be dealt in detail in General organic chemistry]***

Illustrations

Illustration 8. Explain the structure of CO_3^{2-} ion in terms of resonance.

Solution. The single Lewis structure based on the presence of two single bonds and one double bond between carbon adn oxygen atoms is inadequate to represent the molecule accurately as it represents un-equal bonds. According to the experimental findings , all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I , II , and III shown below.



I II III

Resonance in CO_3^{2-} , I , II and III represent the three canonical forms.

☞ ***Note :***

Many misconceptions are associated with resonance and the same need to be dispelled. You should remember that :

(i) *The cannomcal forms have no real existence.*

(ii) *The molecule does not exist for a certain fraction of time in one cannonical form and for other fractions of time in other cannonical forms.*

(iii) *There is no such equilibrium between the cannonlcat forms as we have between tautomeric forms (keto and enol) in tautomeriam.*

(iv) *The molecule as such has a single structure which is the resonance hybrid of the cannonical forms and which cannot as such be depicted by a single Lewis structure.*

21.0 BACK BONDING

SL AL

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)

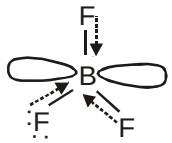
Back bonding increases the bond strength and decreases the bond length

The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example ***Back bonding in boron trihalides***

Boron trihalides :

BF_3	BCl_3	BBr_3	BI_3
↓	↓	↓	↓
sp^2	sp^2	sp^2	unstable (stearic hindrance)

- Observed bond length in BF_3 molecule in found to less than the expected.

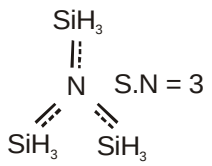


There will be pπ - pπ back bonding between 2p of B atom & 2p of F atom. Bond length of B - F will decreases

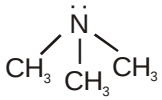
- The extent of back bonding decreases if the atom having vacant orbitals is also having some non-bonded electron pairs on it. So among the atoms of third period the extent of back bonding follows the order Si > P > S > Cl

for example,

Trisilylamine is a planar molecular and does not act as a lewis base while trimethyl is a pyramidal and act as lewis base



Planar

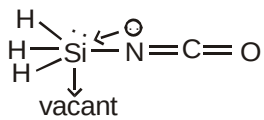


$\ddot{N}(CH_3)_3$ pyramidal

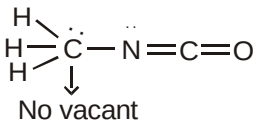
delocalised ℓ.P. S.N. = 3 sp^2 | Localised ℓ.P.S.No. = 4 sp^3

But in a similar compound $N(PH_2)_3$ the shape is found to be pyramidal, so N atom must be sp3 hybridised due to much less extent of back bonding into the vacant orbitals of P.

Silyl isocyanate (SiH_3NCO) is linear but methyl isocyanate (CH_3NCO) is bent explain !



vacant d-orbitals



No vacant orbitals

ℓ.P. of N can be delocalised (Back bonding)

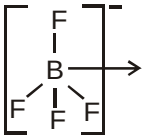
S.N of N = 2 (sp) | S.N = 3 (sp^2)

pπ – dπ back bonding.

Illustrations

Illustration 9. Compare B-F bond length in BF_3 and $[BF_4]^-$.

Solution. $BF_3 + KF \longrightarrow K^+ [BF_4]^-$

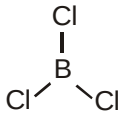


$\rightarrow SP^3$ hybridised [No back bonding]

B–F Bond length $[BF_4]^- > BF_3$

Illustration 10. All boron trihalides are lewis acids also explain their order.

Solution. Boron trihalides are electron deficient molecules therefore act as a Lewis acids

But in $BCl_3 \equiv$ 

$P\pi$ -$P\pi$ back bonding 2p of B & 3p of Cl less effective tendency to accept L.P in $BCl_3 > BF_3$. Lewis acid strength $BF_3 < BCl_3 < BBr_3$.

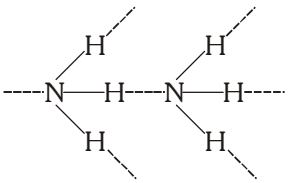
BEGINNER'S BOX–6

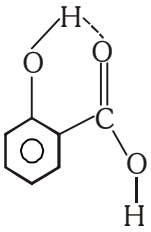
Hydrogen Bond

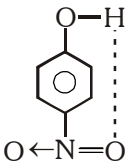
1. The hydrogen bond is strongest in:-
(A) O – H - - - S (B) S – H - - - O (C) F – H - - - F (D) O – H - - - O

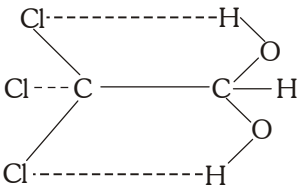
2. H_2O boils at higher temperature than H_2S, because it is capable of forming:-
(A) Ionic bonds (B) Covalent bonds (C) Hydrogen bonds (D) Metallic bonds

3*. In which of the following molecule, the shown hydrogen bond is not possible:-

(A) 

(B) 

(C) 

(D) 

4. The correct order of volatility is:-
(A) $NH_3 < H_2O$ (B) p– nitro phenol < o– nitro phenol
(C) $CH_3OH > CH_3-O-CH_3$ (D) HF > HCl

5. Intramolecular H–bond :-
(A) Decreases Volatility (B) Increases melting point
(C) Increases viscosity (D) Increases vapour pressure

6. Weakest hydrogen bond is :–
(A) O – H ..... N (B) S – H ..... S (C) F – H ..... F (D) N – H ..... N

7. Acetic acid exists as dimer in benzene due to:-
(A) Condensation reaction (B) Hydrogen bonding
(C) Presence of carboxyl group (D) None of the above

8*. Increasing strength of H–bonding (X---H – X) in S, O, F, Cl, N is :–
(A) Cl < S < N < O < F (B) N < Cl < S < O < F
(C) S < Cl < N < O < F (D) S < N < Cl < O < F

9. The high boiling point of water is due to the presence of
(A) Dative bond (B) Covalant bond (C) Hydrogen bond (D) Vander waals bond

10. Maximum no. of hydrogen bonds formed by a water molecule in ice is
(A) 4 (B) 3 (C) 2 (D) 1

22.0 INTERMOLECULAR FORCES (VAN DER WAAL'S FORCES)

SL AL

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

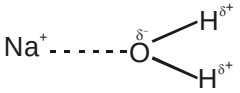
(a) Ion-dipole attraction :
(b) Dipole-dipole attraction :
(c) Ion-induced dipole attraction :
(d) Dipole-induced dipole attraction :
(e) Induced dipole-Induced dipole : (Dispersion force or London forces)

☞ ***Note :***
strength of van der Waal's forces a > b > c > d > e

22.1 Ion-dipole attraction

SL AL

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.



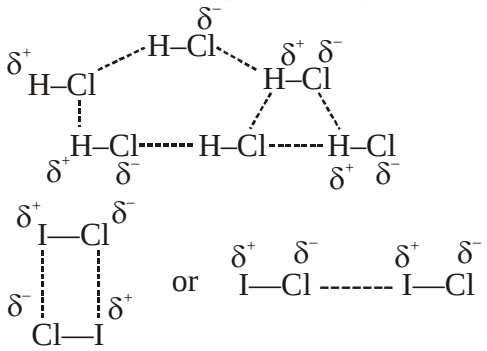
This force is responsible for hydration.

☞ ***Note :***
These are short range forces which are more sensitive to distance as compared to ion–ion attraction (The interaction energy is inversely proportional to square of the distance between species.

22.2 Dipole-dipole interaction

SL AL

In the case of polar molecules which have permanent dipoles, the van der Waals forces are mainly due to electrical interaction between the dipoles. Ends of the dipoles posses partial charges & these charges are shown by (δ). Partial charges are always less than unit electronic charges (1.6×10^{-19}C). Polar molecules interact with neighbouring molecules. These interactions are known as dipole-dipole interactions. For instances, gases such as ammonia, sulphur dioxide, hydrogen fluoride, hydrogen chloride, etc., have permanent dipoles as a result of which there is appreciable dipole interaction directly depends upon the dipole moment of the molecule concerned. This intraction is stronger than the London forces but is weaker that ion-ion interactions because only partial charges are involved.



☞ ***Note :***

The attractive forces decreases with the increase of distance between the dipoles. The interaction energy is inversely proportional to distance between polar molecules. Dipole-Dipole interaction energy between stationary polar molecules (as in solid) is proportional to $1/r^3$ and that between rotating polar molecules is proportional to $1/r^6$, where r is the distance between polar molecules. Besides dipole-dipole interaction, polar molecules can interact by London forces also. Thus cumulative effect is that the total of intermolecular forces in polar molecule increases.

22.3 Ion-induced dipole attraction

SL AL

Exists between ion and non-polar molecules. When a charged ion is introduced into the neighbourhood of an uncharged molecule it polarises the molecule generating dipole–induced dipole interaction.

$$Na^+ \quad \overset{\delta\delta^-}{Cl} — \overset{\delta\delta^+}{Cl}$$

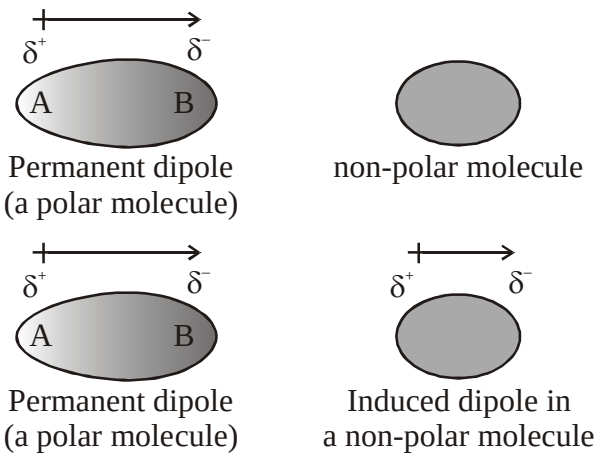
☞ ***Note :***

These are short range forces which are more sensitive to distance as compared to ion–ion attraction (The interaction energy is inversely proportional to fourth power of the distance between species.

