

Crash Course for NEET

CHEMISTRY

Study Package-1

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Aakash

Medical | IIT-JEE | Foundations

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Preface

Dear NEET Aspirant,

This book has been written specifically for the students who get themselves enrolled for the crash course for medical entrance exams, which is a limited days programme. It is meant for the quick brush-up of all the important topics. All the chapters have been written by the experienced faculties who have been preparing the students for qualifying various medical entrance exams. Each chapter covers all the important and must do topics and has been written in such a way that the student can grasp the contents easily.

After the theory portion in the study package, Try Yourself have been given to make the student practise the questions similar to those asked in entrance exams. The sequence of the questions has been kept same as the sequence of theory part so that a student can solve questions as per his/her coverage of theory part. The questions asked in previous AIPMT/NEET exam have also been included. This will help the students to assess the difficulty level in the actual medical entrance exams. We have also added a sample paper of 45 questions covering the entire content of this study package.

As the days are limited, the students should never miss a single class and must cover the syllabus in tandem with the coverage in the classroom. Once the topic is finished, you must do all the questions of same topic given in the form of Try Yourself. If there is any doubt, you can get it clarified from the faculties.

Finally, you are advised to remain focused on your target and must work hard and complete all the necessary work sincerely in a planned manner. You must stay away from all distractions including the mobile phone. All other things can wait but time never waits for anyone. So gear up your preparations to realise your dream of joining the most prestigious and respected profession.

Wishing you a brighter career!

J. C. CHAUDHRY
Managing Director

Analysis of NEET-2019

Subject-wise Report

Subject-wise Difficulty Level

S. No.	SUBJECT	EASY	MEDIUM	DIFFICULT	REMARKS
1	PHYSICS	18	25	2	Medium
2	CHEMISTRY	17	22	6	Medium
3	BOTANY	21	13	14	Easy
4	ZOOLOGY	9	25	8	Medium

Topic-wise Credits & Difficulty Level

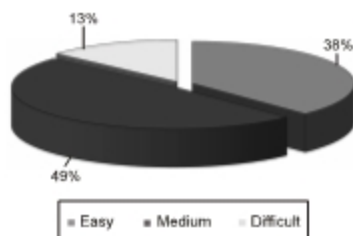
CHEMISTRY

ANALYSIS OF CHEMISTRY PORTION OF NEET 2019

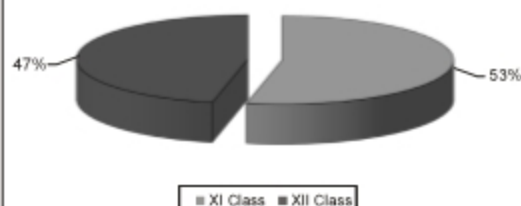
	XI	XII	XI	XII	XI	XII	
	Organic Chemistry	Organic Chemistry	Inorganic Chemistry	Inorganic Chemistry	Physical Chemistry	Physical Chemistry	Total
Easy	2	6	1	2	4	2	17
Medium	2	1	6	3	5	5	22
Difficult	1	0	1	1	2	1	6
Total	5	7	8	6	11	8	45

XI Class	24	XII Class	21
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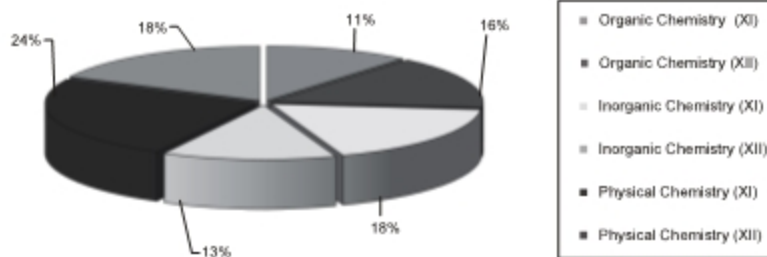
Distributions of Level of Questions in Chemistry



Percentage of Portions asked from Class XI & XII



Topic-Wise Distributions of questions in Chemistry



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Chapter 1

Some Basic Concepts of Chemistry

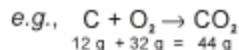
Sub-topics

General Introduction: Importance and scope of chemistry, Laws of chemical combination, Dalton's atomic theory: concept of elements, atoms and molecules, Atomic and molecular masses. Mole concept and molar mass; percentage composition and empirical and molecular formula; chemical reactions, stoichiometry and calculations based on stoichiometry.

Laws of Chemical Combinations

There are five laws of chemical combinations.

- (A) **Law of Conservation of Mass (Lavoisier 1774).** It deals with the mass of reactants and products and states that in a chemical change the total mass of the products is equal to the total mass of the reactants.



Note : In nuclear reactions, the mass of products is found to be slight less than the mass of the reactants.

- (B) **Law of Constant Composition (Proust 1799).** A chemical compound always contains same elements combined together in same proportion by mass e.g., H_2O prepared from any source contains H and O in the ratio of 1 : 8 by mass.
- (C) **Law of Multiple Proportion (Dalton 1804).** When two elements combine to form two or more compounds then the mass of one of which combines with a fixed mass of the other element bears a simple whole number ratio to one another.
- (D) **Law of Reciprocal Proportion (Richter 1792).** It states that when two elements combine separately with a fixed mass of the third element then the ratio in which they do so is either the same or whole number multiple of the ratio in which they combine with each other.
- (E) **Gay Lussac's Law of Combining Volumes.** It states that at a given temperature and pressure, when the gases combine they do so in volumes which bear a simple ratio to each other and also to the volume of gaseous product e.g.,
$$\underset{(1 \text{ L})}{\text{H}_2(\text{g})} + \underset{(1 \text{ L})}{\text{Cl}_2(\text{g})} \rightarrow \underset{(2 \text{ L})}{2\text{HCl}(\text{g})}$$
. The ratio of their volumes is 1 : 1 : 2.

Avogadro's Law

Equal volume of all gases under similar conditions of temperature and pressure contain equal number of molecules e.g., 22.4 litre of every gas at STP (standard temperature and pressure) $T = 273 \text{ K}$, $P = 1 \text{ bar}$ contains equal number of molecules i.e., 6.022×10^{23}

Dalton's Atomic Theory

The main points are

- Matter is made up of extremely small indivisible particles called atoms.
- Atoms of different elements have different masses and atoms of same element have same masses and identical in all respects.

Empirical and Molecular Formula

Empirical formula is the simplest whole number ratio of atoms of each element present in 1 molecule of compound but molecular formula is the actual number of atoms of each element in 1 molecule of compound.

Molecular formula = (Empirical formula) \times n

If n = 1 then E.F. = M.F. other wise both are different E.F. of compound is determined from % composition.

Mole Concept

A mole is the amount of a substance that contains as many entities as there are atoms in exactly 12 g of the carbon - 12 isotope.

1 mole $\equiv N_A$ atoms/molecules/ions/electrons

1 mole \equiv Molecular weight/atomic weight (in gram)

1 mole \equiv Volume of 22.4 lit. of a gas occupied at NTP

1 mole \equiv 1 gram atom or 1 gram molecule

Number of moles \equiv wt./gram atomic wt. or wt./gram mol. wt

or mole is a concept of quantity in terms of number, mass and volume (gases only)

Important formula:

$$(i) \text{ Mole} = \frac{\text{wt. in g}}{\text{mol. wt. / At. wt. (in g)}}$$

$$(ii) \text{ Mole} = \frac{\text{Number of particles given}}{6.022 \times 10^{23}}$$

$$(iii) \text{ Mole} = \text{molarity} \times \text{volume in litre.}$$

$$(iv) \text{ Number of electrons / protons / neutrons / atoms}$$

$$= \text{mole} \times 6.022 \times 10^{23} \times \text{Number of electron / proton / neutron / atoms present in 1 molecule.}$$

$$(v) \text{ Number of molecules} = \text{mole} \times 6.022 \times 10^{23}$$

Chemical Stoichiometry

Stoichiometry is for the determination of quantities of reactant and products involved in balanced chemical reaction. e.g., $H_2 + Cl_2 \rightarrow 2HCl$

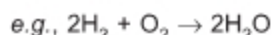
H_2	+	Cl_2	\rightarrow	$2HCl$
i.e., 1 mole		1 mole		2 mole
N_A molecules		N_A molecules		$2N_A$ molecules
$2N_A$ atoms		$2N_A$ atoms		$4N_A$ atoms
$(\text{mol. wt.})_{H_2}$		$(\text{mol. wt.})_{Cl_2}$		$2 \times (\text{mol. wt.})_{HCl}$

Note : For a given balanced equation, information of reactant or product can be determined if information of one of the species is given either in terms of moles, molecules, weight or atoms.

Limiting Reagent

In the given reaction if number of quantities (either in gram/mole/molecules) is present with exact coefficients then it is referred as, reactants are present in exact molar proportions required by chemical equation.

However if exact proportion is not present then the one which gets totally consumed is known as **limiting reagent** (Limiting reagent decides the product quantity for given information).



In above reaction, 2 mole of H_2 reacts exactly with 1 mole of O_2 to give 2 mole of H_2O . If given mole of H_2 is 4 mole and that of O_2 is 0.5 mole, then 0.5 mole O_2 will act as limiting reagent as it is in minimum amount and product formation is given w.r.t. O_2 i.e., 1 mole of H_2O .

Measurement of Concentration

(A) % wt by wt (w/W)

⇒ Weight of solute in gram present in 100 g of solution.

(B) % wt by volume (w/V)

⇒ Weight of solute in gram present in 100 ml of solution.

(C) % by volume (v/V)

⇒ Volume of solute in ml present in 100 ml of solution.

(D) **Molarity** : Number of moles of solute per litre of solution

$$M = \frac{\text{wt/M.wt}}{\text{Volume (ml)}} \times 1000$$

(E) **Normality** : Number of gram equivalents of solute per litre of solution.

$$N = \frac{\text{wt/Eq.wt}}{\text{Volume(ml)}} \times 1000$$

(F) Equivalent = Mole \times n-factor

(G) Normality = Molarity \times n-factor

Dilution of solution

$$(1) \quad \begin{array}{cc} M_1 V_1 & = & M_2 V_2 \\ \text{Moles of solute} & & \text{Moles of solute} \\ \text{before dilution} & & \text{after dilution} \end{array}$$

$$(2) \quad \begin{array}{cc} N_1 V_1 & = & N_2 V_2 \\ \text{Gram equivalents of} & & \text{Gram equivalents of} \\ \text{solute before dilution} & & \text{solute after dilution} \end{array}$$

Mixing of an acid with a base

V_1 volume of N_1 acid is added to V_2 volume of N_2 base

(1) Solution is neutral when $N_1 V_1 = N_2 V_2$

(2) Solution is acidic when $N_1 V_1 > N_2 V_2$

$$\text{Then normality of resulting solution} = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

(3) Solution is basic when $N_2 V_2 > N_1 V_1$

$$\text{Normality of resulting solution} = \frac{N_2 V_2 - N_1 V_1}{V_1 + V_2}$$





Try Yourself

SECTION - A

Objective Type Questions

- The number of moles of Sulphur present in 1 mole of H_2SO_4
(1) 6.02×10^{23} moles of S
(2) 1 mole of S
(3) 4 moles of S
(4) 2 moles of S
- Number of atoms present in 1 mole of NH_3
(1) 4 atoms
(2) N_A atoms
(3) $4N_A$ atoms
(4) $\frac{N_A}{4}$ atoms
- Number of moles present in a gas occupying 22400 ml at STP
(1) 10 moles
(2) 1 mole
(3) N_A moles
(4) $10 N_A$ moles
- Total number of electrons present in 1.6 g of CH_4
(1) 6.022×10^{23} electrons
(2) 6.023×10^{24} electrons
(3) 10 electrons
(4) 1 electron
- Number of moles in 1.8 g of H_2O is equal to number of moles in 18 g glucose (I), 6 g urea (II), or 34.2 g sucrose (III)
(1) I, II, III
(2) I, II
(3) I, III
(4) II, III
- Which of the following has the largest number of atoms?
(1) 0.5 g atom of Cu
(2) 10^{23} atoms of Cu
(3) 0.623 g of Cu
(4) 3.175 g of Cu
- The number of gram atoms in 3.2 gm of Ca
(1) 3.2
(2) 0.08
(3) 0.8
(4) 1.008
- Number of atoms in 1 ml of ammonia gas at STP is
(1) 2.7×10^{19}
(2) 1.08×10^{20}
(3) 10.8×10^{20}
(4) 5.4×10^{19}
- The volume of a drop of water is 0.05 ml and the density of water is 1.0 g/ml. How many water molecules are present in a drop of water?
(1) 1.7×10^{21}
(2) 5.4×10^{23}
(3) 2.2×10^{26}
(4) 1.7×10^{20}
- The number of moles of 'B' required to produce 2.5 moles of AB_4 according to equation
$$\text{A} + 4\text{B} \rightarrow \text{AB}_4$$

(1) 1
(2) 10
(3) 5
(4) 15
- 2 litres of N_2 and 2 litres of H_2 on completion of reaction would give litre of NH_3 at STP
(1) 0.665 L
(2) 1.0 L
(3) 2.00 L
(4) 1.33 L
- Concentration of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in normal blood is approximately 90 mg per 100 mL. What is the molarity of the glucose solution in blood?
(1) 5 M
(2) 0.005 M
(3) 0.05 M
(4) 1 M
- 6 g of monobasic acid is dissolved in 100 ml water to form normal solution. What is equivalent mass of the acid?
(1) 60
(2) 20
(3) 40
(4) 30
- The amount of H_2O formed when 2g H_2 and 1g O_2 are reacted as, $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, is
(1) 3 g
(2) 1.125 g
(3) 4.5 g
(4) 2.50 g

15. For the reaction,
 $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$,
 when 1 mol of ammonia and 1 mol of O_2 are allowed to react then
 (1) 1 mol of H_2O is produced
 (2) 1 mol of NO is produced
 (3) All the oxygen will be consumed
 (4) All the ammonia will be consumed
16. The number of moles present in 720 g of water, is
 (1) 14 mol (2) 24 mol
 (3) 34 mol (4) 40 mol
17. The volume of 2 g of O_2 at NTP is
 (1) 2.4 litre (2) 4.8 litre
 (3) 1.4 litre (4) 1.2 litre
18. How much water is to be added to dilute 10 ml of 10 N HCl to make it decinormal?
 (1) 990 ml (2) 1010 ml
 (3) 100 ml (4) 1000 ml
19. Equal masses of CO_2 and N_2O have
 (1) Same moles
 (2) Same volume at S.T.P.
 (3) Same number of atoms
 (4) All of these
20. Which of the following pair has same number of atoms?
 (1) 18 g water and 64 g SO_2
 (2) 28 g N_2 and 28 g CO
 (3) 100 g CaCO_3 and 18 g NH_4^+
 (4) All of these
3. An excess of AgNO_3 is added to 100 mL of a 0.01 M solution of dichlorotetraaquachromium(III) chloride. The number of moles of AgCl precipitated would be [NEET 2013]
 (1) 0.002 (2) 0.003
 (3) 0.01 (4) 0.001
4. When 22.4 litres of $\text{H}_2(\text{g})$ is mixed with 11.2 litres of $\text{Cl}_2(\text{g})$, each at STP, the moles of HCl(g) formed is equal to [AIPMT 2014]
 (1) 1 mol of HCl(g) (2) 2 mol of HCl(g)
 (3) 0.5 mol of HCl(g) (4) 1.5 mol of HCl(g)
5. 1.0 g of magnesium is burnt with 0.56 g O_2 in a closed vessel. Which reactant is left in excess and how much? (At. wt. Mg = 24; O = 16) [AIPMT 2014]
 (1) Mg, 0.16 g (2) O_2 , 0.16 g
 (3) Mg, 0.44 g (4) O_2 , 0.28 g
6. A mixture of gases contains H_2 and O_2 gases in the ratio of 1 : 4 (w/w). What is the molar ratio of the two gases in the mixture? [AIPMT-2015]
 (1) 2 : 1 (2) 1 : 4
 (3) 4 : 1 (4) 16 : 1
7. What is the mass of the precipitate formed when 50 mL of 16.9% solution of AgNO_3 is mixed with 50 mL of 5.8% NaCl solution? (Ag = 107.8, N = 14, O = 16, Na = 23, Cl = 35.5) [Re-AIPMT-2015]
 (1) 7 g (2) 14 g
 (3) 28 g (4) 3.5 g
8. If Avogadro number N_A is changed from $6.022 \times 10^{23} \text{ mol}^{-1}$ to $6.022 \times 10^{20} \text{ mol}^{-1}$, this would change [Re-AIPMT-2015]
 (1) The ratio of chemical species to each other in a balanced equation
 (2) The ratio of elements to each other in a compound
 (3) The definition of mass in units of grams
 (4) The mass of one mole of carbon
9. 20.0 g of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample? (At. wt. : Mg = 24) [Re-AIPMT-2015]
 (1) 60 (2) 84
 (3) 75 (4) 96

SECTION - B

Previous Years Questions

1. How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0 M HNO_3 ? The concentrated acid is 70% HNO_3 . [NEET 2013]
 (1) 90.0 g conc. HNO_3 (2) 70.0 g conc. HNO_3
 (3) 54.0 g conc. HNO_3 (4) 45.0 g conc. HNO_3
2. 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of solution is [NEET 2013]
 (1) 0.01 M (2) 0.001 M
 (3) 0.1 M (4) 0.02 M

10. Suppose the elements X and Y combine to form two compounds XY_2 and X_3Y_2 . When 0.1 mole of XY_2 weighs 10 g and 0.05 mole of X_3Y_2 weighs 9 g, the atomic weights of X and Y are
[NEET 2016]
- (1) 40, 30
(2) 60, 40
(3) 20, 30
(4) 30, 20
11. A mixture of 2.3 g formic acid and 4.5 g oxalic acid is treated with conc. H_2SO_4 . The evolved gaseous mixture is passed through KOH pellets. Weight (in g) of the remaining product at STP will be
[NEET 2018]
- (1) 1.4
(2) 3.0
(3) 4.4
(4) 2.8
12. In which case is number of molecules of water maximum?
[NEET-2018]
- (1) 18 mL of water
(2) 0.18 g of water
(3) 10^{-3} mol of water
(4) 0.00224 L of water vapours at 1 atm and 273 K
13. The number of moles of hydrogen molecules required to produce 20 moles of ammonia through Haber's process is :
[NEET-2019]
- (1) 10
(2) 20
(3) 30
(4) 40
14. The density of 2 M aqueous solution of NaOH is 1.28 g/cm^3 . The molality of the solution is [Given that molecular mass of NaOH = 40 g mol^{-1}]
[NEET-2019 (Odisha)]
- (1) 1.32 m
(2) 1.20 m
(3) 1.56 m
(4) 1.67 m



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Chapter 2

Structure of Atom

Sub-topics

Atomic number, isotopes and isobars. Concept of shells and subshells, dual nature of matter and light, de Broglie's relationship, Heisenberg uncertainty principle, concept of orbital, quantum numbers, shapes of s, p and d orbitals, rules for filling electrons in orbitals- Aufbau principle, Pauli exclusion principles and Hund's rule, electronic configuration of atoms, stability of half filled and completely filled orbitals.