22.4 Dipole-induced Dipole Interaction

SL AL

A polar molecule may sometimes polarise a neutral molecule which lies in its vicinity and thus induce polarity in that molecule just as a magnet induces magnetic polarity in a neutral piece of iron lying close by. The induced dipole then interacts with the dipole moment of the first molecule and thereby the two molecules are attracted together. The magnitude of this interaction would, evidently, depend upon the magnitude of the dipole moment of the polar molecule and the polarizability of the neutral molecule. Induced dipole moment depend upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule. Molecules of larger size can be easily polarized. High polarisability increases the strength of attractive interactions.



☞ ***Note :***

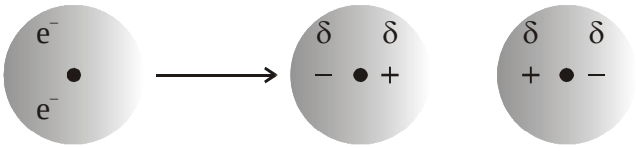
In this case also interation energy is proportional to $1/r^6$ where r is the distance between two molecules.

22.5 Instantaneous dipole- Instantaneous induced dipole attraction

SL AL

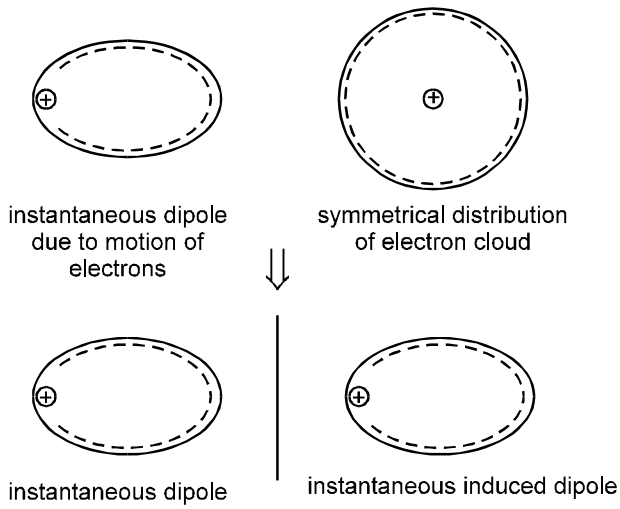
Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentrily even in such atoms and molecules. This can be understod as follows. Suppose we have two atoms 'A' and 'B' in the close vicinity of each other. It may so happens that momentarily electronic charge distrubition in one of the atoms, say 'A', becomes unsymmetrical i.e., the charge cloud is more on one side than the other. This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'.

The temporary dipole of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London and for this reason force of attraction between two temporary dipoles is known as London force. Another name for this force is dispersion force. These forces are always attractive.



Instantaneous uneven distribution of electrons in He atom | Instantaneous dipole | Induced dipole on neighbouring He atom Resultant attractive force

Exists among the non-polar molecules like H_2 , O_2 , Cl_2 etc. in solid or liquid states



☞ ***Note :***

(i) Strength of vander waal force $\propto$ molecular mass.

van der Waal's force $\propto$ Boiling point.

(ii) In this case also interation energy is proportional to $1/r^6$ where r is the distance between two molecules.

Illustrations

Illustration 11. Give the order of boiling point of following

Cl_2 , HCl

Solution. Dispersion force in $Cl_2 - Cl_2$ and dipole-dipole attraction in HCl – HCl

$\therefore$ Boiling point will be high in HCl.

Illustration 12. Arrange the inert gases, according to their increasing order of boiling points

Solution. He < Ne < Ar < Kr < Xe Boiling point

Because strength of van der Waal's force increases down the group with increase in molecular mass.

23.0 METALLIC BOND

SL AL

Metallic bond is defined as the force that binds a metal atom to a number of electrons within its sphere of influence.

23.1 Factors affecting metallic bonding

SL AL

Since it is electrical attraction between delocalised electrons (i.e. mobile electrons) and the positive part of the atom (i.e. kernel) therefore strength of metallic bond depends upon following factors :

- **No. of metallic bonds per atom**
  Larger the number of metallic bonds (number of valence electrons) per atom, stronger is the metallic bonding.
  (i) Alkali metals-only one valence electron and therefore, one metallic bond per atom and thus gives weakest metallic bonding. Hence their melting points are low.
  (ii) Alkaline earth metals-two valence electrons and form two metallic bonds per atom and, therefore, gives a comparatively bit stronger metallicbonding.
  (iii) Transition metals may use inner -d-electrons along with the outers electrons for bonding as (n–1) d and ns have nearly same energy. So in them number of metallic bonds per atoms is quite large (more than two always). Hence their melting points are higher.

- **Type of hybrid orbitals participating in metallic bonding**
  More directional and diffused hybrid orbitals form more stronger metallic bonds. ds hybrid orbitals (in transition metals) are more directional and diffused than sp hybrid orbitals (in alkali & alkaline earth metals)
  Therefore, much stronger metallic bonding takes place in transition metals.

- **Radius of metallic atom**
  Smaller the radius of atom, shorter is the bond length, hence greater is the bond strength.

BEGINNER'S BOX–7

Resonance, Metallic Bonds, Intermolecular forces & Miscellaneous

1. The boiling point of ICl is nearly 40°C higher than that of Br_2 although the two substances have the same relative molecular mass. This is becasue :
(A) ICl is ionic compound
(B) I-Cl bond is stronger than Br - Br bond
(C) ICl is polar covalent molecule while Br_2 is non polar
(D) Ionization energy IP of Iodine is less than that of Br.

2*. The structure of diborane, (B_2H_6) contains
(A) Four (2c–2e) bonds and two (2c–3e) bonds
(B) Two (2c–2e) bonds and two (3c–2e) bonds
(C) Four (2c–2e) bonds and four (3c–2e) bonds
(D) None

3. Boron forms BX_3 type of halides. The correct increasing order of Lewis-acid strength of these halides is
(A) $BF_3 > BCl_3 > BBr_3 > BI_3$
(B) $BI_3 > BBr_3 > BCl_3 > BF_3$
(C) $BF_3 > BI_3 > BCl_3 > BBr_3$
(D) $BF_3 > BCl_3 > BI_3 > BBr_3$

4. Select species which is planar at nitrogen :
(A) $(CH_3)_3N$
(B) $(SiH_3)_3N$
(C) NF_3
(D) NH_3

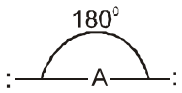
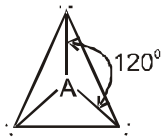
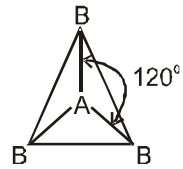
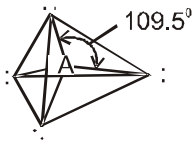
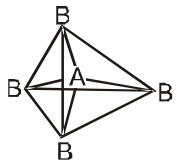
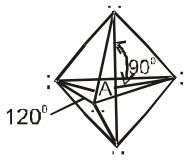
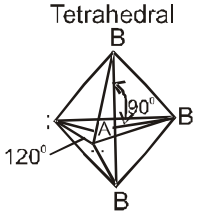
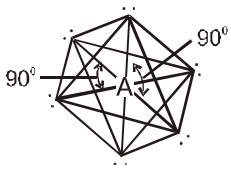
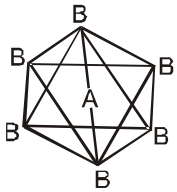
5. Type of back bonding in $(SiH_3)_2O$ is :
(A) $p\pi - d\pi$
(B) $p\pi - p\pi$
(C) $d\pi - d\pi$
(D) None of these

6. Which of the following factors are responsible for origination of vander Waals forces ?
(A) Instantaneous dipole-induced dipole interaction
(B) Dipole-induced dipole interaction
(C) Dipole-dipole interaction
(D) Size of molecule

7*. Which of the following are true ?
(A) Vander Waals forces are responsible for the formation of molecular crystals
(B) Branching lowers the boiling points of isomeric organic compounds due to decrease in vander Waals forces of attraction
(C) In graphite, vander Waals forces act between the carbon layers
(D) In diamond, vander Waals forces act between the carbon layers

GOLDEN KEY POINTS

- Ionic compounds are soluble if hydration energy is greater than lattice energy.
- Covalent character in Ionic compound can be explained with the help of Fajan's rule smaller cation, big anion & pseudo inert gas configuration of cation favours covalent character in ionic compound.
- If an ionic compound is having two or more than two crystalline structures then it is said to be polymorphous.
- Incomplete octect: BeF_2, BF_3, Al_3Cl_3, BCl_3.
- Expansion of octet: PCl_5, SF_6, ClF_3, IF_7.
- A $\sigma-$bond is formed by axial overlap of atomic orbitals and $\pi-$bond is formed by sideways overlap of orbitals.

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Example
2	 Linear	B – A – B Linear	$BeCl_2$,$HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4 , NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

- 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.

  e.g. angular – $SnCl_2$, $PbCl_2$, SO_2 ,

  Unsymmetrical geometry – NH_3, H_2O, NF_3, SF_4, H_2S,

- % Ionic character = $\dfrac{\mu_{Experimental}}{\mu_{Theoretical}} \times 100 = \dfrac{\mu_{(Observed)}}{\mu_{(100\%\ Ionic\ compound)}} \times 100$

- Bond order = $\dfrac{1}{2}(N_b - N_a)$

  A positive bond order ($N_b > N_a$) means a stable molecule while a negative or zero bond order means an unstable molecule.