Atomic number = Number of protons

Isotopes: Same atomic number but different mass number.

Isobars: Same mass number but different atomic number.

Atom

Dalton's atomic theory regarded the atom as the ultimate particle of element. An atom is made up of electron, protons and neutrons.

Except hydrogen all other elements contain all three fundamental particles.

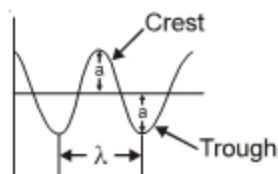
Radiant Energy

Radio wave, Microwave, IR, Visible, UV, X-Rays, γ -Rays, Cosmic Rays

Wavelength decreases \longrightarrow

Frequency increases \longrightarrow

J.C. Maxwell (1864) suggested that radiant energies (the energy which is radiated such as heat, light, X-rays etc) travel in space with the velocity of light ($3.0 \times 10^8 \text{ ms}^{-1}$) in the form of wave. These waves are known as **electromagnetic waves or radiations**. The characteristics of wave motion are :



(a) **Wavelength (λ)** : The distance between two nearest crests or troughs is known as **wavelength**. It is expressed in meters, picometers (pm), nanometers (nm) or Angstrom (\AA) units.
($1 \text{ pm} = 10^{-3} \text{ nm} = 10^{-2} \text{ \AA} = 10^{-10} \text{ cm} = 10^{-12} \text{ m}$).

(b) **Frequency (ν)** : The number of waves that pass a given point in one second is known as frequency of the wave. It is expressed in Hz (hertz) or cps (cycles per second) units ($1 \text{ Hz} = 1 \text{ cps}$).

(c) **Velocity** (v) : The distance travelled by the wave in one second is known as velocity of the wave. It is expressed in ms^{-1} and related to v and λ as : $c = v\lambda$.

$$\text{or } v = c/\lambda \quad \dots (1)$$

(d) **Wave number** ($\bar{\nu}$) : It is reciprocal of wavelength i.e., the number of wavelengths per unit length

$$\bar{\nu} = 1/\lambda \text{ m}^{-1} \quad \dots (2)$$

$$\bar{\nu} = v/c \text{ m}^{-1} \text{ (cf. Eq. 1)} \quad \dots (3)$$

(e) **Amplitude** (a) : It is the height of the crests or depth of the trough of a wave. It determines the intensity (brightness) of the beam of light.

When the different types of electromagnetic radiations are arranged in the increasing or decreasing order of wavelengths or frequencies, the pattern so obtained is called **electromagnetic spectrum**.

Max Planck (1901) introduced Quantum theory. According to this theory the radiant energy is emitted or absorbed not continuously but discontinuously in the form of small packets or bundles of energy known as quanta. **Einstein** (1905) extended this theory and postulated that the energy like light, is not only emitted or absorbed in the form of bundles but also propagated in the form of bundles in space. Each bundle is called a photon, which is considered to be a massless bundle of energy. The energy (E) of the photon is given by the expression :

$$E = h\nu = \frac{hc}{\lambda}$$

where h is **Planck's constant**. Its value is equal to $6.626 \times 10^{-34} \text{ J s}$ (in S.I. units) or $6.626 \times 10^{-27} \text{ erg s}$ (in C.G.S. units).

Bohr Atomic Model

The model is based on the quantum theory of radiation and the classical laws of physics.

Postulate

(a) The path of electron is circular. The force of attraction between nucleus and electron is equal to centrifugal force of the moving electron.

(b) Electrons can revolve only in those orbits for which its angular momentum is an integral multiple of $\frac{h}{2\pi}$.

$$\text{i.e., } mvr = \frac{nh}{2\pi} \quad (m = \text{mass of electron, } v = \text{velocity of electron, } r = \text{radius of orbit})$$

(c) Electron remains in stationary orbit where it does not radiate its energy.

(d) Each stationary orbit is with definite amount of energy (E) and $E_1 < E_2 < E_3 \dots$. Similarly $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3)$.

The Energy of Electron

Total energy (E) = K.E. + P.E.

$$E_n = -\frac{2\pi^2 Z^2 m e^4 k^2}{n^2 h^2}$$

where, $n = 1, 2, 3 \dots$

E = energy of electron in n^{th} orbit

Z = nuclear charge

e = charge of electron

m = mass of electron

h = Planck's constant

$k = 9 \times 10^9 \text{ Nm}^2\text{C}^{-2}$

$$\text{i.e., } E_n = E_1 \times \frac{Z^2}{n^2} \text{ for H-like species}$$

$$\text{i.e., } E = -\frac{21.79 \times 10^{-19} Z^2}{n^2} \text{ J per atom}$$

$$= -\frac{13.6}{n^2} Z^2 \text{ eV per atom}$$

$$= -\frac{313.6 \times Z^2}{n^2} \text{ kcal/mol}$$

$$= -\frac{1312}{n^2} \times Z^2 \text{ kJ/mol}$$

$$\text{K.E.} = \frac{KZe^2}{2r}$$

$$\text{P.E.} = -\frac{KZe^2}{r}$$

$$E_{\text{Total}} = -\frac{KZe^2}{2r}$$

$$\text{KE} = -\text{TE}$$

$$\text{PE} = 2 \times \text{TE}$$

Radii of Orbits

$$r = \frac{n^2 h^2}{4\pi^2 m K Z e^2}$$

By putting value of h , π , m , e and k

$$r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$

$$r = 0.529 \times \frac{n^2}{Z} \times 10^{-10} \text{ m}$$

$$r = 0.529 \times 10^{-8} \times \frac{n^2}{Z} \text{ cm}$$

For H-like atoms.

$$\text{Thus } r_n = r_1 \times n^2$$

Velocity of Electron

$$v = 2.188 \times 10^8 \times \frac{Z}{n} \text{ cm/s}$$

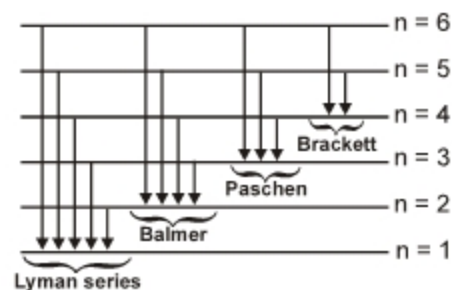
Hydrogen Spectrum

When energy is supplied, the electron moves to higher energy shells depending on the amount of energy absorbed, when it comes back it emits the energy.

For e.g. : If electron comes back from energy level having energy E_2 to energy level having energy E_1 , then energy of emitted radiation is given as $\Delta E = E_2 - E_1 = h\nu$.

Thus, different spectral lines in the spectra of atoms corresponds to different transition of electrons from higher energy level to lower energy levels.

Spectral Series	n_1	n_2	Region
(i) Lyman Series	1	2, 3, 4...	UV
(ii) Balmer Series	2	3, 4	Visible
(iii) Paschen Series	3	4, 5, 6...	IR
(iv) Brackett Series	4	5, 6, 7	IR
(v) Pfund Series	5	6, 7,	IR
(vi) Humphrey Series	6	7, 8	Far IR



Filling of Orbitals

(Rules to write electronic configurations). The electrons in various orbitals are filled according to certain rules.

An understanding of these rules/principles enables us to write electronic configuration of the elements.

- (A) **Aufbau principle** : It states that electrons are filled in the orbitals in order of increasing energy. The energy of the orbitals is governed by $(n + l)$ rule. In simple words, orbitals of lower energy are filled first followed by orbitals of higher energy.
- (B) **$(n + l)$ rule** : Orbitals having lowest value of $(n + l)$ will be filled first. If two orbitals have same value of $(n + l)$, the one having lower value of n will be filled first.

The energy of atomic orbitals for H or H-like species is

$$1s < 2s = 2p < 3s = 3p < 3d < 4s = 4p = 4d = 4f$$

Energy of orbitals of H-atom and H-like species depend only on the value of ' n '.

The energy of orbitals other than H-like species depend upon $n + l$ value and varies as

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

Note : The energy of 3d orbital becomes lower than 4s after the filling of electrons in 3d orbital.

- (C) **Pauli's exclusion principle** : It states that no two electrons can have the same value of the four quantum numbers. This implies that no two electrons are alike in an atom or in other words an orbital can accommodate a maximum of two electrons.
- (D) **Hund's rule** : This rule states that pairing of the electrons in degenerate orbitals, belonging to a particular sub shell (i.e., p , d and f), does not take place till each orbital is occupied by a single electron with parallel spin. The anomalies are observed occurring in a few configurations (particularly transition elements) for example (i) chromium has a configuration of $3d^5 4s^1$ and not $3d^4 4s^2$ and (ii) copper has a configuration of $3d^{10} 4s^1$ and not $3d^9 4s^2$. This is attributable to the extra stability of half filled or completely filled set of degenerate orbitals.
- (E) **Half filled and fully filled** : Electronic configuration are stable since they have more symmetry and more exchange energy.

Important Points

1. Heisenberg uncertainty principle $\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$.

2. **Nodes** : Probability of finding electron is zero. i.e., $\psi^2 = 0$.

Nodes are of two types radial nodes and angular nodes.

Nodes : Total nodes = $(n - 1)$, Radial nodes = $(n - l - 1)$, Angular nodes = l .

Note : d_{z^2} orbital has no angular node.

3. Photoelectric effect, $E = E_0 + KE$,

where

E = energy of radiation

E_0 = threshold energy

K.E. = kinetic energy of ejected electron.





Try Yourself

SECTION - A

Objective Type Questions

- Electromagnetic radiation with maximum wavelength is
 - UV
 - Radiowaves
 - X-rays
 - Infrared
- Energy of Bohr's orbit
 - Increases as we move away from nucleus
 - Decreases as we move away from nucleus
 - Remains the same as we move away from the nucleus
 - First decreases and then increases
- An electron jumps from lower orbit to higher orbit, when
 - Energy is released
 - Energy is absorbed
 - There is no change in energy
 - It radiates energy
- Different spectral lines in Lyman series of hydrogen spectrum lie in
 - UV
 - Visible
 - IR
 - Far IR
- According to Bohr's theory, the angular momentum for an electron of fifth orbit is
 - $5 \frac{h}{\pi}$
 - $2.5 \frac{h}{\pi}$
 - $5 \frac{\pi}{h}$
 - $\frac{25h}{\pi}$
- The spectrum of He^+ is expected to be similar to that of
 - H
 - Na
 - Li^+
 - Na^+
- $E_n = -313.6/n^2$ kcal/mole. If the value of $E = -34.84$ kcal/mole, to which value does 'n' correspond?
 - 4
 - 3
 - 2
 - 1
- The ratio of the difference between first and second Bohr's orbit energy to that between second and third Bohr's orbit energy for H-atom is
 - $\frac{1}{2}$
 - $\frac{91}{35}$
 - $\frac{27}{5}$
 - $\frac{5}{27}$
- The transition of an electron in the hydrogen atom that will emit maximum energy is
 - n_1 to n_2
 - n_4 to n_3
 - n_3 to n_2
 - n_2 to n_1
- Which of the following is correct for 2p-orbitals?
 - $n = 1, l = 2$
 - $n = 1, l = 0$
 - $n = 2, l = 0$
 - $n = 2, l = 1$
- An electron enters the orbital when
 - $(n + l)$ is minimum
 - $(n + l)$ is maximum
 - $(n + m)$ is minimum
 - $(n + m)$ is maximum
- If r_1 is the radius of the first orbit of hydrogen atom, then the radii of second, third and fourth orbits in term of r_1 are
 - r_1^2, r_1^3, r_1^4
 - $4 r_1, 9 r_1, 16 r_1$
 - $8 r_1, 27 r_1, 64 r_1$
 - $2 r_1, 6 r_1, 8 r_1$
- Which of the following statement does not form a part of Bohr's model of hydrogen atom?
 - Angular momentum of electron is quantized
 - The electron in orbit nearest the nucleus has lowest energy
 - Electrons revolve in different orbits around nucleus
 - The position and velocity of electrons in orbit cannot be determined simultaneously

14. Which of the following statement concerning the four quantum numbers is incorrect?
- n gives the size of an orbital
 - l gives the shape of orbital
 - m gives the energy of the electron in orbital
 - s gives the direction of spin of electron in the orbital
15. Number of waves made by electron in fifth Bohr's orbit of hydrogen atom are
- 3
 - 4
 - 5
 - 11
16. If n and l are respectively the principle and azimuthal quantum numbers, then expression for calculating total number of electrons in any energy level is
- $\sum_{l=1}^n 2(2l+1)$
 - $\sum_{l=1}^{n-1} 2(2l+1)$
 - $\sum_{l=0}^{n+1} 2(2l+1)$
 - $\sum_{l=0}^{n-1} 2(2l+1)$
17. The orbital angular momentum of an electron is given by
- $L = n\left(\frac{h}{2\pi}\right)$
 - $L = l\left(\frac{h}{2\pi}\right)$
 - $L = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right)$
 - $L = m\left(\frac{h}{2\pi}\right)$
18. If kinetic energy of a proton is increased nine times, the wavelength of the de-Broglie wave associated with it would become
- 3 times
 - 9 times
 - $\frac{1}{3}$ times
 - $\frac{1}{9}$ times
19. Total number of spectral lines emitted when an electron jumps from $n = 5$ to $n = 1$ in hydrogen atom is
- 1
 - 2
 - 10
 - 6
20. The wave number of limiting line in Lyman series of hydrogen is 109678 cm^{-1} . The wave number of limiting line in Balmer series of He^+ would be
- 54839 cm^{-1}
 - 219356 cm^{-1}
 - 109678 cm^{-1}
 - 438712 cm^{-1}
21. The threshold energy E° is given as
- $E^\circ = E + \text{K.E.}$
 - $E^\circ = E - \text{K.E.}$
 - $E^\circ = h\nu + \text{K.E.}$
 - $E^\circ = \text{K.E.}$
22. The de-Broglie relationship between λ of a moving particle with K.E. is
- $\lambda = \frac{h}{2m(\text{K.E.})}$
 - $\lambda = \frac{\sqrt{2m(\text{K.E.})}}{h}$
 - $\lambda = \frac{h}{\sqrt{2m(\text{K.E.})}}$
 - $\lambda = \frac{h}{\sqrt{m\text{K.E.}}}$
23. The number of radial and angular nodes in $4p$ orbital respectively are
- 2, 0
 - 2, 1
 - 3, 1
 - 1, 2
24. Total number of nodes is given by
- $n - l - 1$
 - l
 - $n - 1$
 - n
25. The correct order of increasing energy of atomic orbitals is
- $5p < 4f < 6s < 5d$
 - $5p < 6s < 4f < 5d$
 - $4f < 5p < 5d < 6s$
 - $5p < 5d < 4f < 6s$
26. In hydrogen atom, energy of first excited state is -3.4 eV . Find out the K.E of the same orbit of hydrogen atom
- 3.4 eV
 - 6.8 eV
 - -13.6 eV
 - 13.6 eV
27. The first emission line in the atomic spectrum of hydrogen in the Balmer series appear at
- [R = Rydberg Constant]
- $\frac{9R}{400}$
 - $\frac{7R}{144}$
 - $\frac{3R}{4}$
 - $\frac{5R}{36}$
28. Azimuthal quantum number of last electron of Na is
- $l = 1$
 - $l = 2$
 - $l = 3$
 - $l = 0$

29. The nineteenth electron of chromium has which of the following set of quantum number?
[Atomic number of Cr = 24]
- | | n | l | m | s |
|-----|-----|-----|-----|---------------|
| (1) | 3 | 0 | 0 | $\frac{1}{2}$ |
| (2) | 3 | 2 | -2 | $\frac{1}{2}$ |
| (3) | 4 | 0 | 0 | $\frac{1}{2}$ |
| (4) | 4 | 1 | -1 | $\frac{1}{2}$ |
30. The uncertainty principle and the concept of wave nature of matter was proposed by and respectively.
- Heisenberg, de-Broglie
 - de-Broglie, Heisenberg
 - Heisenberg, Planck
 - Planck, Heisenberg
31. Which of the following set of quantum numbers belongs to highest energy?
- $n = 4, l = 0, m = 0, s = +\frac{1}{2}$
 - $n = 3, l = 0, m = 0, s = +\frac{1}{2}$
 - $n = 3, l = 1, m = 1, s = +\frac{1}{2}$
 - $n = 3, l = 2, m = 1, s = +\frac{1}{2}$
32. Electromagnetic radiation with minimum wavelength is
- Ultra-violet
 - Microwave
 - X-rays
 - Infrared
33. Which of the following orbital does not exist?
- 3d
 - 3f
 - 5p
 - 7s
34. The shape of the orbital with the value of $l = 1$ and $m = 0$ is
- Spherical
 - Single dumb-bell
 - Square planar
 - Double dumb-bell
35. Which of the following orbital is with the four lobes present on the axis?
- d_{z^2}
 - d_{xy}
 - d_{yz}
 - $d_{x^2 - y^2}$
36. The total number of orbitals in fifth energy level should theoretically be
- 10
 - 25
 - 15
 - 18
37. In an atom which has 2K, 8L, 8M and 2N electrons in the ground state, the total number of electrons having $m = 1$ are
- 20
 - 8
 - 12
 - 10
38. The units for equation $\lambda = \frac{h}{mv}$ are
- $\frac{\text{kgm}^2\text{s}^{-1}}{\text{kgms}^{-1}}$
 - $\frac{\text{kgms}^2}{\text{ms}^{-1}}$
 - $\frac{\text{kg}^2\text{m}^2\text{s}^{-2}}{\text{kgm}^2\text{s}^{-1}}$
 - $\frac{\text{kgms}^{-3}}{\text{kgm}}$
39. The total number of nodes in 5s orbital is
- 4
 - 5
 - 2
 - 0
40. No two electrons of the same atom can have same set of quantum numbers. This is
- Pauli's exclusion principle
 - Uncertainty principle
 - Hund's rule
 - Aufbau principle
41. The radius of the Bohr orbit is given by
- $r = 0.529 \times \frac{Z^2}{n} \text{ \AA}$
 - $r = 0.529 \times \frac{n^2}{Z^2} \text{ \AA}$
 - $r = 0.529 \times \frac{Z}{n^2} \text{ \AA}$
 - $r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$
42. The number of revolutions made by electron is given by [n = number of orbit]
- $\frac{V_n}{2\pi r_n}$
 - $\frac{2\pi r_n}{V_n}$
 - n
 - $n - 1$
43. The potential energy of an electron is given as
- $-\frac{kZe}{r^2}$
 - $-\frac{kZe^2}{r^2}$
 - $-\frac{kZe^2}{r}$
 - $+\frac{kZe^2}{r}$
44. If the radiations emitted falls under visible region it belongs to
- Lyman series
 - Balmer series
 - Paschen series
 - Pfund series

45. The exceptional electronic configuration of Cu(29) is due to
 (1) Stability of half-filled d -sub-shell
 (2) Stability of full-filled d -sub-shell
 (3) Stability of half-filled p -sub-shell
 (4) Stability of full-filled p -sub-shell
46. What is the relation between E_1 and E_2 whose respective wavelengths are 400 Å and 800 Å?
 (1) $E_1 = 2 E_2$ (2) $2 E_1 = E_2$
 (3) $E_1 = E_2$ (4) None of these
47. The threshold energy is given as E_0 and radiation of energy E falls on metal then K.E. is given as
 (1) $\frac{E - E_0}{2}$ (2) $E - E_0$
 (3) $E_0 - E$ (4) $\frac{E}{E_0}$
48. The total number of electrons in a shell is given as
 (1) $(2l + 1)$ (2) $2(2l + 1)$
 (3) $2n^2$ (4) n^2
49. Radius of 2nd shell of which ion is same as the radius of 1st Bohr's orbit of hydrogen?
 (1) He^+ (2) Li^{2+}
 (3) Be^{3+} (4) B^{4+}
50. Balmer series of hydrogen spectrum belongs to
 (1) Visible region (2) UV region
 (3) I.R. region (4) Far I.R. region
3. The orbital angular momentum of a p -electron is given as [AIPMT 2012]
 (1) $\frac{h}{\sqrt{2}\pi}$ (2) $\sqrt{3} \frac{h}{2\pi}$
 (3) $\sqrt{\frac{3}{2}} \frac{h}{\pi}$ (4) $\sqrt{6} \frac{h}{2\pi}$
4. The value of Planck's constant is 6.63×10^{-34} Js. The speed of light is 3×10^{17} nm s^{-1} . Which value is closest to the wavelength in nanometer of a quantum of light with frequency of 6×10^{15} s^{-1} ? [NEET 2013]
 (1) 25 (2) 50
 (3) 75 (4) 10
5. What is the maximum numbers of electrons that can be associated with the following set of quantum numbers? [NEET 2013]
 $n = 3, l = 1$ and $m = -1$
 (1) 6 (2) 4
 (3) 2 (4) 10
6. Based on equation $E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{n^2} \right)$ certain conclusions are written. Which of them is not correct? [AIPMT 2014]
 (1) Larger the value of n , the larger is the orbit radius
 (2) Equation can be used to calculate the change in energy when the electron changes orbit
 (3) For $n = 1$, the electron has a more negative energy than it does for $n = 6$ which means that the electron is more loosely bound in the smallest allowed orbit
 (4) The negative sign in equation simply means that the energy of electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus
7. What is the maximum number of orbitals that can be identified with the following quantum numbers?
 $n = 3, l = 1, m_l = 0$ [AIPMT 2014]
 (1) 1
 (2) 2
 (3) 3
 (4) 4

SECTION - B

Previous Years Questions

1. Maximum number of electrons in a subshell with $l = 3$ and $n = 4$ is [AIPMT 2012]
 (1) 10 (2) 12
 (3) 14 (4) 16
2. The correct set of four quantum numbers for the valence electron of rubidium atom ($Z = 37$) is [AIPMT 2012]
 (1) $5, 0, 0, +\frac{1}{2}$ (2) $5, 1, 0, +\frac{1}{2}$
 (3) $5, 1, 1, +\frac{1}{2}$ (4) $6, 0, 0, +\frac{1}{2}$



8. Calculate the energy in joule corresponding to light of wavelength 45 nm : (Planck's constant $h = 6.63 \times 10^{-34}$ Js; speed of light $c = 3 \times 10^8$ ms $^{-1}$)

[AIPMT 2014]

- (1) 6.67×10^{15} (2) 6.67×10^{11}
(3) 4.42×10^{-15} (4) 4.42×10^{-18}

9. The angular momentum of electron in 'd' orbital is equal to

[AIPMT-2015]

- (1) $0 \hbar$ (2) $\sqrt{6} \hbar$
(3) $\sqrt{2} \hbar$ (4) $2\sqrt{3} \hbar$

10. Two electrons occupying the same orbital are distinguished by

[NEET-2016]

- (1) Spin quantum number
(2) Principal quantum number
(3) Magnetic quantum number
(4) Azimuthal quantum number

11. How many electrons can fit in the orbital for which $n = 3$ and $l = 1$?

[NEET (Phase-2) 2016]

- (1) 2 (2) 6
(3) 10 (4) 14

12. Which of the following pairs of d-orbitals will have electron density along the axes?

[NEET (Phase-2) 2016]

- (1) d_{z^2}, d_{xz} (2) d_{xz}, d_{yz}
(3) $d_{z^2}, d_{x^2-y^2}$ (4) $d_{xy}, d_{x^2-y^2}$

13. Which one is the wrong statement? [NEET-2017]

- (1) de-Broglie's wavelength is given by $\lambda = \frac{h}{mv}$, where m = mass of the particle, v = group velocity of the particle
(2) The uncertainty principle is $\Delta E \times \Delta t \geq \frac{h}{4\pi}$
(3) Half-filled and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement
(4) The energy of 2s orbital is less than the energy of 2p orbital in case of Hydrogen like atoms

14. Which one is a **wrong** statement? [NEET-2018]

- (1) Total orbital angular momentum of electron in 's' orbital is equal to zero
(2) An orbital is designated by three quantum numbers while an electron in an atom is designated by four quantum numbers
(3) The value of m for d_{z^2} is zero
(4) The electronic configuration of N atom is



15. 4d, 5p, 5f and 6p orbitals are arranged in the order of decreasing energy. The correct option is

[NEET-2019]

- (1) $5f > 6p > 5p > 4d$
(2) $6p > 5f > 5p > 4d$
(3) $6p > 5f > 4d > 5p$
(4) $5f > 6p > 4d > 5p$

16. Which of the following series of transitions in the spectrum of hydrogen atom fall in visible region?

[NEET-2019]

- (1) Lyman series
(2) Balmer series
(3) Paschen series
(4) Brackett series

17. Orbital having 3 angular nodes and 3 total nodes is

[NEET-2019 (Odisha)]

- (1) 6 d
(2) 5 p
(3) 3 d
(4) 4 f

18. In hydrogen atom, the de Broglie wavelength of an electron in the second Bohr orbit is

[Given that Bohr radius, $a_0 = 52.9$ pm]

NEET-2019 (Odisha)]

- (1) 105.8 pm
(2) 211.6 pm
(3) 211.6π pm
(4) 52.9π pm



Chapter 3

Classification of Elements and Periodicity in Properties

Sub-topics

Modern periodic law and long form of periodic table, periodic trends in properties of elements- atomic radii, ionic radii, ionization enthalpy, electron gain enthalpy, electronegativity, valence.

Modern periodic table

It is also known as long form or Bohr's table as it is based on Bohr's scheme of the arrangement of elements into four types according to their electronic configuration. Recent work has established that the fundamental property of an atom is atomic number and not the atomic weight. Therefore, atomic number is taken as the basis of the classification of elements.

The modern periodic law may be stated as "The properties of elements are periodic function of their atomic number."

IUPAC Nomenclature for the Superheavy Elements

Atomic Number	Name	Symbol	Atomic Number	Name	Symbol
101	un-nil-unium	Unu	110	un-un-nilium	Uun
102	un-nil-bium	Unb	111	un-un-unium	Uuu
103	un-nil-trium	Unt	112	un-un-bium	Uub
104	un-nil-quadium	Unq	113	un-un-trium	Uut
105	un-nil-pentium	Unp	114	un-un-quadium	Uuq
106	un-nil-hexium	Unh	115	un-un-pentium	Uup
107	un-nil-septium	Uns	116	un-un-hexium	Uuh
108	un-nil-octium	Uno	117	un-un-septium	Uus
109	un-nil-ennium	Une	118	un-un-octium	Uuo
			119	un-un-ennium	Uue
			120	un-bi-nilium	Ubn
			130	un-tri-nilium	Utn
			140	un-quad-nilium	Uqn
			150	un-pent-nilium	Upn

Note : Hyphens have been put in the name for clarity. They should be omitted.

Classification of Elements on the Basis of Electronic Configuration

On the basis of electronic configuration the elements can be classified into the following four types :

- (a) **s-block element** : These elements contain 1 or 2 electrons in s-subshell of outermost shell. Elements of 1 and 2 group belong to this class. These elements enter into chemical reaction by losing valence electrons so as to acquire noble gas configuration in the outermost orbit.

ns^1 (group 1)	ns^2 (group 2)
(alkali metals)	(alkaline earth metals)

These elements generally form electrovalent compounds and basic oxides (except BeO which is amphoteric in nature).

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

13	Boron (B)	Z = 5	$1s^2 2s^2 2p^1$
14	Carbon (C)	Z = 6	$1s^2 2s^2 2p^2$
15	Nitrogen (N)	Z = 7	$1s^2 2s^2 2p^3$
16	Oxygen (O)	Z = 8	$1s^2 2s^2 2p^4$
17	Fluorine (F)	Z = 9	$1s^2 2s^2 2p^5$

The main characteristics of p-block elements are :

- The non-metallic character increases along a period from group 13 to 17.
 - They form covalent compounds among themselves but electrovalent compounds with s-block elements.
 - Their oxides are generally acidic, few are neutral like NO, N₂O, CO and amphoteric like Al₂O₃, Ga₂O₃, PbO etc.
- (c) **d-block elements** : These are called transition elements or 'd' block elements. The elements of group 3 to 12 belong to this class. Their general electronic configuration can be represented as : $(n-1)d^{1-10} ns^{1-2}$

General characteristics of transition (d-block) elements:

- They are metals, hard, malleable, ductile and possess high tensile strength.
 - They are good conductors of heat and electricity.
 - These elements exhibit variable valency.
 - They generally form coloured compounds. This is due to d-d transition mainly.
 - These metals, their alloys and compounds possess marked catalytic activity.
 - They are generally paramagnetic, i.e., attract magnetic lines of force.
- (d) **f-block elements** : They are inner transition elements. These elements are arranged in the two row at the bottom of the periodic table. In the first row 14 elements from atomic number 58 to 71, known as Lanthanides or rare earth elements. The second row of elements from atomic number 90 to 103, known as actinides. Their general electronic configuration can be represented as

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

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

Periodicity

The recurrence of elements with similar properties after certain interval when these are arranged in the increasing order of their atomic numbers is called the periodicity. The properties of elements get repeated after intervals of 2, 8, 8, 18, 18 and 32. This is due to the fact that after these definite intervals, recurrence of similar electronic configuration takes place when the number of valence electrons is the same. Thus there is a regular gradation (gradual increase or decrease in particular property in the same group or period) and repetition in the properties of elements.

(a) Atomic size (or atomic radius) : Atomic radius is the size of the atom of an element. Atomic radius is defined as "the distance from the centre of the nucleus upto the centre of outermost electron." It is measured in Angstrom unit (\AA). It is not possible to measure exact atomic radius as an atom is unstable and it cannot be isolated to get its radius. Moreover, the exact position of the outermost electron is uncertain. The values for radii are obtained from X-ray measurements. Following points are to be noted in this reference :

- (i) The size of an atom or ion decreases in a period as we move from left to right.
- (ii) The atomic radius generally increases in a group with the increase in atomic number.
- (iii) **A positive ion (cation) is smaller than the corresponding atom :** A positive ion or cation is formed by the loss of one or more electrons from an atom and the number of protons remains the same in the nucleus. Thus the ratio of the positive charge in the nucleus to the number of electrons *i.e.*, effective nuclear charge increases. Hence the force of attraction of nucleus to the outer electrons increases thus decreasing the size of cation. In case of alkali metals, the removal of an electron removes the entire outermost shell.
- (iv) **A negative ion (anion) is bigger than the corresponding atom :** In the formation of negative ion (anion) one or more electrons(s) are added to the atom. This results in decrease of effective nuclear charge, which in turn decreases the force of attraction and increases the size of an anion or the pull exercised by the nucleus on the electron become less *i.e.*, they move a little farther resulting in an increase in the ionic size.

Note : Size of Iso-electronic ions : These are such cations or anions which carry the same number of electrons. The size of such ions depends upon the effective nuclear charge. Greater the nuclear charge of an ion, greater will be the force of attraction for same number of electrons. As a result, the size of the ion decreases. For example

N^{3-} , O^{2-} , F^- , Na^+ , Mg^{2+} and Al^{3+} are isoelectronic ions, among these N^{3-} is largest (1.71 \AA) and Al^{3+} is smallest (0.50 \AA).

(b) Ionisation Potential or Ionisation Energy : It may be defined as "the energy required to remove an electron from the outermost orbit of an isolated gaseous atom in its ground state." In an atom, the energy required to remove first electron from a gaseous atom is called the first ionisation energy.

The energy required to remove one electron from a unipositive ion to form a bipositive ion is called second ionisation energy. The second ionisation energy is always higher (more) than the first. This is due to the fact that a unipositive ion left after the removal of one electron from the atom, the electrons are more firmly bound to the nucleus than in the atom *i.e.* second electron has to be removed against the relative increase in nuclear charge, hence more energy is needed to remove the second electron.

Factors on which ionisation energy depends

- (i) Greater the size of an atom, lesser will be the force of attraction of its nucleus for the valence electron.
- (ii) **Nuclear charge :** Greater the magnitude of nuclear charge (along a period) greater will be the force of attraction of the nucleus for the valence electrons.

(iii) **Screening or Shielding effect** : The effect of reduction of force of attraction by the electrons present between nucleus and valence electrons is called screening effect. Greater the number of electrons between nucleus and valence electrons, lesser will be the electron nucleus attraction and lesser will be ionisation potential. $s > p > d > f$ is order of screening or shielding effect for same value of n .

(iv) **Penetration of sub-shells** : Ionisation energy also depends upon the type *i.e.*, s , p , d or f electrons which are to be removed. s -electrons are closer to the nucleus (more penetrated towards nucleus) and are more tightly held than p , d , or f electrons. Hence ionisation energy decreases in the order of $s > p > d > f$.

(v) **Stable configuration** : Atoms/ions having half filled or full filled orbitals require more energy to remove electron than the next member of same period.

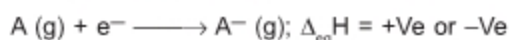
Ex. : I.E.₁ of nitrogen > I.E.₁ of oxygen.

The periodicity of ionisation energy in the light of above factors may be summarised as follows :

Down a group : As we go down a group, the I.E. goes on decreasing.

Along a period : As we go from left to right in the periodic table the ionisation energy goes on increasing in general.

(c) **Electron gain enthalpy** : It is possible to add an electron to any atom, ion or molecule. The enthalpy change in this process is called the **electron gain enthalpy** of the species.



Electron gain enthalpy just defined is actually first electron gain enthalpy. It may be noted that for the addition of second electron, energy is supplied to $A^-(g)$ to form $A^{2-}(g)$. The energy supplied to convert $A^-(g)$ to form $A^{2-}(g)$ is called second electron affinity of A . It is given a positive sign *i.e.*, net energy is absorbed.

The magnitude of electron affinity is influenced by the following factors

(a) **Atomic radius** : Electron affinity decreases as the atomic radius increases.

(b) **Nuclear charge** : Electron affinity increases as the nuclear charge increases.

(c) **Screening effect** : Electron affinity increases as the shielding or screening effect decreases.

The periodic variation of this property is as follows :

(i) The electron affinity decreases in a group as seen in Cl, Br and I. The members of 2nd period have generally lower electron affinity than the next lower members in their respective groups. Chlorine has highest electron affinity.

(ii) In a period, the electron affinity values generally increase on moving from left to right. Be, Mg and noble gases have almost zero electron affinities. N and P have unexpected lower values of electron affinities due to half filled p -orbitals.

Although electron affinity decreases down the group but fluorine is found to have lower electron affinity than chlorine. The reason for this is that fluorine has a very small size, so there is electron repulsion, which results in less evolution of energy in the formation of F^- ion.

(d) **Electronegativity**: It may be defined as : "The tendency of an atom to attract shared electron pair towards itself in a molecule". The small atoms attract electrons more strongly than larger ones hence they are more electronegative.

The numerical value of electronegativity depends upon the ionisation potential and electron affinity. Higher ionisation potential and higher electron affinity both imply higher electronegativity. To measure electronegativity an arbitrary scale was developed by Linus Pauling which is known as electronegativity scale. On this scale fluorine has maximum electronegativity of 4.0 and Li has a value of 1.0 while inert gas have no value of electronegativity.

The value of electronegativity show periodic variations as given below

Generally in a group electronegativity generally decreases from top to bottom due to increase in size of atom.

F	Cl	Br	I	At
4.0	3.0	2.8	2.5	2.2

In a period electronegativity increases from left to right

Li	Be	C	N	O	F
1.0	1.5	2.5	3.0	3.5	4.0

Diagonal Relationship

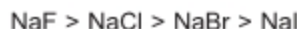
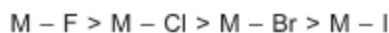
First three elements of second period *i.e.*, lithium, beryllium and boron show resemblance in properties with the elements of the next higher group of the third period *i.e.*, with diagonally opposite elements. This is referred to as **diagonal relationship**.