  Bond order $\propto$ Bond strength

  $\propto \dfrac{1}{\text{Bond length}}$

  $\propto$ Stability

- Energy of Molecular orbital is given by experimental order not by (n + *l*) rule.

- $\overset{-\delta}{A}.....\overset{+\delta}{H}—\overset{-\delta}{B} \Rightarrow$ Hydrogen bond can be intermolecular or intramolecular hydrogen bonding.

  Intermolecular H - bond $\Rightarrow$ ROH, H_2O, ROH & H_2O

  Intramolecular H -bond $\Rightarrow$ Salicylic acid, Maleic acid.

- Vander wall's force are weakest type of intermolecular force. These are non-directional, non-valence cohesive forces. V.W. force $\propto$ Molecular weight $\propto$ Boiling point.

SOME WORKED OUT ILLUSTRATION

Illustration 1*.

If it is known that on heating a ionic compound of a polyhalide with a cation it decomposese into more stable halide of that cation due to high lattice energy, for example

$CsI_3 \xrightarrow{\Delta} CsI + I_2$

The complex compound Rb[IBrCl] after strong heating will

(A) RbI + BrCl (B) RbCl + IBr (C) RbBr + ICl (D) None

Solution.

(B)

$(L.E.)_{RbCl} > (L.E.)_{RbBr} > (L.E.)_{RbI}$ and more stable compound is formed first.

Illustration 2.

Which of the following overlaps is ***incorrect*** [assuming z-axis to be the internuclear axis]

(a) $2p_y + 2p_y \rightarrow \pi\, 2p_y$ (b) $2p_z + 2p_z \rightarrow \sigma\, 2p_z$

(c) $2p_x + 2p_x \rightarrow \pi\, 2p_x$ (d) $1s + 2p_y \rightarrow \pi\, (1s\text{-}2p_y)$

(A) 'a' & 'b' (B) 'b' & 'd' (C) only 'd' (D) None of these

Solution.

(C)

Orbitals should have same orientation & energy.

Illustration 3.

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^-

Solution.

(B)

Polarization $\propto$ Charge.

Illustration 4.

In which of the following molecule bonding is taking place in excited state

(A) CH_4 (B) BF_3 (C) ICl (D) PCl_3

Solution.

(A)

sp^3 hybridisation in Carbon

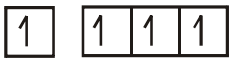


Illustration 5.

Consider the structures of the following two molecules

X : $F_2C = C = CF_2$

Y : $F_2B - C \equiv C - BF_2$

In which of these two it is impossible for all the four F atoms to lie in the same plane

(A) X (B) Y (C) both (D) none

Solution.

(A)

In cumulated dienes, planes will be perpendicular.

Illustration 6*.

Match the isostructure pairs

Hint : Having same hybridization and same Number of lone pair

(a)	SF_4	***(i)***	IF_6^+
(b)	PCl_5	***(ii)***	ClF_4^+
(c)	ICl_3	***(iii)***	$SnCl_5^-$
(d)	I_3^-	***(iv)***	ClF_3
(e)	ICl_4^-	***(v)***	ClF_2^-
(f)	PCl_6^-	***(vi)***	XeF_4

Solution.

(a-ii),(b-iii),(c- iv), (d-v),(e-vi),(f-i).

Illustration 7.

VESPR theory does not state

(A) the order of repulsion between different pair of electrons is $\ell p - \ell p > \ell p - bp > bp - bp$ (ℓp = lone pair electrons, bp = bond pair electrons.)

(B) as the number of lone pair of electrons on central atom increase, the deviation in BA from normal BA (Bond-Angle) also increase.

(C) the number of lone pair on O in H_2O is 1 while on N in NH_3 is 2.

(D) the structures of Xenon-fluorides and Xenon-oxyfluorides could be explained on the basis of VESPR theory.

Solution.

(C)

H_2O has 2 lone pair.

Illustration 8.

The correct expected order of decreasing lattice energy is

(A) CaO > $MgBr_2$ > CsI
(B) $MgBr_2$ > CaO > CsI
(C) CsI > $MgBr_2$ > CaO
(D) CsI > CaO > $MgBr_2$

Solution.

(A)

Lattice energy depends on charge & inversely depends on size.

Illustration 9*.

Which of the following is ionic solid :

(A) XeF_6 (s)
(B) PBr_5(s)
(C) CaC_2(s)
(D) All

Solution.

All are ionic solids

XeF_6 (S) consists XeF_5^+ & F^-

PBr_5 (s)..... PBr_4^+ & Br^-

CaC_2(s) ..... Ca^{++} & C_2^{--}

Illustration 10.

The correct order of increasing s character (in percentage) in the hybrid orbitals in below molecules / ions is (assume all hybrid orbitals are exactly equivalent) :

CO_3^{2-}	XeF_4	I_3^-	NCl_3	$BeCl_2$ (g)
I	II	III	IV	V

(A) II < III < IV < I < V
(B) II < IV < III < V < I
(C) III < II < I < V < IV
(D) II < IV < III < I < V

Solution.

(A)

CO_3^{2-} – sp^2

XeF_4 – sp^3d^2

I_3^- – sp^3d

NCl_3 – sp^3

$BeCl_2$(g) – sp

Illustration 11.

Which of the following is correct about the bond angle.

(A) $OF_2 < H_2O < Cl_2O < ClO_2$
(B) $PF_3 < PCl_3 < PBr_3 < PI_3$
(C) $NH_3 > NF_3$
(D) $KrF_4 < SF_2 < N_2H_2$

Solution.

(ABCD)

All given order are correct

$OF_2 < H_2O < Cl_2O < ClO_2$

sp^3 sp^3 sp^3 sp^3

low bp-bp larger

repulsion size of Cl

$PF_3 < PCl < PBr_3 < PI_3$

97.7° 100.3° 101.0° 102°

NH_3 > NF_3
107° 104°
KrF_4 > SF_2 < N_2H_2
sp^3d^2 Sp^3 sp^2 (< 120°)
(90°C) (< 109°28') sp^2(< 120°)
All gives order are order are correct

Illustration 12.

On the basis of MOT which is ***correct*** -
(A) The bond order for C_2 molecule is two and both bonds are π-bonds
(B) The LUMO in this molecule is σ2p molecular orbital
(C) The HOMO in this molecule are π type of antibonding m.o. containing total 4 electrons
(D) None of the above is correct

Solution.

(A)
LUMO is lowest unoccupied molecular orbital.
HOMO is highest occupied molecular orbital.

Illustration 13.

Which of the following statements is not correct from the point of view of molecular orbital?
(A) Be_2 is not a stable molecule
(B) He_2 is not stable but He_2^+ is expected to exist
(C) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules
(D) The order of energies of molecular orbitals in F_2 molecule is $\pi^b 2p_x < \sigma^b 2p_z$

Solution.

(D)
Correct order of energy in F_2 $\pi^b 2p_x > \sigma^b 2p_z$.

Illustration 14.

Match the following :

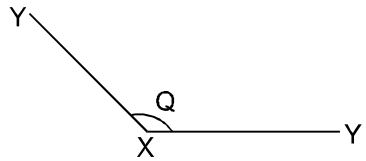
Column	***Column***
(A) N_2^+ is stable than N_2^-	(p) due to one have higher electrons in antibonding than other
(B) NO can easily loss its electron than N_2	(q) one have B.O. 3 and other have 2.5
(C) NO have large bond length than NO^+	(r) both are paramagnetic with same bond order
(D) He_2^+ exist but less stable than H_2^+	(s) one paramagnetic and other diamagnetic

Solution.

(A) - p, r (B)- p, q, s (C)- q, s (D) - p, r
Using their molecular orbital configuration.

Illustration 15.

Which bond angle Q would result in the maximum dipole moment for the triatomic molecule XY_2 shown below



(A) Q = 90° (B) Q = 120° (C) Q = 150° (D) 180°

Solution.

$R = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$; as $\theta \uparrow$, $R \downarrow$

Illustration 16.

Which of the following molecule is/are non polar
(A) XeF_2 (B) PCl_3F_2 (C) XeF_4 (D) All

Solution.

(D)

Illustration 17.

The dipole moment of HBr is 2.60×10^{-30} C.m, and the interatomic spacing is 1.41Å. What is the percent ionic character of HBr?

Solution.

The dipole moment of a 100% ionic "molecule" at the given internuclear distance would be

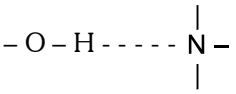
$(1.60 \times 10^{-19}C)\ (1.41 \times 10^{-10}m) = 2.26 \times 10^{-29}$ C.m

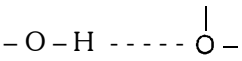
The actual dipole is less; the percent ionic character is given by

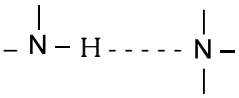
$$\frac{2.60 \times 10^{-30}\,C.m}{2.26 \times 10^{-29}\,C.m} \times 100\% = 11.5\%$$

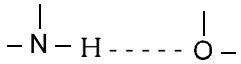
Illustration 18.

Consider the following sets of H-bonds

P : 

Q : 

R : 

S : 

The correct order of H-bond strengths is :

(A) Q > P > S > R (B) R > Q > S > P (C) R > S > P > Q (D) P > Q > R > S

Solution.

Nitrogen is less electronegative than oxygen so electron pair is easily available for bonding

Illustration 19.