	I	II	III	IV
II Period	Li	Be	B	C
	↘	↘	↘	
III Period	Na	Mg	Al	Si

Thus lithium resembles with magnesium, beryllium with aluminium and boron with silicon due to same charge over radius ratio [Ionic potential].

Properties of Halides, Hydroxides, Sulphates of Alkali & Alkaline Earth Metals

- (a) Melting point of alkali metal halides follow following order



This due to decrease in charge density of halide ions.

- (b) The order of melting point of chlorides of alkali metals is as follows :



- (c) The melting point of LiCl is lowest because it is covalent.
- (d) The solubility of alkali metal carbonates in water at 298 K increases down the group from lithium to cesium.
- (e) The basic character of oxides and hydroxides of group 1 and group 2 increases down the group because metallic character increases down the group *e.g.*, LiOH is least basic whereas CsOH is strongly basic. $Be(OH)_2$ is amphoteric, $Mg(OH)_2$ is a weak base, $Ca(OH)_2$ and $Sr(OH)_2$ are moderately strong bases, $Ba(OH)_2$ is strong base.
- (f) The solubility of hydroxides of group 1 and group 2 in water increases down the group.
- (g) The solubility of sulphates, carbonates and phosphates decreases down the group because lattice energy dominates over hydration energy in group 2 *e.g.*, $MgSO_4$ is soluble in water whereas $BaSO_4$ is insoluble in water.
- (h) Li_2CO_3 is thermally unstable whereas other alkali metal carbonates are thermally stable.
- (i) Thermal stability of carbonates of group 2 increases down the group due to increase in lattice energy.





Try Yourself

SECTION - A

Objective Type Questions

- If the atomic number of element is 33, it belongs to
 - 1st group
 - 2nd group
 - 13th group
 - 15th group
- The elements with atomic numbers 2, 10, 18, 36, 54, 86 are called
 - Noble gases
 - Rare metals
 - Noble metals
 - Halogens
- The least electronegative element has the following electronic configuration
 - ns^2np^5
 - ns^2np^4
 - ns^2np^3
 - ns^2np^6
- Atomic number of next inert gas if discovered will be
 - 87
 - 104
 - 118
 - 132
- Ce_{58} is a member of
 - s-block elements
 - p-block elements
 - d-block elements
 - f-block elements
- The element having lowest first ionization potential among Sr, As, S and F is
 - Sr
 - As
 - S
 - F
- The element having least difference in the values of first and second ionization potential is
 - Na
 - K
 - Li
 - Mg
- The first four ionization energy values of an element are 191, 578, 872 and 5962 kcal. The number of valence electrons in the element is
 - 1
 - 2
 - 3
 - 4
- Which of the following configuration is associated with biggest jump between 2nd and 3rd IE?
 - $1s^2 2s^2 2p^2$
 - $1s^2 2s^2 2p^6 3s^1$
 - $1s^2 2s^2 2p^6 3s^2$
 - $1s^2 2s^2 2p^1$
- Find the incorrect statement
 - IE₁ of N is higher than oxygen
 - Oxygen is more electronegative than nitrogen
 - Electron affinity of Fluorine is higher than that of chlorine
 - Smallest atom of periodic table is H
- The electronegativity of Be is almost same as
 - Al
 - Mg
 - Na
 - Li
- Ease of formation of the anion is favoured by
 - Lower value of ionization potential
 - Lower value of electron affinity
 - Higher value of electron affinity
 - Lower value of electronegativity
- When a neutral atom is converted into a cation its
 - Atomic weight increases
 - Atomic weight decreases
 - Size increases
 - Size decreases
- Ionization potential of Na would be numerically the same as
 - Electron affinity of Na^+
 - Electronegativity of Na^+
 - Electron affinity of Ne
 - Ionization potential of Mg
- With the increase of atomic number in a period there is
 - Increase in electropositive character
 - Decrease in electropositive character
 - Increase in size
 - Decrease in ionisation energy regularly

16. On going down group in the periodic table (Example Li to Cs in group I or Be to Ra in group 2). The expected trend of change in atomic radius is a
- (1) Continuous increase
 - (2) Continuous decrease
 - (3) Periodic one, an increase followed by a decrease
 - (4) Periodic one, a decrease followed by an increase
17. In a group of periodic table, as the atomic number increases
- (1) Electropositive nature goes on increasing
 - (2) Ionization potential goes on increasing
 - (3) Electronegativity goes on increasing
 - (4) Non-metallic character goes on increasing
18. Elements in the same vertical group of the periodic table have generally the same
- (1) Atomic number
 - (2) Number of isotopes
 - (3) Number of electrons
 - (4) Number of electrons in the valence shell
19. The process requiring absorption of energy is
- (1) $F \rightarrow F^-$
 - (2) $H \rightarrow H^+$
 - (3) $Cl \rightarrow Cl^-$
 - (4) $O \rightarrow O^-$
20. Which element has the greatest tendency to lose electrons?
- (1) F
 - (2) S
 - (3) Cs
 - (4) C
21. As one moves along a given row in the periodic table, ionisation energy
- (1) Remains unchanged
 - (2) Increases from left to right with some exceptions
 - (3) Increases then decreases
 - (4) Decreases from left to right
22. Electronegativity of the following elements increases in the order
- (1) C, N, Si, P
 - (2) N, Si, C, P
 - (3) Si, P, C, N
 - (4) P, Si, N, C
23. Which of the following elements should have the maximum electronegative character?
- (1) Oxygen
 - (2) Nitrogen
 - (3) Fluorine
 - (4) Astatine
24. Which of the following element has the lowest first ionisation potential?
- (1) Na
 - (2) F
 - (3) Cs
 - (4) I
25. Which of the following is a correct statement?
- (1) Ionic radius of a metal is same as its atomic radius
 - (2) The ionic radius of a metal is always greater than its atomic radius
 - (3) The atomic radius of a non-metal is more than its ionic radius
 - (4) The ionic radius of a metal is less than its atomic radius
26. Element with lowest ionisation potential is
- (1) Fluorine
 - (2) Chlorine
 - (3) Bromine
 - (4) Iodine
27. Ease of formation of cation is favoured by
- (1) Lower value of ionization potential
 - (2) Higher value of ionization potential
 - (3) Higher value of electron affinity
 - (4) Higher value of electronegativity
28. Consider the iso-electronic series : K^+ , S^{2-} , Cl^- and Ca^{2+} . The radii of the ions decreases as
- (1) $Ca^{2+} > K^+ > Cl^- > S^{2-}$
 - (2) $Cl^- > S^{2-} > K^+ > Ca^{2+}$
 - (3) $S^{2-} > Cl^- > K^+ > Ca^{2+}$
 - (4) $K^+ > Ca^{2+} > S^{2-} > Cl^-$
29. Which of the following is not correct for iso-electronic ions?
- (1) They have the same number of electrons around their nuclei equal to number of protons and have no charge
 - (2) Higher the atomic number, higher will be positive charge in a series of isoelectronic cations
 - (3) Isoelectronic ions have different atomic number
 - (4) An isoelectronic series may have both positively and negatively charged ions
30. Which of the following has positive electron gain enthalpy?
- (1) Rn
 - (2) Cl
 - (3) F
 - (4) Br

SECTION - B

Previous Years Questions

1. Identify the
- wrong**
- statement in the following

[AIPMT 2012]

- (1) Atomic radius of the elements increases as one moves down the first group of the periodic table
- (2) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table
- (3) Amongst isoelectronic species, smaller the positive charge on the cation, smaller is the ionic radius
- (4) Amongst isoelectronic species, greater the negative charge on the anion, larger is the ionic radius

- 2.
- Be^{2+}
- is isoelectronic with which of the following ions?

[AIPMT 2014]

- (1) H^+
- (2) Li^+
- (3) Na^+
- (4) Mg^{2+}

3. The species
- Ar
- ,
- K^+
- and
- Ca^{2+}
- contain the same number of electrons. In which order do their radii increase?

[AIPMT-2015]

- (1) $\text{K}^+ < \text{Ar} < \text{Ca}^{2+}$
- (2) $\text{Ar} < \text{K}^+ < \text{Ca}^{2+}$
- (3) $\text{Ca}^{2+} < \text{Ar} < \text{K}^+$
- (4) $\text{Ca}^{2+} < \text{K}^+ < \text{Ar}$

4. In which of the following options, the order of arrangement does
- not**
- agree with the variation of property indicated against it?

[NEET-2016]

- (1) $\text{Li} < \text{Na} < \text{K} < \text{Rb}$ (increasing metallic radius)
- (2) $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$ (increasing ionic size)
- (3) $\text{B} < \text{C} < \text{N} < \text{O}$ (increasing first ionisation enthalpy)
- (4) $\text{I} < \text{Br} < \text{Cl} < \text{F}$ (increasing electron gain enthalpy)

5. The element
- $Z = 114$
- has been discovered recently. It will belong to which of the following family group and electronic configuration? [NEET-2017]

- (1) Halogen family, $[\text{Rn}] 5f^{14}6d^{10}7s^27p^5$
- (2) Carbon family, $[\text{Rn}] 5f^{14}6d^{10}7s^27p^2$
- (3) Oxygen family, $[\text{Rn}] 5f^{14}6d^{10}7s^27p^4$
- (4) Nitrogen family, $[\text{Rn}] 5f^{14}6d^{10}7s^27p^6$

6. For the second period elements the correct increasing order of first ionisation enthalpy is:

[NEET-2019]

- (1) $\text{Li} < \text{Be} < \text{B} < \text{C} < \text{N} < \text{O} < \text{F} < \text{Ne}$
- (2) $\text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne}$
- (3) $\text{Li} < \text{B} < \text{Be} < \text{C} < \text{N} < \text{O} < \text{F} < \text{Ne}$
- (4) $\text{Li} < \text{Be} < \text{B} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne}$

7. Match the oxide given in column A with its property given in column B

[NEET-2019 (Odisha)]

Column-A

Column-B

- | | |
|------------------------------|----------------|
| (i) Na_2O | (a) Neutral |
| (ii) Al_2O_3 | (b) Basic |
| (iii) N_2O | (c) Acidic |
| (iv) Cl_2O_7 | (d) Amphoteric |

Which of the following options has all correct pairs?

- (1) (i)-(b), (ii)-(d), (iii)-(a), (iv)-(c)
- (2) (i)-(b), (ii)-(a), (iii)-(d), (iv)-(c)
- (3) (i)-(c), (ii)-(b), (iii)-(a), (iv)-(d)
- (4) (i)-(a), (ii)-(d), (iii)-(b), (iv)-(c)



Chapter 4

Chemical Bonding and Molecular Structure

Sub-topics

Valence electrons, ionic bond, covalent bond, bond parameters, Lewis structure, polar character of covalent bond, valence bond theory, resonance, geometry of molecules, VSEPR theory, concept of hybridization involving s, p and d orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules (qualitative idea only). Hydrogen bond.

Chemical Bond

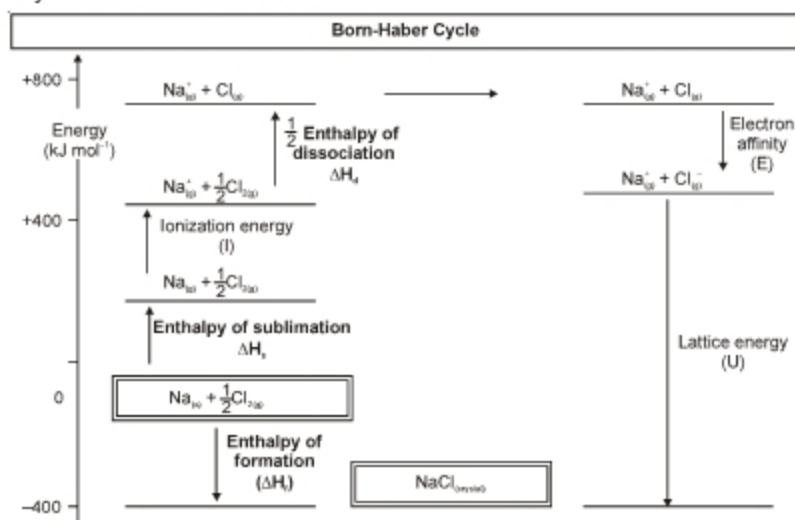
- Ionic Bond** : The bond formed between the positive and negative ions as a result of the electrostatic force of attraction is termed as electrovalent bond i.e., ionic bond. e.g., NaCl.
- Covalent Bond** : Two atoms joined by equal sharing of one pair of electron are said to be joined by a single covalent bond e.g., Cl_2 .
Depending upon the number of electrons shared by each atom in bond formation, single, double or triple bond is formed.
Number of electrons shared is known as covalency. e.g., Hydrogen has covalency 1, oxygen has 2.
- Dative Bond** : Bond formation in which the electron pair used for sharing is donated solely by one of the combining atoms. The bond is also known as **semi-polar, co-ordinate, dative, co-ionic or donor-acceptor bond**. e.g., $[\text{BF}_3 \leftarrow \text{NH}_3]$.

Ionic Bond

Born - Haber Cycle

Born-Haber cycle determines the lattice enthalpy. The calculation is based on the Hess's law, which state that the enthalpy of reaction is the same, whether it is carried out in single step or more than one step.

e.g., Born-Haber cycle for the formation of NaCl.



Born-Haber cycle for the formation of NaCl.

Lattice Energy

Energy required to completely separate one mole of a solid ionic compound into its gaseous constituent ions is known as lattice energy.

Higher the charge higher is the lattice energy. Smaller the distance between cation and anion higher is the lattice energy. Lattice Energy is directly proportional to charge on ion and inversely proportional to radius of cation and anion.

Fajan's Rule

The (ionic) bond is not 100% ionic. Some percentage of covalent character is present in ionic bond, due to which observed physical properties like melting point, solubility are different than expected.

Percentage covalent character is due to polarisation power of cation and polarisability of anion. The percentage covalent character is given by **Fajan's Rule**. It states that, percentage covalent character is higher if

- (A) Size of cation is small or
- (B) Size of anion is large or
- (C) Charge on cation and anion is higher

Size of Cation : The smaller the cation, more will be its effective nuclear charge and thus valence shell of anions will be pulled more effectively towards cation nucleus to show more polarisation.

Polarizing power : $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$

\therefore Covalent character : $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$.

Size of Anion : The larger the anion, lesser will be its effective nuclear charge, less tightly its valence shells will be held towards its own nucleus and therefore more effectively will be pulled towards cation nucleus to show more polarisation.

Polarization in anion : $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

\therefore Covalent character : $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$

Charge on Cation : Higher is the oxidation state of cation, more will be the deformation of anion and thus more covalent will be the molecule.

Polarization power : $\text{Fe}^{+2} < \text{Fe}^{+3}$

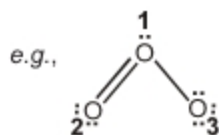
\therefore Covalent character : $\text{FeCl}_2 < \text{FeCl}_3$

Covalent Bond

Lewis Structure and Formal Charge

While drawing lewis structure of a compound or ion formal charge (F.C.) is given to each atom.

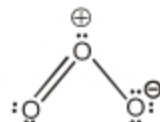
$$\text{F.C.} = [\text{Total no. of valence electron}] - [\text{Total no. of non-bonding (lone pair) electrons}] - \frac{1}{2} [\text{Total no. of shared electrons}]$$



$$\text{F.C. (for 1 O)} = 6 - 2 - \frac{1}{2}(6) = +1; \quad \text{F.C. (for 2 O)} = 6 - 4 - \frac{1}{2}(4) = 0$$

$$\text{F.C. (for 3 O)} = 6 - 6 - \frac{1}{2}(2) = -1$$

Therefore the formal charges on oxygen atom in the lewis structure of O_3 is written as



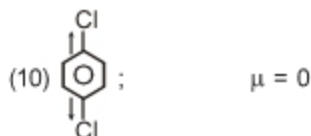
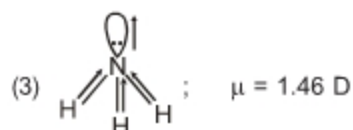
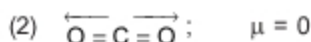
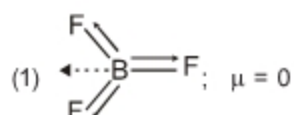
Note : The structure with lesser formal charges is lowest energy structure and most stable.

Dipole Moment (M)

Dipole moment is product of the magnitude of charge developed on any of the atom and the distance between the atoms. ($\mu = q \times d$), where q = charge developed and d = distance between two atoms. The unit of dipole moment is debye (D). $1 \text{ debye} = 1 \times 10^{-18} \text{ esu cm}$.

- (a) Dipole moment is a vector quantity.
 (b) Molecule with more than one bond will have more than one dipole moment. The resultant dipole moment of the molecule is given as $\mu_{\text{res}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$.
 (c) Dipole moment can predict whether a molecule is polar or non-polar.
 (d) Dipole moment is zero for symmetrical and planar species.
 (e) Dipole moment helps to determine percentage ionic character which can be calculated as:-

$$\% \text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Calculated dipole moment}} \times 100$$

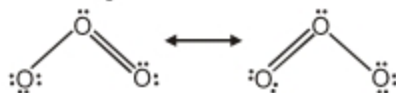
Dipole moment for some molecules

Valence bond theory: When two atoms come closer to each other, the new force come into operation i.e. force of repulsion and force of attraction. If attractive force > Repulsive force then molecule formed.

Resonance Structure

Single Lewis structure can't give the exact information or can't describe the molecule. Canonical structures with similar energy, position of nuclei, bonding and non-bonding pairs of electrons, whose one resonance hybrid structure describes molecule accurately.

e.g., The bond length of O—O in ozone is neither single bond length nor double bond length. It is in-between the two due to presence of resonance in O_3 .



Valence Shell Electron Pair Repulsion Theory (VSEPR)

- (a) A number of physical and chemical properties of molecules are affected by the geometry and shape of molecules.
- (b) VSEPR theory gives the information of shape of molecules.
- (c) The arrangement of bonded pair electron and lone pair electron is done to minimize the repulsion.

The order of repulsion is

Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair.

- (d) These repulsion result in deviations from ideal shape and alterations in bond angles in molecules.

S.No.	Type of hybridisation	No. of hybridised orbitals	Bond pair	Lone Pair	Geometry	Shape	Examples
1.	sp	2	2	–	Linear	Linear	CO_2
2.	sp^2	3	3	–	Trigonal Planar	Trigonal Planar	BF_3
			2	1	Trigonal Planar	V-shape	SO_2
3.	sp^3	4	4	–	Tetrahedral	Tetrahedral	CH_4
			3	1	Tetrahedral	Pyramidal	NH_3
			2	2	Tetrahedral	V-shape	H_2O
4.	sp^3d	5	5	–	Trigonal Bipyramidal	Trigonal Bipyramidal	PCl_5
			4	1	Trigonal Bipyramidal	See-saw	SF_4
			3	2	Trigonal Bipyramidal	T-shape	ClF_3
			2	3	Trigonal Bipyramidal	Linear	ICl_2^-
			6	–	Square Bipyramidal	Square Bipyramidal (octahedral)	SF_6
5.	sp^3d^2	6	5	1	Square Bipyramidal	Square Pyramidal	IF_5
			4	2	Square Bipyramidal	Square Planar	XeF_4
			7	–	Pentagonal Bipyramidal	Pentagonal Bipyramidal	IF_7
6.	sp^3d^3	7	6	1	Pentagonal Bipyramidal	Distorted Square Bipyramidal	XeF_8

Concept of Hybridization

- (a) Orbitals of nearly same energy hybridise.
- (b) Number of hybridized orbitals formed = number of orbitals mixed.
- (c) Hybridised orbitals have identical shape and energy.
- (d) Hybridized orbitals have different orientation in space.
 sp hybridisation = 2 hybridised orbitals at 180° .
 sp^2 hybridisation = 3 hybridised orbitals at 120° .
 sp^3 hybridisation = 4 hybridised orbitals at $109^\circ 28'$.
- (e) Hybridized orbitals show only head on overlapping and thus only form sigma bond.
- (f) Presence of lone pair of electron on hybridised orbitals show distorted geometry of molecules and decrease the bond angle.

Molecular Orbital Theory

- (a) Linear combination of atomic orbitals (**LCAO**) method is used for the formation of molecular orbitals.
- (b) For two atomic orbitals A and B, whose wave function is given as ψ_A and ψ_B . Then molecular orbitals (MO) are given as $\psi_{MO} = \psi_A \pm \psi_B$.
- (c) The σ or π molecular orbital formed by the addition of atomic orbitals is called **bonding molecular orbitals**. And σ^* or π^* molecular orbital formed by the subtraction of atomic orbitals is called **antibonding molecular orbital**.
- (d) Molecular orbital configuration for diatomic molecules upto 14 electrons.
 $\Rightarrow \sigma 1s \sigma^* 1s \sigma 2s \sigma^* 2s \{\pi 2p_x, \pi 2p_y\} \sigma 2p_z \{\pi^* 2p_x, \pi^* 2p_y\} \sigma^* 2p_z$

Note : In CO molecule energy of $\sigma^* 2s$ is higher than energy of $\sigma 2p_z$.

- (e) Molecular orbital configuration for diatomic molecules with more than 14 electrons.
 $\Rightarrow \sigma 1s \sigma^* 2s \sigma 2s \sigma^* 2s \sigma 2p_z \{\pi 2p_x, \pi 2p_y\} \{\pi^* 2p_x, \pi^* 2p_y\} \sigma^* 2p_z$
- (f) Molecular orbitals are arranged with increasing order of energy level.
- (g) $\pi 2p_x$ and $\pi 2p_y$ similarly $\pi^* 2p_x$ and $\pi^* 2p_y$ have same energy and follow Hund's rule.
- (h) Bond order = $\frac{1}{2}$ [Bonding electrons – Antibonding electrons].
- (i) Bond order \propto Bond strength $\propto \frac{1}{\text{Bond length}}$.

e.g., $N_2 = 14$ electrons

\therefore Molecular orbital configuration

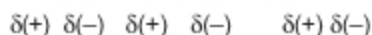
$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \{\pi 2p_x^2, \pi 2p_y^2\} \sigma 2p_z^2 \{\pi^* 2p_x, \pi^* 2p_y\} \sigma^* 2p_z$$

$$\text{B.O} = \frac{1}{2} [10 - 4] = 3$$

As no unpaired electron hence N_2 is diamagnetic.

Hydrogen bond

Bonding between H and highly electronegative species i.e. N, O and F.



Due to hydrogen bonding m.pt./b.pt., solubility is exceptionally higher.




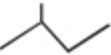



Try Yourself

SECTION - A

Objective Type Questions

- The types of bonds present in $[\text{NH}_3 \cdot \text{BF}_3]$ are
 - Covalent
 - Ionic
 - Covalent and co-ordinate
 - Covalent and ionic
- Formal charge of S atom in SO_3 is
 - Zero
 - +6
 - 6
 - +3
- Which of the following will have the highest lattice energy?
 - LiCl
 - MgCl₂
 - NaCl
 - CsCl
- Bond order in benzene is
 - 3
 - 1.5
 - 2
 - 4
- Which of the following are isolobal?
 - BH_4^- and NH_4^+
 - CO_2 and SO_2
 - N_2 and NO
 - All of these
- Which of the following are paramagnetic?
 - NO
 - N_2^+
 - B_2
 - All of these
- LCAO stands for
 - Location combined for atomic orbital
 - Locus combine of atomic orbital
 - Linear combination of atomic orbital
 - Locus combination of atomic origin
- The d-orbitals involved in the formation of SF_6 are
 - $d_{z^2}, d_{x^2-y^2}$
 - $d_{xy}, d_{x^2-y^2}$
 - d_{yz}, d_{xz}
 - $d_{z^2}, d_{x^2-y^2}$
- Which of these does not exist in nature?
 - Be_2
 - Ne_2
 - Ar_2
 - All of these
- Resonance is not shown by the species
 - SO_2
 - HCl
 - CO_3^{2-}
 - NO_3^-
- Percentage covalent character is highest in
 - NaF
 - NaCl
 - NaBr
 - NaI
- The percentage ionic character will be higher if
 - Polarisation is high, polarising power is low
 - Polarisation is low, polarising power is low
 - Polarisation is high, polarising power is high
 - Polarisation is low, polarising power is high
- Dipole moment is zero for which of the following pair of molecules?
 - BF_3, SO_2
 - $\text{BF}_3, \text{CCl}_4$
 - $\text{SO}_2, \text{CHCl}_3$
 - $\text{CCl}_4, \text{cis-C}_2\text{H}_2\text{Cl}_2$
- Dipole moment is maximum and minimum respectively for which of the following molecule?
 - NF_3, NH_3
 - NH_3, NF_3
 - $\text{CO}_2, p\text{-dichlorobenzene}$
 - $\text{Trans-C}_2\text{H}_2\text{Cl}_2, \text{cis-C}_2\text{H}_2\text{Cl}_2$
- XeO_2F_2 is
 - sp^3d hybridised
 - sp^3d^2 hybridised
 - sp^3 hybridised
 - sp^3d^3 hybridised
- In I_3^- ion
 - Central element is sp^3d hybridised
 - Geometry is trigonal bipyramidal
 - Shape is linear
 - All of these
- The hybridisation is same for
 - CO_2 and BF_3
 - SO_2 and CO_3^{2-}
 - ClF_3 and NH_3
 - CH_4 and ICl_2^-

18. For ClF_3 and ICl_2^- ion
- Hybridisation and shape both are same
 - Hybridisation is same but shape are different
 - Hybridisation is different but shape is same
 - Hybridisation and shape both are different
19. Which among the following is with square pyramidal shape?
- PCl_5
 - SF_4
 - IF_5
 - IF_7
20. Which of the following is with two lone pairs and two bond pairs of electrons on central atom in its structure?
- H_2O
 - CO_3^{2-}
 - NH_3
 - SF_4
21. The hydrocarbon with variety of hybridisation of carbon atom
- $\text{CH} \equiv \text{CH}$
 - 
 - 
 - 
22. In propadiene the carbon atoms are
- sp^2 and sp hybridised
 - sp and sp^3 hybridised
 - Only sp^2 hybridised
 - Only sp hybridised
23. XeF_6 is with shape
- Pentagonal bipyramidal
 - Pentagonal pyramidal
 - Distorted square bipyramidal
 - Square planar
24. Number of H-bonds formed by a molecule of H_2O in ice
- 2
 - 1
 - 4
 - 3
25. The interaction between Li^+ and H_2O in aqueous solution is
- Dipole-dipole interaction
 - Ion-dipole interaction
 - Dispersion forces
 - Dipole-induced dipole interaction
2. Which of the following species contains three bond pairs and one lone pair around the central atom?
- [AIPMT 2012]
- NH_2^-
 - PCl_3
 - H_2O
 - BF_3
3. The pair of species with the same bond order is
- [AIPMT 2012]
- NO , CO
 - N_2 , O_2
 - O_2^{2-} , B_2
 - O_2^+ , NO^+
4. Bond order of 1.5 is shown by
- [AIPMT 2012]
- O_2^{2-}
 - O_2
 - O_2^+
 - O_2^-
5. During change of O_2 to O_2^- ion, the electron adds on which one of the following orbitals?
- [AIPMT 2012]
- π^* orbitals
 - π orbitals
 - σ^* orbitals
 - σ orbitals
6. Four diatomic species are listed below. Identify the correct order in which the bond order is increasing in them
- [AIPMT 2012]
- $\text{NO} < \text{O}_2^- < \text{C}_2^{2-} < \text{He}_2^+$
 - $\text{O}_2^- < \text{NO} < \text{C}_2^{2-} < \text{He}_2^+$
 - $\text{C}_2^{2-} < \text{He}_2^+ < \text{O}_2^- < \text{NO}$
 - $\text{He}_2^+ < \text{O}_2^- < \text{NO} < \text{C}_2^{2-}$
7. Which of the following is electron-deficient?
- [NEET 2013]
- $(\text{SiH}_3)_2$
 - $(\text{BH}_3)_2$
 - PH_3
 - $(\text{CH}_3)_2$
8. Which one of the following molecules contains no π bond?
- [NEET 2013]
- H_2O
 - SO_2
 - NO_2
 - CO_2
9. Which of the following is a polar molecule?
- [NEET 2013]
- SF_4
 - SiF_4
 - XeF_4
 - BF_3
10. Which of the following is paramagnetic?
- [NEET 2013]
- O_2^-
 - CN^-
 - NO^+
 - CO
11. Which of the following molecules has the maximum dipole moment?
- [AIPMT 2014]
- CO_2
 - CH_4
 - NH_3
 - NF_3

SECTION - B

Previous Years Questions

1. Which **one** of the following pairs is isostructural (i.e. having the same shape and hybridization)?
- [AIPMT 2012]
- $[\text{NF}_3 \text{ and } \text{BF}_3]$
 - $[\text{BF}_4^- \text{ and } \text{NH}_4^+]$
 - $[\text{BCl}_3 \text{ and } \text{BrCl}_3]$
 - $[\text{NH}_3 \text{ and } \text{NO}_3^-]$

12. Which one of the following species has plane triangular shape? [AIPMT 2014]

(1) N_3 (2) NO_3^-
(3) NO_2^- (4) CO_2

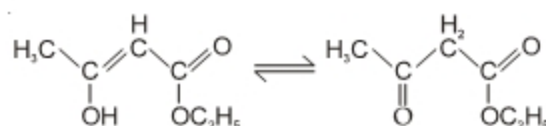
13. Which of the following organic compounds has same hybridization as its combustion product $-(CO_2)$? [AIPMT 2014]

(1) Ethane (2) Ethyne
(3) Ethene (4) Ethanol

14. Maximum bond angle at nitrogen is present in which of the following? [AIPMT-2015]

(1) NO_3^- (2) NO_2
(3) NO_2^- (4) NO^+

15. The enolic form of ethyl acetoacetate as below has [AIPMT-2015]



(1) 9 sigma bonds and 1 pi-bond
(2) 18 sigma bonds and 2 pi-bonds
(3) 16 sigma bonds and 1 pi-bond
(4) 9 sigma bonds and 2 pi-bonds

16. Which of the following species contains equal number of σ - and π - bonds? [AIPMT-2015]

(1) $CH_2(CN)_2$ (2) HCO_3^-
(3) XeO_4 (4) $(CN)_2$

17. The correct bond order in the following species is [AIPMT-2015]

(1) $O_2^- < O_2^+ < O_2^{2+}$ (2) $O_2^{2+} < O_2^+ < O_2^-$
(3) $O_2^{2+} < O_2^- < O_2^+$ (4) $O_2^+ < O_2^- < O_2^{2+}$

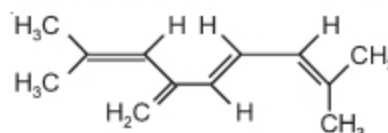
18. Which of the following pairs of ions are isoelectronic and isostructural? [AIPMT-2015]

(1) ClO_3^- , SO_3^{2-} (2) CO_3^{2-} , SO_3^{2-}
(3) ClO_3^- , CO_3^{2-} (4) SO_3^{2-} , NO_3^-

19. Which of the following options represents the correct bond order? [AIPMT-2015]

(1) $O_2^- < O_2 > O_2^+$ (2) $O_2^- > O_2 > O_2^+$
(3) $O_2^- < O_2 < O_2^+$ (4) $O_2^- > O_2 < O_2^+$

20. The total number of π -bond electrons in the following structure is [AIPMT-2015]



(1) 16 (2) 4
(3) 8 (4) 12

21. Decreasing order of stability of O_2 , O_2^- , O_2^+ and O_2^{2-} is [Re-AIPMT-2015]

(1) $O_2 > O_2^+ > O_2^{2-} > O_2^-$
(2) $O_2^- > O_2^{2-} > O_2^+ > O_2$
(3) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
(4) $O_2^{2-} > O_2^- > O_2 > O_2^+$

22. In which of the following pairs, both the species are not isostructural? [Re-AIPMT-2015]

(1) NH_3 , PH_3
(2) XeF_4 , XeO_4
(3) $SiCl_4$, PCl_4^+
(4) Diamond, silicon carbide

23. Predict the correct order among the following [NEET-2016]

(1) lone pair - bond pair > bond pair - bond pair > lone pair - lone pair
(2) lone pair - lone pair > lone pair - bond pair > bond pair - bond pair
(3) lone pair - lone pair > bond pair - bond pair > lone pair - bond pair
(4) bond pair - bond pair > lone pair - bond pair > lone pair - lone pair

24. Consider the molecules CH_4 , NH_3 and H_2O . Which of the given statements is false? [NEET-2016]

(1) The $H-C-H$ bond angle in CH_4 is larger than the $H-N-H$ bond angle in NH_3
(2) The $H-C-H$ bond angle in CH_4 , the $H-N-H$ bond angle in NH_3 , and the $H-O-H$ bond angle in H_2O are all greater than 90°
(3) The $H-O-H$ bond angle in H_2O is larger than the $H-C-H$ bond angle in CH_4
(4) The $H-O-H$ bond angle in H_2O is smaller than the $H-N-H$ bond angle in NH_3

25. Which one of the following compounds shows the presence of intramolecular hydrogen bond? [NEET (Phase-2) 2016]

(1) H_2O_2
(2) HCN
(3) Cellulose
(4) Concentrated acetic acid

26. The hybridizations of atomic orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ respectively are

[NEET (Phase-2) 2016]

- (1) sp , sp^3 and sp^2 (2) sp^2 , sp^3 and sp
 (3) sp , sp^2 and sp^3 (4) sp^2 , sp and sp^3

27. Which of the following pairs of ions is isoelectronic and isostructural? [NEET (Phase-2) 2016]

- (1) CO_3^{2-} , NO_3^- (2) ClO_3^- , CO_3^{2-}
 (3) SO_3^{2-} , NO_3^- (4) ClO_3^- , SO_3^{2-}

28. The correct geometry and hybridization for XeF_4 are [NEET (Phase-2) 2016]

- (1) Octahedral, sp^3d^2
 (2) Trigonal bipyramidal, sp^3d
 (3) Planar triangle, sp^3d^3
 (4) Square planar, sp^3d^2

29. Among the following, which one is a wrong statement? [NEET (Phase-2) 2016]

- (1) PH_5 and BiCl_5 do not exist
 (2) $p\pi-d\pi$ bonds are present in SO_2
 (3) SeF_4 and CH_4 have same shape
 (4) I_3^+ has bent geometry

30. Which of the following pairs of compounds is isoelectronic and isostructural? [NEET-2017]

- (1) BeCl_2 , XeF_2 (2) TeI_2 , XeF_2
 (3) IBr_2^- , XeF_2 (4) IF_3 , XeF_2

31. The species, having bond angles of 120° is

[NEET-2017]

- (1) PH_3 (2) ClF_3
 (3) NCl_3 (4) BCl_3

32. Which one of the following pairs of species have the same bond order? [NEET-2017]

- (1) CO , NO (2) O_2 , NO^+
 (3) CN^- , CO (4) N_2 , O_2^-

33. In the structure of ClF_3 , the number of lone pair of electrons on central atom 'Cl' is [NEET-2018]

- (1) One (2) Two
 (3) Three (4) Four

34. Magnesium reacts with an element (X) to form an ionic compound. If the ground state electronic configuration of (X) is $1s^2 2s^2 2p^3$, the simplest formula for this compound is [NEET-2018]

- (1) Mg_2X_3 (2) MgX_2
 (3) Mg_3X_2 (4) Mg_2X

35. Consider the following species :

 CN^+ , CN^- , NO and CN

Which one of these will have the highest bond order? [NEET-2018]

- (1) NO (2) CN^-
 (3) CN (4) CN^+

36. Which of the following diatomic molecular species has only π bonds according to Molecular Orbital Theory? [NEET-2019]

- (1) O_2 (2) N_2
 (3) C_2 (4) Be_2

37. Match the Xenon compounds in **Column-I** with its structure in **Column-II** and assign the correct code: [NEET-2019]

Column-I**Column-II**

- | | |
|---------------------|----------------------------|
| (a) XeF_4 | (i) Pyramidal |
| (b) XeF_6 | (ii) Square planar |
| (c) XeOF_4 | (iii) Distorted octahedral |
| (d) XeO_3 | (iv) Square pyramidal |

Code:

- | | (a) | (b) | (c) | (d) |
|-----|-------|-------|-------|------|
| (1) | (i) | (ii) | (iii) | (iv) |
| (2) | (ii) | (iii) | (iv) | (i) |
| (3) | (ii) | (iii) | (i) | (iv) |
| (4) | (iii) | (iv) | (i) | (ii) |

38. Which of the following is paramagnetic?

[NEET-2019 (Odisha)]

- (1) O_2 (2) N_2
 (3) H_2 (4) Li_2

39. Which of the following is the correct order of dipole moment? [NEET-2019 (Odisha)]

- (1) $\text{H}_2\text{O} < \text{NF}_3 < \text{NH}_3 < \text{BF}_3$
 (2) $\text{NH}_3 < \text{BF}_3 < \text{NF}_3 < \text{H}_2\text{O}$
 (3) $\text{BF}_3 < \text{NF}_3 < \text{NH}_3 < \text{H}_2\text{O}$
 (4) $\text{BF}_3 < \text{NH}_3 < \text{NF}_3 < \text{H}_2\text{O}$

40. The number of hydrogen bonded water molecule(s) associated with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is

[NEET-2019 (Odisha)]

- (1) 5 (2) 3
 (3) 1 (4) 2



Chapter 5

States of Matter

Sub-topics

Three states of matter, intermolecular interactions, types of bonding, melting and boiling points, role of gas laws of elucidating the concept of the molecule, Boyle's law, Charles's law, Gay Lussac's law, Avogadro's law, ideal behaviour of gases, empirical derivation of gas equation. Avogadro number, ideal gas equation. Kinetic energy and molecular speeds (elementary idea), deviation from ideal behaviour, liquefaction of gases, critical temperature. Liquid State- Vapour pressure, viscosity and surface tension (qualitative idea only, no mathematical derivations).