Column-I		***Column-II***	
(A)	HCl < HF	***(p)***	Intermolecular forces
(B)	$PH_3 < NH_3$	***(q)***	Dipole moment
(C)	$H_2O < D_2O$	***(r)***	Boiling point
(D)	$H_2S < H_2O$	***(s)***	Molar mass

Solution.

(A – p, q, r) ; (B – p, q, r) ; (C – p, q, r, s) ; (D –p,q,r)

(A) In HF hydrogen bonding takes place and dipole moment is more than HCl.

(B) In NH_3 hydrogen bonding takes place which is absent in PH_3.

(C) In D_2O dipole moment is more than H_2O as D is less electronegative than hydrogen

(D) In H_2O hydrogen bonding is present

Illustration 20.

I. When ice is melted hydrogen bond starts breaking molecule of water come closer by moving into vacant space. As a result density of water decreases upto 4°C.

II. Due to open cage like structure, ice has a relatively large volume for a given mass of liquid water.

III. In ice there are four water molecules attached tetrahedrally.

Which of the above statement is true.

(A) I, II and III (B) I and III (C) II and III (D) II only

Solution.

I. density of water increases up to 4°C

II. in case of ice each water molecule is attached with other molecules tetrahedrally forming a cage like structure.

Illustration 21*.

Which of the following conditions is required for the formation of the hydrogen bond

(A) Hydrogen atom should be bonded to a highly electronegative atom

(B) The size of electronegative atom should be small

(C) There should be a lone pair of electron on the electronegative atom.

(D) All of the above

Solution.

(D)

Illustration 22.

Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false.

S_1 : HF boils at a higher temperature than HCl S_2 : HBr boils at lower temperature than HI

S_3 : Bond length of N_2 is less than N_2^+

S_4 : Enthalpy of formation of HCl is equal to the bond energy of HCl.

(A) T F T T (B) T T F F (C) T T T F (D) T T T T

Solution.

S_1 : Due to intermolecular H-bonding in HF it boils at higher temperature than HCl

S_2 : Mol. wt. of HBr < Mol. wt. of HI

S_3 : Bond order of N_2 is more than N_2^+ .

*****

ANSWERS

BEGINNER'S BOX-1

1.	(C)	2.	(A)	3.	(B)	4.	(C)	5.	(A)
6.	(A)	7.	(B)	8.	(C)	9.	(D)	10.	(B)
11.	(C)	12.	(A)	13.	(B)	14.	(C)		

BEGINNER'S BOX-2

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

BEGINNER'S BOX-3

1.	(C)	2.	(D)	3.	(C)	4.	(B)	5.	(D)
6.	(D)	7.	(C)	8.	(C)	9.	(C)	10.	(C)
11.	(B)	12.	(A)	13.	(B)				

BEGINNER'S BOX-4

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

BEGINNER'S BOX-5

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

BEGINNER'S BOX-6

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

BEGINNER'S BOX-7

1.	(C)	2.	(D)	3.	(B)	4.	(B)	5.	(A)
6.	(ABC)	7.	(ABC)						

EXERCISE – 1 MCQ (SINGLE CHOICE CORRECT)

1. 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

2. The compound which contains ionic as well as covalent bonds is
(A) $C_2H_4Cl_2$ (B) CH_3I (C) KCN (D) H_2O_2

3. A bond formed between two like atoms cannot be
(A) ionic (B) covalent (C) coordinate (D) metallic

4. Which of the following contains electrovalent and polar covalent bonds ?
(A) CH_4 (B) H_2O_2 (C) NH_4Cl (D) HCN

5*. PCl_5 exists but NCl_5 does not because :
(A) Nitrogen has no vacant 2d-orbitals (B) NCl_5 is unstable
(C) Nitrogen atom is much smaller than P (D) Nitrogen is highly inert

6*. Which of the following has/have a strong covalent bond?
(A) Cl-F (B) F-F (C) C-Cl (D) C-F

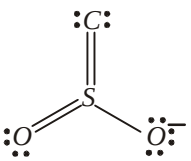
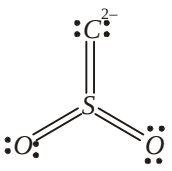
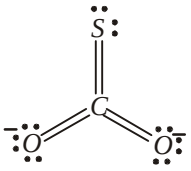
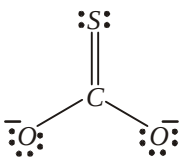
7. Which of the following species are hypervalent?
1. PCl_5, 2. BF_3, 3. XeF_2 , 4. CO_3^{2-}
(A) 1, 2, 3 (B) 1, 3 (C) 3, 4 (D) 1, 2

8. The types of bond present in N_2O_5 are
(A) only covalent (B) only ionic (C) ionic and covalent (D) covalent & coordinate

9. NH_3 and BF_3 combine readily because of the formation of :
(A) a covalent bond (B) a hydrogen bond (C) a coordinate bond (D) an ionic bond

10. Which of the following molecule does not have coordinate bonds?
(A) CH_3–NC (B) CO (C) O_3 (D) CO_3^{2-}

11. The possible structure(s) of monothiocarbonate ion is :

(A) 
(B) 
(C) 
(D) 

12. In the following compound $\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-C\equiv CH$, the C_2-C_3 bond is of the type :

(A) $sp-sp^2$ (B) sp^3-sp^3 (C) $sp-sp^3$ (D) sp^2-sp^3

13. 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^+

14. Maximum bond energy is in :

(A) F_2 (B) N_2 (C) O_2 (D) equal

15. The hybridisation and shape of BrF_3 molecule are :

(A) sp^3d and bent T shape (B) sp^2d^2 and tetragonal

(C) sp^3d and bent (D) none of these

16. The shape of methyl cation (CH_3^+) is likely to be:

(A) linear (B) pyramidal (C) planar (D) spherical

17. The structure of XeF_2 involves hybridization of the type :

(A) sp^3 (B) dsp^2 (C) sp^3d (D) sp^3d^2

18*. In the context of carbon, which of the following is arranged in the correct order of electronegativity :

(A) $sp > sp^2 > sp^3$ (B) $sp^3 > sp^2 > sp$ (C) $sp^2 > sp > sp^3$ (D) $sp^3 > sp > sp^2$

19*. When $2s-2s, 2p-2p$ and $2p-2s$ orbitals overlap, the bond strength decreases in the order :

(A) $p-p > s-s > p-s$ (B) $p-p > p-s > s-s$

(C) $s-s > p-p > p-s$ (D) $s-s > p-s > p-p$

20. Carbon atoms in $C_2(CN)_4$ are :

(A) sp-hybridized (B) sp^2-hybridized

(C) sp- and sp^2 hybridized (D) sp, sp^2 and sp^3 - hybridized

21. The structure of XeF_6 in vapour phase is

(A) pentagonal bipyramidal (B) trigonal bipyramidal

(C) capped octahedron (D) square bipyramidal

22. The formal charges on the three O-atoms in O_3 molecule are

(A) 0, 0, 0 (B) 0, 0, –1 (C) 0, 0, +1 (D) 0, +1, –1

23*. Which of the following has been arranged in order of decreasing dipole moment ?

(A) $CH_3Cl > CH_3F > CH_3Br > CH_3I$
(B) $CH_3F > CH_3Cl > CH_3Br > CH_3I$
(C) $CH_3Cl > CH_3Br > CH_3I > CH_3F$
(D) $CH_3F > CH_3Cl > CH_3I > CH_3Br$

24. The experimental value of the dipole moment of HCl is 1.03 D. The length of the $H-Cl$ bond is $1.275\mathring{A}$. The percentage of ionic character in HCl is :

(A) 43
(B) 21
(C) 17
(D) 7

25*. If ethylene molecule lies in X-Y plane then nodal planes of the π-bond will lie in

(A) XZ plane
(B) YZ plane
(C) In a plane that bisects C–C axis
(D) XY plane

26. Which of the following models best describes the bonding between layer of the graphite structure ?

(A) metallic bonding
(B) ionic bonding
(C) non-metallic covalent bonding
(D) van der Waals forces

27. Ethanol has a higher boiling point than dimethyl ether though they have the same molecular weight. This is due to :

(A) resonance
(B) coordinate bonding
(C) hydrogen bonding
(D) ionic bonding

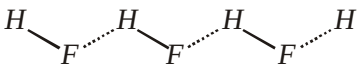
28. Which of the following compounds would have significant intermolecular hydrogen bonding ?

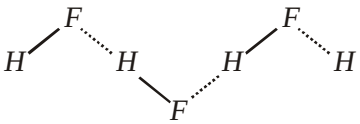
HF, CH_3OH, N_2O_4, CH_4

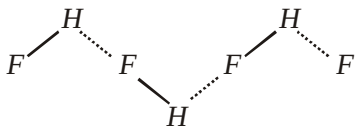
(A) HF, N_2O_4
(B) HF, CH_4, CH_3OH
(C) HF, CH_3OH
(D) CH_3OH, CH_4

29. The H bond in solid HF can be best represented as:

(A) $H-F....H-F....H-F$

(B) 

(C) 

(D) 

30. Two ice cubes are pressed over each other and unite to form one cube. Which force is responsible for holding them together :

(A) van der Waal's forces
(B) Covalent attraction
(C) Hydrogen bond formation
(D) Dipole-dipole attraction

EXERCISE – 2 MCQ (ONE OR MORE CHOICE CORRECT)

1. Which of the following statement(s) is/are correct regarding ionic compounds?
(A) They are good conductors of electricity at room temperature in aqueous solution.
(B) They are generally soluble in polar solvents.
(C) They consist of ions.
(D) They generally have high melting and boiling points.

2*. Which of the following compounds contain ionic, covalent and cordinate bonds?
(A) NH_4Cl (B) KCN (C) $NaBF_4$ (D) NaOH

3. The octet rule is not obeyed in :
(A) CO_2 (B) BCl_3 (C) PCl_5 (D) SiF_4

4. To which of the following species octet rule is not applicable :
(A) BrF_5 (B) SF_6 (C) IF_7 (D) *CO*

5. Pick out among the following species isoelectronic with CO_2 :
(A) N_3^- (B) $(CNO)^-$ (C) $(NCN)^{2-}$ (D) NO_2^-

6*. Which of the following statement(s) is / are not correct ?
(A) Hybridization is the mixing of atomic orbitals of large energy difference.
(B) sp^2 – hybrid orbitals are formed from two *p* - atomic orbitals and one *s*- atomic orbital
(C) sp^3d^2 – hybrid orbitals are all at 90° to one another
(D) sp^3 –hybrid orbitals are directed towards the corners of a regular tetrahedron

7. Which of the following species is (are) isostructural with XeF_4 ?
(A) ICl_4^- (B) I_3^- (C) BrF_4^- (D) XeO_4

8. Which of the following statements is/are correct ?
(A) NH_2^+ shows sp^2 – hybridisation whereas NH_2^- shows sp^3 – hybridisation
(B) $Al(OH)_4^-$ has a regular tetrahedral geometry
(C) sp^2 – hybridized orbitals bonded to same substituents have equal *s*- and *p*- character
(D) Hybridized orbitals always form σ - bonds

9. There is change in the hybridisation when :
(A) NH_3 combines with H^+
(B) AlH_3 combines with H^-
(C) NH_3 forms NH_2^-
(D) SiF_4 forms SiF_6^{2-}

10. State the wrong statement :
(A) Free rotation around the single bond is not possible.
(B) *p*-orbitals always overlap sideways
(C) *s*-orbitals never form π - bonds
(D) There can be more than one sigma bond between two atoms

11. Which of the following has (have) regular octahedral geometry :
(A) $SbCl_6^-$ (B) $SnCl_6^{2-}$ (C) XeF_6 (D) IO_6^{5-}

12. Which of the following have same shape as NH_2^+ ?
(A) CO_2 (B) $SnCl_2$ (C) SO_2 (D) $BeCl_2$

13. Which of the following is (are) linear ?
(A) I_3^- (B) I_3^+ (C) $PbCl_2$ (D) XeF_2

14. Which of the following compounds possesses zero dipole moment?
(A) Water (B) Benzene
(C) Carbon tetrachloride (D) Boron trifluoride

15. Which of the following compounds has bond angle as nearly 90° ?
(A) NH_3 (B) H_2S (C) H_2O (D) SF_6

16*. For propadiene $\underset{1}{H_2C} = \underset{2}{C} = \underset{3}{CH_2}$, correct statement(s) is / are :
(A) Molecule is non planar
(B) Molecule is nonpolar
(C) Nodal plane of π-bond formed by C_1 & C_2 is perpendicular to that of formed by C_2 & C_3.
(D) Nodal plane of π-bond formed by C_1 & C_2 is coplanar with that of formed by C_2 & C_3.

17. Which of the following bonds/forces is/are weakest?
(A) covalent bond (B) vander Waals force
(C) hydrogen bond (D) london force

18. Which of the following molecules have intermolecular hydrogen bonds ?
(A) KH_2PO_4 (B) H_3BO_3 (C) $C_6H_5CO_2H$ (D) CH_3OH

19. Which of the following have dipole moment ?
(A) nitrobenzene (B) *p*-chloronitrobenzene (C) *m*-dichlorobenzene (D) *o*-dichlorobenzene

Match the Column

20*.

Column-I	***Column-II***
(A) O_3	(p) covalent bond
(B) $H_2O_{(\ell)}$	(q) Co-ordinate bond
(C) $CuSO_4 . 5H_2O$	(r) Hydrogen bond
(D) $(NH_4)_2SO_4$	(s) Ionic bond

21.

Column-I	***Column-II***
(A) N_2^+ is stable than N_2^- / In N_2^+ & N_2^-	(p) due to one have higher electrons in antibonding than other
(B) NO can easily loss its electron than N_2 / In NO & N_2	(q) one have B.O. 3 and other have 2.5
(C) NO have large bond length than NO^+ / In NO & NO^+	(r) both are paramagnetic with same bond order
(D) He_2^+ exist but less stable than H_2^+ / In He_2^+ & H_2^+	(s) one paramagnetic and other diamagnetic

22*.

Column I	***Column II***
(A) BrF_3	(p) Atleast one angle ≤ 90°
(B) TeF_5^-	(q) Central atom is sp^3d^2 hybridised
(C) IF_7	(r) Non planar
(D) XeF_4	(s) Polar

23*. **Column I** | **Column II**

(A) $I(CN)_2^-$ | (p) Having $p\pi$–$p\pi$ bond & $\mu_D = 0$
(B) CO_3^{2-} | (q) Having $p\pi$–$d\pi$ bond & $\mu_D \neq 0$
(C) XeO_2F_2 | (r) Planar
(D) SOF_4 | (s) Central atom is sp^3d

Comprehension Based Questions

Comprehension-1

In order to explain the shape and geometry of molecules. The valence bond theory was supplemented by the concept of Hybridization. This is a Hypothetical concept and has been introduced by Pauling and Slater. According to this concept any number of atomic orbitals of an atom which differ in energy slightly may mix with each other to form new orbitals called hybrid orbitals. The process of mixing or amalgamation of atomic orbitals of nearly same energy to produced a set of entirely new orbitals of equivalent energy is known as Hybridization.

24. The hybridization of carbon atoms in C – C single bond of H – C ≡ C – CH = CH_2 is :
(A) $sp^3 - sp^3$ (B) $sp^2 - sp^3$ (C) $sp - sp^2$ (D) $sp^3 - sp$

25. In XeF_2, XeF_4 and XeF_6 the number of lone pairs on Xe is respectively :
(A) 2, 3, 1 (B) 1, 2, 3 (C) 4, 1, 2 (D) 3, 2, 1

26. Which of the following is the correct set :
(A) H_2O ; sp^3, angular
(B) H_2O ; sp^2, linear
(C) NH_3 ; sp^2, pyramidal
(D) BF_3 ; sp^3, trigonal planar

27. In NO_3^- ion, number of bond pair and lone pairs of electrons on nitrogen atom are :
(A) 2, 2 (B) 3, 1 (C) 1, 3 (D) 4, 0

28. T-shape is exhibited by molecule :
(A) ClF_3 (B) $CHCl_3$ (C) CCl_4 (D) PCl_5

Comprehension-2

The molecular orbital with the lowest energy is filled first. Thus σ (1s) is filled first where as σ^* (2p) is filled in the last, also the maximum number of electron in bonding and antibonding molecular orbtitals are according to Pauli and Hund's rule. As an electron in an antibonding molecular orbital cancels out the stability introduced by the electron in a bonding molecular orbital, it means that in order for bonding of atoms to occur there should be an excess of bonding electrons over antibonding electrons. In case where the number of bonding and antibonding electrons are equal, no bond will be formed between the atoms. With the help of above discussion, we can define easily bond order, relative bond length, relative stability and magnetic properties for a molecule.
Read the above paragraph carefully and give the answer of following questions :

29*. In an antibonding molecular orbital, there is a point between the two probability contours of hydrogen atoms. This is called.
(A) antinode
(B) node
(C) a plane where electron charge density is maximum
(D) A and C both are correct

30*. According to MOT which statement is correct about Boron molecule ?
(A) it is diamagnetic in nature
(B) it is paramagnetic in nature having magnetic moment 2.8 B.M. by using spin only formula
(C) it is paramagnetic but having magnetic moment 1.7 B.M.
(D) its bond order is 2

31*. Which of the following are paramagnetic in nature ?
(A) B_2, N_2 and C_2 (B) O_2, B_2, N_2^- and O_2^- (C) O_2^{--}, N_2^+ and CO (D) B_2, C_2 and F_2

EXERCISE – 3 SUBJECTIVE

1*. **(a)** The structures of N_2O_3 and P_2O_3 are different. Explain.
(b) Among H–I, H–Br and H–Cl bonds which is weakest?

2. Suppose that the stability of carbonates when heated depends on the ability of the metal cation to polarize the carbonate ion and remove an oxide ion from it, so releasing CO_2.
(a) Predict the order of thermal stability of the group 1 and 2 metal carbonates ?
(b) Comment on the likely stability of aluminium carbonate ?

3*. Example the following :
(i) Boron trichloride has triangular planar geometry whereas aluminium trichloride has tetrahedral dimeric structure.
(ii) Barium sulphate is sparingly soluble in water whereas beryllium sulphate is freely soluble.
(iii) Dioxygen (O_2) molecule is stable whereas disulphur (S_2) is unstable at the room temperature.

4*. Assuming Z-axis as molecular axis, lable the molecular orbitals formed by the following combination of atomic orbitals :
(i) 1s + 1s **(ii)** $2p_y - 2p_y$ **(iii)** $2p_z + 2p_z$ **(iv)** 2s + 2s
(v) $2p_x + 2p_x$

5. When a magnet is dipped in a jar of liquid O_2, some O_2 clings to it. Why ?

6. A diatomic molecule has a dipole moment of 1.2 D. If the bond distance is 0.1 Å, what fraction of an electron charge, *e* exist on each atom?

7. Through the electronegativities of nitrogen and chlorine are same, NH_3 exists as liquid whereas HCl as gas. Why?

8*. The percent ionic character in HCl is 18.08. The observed dipole moment is 1.08 D. Find the internuclear distance in HCl.

9. Dipole moment of LiF was experimentally determined and was found to be 6.32 D. Calculate percentage ionic character in LiF molecule Li – F bond length is 0.156 nm.