The three **states of matter** are the result of competition between molecular energy and thermal energy.

- (i) Molecular energy > thermal energy → Solid state
- (ii) Molecular energy = thermal energy → Liquid state
- (iii) Molecular energy < thermal energy → Gaseous state

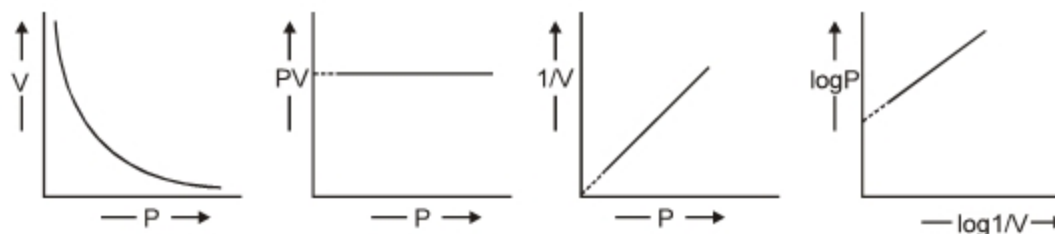
Intermolecular Forces :

- (i) **Dipole - Dipole interaction** - Exist between molecules having permanent dipoles.
- (ii) **Ion - dipole interaction** - Exist between ion and polar molecule. Strength of this depends on size and charge of the ion and on magnitude and of the dipole moment and size of polar molecule.
- (iii) **Ion - induced dipole interaction and dipole - induced dipole interactions** - The attractive interaction between an ion and the induced dipole is called ion-induced dipole interaction. And attractive interaction between a polar molecule and the induced dipole is called dipole - induced dipole interaction.
- (iv) **Dispersion forces** - The attractive forces between non polar substance such as O_2 , N_2 or monoatomic gases.

Gaseous State

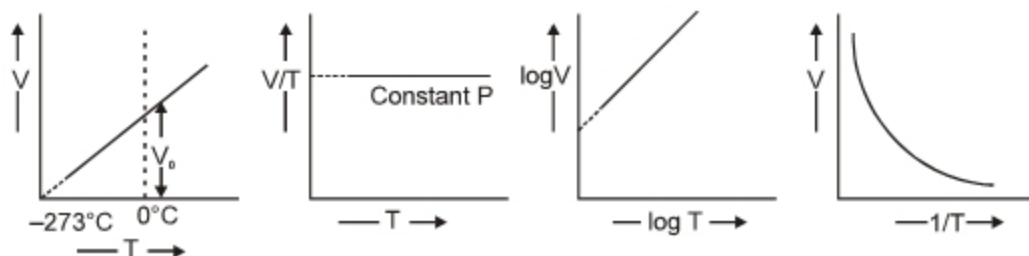
1. Gas Laws

(A) **Boyle's Law** : $P \propto \frac{1}{V}$ at constant n and T.



(B) **Charles's Law** : $V \propto T$ at constant n and P .

$$V_t = V_0 \left(1 + \frac{t}{273} \right)$$



(C) **Avogadro Law** : $V \propto n$ (P and T constant); 1 mole of every gas at STP occupies volume = 22.4 L.

2. **Ideal Gas Equation** : $PV = nRT$.

Note : All the laws are followed when gas shows ideal behaviour.

Numerical value of R : $R = PV / nT$

- (a) $R = (1 \times 22.4) / (1 \times 273) = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$
- (b) $R = (76 \times 13.6 \times 981) \times 22400 / (1 \times 273) = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$
- (c) $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
- (d) $R = 1.98 \text{ cal K}^{-1} \text{ mol}^{-1}$

3. **Dalton's Law of Partial Pressures**: The total pressure exerted by a mixture of two or more **non-reacting gases** in a definite volume is equal to the sum of individual pressures which each gas would exert if it occupies the same volume at a constant temperature

$$P = p_1 + p_2 + p_3 \dots, P = (n_1 + n_2 + \dots) \frac{RT}{V}$$

p_{gas} = mole fraction of gas \times Total pressure.

$$= \frac{\text{no. of moles of gas}}{\text{Total no. of moles of all gases}} \times \text{Total pressure}$$

Note : $P (\text{moist}) = P (\text{dry gas}) + P (H_2O \text{ vapours})$

$P (\text{dry gas}) = P (\text{moist}) - \text{aqueous tension.}$

4. **Gay Lussac's law**

$P \propto T$ at constant volume and n .

5. **Graham's law of diffusion**: At constant pressure and temperature rate of diffusion of gases is inversely proportional to the square root of their densities

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Kinetic Molecular Model of Gas - Kinetic Theory of Gases

Postulates

- (a) A gas consists of tiny particles, either atoms or molecules, moving in random motion.
- (b) The volume of the particle themselves is negligible compared with total volume of the container, most of the volume is empty space.

- (c) There is no force of attraction or repulsion between particles.
- (d) Collisions of the gas particles, either with other particles or with walls of container are perfectly elastic *i.e.* total kinetic energy of the gas particles remains constant.
- (e) The average kinetic energy of the colliding molecules is directly proportional to its absolute temperature.

Based on Kinetic-Molecular Theory

$$PV = \frac{1}{3}mNu^2$$

m = Mass of one molecule

N = Number of molecules in the container

u = Root mean square velocity

$$\text{KE of } n \text{ moles} = \frac{3}{2}nRT, \text{ for } n = 1 \quad \boxed{\text{KE} = \frac{3}{2}RT}$$

$$\text{Average KE per molecule} = \frac{3}{2} \frac{RT}{N_0} = \frac{3}{2}kT, \text{ } k = \text{Boltzmann's constant}$$

Distribution of Molecular Speeds

$$(i) \text{ Root mean square velocity } (\mu_{rms}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

$$(ii) \text{ Average velocity } (\mu_{av}) = \sqrt{\frac{8RT}{\pi M}}$$

$$(iii) \text{ Most probable velocity } (\mu_{mp}) = \sqrt{\frac{2RT}{M}}$$

Note : $\mu_{rms} > \mu_{av} > \mu_{mp}$

Deviation from ideal behaviour

1. Ideal gas behaviour is shown at high temperature and low pressure.
2. Ideal gas starts deviating at low temperature and high pressure. *i.e.*, it shows real gas behaviour.
3. Real gas follows van der Waals gas equation.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \text{ for } n \text{ mole}$$

where a ($\text{atmL}^2 \text{mol}^{-2}$) is pressure correction constant and b (L mol^{-1}) is volume correction constant.

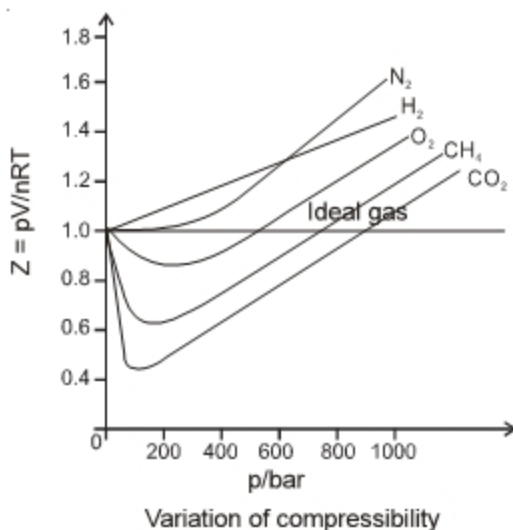
$$P_{\text{real}} < P_{\text{ideal}} \text{ \& } V_{\text{real}} > V_{\text{ideal}}$$

4. The quantitative description of the deviation for real gas from ideal gas behaviour is given by compressibility factor 'Z'.

$$Z = \frac{PV}{nRT} = \frac{PV_m}{RT} \quad V_m = \text{molar volume.}$$

$Z = 1$ For ideal gas.

$Z > 1$ or $Z < 1$ for real gases.



5. Critical temperature (T_c) = $\frac{8a}{27Rb}$, Temperature above which a gas can not be liquefied by applying pressure. Critical pressure (P_c) = $\frac{a}{27b^2}$, Critical volume (V_c) = $3b$.
6. Inversion temperature is a temperature below which if gas is allowed to expand adiabatically it causes cooling effect, above this temperature heating takes place and at this temperature neither heating, nor cooling occurs.
Inversion temperature $T_i = \frac{2a}{bR} = 2T_b$, where T_b is Boyle's temperature.
7. Boyle's temperature (T_B): $T_B = \frac{a}{Rb}$. Temperature at which gases behaves ideally for a long range of pressure.

Liquid State

A liquid is composed of molecules that are constantly moving about at random, each undergoing billions of collisions per second. However strong attractive forces of the dipole-dipole, H-bonds, prevent them from moving as freely and as far apart as in a gas.

- (a) **Vapour Pressure:** Pressure exerted by vapours of the liquid over the surface of liquid at equilibrium is called vapour pressure.

Vapour pressure depends upon nature of liquid and temperature.

- (b) **Viscosity:** Liquids flows as if they were divided into layers flowing over one another. Resistance offered to this flow is due to friction between two liquid layers and is called viscosity. Reciprocal of viscosity is called fluidity.

$\eta = \pi Pr^4/8Vl$ viscosity of a liquid decreases with rise of temperature.

Coefficient of viscosity: The force in newtons per square metre required to maintain a difference of velocity of one metre per second between two parallel layers of the liquid at a distance of one metre from each other. It is expressed in $\text{kg m}^{-1} \text{s}^{-1}$. Liquids having stronger attractive forces are more viscous.

- (c) **Surface tension:** The force that acts at right angles to an imaginary line of unit length at the surface of the liquid at rest. It is expressed in J m^{-2} or N m^{-1} . Surface tension generally decreases with the rise of temperature. Liquids exhibit capillary action and make spherical drops, this can be explained on the basis of surface tension.





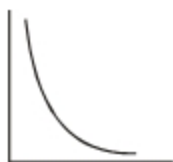
Try Yourself

SECTION - A

Objective Type Questions

1. A sample of 5 litre gas in open vessel is taken at 300 K temperature and it is heated upto 450 K, then what fraction of gas will escape out with respect to final volume?
 (1) 50% (2) 25%
 (3) 33.33% (4) 100%

2. The graph for Boyle's law is plotted at constant temperature is given as

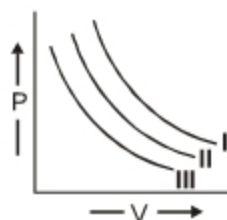


The graph is

- (1) $\frac{1}{V}$ vs P (2) V vs P
 (3) PV vs P (4) log P vs V
3. When the temperature is raised through 1°C the volume is increased by $\frac{1}{273}$ times of the original volume. This is
 (1) Boyle's Law
 (2) Charles' Law
 (3) Avogadro Law
 (4) Graham's Law
4. Two flasks of equal volumes have been joined by a narrow tube of negligible volume. Initially both flasks are at 300 K containing 0.60 mol of O_2 gas at 0.5 atm pressure. One of the flasks is then placed in a thermostat at 600 K. Calculate number of moles of O_2 gas in each flask
 (1) 0.4 at 300 K, 0.6 at 600 K
 (2) 0.4 at 300 K, 0.2 at 600 K
 (3) 0.4 at 600 K, 0.2 at 300 K
 (4) 0.2 at 600 K, 0.2 at 600 K

5. If 10 gm of a gas at atmospheric pressure is cooled from 273°C to 0°C keeping the volume constant, its pressure would become
 (1) $\frac{1}{2}$ atm (2) $\frac{1}{273}$ atm
 (3) 2 atm (4) 273 atm

6. I, II, III are three isotherms respectively at T_1 , T_2 , T_3 . Temperature will be in order



- (1) $T_1 = T_2 = T_3$
 (2) $T_1 < T_2 < T_3$
 (3) $T_1 > T_2 > T_3$
 (4) $T_1 > T_2 = T_3$
7. A gas at a pressure of 5 atm is heated from 0°C to 546°C and simultaneously compressed to $\frac{1}{3}$ rd of its original volume. Hence final pressure is
 (1) 10 atm (2) 45 atm
 (3) 30 atm (4) 5 atm
8. A 1 L flask contains 32 g O_2 gas at 27°C . What mass of O_2 must be released to reduce the pressure in the flask to 12.315 atm?
 (1) 8 g (2) 16 g
 (3) 24 g (4) 32 g
9. Which of the following gas is most easily liquefied?
 (1) N_2
 (2) NH_3
 (3) CO
 (4) All are easily liquefiable

10. If 300 mL of a gas weighs 0.368 g at STP, molar mass of the gas is
 (1) 27.48 g mol⁻¹ (2) 110.4 g mol⁻¹
 (3) 54.98 g mol⁻¹ (4) 55.2 g mol⁻¹
11. A sample of gas at 0°C and 1 atm pressure occupies 300 L. What change in temperature is necessary to adjust the pressure of that gas to 1.5 atm after it has been transferred to 200 L container?
 (1) 273° (2) 0°
 (3) 5° (4) 10°
12. The r.m.s. velocity of hydrogen is $\sqrt{7}$ times the r.m.s. of nitrogen. If T is the temperature of the gas then
 (1) $T_{H_2} = T_{N_2}$ (2) $T_{H_2} > T_{N_2}$
 (3) $T_{H_2} < T_{N_2}$ (4) $T_{H_2} = \sqrt{7} T_{N_2}$
13. At what temperature will the total KE of 0.3 mol of He be the same as the total KE of 0.40 mol of Ar at 400 K?
 (1) 533 K (2) 400 K
 (3) 346 K (4) 300 K
14. The relative rate of diffusion of a certain gas (molar mass = 128) as compared to oxygen is
 (1) 2 times (2) $\frac{1}{4}$ times
 (3) $\frac{1}{8}$ times (4) $\frac{1}{2}$ times
15. If 4 g of oxygen diffuses through a very narrow hole, how much hydrogen would have diffused under identical conditions?
 (1) 16 g (2) 1 g
 (3) $\frac{1}{4}$ g (4) 64 g
16. Ratio of molecular weights of A and B is $\frac{4}{25}$ then ratio of rate of diffusion will be
 (1) 5 : 1 (2) 5 : 2
 (3) 25 : 3 (4) 25 : 4
17. 100 ml of an ideal gas is heated in an open vessel from 300 K to 400 K. The volume of gas that will remain in the vessel is
 (1) 133 ml (2) 100 ml
 (3) 33 ml (4) 67 ml
18. Two bulbs of volume 5 L and 10 L containing an ideal gas at 9 atm and 6 atm respectively is opened. What is the final pressure in the two bulbs if the temperature remains constant?
 (1) 15 atm (2) 7 atm
 (3) 12 atm (4) 21 atm
19. If pressure of a fixed quantity of a gas is increased 4 times keeping the temperature constant, the r.m.s velocity will be
 (1) 4 times (2) 2 times
 (3) Same (4) $\frac{1}{2}$ times
20. According to kinetic theory of gases there are
 (1) Intermolecular attractions
 (2) Molecules have considerable volume
 (3) No intermolecular attraction
 (4) The velocity of molecules decreases for each collision
21. A sample of gas at 1.2 atm and 27°C is heated at constant pressure to 57°C. Its final volume is found to be 4.75 litre. What was its original volume?
 (1) 4.32 L (2) 5.02 L
 (3) 4 L (4) 10 L
22. What is the ratio of the average kinetic energy per mole of H₂ to that of CO₂ at 300 K?
 (1) 1 : 1 (2) 44 : 2
 (3) 1 : 11 (4) None of these
23. A vessel has 6 g of oxygen at a pressure P and temperature 400 K. A small hole is made in it so that O₂ leaks out. How much O₂ leaks out if the pressure is $\frac{P}{2}$ and temperature is 300 K?
 (1) 5 g (2) 4 g
 (3) 2 g (4) 3 g
24. At what temperature the r.m.s. velocity of oxygen will be same as that of methane at 27°C?
 (1) 54°C
 (2) 327 K
 (3) 600 K
 (4) 573 K
25. Boyle's temperature T_b is equal to
 (1) $\frac{a}{b}$ (2) $\frac{a}{Rb}$
 (3) $\frac{2a}{Rb}$ (4) $\frac{a}{2Rb}$

26. The critical temperature of gas is related to van der Waal's constant as

$$(1) T_c = 3b \quad (2) T_c = \frac{a}{27b^2}$$

$$(3) T_c = \frac{8a}{27Rb} \quad (4) T_c = \frac{a}{2Rb}$$

27. T_c and P_c of gas are 400 K and 41 atm respectively. Then V_c is

$$(1) \frac{400R}{41} \quad (2) \frac{41R}{400}$$

$$(3) \frac{150R}{41} \quad (4) \text{None of these}$$

28. The gas behaves ideally at

- (1) High temperature, low pressure
- (2) High temperature, high pressure
- (3) Low temperature, high pressure
- (4) Low temperature, low pressure

29. Least liquefiable gas is

- (1) He
- (2) CH₄
- (3) N₂
- (4) O₂

30. Compressibility factor (Z) of real gas at critical state is

- (1) $Z = 1$
- (2) $Z > 1$
- (3) $Z < 1$
- (4) Either (1) or (2)

SECTION - B

Previous Years Questions

1. A certain gas takes three times as long to effuse out as helium. Its molecular mass will be

[AIPMT 2012]

- (1) 27 u
- (2) 36 u
- (3) 64 u
- (4) 9 u

2. For real gases van der Waal's equation is written

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad \text{[AIPMT 2012]}$$

where 'a' and 'b' are van der Waal's constants.

Two sets of gases are :

- (I) O₂, CO₂, H₂ and He
- (II) CH₄, O₂ and H₂

The gases given in set-I in increasing order of 'b' and gases given in set-II in decreasing order of 'a', are arranged below. Select the correct order from the following :

- (1) (I) He < H₂ < CO₂ < O₂ (II) CH₄ > H₂ > O₂
- (2) (I) O₂ < He < H₂ < CO₂ (II) H₂ > O₂ > CH₄
- (3) (I) H₂ < He < O₂ < CO₂ (II) CH₄ > O₂ > H₂
- (4) (I) H₂ < O₂ < He < CO₂ (II) O₂ > CH₄ > H₂

3. Maximum deviation from ideal gas is expected from [NEET 2013]

- (1) N₂(g)
- (2) CH₄(g)
- (3) NH₃(g)
- (4) H₂(g)

4. Dipole-induced dipole interactions are present in which of the following pairs? [NEET 2013]

- (1) Cl₂ and CCl₄
- (2) HCl and He atoms
- (3) SiF₄ and He atoms
- (4) H₂O and alcohol

5. Equal masses of H₂, O₂ and methane have been taken in a container of volume V at temperature 27°C in identical conditions. The ratio of the volumes of gases H₂ : O₂ : methane would be

[AIPMT 2014]

- (1) 8 : 16 : 1
- (2) 16 : 8 : 1
- (3) 16 : 1 : 2
- (4) 8 : 1 : 2

6. A gas such as carbon monoxide would be most likely to obey the ideal gas law at [Re-AIPMT 2015]

- (1) High temperatures and high pressures
- (2) Low temperatures and low pressures
- (3) High temperatures and low pressures
- (4) Low temperatures and high pressures

7. Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape? [NEET-2016]

- (1) $\frac{1}{2}$
- (2) $\frac{1}{8}$
- (3) $\frac{1}{4}$
- (4) $\frac{3}{8}$

8. The correction factor 'a' to the ideal gas equation corresponds to [NEET-2018]

- (1) Density of the gas molecules
- (2) Volume of the gas molecules
- (3) Forces of attraction between the gas molecules
- (4) Electric field present between the gas molecules

9. Given van der Waals constant for NH_3 , H_2 , O_2 and CO_2 are respectively 4.17, 0.244, 1.36 and 3.59, which one of the following gases is most easily liquefied? [NEET-2018]
- (1) NH_3
(2) H_2
(3) CO_2
(4) O_2
10. A gas at 350 K and 15 bar has molar volume 20 percent smaller than that for an ideal gas under the same conditions. The **correct** option about the gas and its compressibility factor (Z) is : [NEET-2019]
- (1) $Z > 1$ and attractive forces are dominant
(2) $Z > 1$ and repulsive forces are dominant
(3) $Z < 1$ and attractive forces are dominant
(4) $Z < 1$ and repulsive forces are dominant
11. The volume occupied by 1.8 g of water vapour at 374°C and 1 bar pressure will be [Use $R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}$] [NEET-2019 (Odisha)]
- (1) 5.37 L
(2) 96.66 L
(3) 55.87 L
(4) 3.10 L
12. In water saturated air, the mole fraction of water vapour is 0.02. If the total pressure of the saturated air is 1.2 atm, the partial pressure of dry air is [NEET-2019 (Odisha)]
- (1) 0.98 atm
(2) 1.18 atm
(3) 1.76 atm
(4) 1.176 atm



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Chapter 6

Thermodynamics

Sub-topics

First law of thermodynamics-internal energy and enthalpy, heat capacity and specific heat, measurement of ΔU and ΔH , Hess's law of constant heat summation, enthalpy of : bond dissociation, combustion, formation, atomization, sublimation, phase transition, ionization, solution and dilution. Introduction of entropy as state function, Second law of thermodynamics, Gibbs energy change for spontaneous and non-spontaneous process, criteria for equilibrium and spontaneity. Third law of thermodynamics- Brief introduction.

Thermodynamics

Thermodynamics deals with energy in its various forms and their interconversion.

System

Thermodynamic system refers to any part of the real world under study and rest is referred as surrounding

- (i) **Open system** : Matter and energy both gets exchanged.
- (ii) **Close system** : Only energy can exchange (heat or work) not matter.
- (iii) **Isolated system** : Neither matter nor energy gets exchanged.

State of System

Condition where all the macroscopic properties of system have definite values (*i.e.*, temperature, pressure, volume known as **state variable** fix the state of system).

Properties of System

- (i) **State Function and Path Function** : Properties that depend on path which is followed during thermodynamic processes are path function *e.g.*, work and heat. And state function are those properties of system whose value depends only upon state of the system and is independent of path followed. *e.g.*, pressure, volume, temperature, internal energy (E), enthalpy (H), entropy (S).
- (ii) **Extensive and Intensive Properties** : Extensive Properties : Properties of system which depends upon the amount of substance present in system. *e.g.*, mass, volume, surface area, entropy, enthalpy. Intensive Properties : Properties of the system whose value is independent of the amount of substance present in system. *e.g.*, Temperature, pressure.

Thermodynamic Process

When a thermodynamic system undergoes a change of state, this process from initial state to final state is known as **thermodynamic process**.

- (i) **Reversible process** : Process where change is carried out so slowly that system and surrounding are always in equilibrium.

- (ii) **Isothermal process** : $\Delta T = 0$.
- (iii) **Isobaric process** : $\Delta P = 0$.
- (iv) **Isochoric process** : $\Delta V = 0$.
- (v) **Adiabatic process** : Process does not exchange heat with surrounding.

Internal Energy (U.E.)

The energy of a thermodynamic system under given condition is called internal energy.

Internal energy (U.E.) = Kinetic energy (K.E.) + potential energy (P.E.) + vibrational energy (V.E.) + rotational energy (R.E) or sum of all kinds of energies.

First Law of Thermodynamics

- (i) Energy can neither be created nor destroyed.
- (ii) The total energy of the universe is constant.
- (iii) The mass and energy of an isolated system remains constant.
- (iv) The total energy of a system and its surrounding must remain constant, although it may be changed from one form to other.

Mathematically, $\Delta U = q + W$... (1)

Sign Convention :

$W = +ve$ work done on the system

$W = -ve$ work done by the system

$q = +ve$ heat is absorbed by the system

$q = -ve$ heat is evolved by the system.

Work

$W = -P\Delta V \rightarrow$ for **irreversible isothermal** process.

$$W = -2.303nRT \log \frac{V_2}{V_1} \rightarrow \text{for reversible isothermal process}$$

$$W = -2.303nRT \log \frac{P_1}{P_2} \text{ for reversible isothermal process}$$

$W = 0$, for free expansion

Enthalpy

For the process or a chemical reaction carried out at constant volume, the heat absorbed/evolved is equal to the corresponding change in internal energy (ΔU) or (ΔE).

Many of the reactions are carried out at constant pressure. To measure heat changes at constant pressure it is useful to define new state function called **enthalpy** (H).

i.e., internal energy and PV energy of any system under a particular set of conditions is known as enthalpy (H) i.e., $H = U + PV$ and for reaction i.e., process

$$\Delta H = \Delta U + \Delta n_g RT \quad \dots (2)$$

Δn_g = number of moles of gaseous product – number of moles of gaseous reactant.

Note : ΔH is a state function and is the extensive property.

Standard Enthalpy Changes ΔH°

S. No.	Name of Enthalpy Changed		Definition	Example
1.	Enthalpy of combustion	ΔH_C°	It is the energy which is released when 1 mole of substance is burnt completely with excess amount of oxygen	(i) $C + O_2 \rightarrow CO_2$ (ii) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
2.	Enthalpy of formation	ΔH_f°	It is the energy which is released or absorbed when 1 mole of substance/compound is formed from its elements in their most stable state.	(i) $H_2 + S + 2O_2 \rightarrow H_2SO_4$ (ii) $S + \frac{3}{2}O_2 \rightarrow SO_3$
3.	Enthalpy of atomisation	ΔH_a°	It is the energy which is absorbed when 1 mole of substance broken up into its isolated atoms in the gas phase	(i) $Na(s) \rightarrow Na(g)$
4.	Enthalpy of neutralization	ΔH_N°	It is the energy which is released (fix for strong acid - strong base neutralization i.e. -57.1 kJ or -13.7 kcal) when one mole of water is formed by the neutralization of an acid by a base. [one equivalent of acid and one equivalent of base]	(i) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ (ii) $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
5.	Enthalpy of fusion	ΔH_f°	It is the energy which is absorbed when 1 mole of liquid is formed from the solid at its melting point.	(i) $H_2O(s) \rightarrow H_2O(l)$
6.	Enthalpy of solution	ΔH_S°	It is the amount of heat change when 1 mole of solute is dissolved in excess amount of solvent	(i) $KCl + aq \rightarrow KCl(aq)$ $\Delta H = 4.4$ kcal

Enthalpy of reaction can also be calculated using bond energy

$$\Delta H_{\text{reaction}} = \sum \text{Bond energy of reactants} - \sum \text{Bond energy of products}$$

Heat Capacity (C)

Heat Capacity (C) : Quantity of heat required to raise the temperature of a substance by one degree celsius at constant volume is C_v and C_p is at constant pressure.

$$C_p = \frac{q_p}{T}, C_v = \frac{q_v}{T}$$

$$\text{i.e., } q_v = C_v \Delta T$$

Molar Heat Capacity - Heat capacity for one mole of substance is called molar heat capacity whereas specific heat capacity is heat capacity for per gram of substance.

$$q = C \times M \times \Delta T;$$

$$\gamma = \frac{C_p}{C_v};$$

if $\gamma = 1.67$, gas is monoatomic

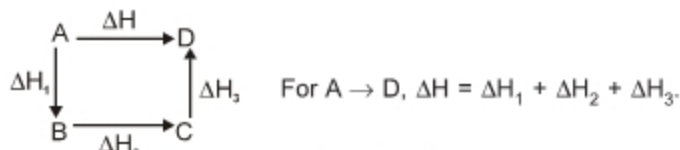
$\gamma = 1.40$; gas is diatomic or linear triatomic

$\gamma = 1.33$; gas is non-linear triatomic

Hess's Law

If a reaction is the sum of two or more constituent reactions, then ΔH for the overall process must be sum of the ΔH of the constituent reactions.

The enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps.



Enthalpy of reaction can also be calculated using bond energy.

$$\Delta H_{\text{reaction}} = \sum \text{Bond energy of reactants} - \sum \text{Bond energy of products}$$

2nd law of thermodynamics: Entropy of the universe always increases.

Entropy and Entropy Change

Entropy is measure of randomness. Higher the disorder higher is the entropy.

Entropy for solid < liquid < gas

$$\Delta S = \frac{q_{\text{rev}}}{T}; \quad \Delta S = 2.303 nR \log \frac{V_2}{V_1} \quad \dots(3)$$

where q_{rev} = Heat absorbed when the process is carried out reversibly and isothermally.

Entropy change is given in unit of J/K or JK⁻¹.

Gibb's Energy and Gibb's Free Energy Change

Gibb's free energy is criteria for spontaneity of reaction. It is maximum possible useful work that can be derived from process.

$$\Delta G = \Delta H - T\Delta S \quad \dots(4)$$

- (i) If ΔG_{sys} is negative (<0), the process is spontaneous.
- (ii) If ΔG_{sys} is positive (>0), the process is non-spontaneous.
- (iii) If $\Delta G_{\text{sys}} = 0$, the system has attained equilibrium.
- (iv) Spontaneity of the reaction :

ΔH	$T\Delta S$	ΔG	Temperature	Nature of reaction
+ve	-ve	+ve	All temperature	Non-spontaneous
-ve	+ve	-ve	All temperature	Spontaneous
+ve	+ve	+ve	Low temperature	Non-spontaneous
		-ve	High temperature $T > \frac{\Delta H}{\Delta S}$	Spontaneous
-ve	-ve	-ve	Low temperature $T < \frac{\Delta H}{\Delta S}$	Spontaneous
		+ve	High temperature	Non-spontaneous

Third law of thermodynamics: The absolute entropy of a perfectly crystalline substance at absolute zero temperature is zero.





Try Yourself

SECTION - A

Objective Type Questions

- Tea placed in thermos flask is an example of
 - Open system
 - Close system
 - Isolated system
 - It can't act as system
- Gaseous system is placed with pressure P_1 , volume V_1 and temperature T_1 , it undergoes thermodynamic changes where temperature is remaining constant, it is
 - Adiabatic process
 - Isothermal process
 - Isobaric process
 - Isochoric process
- The respective examples of extensive and intensive properties are
 - Enthalpy, entropy
 - Entropy, enthalpy
 - Entropy, temperature
 - Temperature, entropy
- State function are properties which
 - Depends on path
 - Depends on amount
 - Independent of path
 - All of these
- According to first law of thermodynamics
 - $\Delta U = q \times w$
 - $\Delta U = q + \Delta H$
 - $\Delta U = q + w$
 - $\Delta U = q + W$
- System with internal energy E_1 absorbs 200 cal of heat and work is done on it of 4.184 J. The final internal energy E_2 is
 - $(E_1 + 200)$ cal
 - $(E_1 + 201)$ cal
 - $(E_1 + 1)$ cal
 - $(E_1 - 201)$ cal
- If 'r' is the work done on the system and 's' is heat evolved by the system then,
 - $\Delta E = r + s$
 - $\Delta E = r - s$
 - $\Delta E = r$
 - $\Delta E = s$
- For the reaction,

$$aA(s) + bB(g) \longrightarrow dD(s) + cC(g).$$
 Then
 - $\Delta H - \Delta E = (b - d) RT$
 - $\Delta H - \Delta E = (c - b) RT$
 - $\Delta H - \Delta E = (a + b) - (c + d) RT$
 - $\Delta H - \Delta E = (a - d) RT$
- Which of the following is an exothermic process?
 - $C(s) + O_2(g) \longrightarrow CO_2(g)$
 - $NaOH + HCl \longrightarrow NaCl + H_2O$
 - Both (1) & (2)
 - $H_2(g) \longrightarrow 2H(g)$
- For the given reactions, $A \longrightarrow D$, $\Delta H = x$. Steps involved are

$$A \longrightarrow B \quad \Delta H_1 = x_1$$

$$B \longrightarrow C \quad \Delta H_2 = ?$$

$$C \longrightarrow D \quad \Delta H_3 = x_3$$
 - $\Delta H_2 = x - (x_1 + x_3)$
 - $\Delta H_2 = x + x_1 + x_3$
 - $\Delta H_2 = x_1 - x_3 - x$
 - $\Delta H_2 = (x_1 + x) - x_3$
- Which will be with maximum positive entropy change?
 - Solid \longrightarrow Liquid
 - Liquid \longrightarrow Gas
 - Solid \longrightarrow Gas
 - Gas \longrightarrow Solid
- Two free atoms $A(g)$ and $B(g)$ are combining to give $AB(g)$
 - The energy will release
 - The entropy will decrease
 - Both (1) & (2)
 - Can't predict change in state function
- Though N_2 and O_2 are in atmosphere but they are not forming oxides at room temperature as ΔG for reaction is
 - Zero
 - Negative
 - Positive
 - They are not present in atmosphere
- At all temperature reaction is spontaneous if
 - $\Delta H = +ve, \Delta S = +ve$
 - $\Delta H = +ve, \Delta S = -ve$
 - $\Delta H = -ve, \Delta S = -ve$
 - $\Delta H = -ve, \Delta S = +ve$

15. At low temperature reaction will be spontaneous if
 (1) ΔH and ΔS both are negative and $\Delta H > T\Delta S$ (magnitude)
 (2) ΔH and ΔS both are negative and $\Delta H < T\Delta S$ (magnitude)
 (3) ΔH is positive and ΔS is negative
 (4) ΔH and ΔS both are positive
16. Work done corresponding to 200 cal of heat is
 (1) 83.68 J (2) 836.8 J
 (3) 0.836 J (4) 8.36 J
17. Calculate the temperature at which the reaction given below is at equilibrium

$$\text{Ag}_2\text{O(s)} \rightleftharpoons 2\text{Ag(s)} + \frac{1}{2}\text{O}_2\text{(g)}$$

 Given $\Delta H^\circ = 30.5 \text{ kJ mol}^{-1}$
 $\Delta S^\circ = 0.066 \text{ kJ K}^{-1}$
 (1) 462.12 K (2) 462.12°C
 (3) 46.21 K (4) 46.21°C
18. Calculate the enthalpy of vaporization for 1 gm of water from the following

$$\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(g)}$$

 $\Delta H = -51 \text{ kcal}$

$$\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(l)}$$

 $\Delta H = -68.3 \text{ kcal}$
 (1) 11.3 kcal (2) 0.961 kcal
 (3) 113 kcal (4) None of these
19. Calculate work done during the process when one mole of a gas is allowed to expand freely into vacuum.
 (1) 101.3 J (2) 1.013 J
 (3) Zero (4) Insufficient data
20. In a reaction, all reactant and products are liquid, then
 (1) $\Delta H > \Delta E$ (2) $\Delta H < \Delta E$
 (3) $\Delta H = \Delta E$ (4) Unpredictable
21. Entropy decreases in
 (1) Rusting of iron
 (2) Melting of ice
 (3) Vapourisation of camphor
 (4) Crystallisation of sucrose from solution
22. Evaporation of a liquid is accompanied by
 (1) Decrease in entropy
 (2) Increase in enthalpy
 (3) Decrease in enthalpy
 (4) No change in free energy
23. The standard heat of formation for $\text{CCl}_4\text{(g)}$, $\text{H}_2\text{O(g)}$, $\text{CO}_2\text{(g)}$ and HCl(g) are -25.5 , -57.8 , -94.1 and -22.1 kcal , respectively. Calculate ΔH_{298} for the reaction,

$$\text{CCl}_4\text{(g)} + 2\text{H}_2\text{O(g)} \longrightarrow \text{CO}_2\text{(g)} + 4\text{HCl(g)}$$