10. Based upon M.O. theory state reason for the paramagnetic characater of CN, the diamagnetic character of CN^-, the stability of CN^- and calculate their respective bond orders.

11*. Draw the structure of following compound
(i) S_8 **(ii)** N_2H_4 **(iii)** P_4O_{10} **(iv)** $POCl_3$
(v) $XeOF_4$ **(vi)** C_3O_2 **(vii)** BrF_5

12. In solid $\overset{+}{Na}\overset{-}{Cl}$ one Na^+ is surrounded by six Cl^- ions find out total number of directional bonds formed by each Na^+ with Cl^- ions.

13. Using *VSEPR* theory identify the type of hybridisation and draw the structure of OF_2 .

14. What should be the structure shape of the following as per *VSEPR* theory ?
(a) XeF_2 (b) XeF_4 (c) PBr_5 (d) OF_2 (e) I^-_3 (f) I^+_3

15. Which will have a higher boiling point, Br_2 or ICl , & why?

16. Arrange noble gases , in the increasing order of b.p.

EXERCISE – 4 RECAP OF AIEEE/JEE (MAIN)

1. In which of the following species is the underlined carbon having sp^3 - hybridisation ? ***[AIEEE 2002]***

(A) $CH_3–\underline{C}OOH$ (B) $CH_3\underline{C}H_2OH$ (C) $CH_3\underline{C}OCH_3$ (D) $CH_2=\underline{C}H–CH_3$

2. Which of the following statements is true ? ***[AIEEE 2002]***

(A) HF is less polar than HBr

(B) Water does not contain any ions

(C) Chemical bond formation takes place when forces of attraction overcome the forces of repulsion

(D) In covalent bond, transfer of electrons takes place

3*. The reason for double helical structure of DNA is operation of : ***[AIEEE 2003]***

(A) dipole-dipole interaction (B) hydrogen bonding

(C) electrostatic attractions (D) vander Walls' forces

4*. Which one of the following pairs of molecules will have permanent dipole moments for both members ***[AIEEE 2003]***

(A) NO_2 and CO_2 (B) NO_2 and O_3 (C) SiF_4 and CO_2 (D) SiF_4 and NO_2

5. The pair of species having identical shapes for molecules of both species is ***[AIEEE 2003]***

(A) XeF_2, CO_2 (B) BF_3, PCl_3 (C) PF_5, IF_5 (D) CF_4, SF_4

6*. The correct order of bond angles (smallest first) in H_2S, NH_3, BF_3 and SiH_4 is :– ***[AIEEE–2004]***

(A) $H_2S < NH_3 < SiH_4 < BF_3$ (B) $NH_3 < H_2S < SiH_4 < BF_3$

(C) $H_2S < SiH_4 < NH_3 < BF_3$ (D) $H_2S < NH_3 < BF_3 < SiH_4$

7. The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for these two species ? ***[AIEEE–2004]***

(A) Bond length in NO^+ is equal to that in NO (B) Bond length in NO is greater than in NO^+

(C) Bond length in NO^+ is greater than in NO (D) Bond length is unpredictable

8. The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are respectively ***[AIEEE–2004]***

(A) sp^3 and sp^2 (B) sp^2 and sp^3 (C) sp^2 and sp^2 (D) sp^3 and sp^3

9*. Beryllium and aluminium exhibit many properties which are similar. But, the two elements differ in

(A) Forming covalent halides (B) Forming polymeric hydrides ***[AIEEE–2004]***

(C) Exhibiting maximum covalency in compounds (D) Exhibiting amphoteric nature in their oxides

10. Which one of the following species is diamagnetic in nature ? ***[AIEEE-2005]***

(A) He_2^+ (B) H_2 (C) H_2^+ (D) H_2^-

11. lattice energy of an ionic compound depends upon ***[AIEEE-2005]***

(A) charge on the ion only (B) size of the ion only

(C) packing of the ion only (D) charge and size of the ion

12. The molecular shapes of SF_4, CF_4 and XeF_4 are **[AIEEE-2005]**
(A) the same with 2, 0 and 1 lone pair of electrons on the central atom, respecitvely
(B) the same with 1, 1 and 1 lone pair of electrons on the central atoms, respectively
(C) different with 0, 1 and 2 lone pair of electrons on the central atoms, respectively
(D) different with 1, 0 and 2 lone pair of electrons on the central atoms, respectively

13. Of the following sets which one does not contain isoelectronic species ? **[AIEEE-2005]**
(A) PO_4^{3-}, SO_4^{2-}, ClO_4^- (B) CN^-, N_2, C_2^{2-} (C) SO_3^{2-}, CO_3^{2-}, NO_3^- (D) BO_3^{3-}, CO_3^{2-}, NO_3^-

14. The number and type of bond between two carbon atom in calcium carbide are : **[AIEEE 2005]**
(A) One sigma, one pi (B) One sigma, two pi (C) Two sigma, one pi (D) Two sigma, two pi

15. Which of the following molecules\ions does not contain unpaired electrons? **[AIEEE-2006]**
(A) N_2^+ (B) O_2 (C) O_2^{2-} (D) B_2

16. Among the following mixtures, dipole-dipole as the major interaction, is present in **[AIEEE-2006]**
(A) KCI and water (B) benzene and carbon tetrachloride
(C) benzene and ethanol (D) acetonitrile and acetone

17. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct? **[AIEEE-2006]**
(A) MCl_2 is more ionic than MCl_4
(B) MCl_2 is more easily hydrolysed than MCl_4
(C) MCl_2 is more volatile than MCl_4
(D) MCl_2 is more soluble in anhydrous ethanol than MCl_4

18*. In which of the following molecules/ions are all the bonds ***not*** equal? **[AIEEE-2006]**
(A) XeF_4 (B) BF_4^- (C) SF_4 (D) SiF_4

19*. In which of the following ionizion processes, the bond order has increased and the magnetic behaviour has changed **[AIEEE-2007]**
(A) $NO \rightarrow NO^+$ (B) $O_2 \rightarrow O_2^+$ (C) $N_2 \rightarrow N_2^+$ (D) $C_2 \rightarrow C_2^+$

20. Which of the following hydrogen bonds is the strongest **[AIEEE-2007]**
(A) F–H.....F (B) O–H.....O (C) O–H.....F (D) O–H.....N

21. Which of the following species exhibits the diamagnetic behaviour **[AIEEE-2007]**
(A) O_2^+ (B) O_2 (C) NO (D) O_2^{2-}

22. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+, Ca^{+2}, Mg^{+2}, Be^{+2}
(A) $Be^{+2} < K^+ < Ca^{+2} < Mg^{+2}$ (B) $K^+ < Ca^{+2} < Mg^{+2} < Be^{+2}$
(C) $Ca^{+2} < Mg^{+2} < Be^{+2} < K^+$ (D) $Mg^{+2} < Be^{+2} < K^+ < Ca^{+2}$ **[AIEEE-2007]**

23. which one of the following pairs of species have the same bond order? **[AIEEE-2008]**
(A) CN^- and NO^+ (B) CN^- and CN^+ (C) O_2^- and CN^- (D) NO^+ and CN^+

24*. Using MO theory predict which of the following species has the shortest bond length? **[AIEEE-2009]**

(A) O_2^- (B) O_2^{2-} (C) O_2^{2+} (D) O_2^+

25. Among the following the maximum covalent character is shown by the compound :- **[AIEEE-2011]**

(A) $AlCl_3$ (B) $MgCl_2$ (C) $FeCl_2$ (D) $SnCl_2$

26. The structure of IF_7 is :- **[AIEEE-2011]**

(A) octahedral (B) pentagonal bipyramid
(C) square pyramid (D) trigonal bipyramid

27. The hybridisation of orbitals of N atom in NO_3^-, NO_2^+ and NH_4^+ are respectively :- **[AIEEE-2011]**

(A) sp, sp^3, sp^2 (B) sp^2, sp^3, sp (C) sp, sp^2, sp^3 (D) sp^2, sp, sp^3

28. Which of the following has maximum number of lone pairs associated with Xe ? **[AIEEE-2011]**

(A) XeO_3 (B) XeF_4 (C) XeF_6 (D) XeF_2

29. The number of types of bonds between two carbon atoms in calcium carbide is :- **[AIEEE-2011]**

(A) One sigma, two pi (B) One sigma, one pi (C) Two sigma, one pi (D) Two sigma, two pi

30*. Ortho-Nitrophenol is less soluble in water than p– and m– Nitrophenols because :- **[AIEEE-2012]**

(A) Melting point of o–Nitrophenol is lower than those of m– and p– isomers
(B) o–Nitrophenol is more volatile in steam than those of m– and p– isomers
(C) o–Nitrophenol shows Intramolecular H–bonding
(D) o–Nitrophenol shows Intermolecular H–bonding

31. In which of the following pairs the two species are not isostructural ? **[AIEEE-2012]**

(A) AlF_6^{3-} and SF_6 (B) CO_3^{2-} and NO_3^- (C) PCl_4^+ and $SiCl_4$ (D) PF_5 and BrF_5

32. Which one of the following molecules is expected to exhibit diamagnetic behaviour ? **[JEE (MAIN) 2013]**

(A) C_2 (B) N_2 (C) O_2 (D) S_2

33. In which of the following pairs of molecules/ions, both the species are not likely to exist ? **[JEE (MAIN) 2013]**

(A) H_2^+, He_2^{2-} (B) H_2^-, He_2^{2-} (C) H_2^{2+}, He_2 (D) H_2^-, He_2^{2+}

34*. Which of the following exists as covalent crystals in the solid state ? **[JEE (MAIN) 2013]**

(A) Iodine (B) Silicon (C) Sulphur (D) Phosphorus

35. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of :- **[JEE (MAIN) 2013]**

(A) $Li_2 < Li_2^+ < Li_2^-$ (B) $Li_2^- < Li_2^+ < Li_2$ (C) $Li_2 < Li_2^- < Li_2^+$ (D) $Li_2^- < Li_2 < Li_2^+$

36. Which one of the following properties is not shown by NO ? **[JEE (MAIN) 2014]**

(A) It is diamagnetic in gaseous state
(B) It is a neutral oxide
(C) It combines with oxygen to form nitrogen dioxide
(D) It's bond order is 2.5

37*. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is : **[JEE (MAIN) 2015]**

(A) ion–ion interaction (B) ion–dipole interaction (C) London force (D) Hydrogen bond

38. Which among the following is the most reactive ? **[JEE (MAIN) 2015]**

(A) Cl_2 (B) Br_2 (C) I_2 (D) ICl

39*. The species in which the N atom is in a state of sp hybridization is: **[JEE (MAIN) 2016]**

(A) NO_2^+ (B) NO_2^- (C) NO_3^- (D) NO_2

40. The pair in which phosphorous atoms have a formal oxidation state of + 3 is :- **[JEE-MAINS-2016]**

(A) Pyrophosphorous and pyrophosphoric acids (B) Orthophosphorous and pyrophosphorous acids
(C) Pyrophosphorous and hypophosphoric acids (D) Orthophosphorous and hypophosphoric acids

41. The group of molecules having identical shape is : **[JEE-MAINS-2016]**

(A) SF_4, XeF_4, CCl_4 (B) ClF_3, $XeOF_2$, XeF_3^+ (C) PCl_5, IF_5, XeO_2F_2 (D) BF_3, PCl_3, XeO_3

42. ***Assertion :*** Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity. **[JEE-MAINS-2016]**

Reason : Hybridization of carbon in diamond and graphite are sp^3 and sp^2, respectively.

(A) Assertion is incorrect statement, but the reason is correct.
(B) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.
(C) Both assertion and reason are incorrect.
(D) Both assertion and reson are correct, but the reason is not the correct explanation for the assertion.

43. Aqueous solution of which salt will not contain ions with the electronic configuration $1s^22s^22p^63s^23p^6$? **[JEE-MAINS-2016]**

(A) NaCl (B) CaI_2 (C) KBr (D) NaF

44. The correct sequence of decreasing number of π-bonds in the structures of H_2SO_3, H_2SO_4 and $H_2S_2O_7$ is :- **[JEE-MAINS-2017]**

(A) $H_2S_2O_7 > H_2SO_4 > H_2SO_3$ (B) $H_2SO_3 > H_2SO_4 > H_2S_2O_7$
(C) $H_2S_2O_7 > H_2SO_3 > H_2SO_4$ (D) $H_2SO_4 > H_2S_2O_7 > H_2SO_3$

45. The increasing order of the boiling points for the following compounds is:- **[JEE-MAINS-2017]**

(I) C_2H_5OH (II) C_2H_5Cl (III) $C_2H_5CH_3$ (IV) $C_2H_5OCH_3$

(A) (III) < (II) < (I) < (IV) (B) (II) < (III) < (IV) < (I) (C) (IV) < (III) < (I) < (II) (D) (III) < (IV) < (II) < (I)

46. The number of P–OH bonds and the oxidation state of phosphorus atom in pyrophosphoric acid ($H_4P_2O_7$) respectively are:- **[JEE-MAINS-2017]**

(A) five and four (B) five and five (C) four and five (D) four and four

47. The group having triangular planar structures is :- **[JEE-MAINS-2017]**

(A) CO_3^{2-}, NO_3^-, SO_3 (B) NCl_3, BCl_3, SO_3 (C) NH_3, SO_3, CO_3^{2-} (D) BF_3, NF_3, CO_3^{2-}

48. The number of S=O and S–OH bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are : **[JEE-MAINS-2017]**

(A) (2 and 4) and (2 and 4) (B) (4 and 2) and (2 and 4)
(C) (2 and 2) and (2 and 2) (D) (4 and 2) and (4 and 2)

49. Total number of lone pair of electrons in I_3^- ion is **[JEE (MAIN) 2018]**

(A) 6 (B) 9 (C) 12 (D) 3

50. According to molecular orbital theory, which of the following will not be a viable molecule ? **[JEE (MAIN) 2018]**

(A) He_2^+ (B) H_2^- (C) H_2^{2-} (D) He_2^{2+}

51. The number of 2–centre–2–electron and 3–centre–2–electron bonds in B_2H_6, respectively, are **[JEE-MAIN-2019]**

(A) 2 and 4 (B) 2 and 1 (C) 2 and 2 (D) 4 and 2

52. The element that shows greater ability to form pπ–pπ multiple bonds, is : **JEE-MAIN-2019]**

(A) Si (B) Ge (C) Sn (D) C

53. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic ? **[JEE-MAIN-2019]**

(A) $N_2 \rightarrow N_2^+$ (B) $NO \rightarrow NO^+$ (C) $O_2 \rightarrow O_2^{2-}$ (D) $O_2 \rightarrow O_2^+$

54. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^- ? **[JEE-MAIN-2019]**

(A) Both are unstable (B) Li_2^+ is unstable and Li_2^- is stable

(C) Li_2^+ is stable and Li_2^- is unstable (D) Both are stable

55. Two pi and half sigma bonds are present in : **[JEE-MAIN-2019]**

(A) N_2+ (B) N_2 (C) O_2+ (D) O_2

56. The correct order of hydration enthalpies of alkali metal ions is - **[JEE-MAIN 2019]**

(A) $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ (B) $Li^+ > Na^+ > K^+ > Cs^+ > Rb^+$

(C) $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$ (D) $Na^+ > Li^+ > K^+ > Cs^+ > Rb^+$

57. The ion that has sp^3d^2 hybridization for the central atom, is : **[JEE-MAIN 2019]**

(A) $[ICI_2]^-$ (B) $[IF_6]^-$ (C) $[ICI_4]^-$ (D) $[BrF_2]^-$

58. Among the following molecules / ions, $C_2^{2-}, N_2^{2-}, O_2^{2-}, O_2$ which one is diamagnetic and has the shortest bond length ? **[JEE-MAIN 2019]**

(A) C_2^{2-} (B) N_2^{2-} (C) O_2 (D) O_2^{2-}

59. The correct statement about ICl_5 and ICl_4^- is **[JEE-MAIN 2019]**

(A) ICl_5 is trigonal bipyramidal and ICl_4^- is tetrahedral.

(B) ICl_5 is square pyramidal and ICl_4^- is tetrahedral.

(C) ICl_5 is square pyramidal and ICl_4^- is square planar.

(D) Both are isostructural.

60. Among the following, the molecule expected to be stabilized by anion formation is : ***[JEE-MAIN 2019]***

C_2, O_2, NO, F_2

(A) NO (B) C_2 (C) F_2 (D) O_2

61. Among the following species, the diamagnetic molecule is ***[JEE-MAIN 2019]***

(A) O_2 (B) NO (C) B_2 (D) CO

62. During the change of O_2 to O_2^-, the incoming electron goes to the orbital : ***[JEE-MAIN 2019]***

(A) $\sigma^*\ ^2P_z$ (B) $\pi\ ^2P_y$ (C) $\pi^*\ ^2P_x$ (D) $\pi\ ^2P_x$

63. The correct statement among the following is ***[JEE-MAIN 2019]***

(A) $(SiH_3)_3N$ is pyramidal and more basic than $(CH_3)_3N$

(B) $(SiH_3)_3N$ is planar and more basic than $(CH_3)_3N$

(C) $(SiH_3)_3N$ is pyramidal and less basic than $(CH_3)_3N$

(D) $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$

EXERCISE – 5 RECAP OF IIT-JEE/JEE (ADVANCED)

1*. The percentage of p-character in the orbitals forming P–P bonds in P_4 is **[JEE 2007]**
(A) 25 (B) 33 (C) 50 (D) 75

2. The structure of XeO_3 is **[JEE 2007]**
(A) linear (B) planar (C) pyramidal (D) T-shaped

3. ***Statement-1*** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.
because
Statement-2 : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. **[JEE 2007]**
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.

4. ***Statement-1*** : In water, orthoboric acid behaves as a weak monobasic acid.
because
Statement-2 : In water, orthoboric acid acts as a proton donor. **[JEE 2007]**
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.

5*. The nitrogen oxide(s) that contain(s) N–N bond(s) is/are **[JEE 2009]**
(A) N_2O (B) N_2O_3 (C) N_2O_4 (D) N_2O_5

6. The species having pyramidal shape is/are : **[JEE 2010]**
(A) SO_3 (B) BrF_3 (C) SiO_3^{--} (D) OSF_2

7*. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are) **[JEE 2012]**
(A) sp and sp^3 (B) sp and sp^2 (C) only sp^2 (D) sp^2 and sp^3

8. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen- **[JEE 2012]**
(A) HNO_3, NO, NH_4Cl, N_2 (B) HNO_3, NO, N_2, NH_4Cl
(C) HNO_3, NH_4Cl, NO, N_2 (D) NO, HNO_3, NH_4Cl, N_2

9. The shape of XeO_2F_2 molecule is : **[JEE 2012]**
(A) Trigonal bipyramidal (B) Square planar (C) tetrahedral (D) see-saw

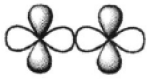
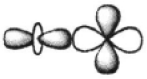
10. The total number of lone-pairs of electrons in melamine is. **[JEE 2013]**

11*. Hydrogen bonding plays a central role in the following phenomena: **[JEE 2014]**
(A) Ice floats in water
(B) Higher Lewis basicity of primary amines than tertiary amines in aqueous solution
(C) Formic acid is more acidic than acetic acid.
(D) Dimerisation of acetic acid in benzene.

12*. Assuming 2s-2p mixing is NOT operative, the paramagnetic species among the following is **[JEE 2014]**

(A) Be_2 (B) B_2 (C) C_2 (D) N_2

13. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists. **[JEE 2014]**

List-I		***List-II***
P.		***1.*** p – d π antibonding
Q.		***2.*** d – d σ bonding
R.		***3.*** p – d π bonding
S.		***4.*** d – d σ antibonding

Code:

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

14. The correct statement(s) regarding, (i) $HClO_2$, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$, is(are) **[JEE 2015]**

(A) The number of Cl = O bonds in (ii) and (iii) together is two

(B) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three

(C) The hybridization of Cl in (iv) is sp^3

(D) Amongst (i) to (v), the strongest acid is (i)

15. 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 molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d–orbital(s) is

[Atomic number : S = 16, Cl = 17, I = 53 and Xe = 54] **[JEE 2015]**

16. The total number of lone pairs of electrons in N_2O_3 is **[JEE 2015]**

17*. According to Molecular Orbital Theory, **[JEE 2016]**

(A) C_2^{2-} is expected to be diamagnetic.

(B) O_2^{2+} is expected to have a longer bond length than O_2.

(C) N_2^+ and N_2^- have the same bond order.

(D) He_2^+ has the same energy as two isolated He atoms.

18*. The compound(s) with TWO lone pairs of electrons on the central atom is(are) **[JEE 2016]**

(A) BrF_6 (B) ClF_3 (C) XeF_4 (D) SF_4

19. The crystalline form of borax has **[JEE 2016]**

(A) Tetranuclear $[B_4O_5(OH)_4]^{2-}$ 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

20. The order of the oxidation state of the phosphorus atom in H_3PO_2 , H_3PO_4 , H_3PO_3 and $H_4P_2O_6$ is **[JEE 2017]**

(A) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$
(B) $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$
(C) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$
(D) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$

21. 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.

(A) $BeCl_2$, CO_2, BCl_3, $CHCl_3$
(B) SO_2, C_6H_5Cl, H_2Se, BrF_5
(C) BF_3, O_3, SF_6, XeF_6
(D) NO_2, NH_3, $POCl_3$, CH_3Cl

22. Among B_2H_6, $B_3N_3H_6$, N_2O, N_2O_4, $H_2S_2O_3$ and $H_2S_2O_8$, the total number of molecules containing covalent bond between two atoms of the same kind is ————

ANSWERS

EXERCISE-1

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
B	C	A	C	A	D	B	D	C	D	D	D	C	B	A
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
D	D	C	B	A	C	C	A	B	C	C	D	A	C	D
26	**27**	**28**	**29**	**30**										
D	C	C	C	C										

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	ABCD	AC	BC	ABC	ABC	AC	AC	ABC	BD	ABD
Que.	11	12	13	14	15	16	17	18	19	
Ans.	ABD	BC	AD	BCD	BD	ABC	BD	ABCD	ABCD	

- ***Match the Column***

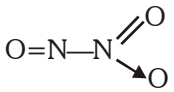
20. A - (p, q), B - (p, r), C - (p, q, r, s), D - (p, q, s)
21. A - (p, r), B - (p, q, s), C - (p, q, s), D - (p, r)
22. A - (p, s), B - (p, q, r, s), C - (p, r), D - (p, q)
23. A - (p, r, s), B - (p, r), C - (q, s), D - (q, s)

- ***Comprehension Based Questions***

Comprehension 1 : **24.** (C) **25.** (D) **26.** (A) **27.** (D) **28.** (A)

Comprehension 2 : **29.** (B) **30.** (B) **31.** (B)

EXERCISE-3

1. **(a)** 

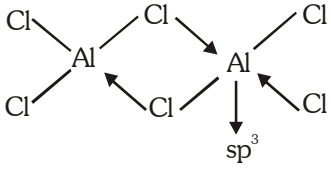
while in P_2O_3 π bond between P and O is not so stable so it form cyclic structure.

(b) H–I is weakest bond due to longest bond length as I atom is largest in size.

2. **(a)** Stable of carbonates increases down the group.

(b) $Al_2(CO_3)_3$ is very lesser stable as Al^{3+} due to its larger polarizing power polarize CO_3^{2-} largely so it is unstable.

3. In BCl_3 dimerization does not take place so its hybridization state $\rightarrow sp^2$
and structure is planar triangular while $AlCl_3$ gets dimirized due to which Al can form 4σ bonds. So hybridization state of Al $\rightarrow sp^3$



4. $1s + 1s \longrightarrow \sigma$ $\quad$ $2py + 2py \longrightarrow \pi$

$2pz + 2pz \longrightarrow \sigma$ $\quad$ $2s + 2s \longrightarrow \sigma$

$2px + 2px \longrightarrow \pi$

5. due to paramagnetic behaviour of O_2 it sticks to magnet.

6. $\mu = Q \times d$

$1.2\times3.3\times10^{-30} = Q\times0.1\times10^{-10}$

$$Q = \frac{1.2\times3.3\times10^{-30}}{10^{-10}} = 1.2\times3.3\times10^{-20} = 3.96\times10^{-20} = 0.396\times10^{-19}$$

$$\text{Fraction of charge} = \frac{0.396\times10^{-19}}{1.6\times10^{-19}} = \frac{0.396}{1.6} = 0.2475$$

7. In NH_3 due to inter molecular H–bond molecular association takes place so it exist as liquid but in HCl due to larger size of Cl atom it can't form intermolecular H–bond so molecular associations do not take place.

8. $$\%\text{ ionic character} = \frac{\mu_{obs}}{\mu_{cal}}\times100$$

$$\Rightarrow \quad 18.08 = \frac{1.08\times10^{-18}}{4.8\times10^{-8}\times d}\times100$$

$$d = \frac{1.08\times10^{-18}\times100}{4.8\times10^{-8}\times18.08} = 1.244\times10^{-10}\,M$$

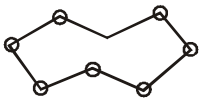
9. $$\%\text{ ionic character} = \frac{\mu_{obs}}{\mu_{cal}}\times100 = \frac{6.32\times10^{-18}}{4.8\times10^{-10}\times0.156\times10^{-7}}\times100 = \frac{6.32\times10^{-1}}{4.8\times0.156}\times100 = 84.4\%$$

10. C + N = 6 + 7 = 13 electron.

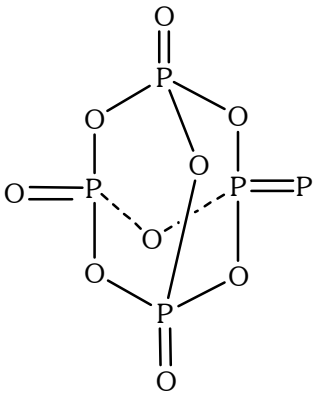
$$\text{Bo of CN} = \frac{\text{B molecular} - \text{AB molecular}}{2} = \frac{9-4}{2} = 2.5$$

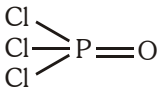
$$C\overline{N} = \frac{10-4}{2} = 3$$

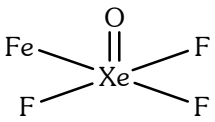
in $C\overline{N}$ 14 electron are present and all are paired.

11. ***(i)*** $S_8 \longrightarrow$ 

(ii) $N_2H_4 \longrightarrow H_2\ddot{N}—\ddot{N}H_2$

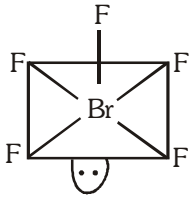
(iii) $P_4H_{10} \longrightarrow$ 

(iv) $POCl_3 \longrightarrow$ 

(v) $XeOF_4 \longrightarrow$ 

(vi) $C_3O_2 \longrightarrow O = C = C = C = O$

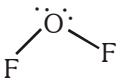
(viii) $BrF_5 \longrightarrow$



12. Zero directional bond.

13. $OF_2 \longrightarrow$ hybridization = sp^3

Shape $\longrightarrow$ V – shape



14. $XeF_2 \longrightarrow$ linear, sp^3d

$XeF_4 \longrightarrow$ square planar, sp^3d^2

$PBr_5 \longrightarrow$ triangular Bi Pyramidal sp^3d.

$OF_2 \longrightarrow$ v–shape, sp^3

$I_3^- \longrightarrow$ sp^3d linear

$I_3^+ \longrightarrow$ sp^3 v–shape

15. ICl will have larger Boiling point as it is polar while Br_2 is non polar.

16. Boiling of noble gases $\propto$ mol mass

$\propto$ size

He < Ne < Ar < Kr < Xe < Rn

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	B	C	B	B	A	A	B	B	C	B
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	D	D	C	B	C	D	A	C	A	A
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	D	B	A	C	A	B	D	D	A	C
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	AB	C	B	B	A	B	D	A	B
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	B	D	D	A	D	C	A	D	B	C
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	D	D	B	D	A	A	C	A	C	B
Que.	61	62	63							
Ans.	D	C	D							

EXERCISE-5

1.	(D)	**2.**	(C)	**3.**	(D)	**4.**	(C)	**5.**	(ABC)
6.	(D)	**7.**	(B)	**8.**	(B)	**9.**	(D)	**10.**	(6)
11.	(ABD)	**12.**	(C)	**13.**	(C)	**14.**	(BC)	**15.**	(4)
16.	(8)	**17.**	(AC)	**18.**	(BC)	**19.**	(ACD)	**20.**	(A)
22.	(2,4)	**23.**	(4)						

Important Notes

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