 (1) -41.4 kcal (2) 41.4 kcal
 (3) 414 kcal (4) -414 kcal
24. An athlete takes 100 gm of glucose of energy equivalent to 1560 kJ. How much amount of energy is uptaken by 1 gm molecule of glucose?
 (1) 15.6 kJ (2) 2808 kJ
 (3) 1560 kJ (4) 28.08 kJ
25. For strong acid strong base neutralisation energy released for $1\text{H}_2\text{O}$ formation is -57.1 kJ . If 0.25 mole of strong monoprotic acid is reacted with 0.5 mole of strong base then the enthalpy of reaction is
 (1) $-(0.25 \times 57.1)$ (2) 0.5×57.1
 (3) 0.25×57.1 (4) $-(0.5 \times 57.1)$
26. Using bond energy data, calculate heat of formation of isoprene

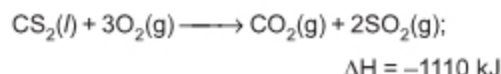
$$5\text{C(s)} + 4\text{H}_2\text{(g)} \longrightarrow \text{H}_2\text{C}=\underset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2$$

 Given C-H, H-H, C-C, C=C and C(s) \rightarrow C(g) respectively as 98.8 kcal, 104 kcal, 83 kcal, 147 kcal, 171 kcal
 (1) -20.6 kcal (2) 20.6 kcal
 (3) 40 kcal (4) 50 kcal
27. A system absorb 20 kJ of heat and also does 10 kJ of work. The net internal energy of the system
 (1) Increases by 10 kJ (2) Decreases by 10 kJ
 (3) Increases by 30 kJ (4) Decreases by 30 kJ
28. 2 moles of hydrogen expand isothermally and reversibly at 27°C from 15 to 30 litre. The work done in calories is
 (1) $2763.6 \log 2 \text{ cal}$ (2) $-2763.6 \log 2 \text{ cal}$
 (3) $-27 \log 20 \text{ cal}$ (4) $276.3 \log 2 \text{ cal}$
29. What is the enthalpy of combustion for the given reaction?

$$2\text{HC}\equiv\text{CH} + 5\text{O}_2 \rightarrow 4\text{CO}_2 + 2\text{H}_2\text{O}$$

 The bond energies of C-H, C \equiv C, O=O, C=O and O-H bonds are p, q, r, s and t respectively
 (1) $[8s + 4t] - [4p + q + 5r]$
 (2) $[4p + 2q + 5r] - [8s + 4t]$
 (3) $[4p + 2q + 5r + 8s + 4t]$
 (4) $[2p + q + 5r] - [8s + 4t]$

30. Given that,



The heat of formation of CS_2 is

- (1) 125 kJ mol⁻¹ (2) 31.25 kJ mol⁻¹
(3) 62.5 kJ mol⁻¹ (4) 250 kJ mol⁻¹

31. For reaction, $\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$. Which one of the following statement is correct at constant T and P?

- (1) $\Delta H = \Delta E$ (2) $\Delta H < \Delta E$
(3) $\Delta H > \Delta E$ (4) Cannot predict

32. A reaction is not feasible at all temperatures if

- (1) ΔH is positive and ΔS is also positive
(2) ΔH is positive and ΔS is negative
(3) ΔH is negative and ΔS is also negative
(4) ΔH is negative and ΔS is positive

33. Which of the following process will have ΔH positive?

- (1) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$
(2) $\text{C(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$
(3) $\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$
(4) $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g})$

34. A cylinder of gas is assumed to contain 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day. The cylinder will last (given that ΔH for combustion of butane is -2658 kJ)

- (1) 20 days (2) 35 days
(3) 26 days (4) 31 days

35. At 298 K the standard enthalpies of formation $\text{H}_2\text{O(l)}$ and $\text{H}_2\text{O}_2(\text{l})$ are -286.0 kJ mol⁻¹ and -188.0 kJ mol⁻¹. The enthalpy change for reaction



- (1) -948 kJ mol⁻¹
(2) -196 kJ mol⁻¹
(3) +196 kJ mol⁻¹
(4) +948 kJ mol⁻¹

SECTION - B

Previous Years Questions

1. In which of the following reactions, standard reaction entropy change (ΔS°) is positive and standard Gibbs energy change (ΔG°) decreases sharply with increasing temperature? [AIPMT 2012]

- (1) $\text{Mg(s)} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{MgO(s)}$
(2) $\frac{1}{2}\text{C graphite} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \frac{1}{2}\text{CO}_2(\text{g})$
(3) $\text{C graphite} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO(g)}$
(4) $\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$

2. Standard enthalpy of vapourisation $\Delta_{\text{vap}}H^\circ$ for water at 100° C is 40.66 kJ mol⁻¹. The internal energy of vapourisation of water at 100°C (in kJ mol⁻¹) is

[AIPMT 2012]

- (1) +43.76 (2) +40.66
(3) +37.56 (4) -43.76

(Assume water vapour to behave like an ideal gas)

3. The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is [AIPMT 2012]

- (1) 5.260 cal/(mol K)
(2) 0.526 cal/(mol K)
(3) 10.52 cal/(mol K)
(4) 21.04 cal/(mol K)

4. Equal volumes of two monoatomic gases, A and B, at same temperature and pressure are mixed. The ratio of specific heats (C_p/C_v) of the mixture will be: [AIPMT 2012]

- (1) 0.83 (2) 1.50
(3) 3.3 (4) 1.67

5. A reaction having equal energies of activation for forward and reverse reactions has [NEET 2013]

- (1) $\Delta G = 0$ (2) $\Delta H = 0$
(3) $\Delta H = \Delta G = \Delta S = 0$ (4) $\Delta S = 0$

6. For the reaction, $\text{X}_2\text{O}_4(\text{l}) \longrightarrow 2\text{XO}_2(\text{g})$
 $\Delta U = 2.1 \text{ kcal}$, $\Delta S = 20 \text{ cal K}^{-1}$ at 300 K

Hence, ΔG is

[AIPMT 2014]

- (1) 2.7 kcal (2) -2.7 kcal
(3) 9.3 kcal (4) -9.3 kcal

7. The heat of combustion of carbon to CO_2 is -393.5 kJ/mol . The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is

[Re-AIPMT 2015]

- (1) -630 kJ (2) -3.15 kJ
(3) -315 kJ (4) $+315 \text{ kJ}$

8. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is

[NEET-2016]

- (1) $\Delta H < 0$ and $\Delta S < 0$ (2) $\Delta H < 0$ and $\Delta S = 0$
(3) $\Delta H > 0$ and $\Delta S < 0$ (4) $\Delta H < 0$ and $\Delta S > 0$

9. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f , the entropy change is given by

[NEET (Phase-2) 2016]

(1) $\Delta S = nR \ln \left(\frac{p_f}{p_i} \right)$ (2) $\Delta S = nR \ln \left(\frac{p_i}{p_f} \right)$

(3) $\Delta S = nRT \ln \left(\frac{p_f}{p_i} \right)$ (4) $\Delta S = RT \ln \left(\frac{p_i}{p_f} \right)$

10. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L . The change in internal energy ΔU of the gas in joules will be

[NEET-2017]

- (1) 1136.25 J (2) -500 J
(3) -505 J (4) $+505 \text{ J}$

11. For a given reaction, $\Delta H = 35.5 \text{ kJ mol}^{-1}$ and $\Delta S = 83.6 \text{ JK}^{-1} \text{ mol}^{-1}$. The reaction is spontaneous at : (Assume that ΔH and ΔS do not vary with temperature)

[NEET-2017]

- (1) $T < 425 \text{ K}$ (2) $T > 425 \text{ K}$
(3) All temperatures (4) $T > 298 \text{ K}$

12. The bond dissociation energies of X_2 , Y_2 and XY are in the ratio of $1 : 0.5 : 1$. ΔH for the formation of XY is -200 kJ mol^{-1} . The bond dissociation energy of X_2 will be

[NEET-2018]

- (1) 200 kJ mol^{-1}
(2) 100 kJ mol^{-1}
(3) 400 kJ mol^{-1}
(4) 800 kJ mol^{-1}

13. Under isothermal condition, a gas at 300 K expands from 0.1 L to 0.25 L against a constant external pressure of 2 bar . The work done by the gas is

(Given that $1 \text{ L bar} = 100 \text{ J}$)

[NEET-2019]

- (1) -30 J (2) 5 kJ
(3) 25 J (4) 30 J

14. In which case change in entropy is negative?

[NEET-2019]

- (1) Evaporation of water
(2) Expansion of a gas at constant temperature
(3) Sublimation of solid to gas
(4) $2\text{H(g)} \rightarrow \text{H}_2\text{(g)}$

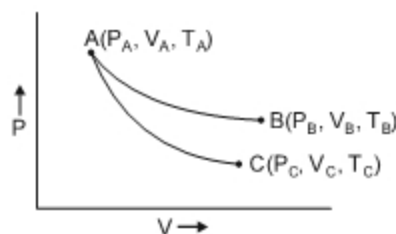
15. An ideal gas expands isothermally from 10^{-3} m^3 to 10^{-2} m^3 at 300 K against a constant pressure of 10^5 Nm^{-2} . The work done on the gas is

[NEET-2019 (Odisha)]

- (1) -900 kJ
(2) $+270 \text{ kJ}$
(3) -900 J
(4) $+900 \text{ kJ}$

16. Reversible expansion of an ideal gas under isothermal and adiabatic conditions are as shown in the figure.

[NEET-2019 (Odisha)]

AB \rightarrow Isothermal expansionAC \rightarrow Adiabatic expansionWhich of the following options is **not** correct?

- (1) $T_C > T_A$
(2) $\Delta S_{\text{isothermal}} > \Delta S_{\text{adiabatic}}$
(3) $T_A = T_B$
(4) $w_{\text{isothermal}} > w_{\text{adiabatic}}$



Chapter 7

Equilibrium

Sub-topics

Equilibrium in physical and chemical processes, dynamic nature of equilibrium, law of chemical equilibrium, equilibrium constant, factors affecting equilibrium-Le Chatelier's principle; ionic equilibrium- ionization of acids and bases, strong and weak electrolytes, degree of ionization, ionization of polybasic acids, acid strength, concept of pH., Hydrolysis of salts (elementary idea)., buffer solutions, Henderson equation, solubility product, common ion effect (with illustrative examples).

Types of Equilibria :

- (1) Physical equilibrium e.g., $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$
- (2) Chemical equilibrium e.g., $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$
- (3) Ionic equilibrium e.g., $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

Chemical Equilibrium

At same given set of condition, the rate at which products are produced from reactants equals the rate at which reactants are produced from products is known as equilibrium of reaction.

e.g., $aA + bB \rightleftharpoons cC + dD$



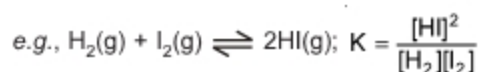
$$\left. \begin{array}{l} \text{Rate of forward reaction (1)} \\ r_f = k_f [A]^a [B]^b \\ \text{Rate of backward reaction (2)} \\ r_b = k_b [C]^c [D]^d \end{array} \right\} \text{According to law of mass action}$$

At equilibrium $r_f = r_b$

$$\therefore \frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\frac{k_f}{k_b} = K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ where } K = \text{equilibrium constant, } k_f \text{ and } k_b \text{ are rate constants for forward and backward reaction}$$

$$\therefore K = \frac{[\text{Product}]}{[\text{Reactant}]}$$



Note : Pure liquid and pure solid entities are not taken in equation as its activity is taken as 1

1. Equilibrium constant K in terms of concentration and pressure (K_p and K_c)

According to law of mass action rate is directly proportional to activity. Here activity is replaced by concentration or by partial pressure term for gaseous species.



$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \text{ and } K_p = \frac{p_{\text{PCl}_3} p_{\text{Cl}_2}}{p_{\text{PCl}_5}}$$

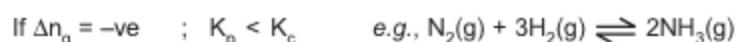
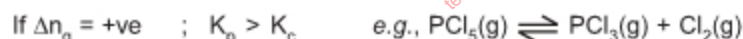
2. Relation between K_p and K_c : K_p and K_c for same reaction are related as;

$$K_p = K_c(RT)^{\Delta n_g}$$

Δn_g = Number of moles of gaseous product – number of moles of gaseous reactant

T = Absolute temperature

R = Gas constant



3. Degree of dissociation : (α)



Int. moles 1 0 0

Eq. moles $1 - \alpha$ α α

Eq. conc. $\frac{1 - \alpha}{V}$ $\frac{\alpha}{V}$ $\frac{\alpha}{V}$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\alpha^2 / V^2}{(1 - \alpha) / V} = \frac{\alpha^2}{(1 - \alpha)V}$$

This approximation is valid if $\alpha < 0.05$

if $\alpha \ll 1$, then $1 - \alpha \approx 1$

$$\therefore K_c = \frac{\alpha^2}{V} \quad \therefore \alpha = \sqrt{K_c \cdot V}$$

4. Degree of dissociation from vapour density

$$\alpha = \frac{D - d}{(n - 1)d}$$

where D = Vapour density before dissociation

d = Vapour density after dissociation

n = Number of moles obtained from one mole of dissociating species

Note : This formula is not applicable for the reactions, in which $\Delta n_g = 0$

5. Le Chatelier's Principle

"When the reaction is already at equilibrium and if it is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to decrease the effect of the change".

Factors influencing Equilibrium Reaction

- Concentration
- Pressure
- Inert Gas
- Catalyst
- Temperature

A. Concentration

- If concentration of reactant increased reaction shifts in forward direction.
- If concentration of reactant decreased reaction shifts in backward direction.
- If concentration of product increased reaction shifts in backward direction.
- If concentration of product decreased reaction shifts in forward direction.

B. Pressure : Effect of pressure depends on the Δn_g of reaction

$$\Delta n_g = 0$$

- (i) $\uparrow P$ Reaction unaltered $\downarrow P \Rightarrow$ e.g. : $H_2 + I_2 \rightleftharpoons 2HI$

$$\Delta n_g = +ve$$

- (ii) $\uparrow P \xleftarrow{\text{Backward}} \xrightarrow{\text{Forward}} \downarrow P \Rightarrow$ e.g. : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$$\Delta n_g = -ve$$

- (iii) $\uparrow P \xrightarrow{\text{Forward}} \xleftarrow{\text{Backward}} \downarrow P \Rightarrow$ e.g. : $N_2 + 3H_2 \rightleftharpoons 2NH_3$

C. Inert Gas : Effect of addition of inert gas is studied either at constant pressure or constant volume at equilibrium.

Inert gas	$\Delta n_g = 0$	$\Delta n_g = -ve$	$\Delta n_g = +ve$
At. constant V	No effect	No effect	No effect
At. constant P	No effect	$\xleftarrow{\text{Backward}}$	$\xrightarrow{\text{Forward}}$

D. Catalyst : Addition of catalyst decreases the energy of activation and increases the rate of forward and backward reaction equally and hence doesn't influence equilibrium. It only decreases the time of attainment of equilibrium.

- E. Temperature :** With increase or decrease in temperature reaction either shifts in forward or backward direction and it also changes the **equilibrium constant**.

	Endothermic Reaction $\Delta + R \rightleftharpoons P$	Exothermic Reaction $R \rightleftharpoons P + \Delta$
(1)	Increase in temperature, shifts reaction in forward direction	Increase in temperature, shifts reaction in backward direction
(2)	Decrease in temperature, shifts reaction in backward direction	Decrease in temperature, shifts reaction in forward direction

For Endothermic Reaction : If K_1 is equilibrium constant at temperature T_1 and K_2 is equilibrium constant at temperature T_2 if $T_2 > T_1$; $K_2 > K_1$.

For Exothermic Reaction : If K_1 is equilibrium constant at temperature T_1 and K_2 is equilibrium constant at temperature T_2 if $T_2 > T_1$ $K_2 < K_1$.

Note : Only temperature factor changes equilibrium constant value rest only shifts the direction of the equilibrium.

Variation of equilibrium constant with temperature.

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

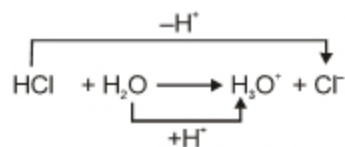
It is called as clayperon – clausius equation.

K_1 = equilibrium constant at temperature T_1

K_2 = equilibrium constant at temperature T_2

Ionic Equilibrium in Solutions

1. Conjugated Acid - Base Theory



$HCl \rightarrow$ acid; $Cl^- \rightarrow$ conjugate base

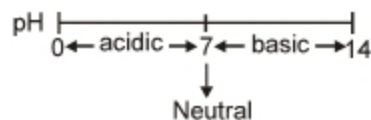
$H_2O \rightarrow$ base; $H_3O^+ \rightarrow$ conjugate acid

Note : For strong acid its conjugate base is weak and for weak acid its conjugate base is strong.

2. pH Scale

The pH of a solution is defined as negative logarithm of hydrogen ion concentration. At low concentration the activity of hydrogen ion is numerically equal to its molarity represented by $[H^+]$.

$$pH = -\log[H^+] \quad \text{and} \quad pOH = -\log[OH^-]$$



e.g., pH for 10^{-3} M HCl is 3.

Note : $pH + pOH = pK_w$ i.e., $pH + pOH = 14$.

3. Ostwald Dilution Law (For weak Electrolyte)

Consider a binary electrolyte AB (acid or base) which dissociates into A^+ and B^- and the equilibrium state is represented by equation



Initially C 0 0

At. Equilibrium $C(1 - \alpha)$ $C\alpha$ $C\alpha$

\therefore Dissociation constant is given as

$$K_a = \frac{[A^+][B^-]}{[AB]} = \frac{(C\alpha)(C\alpha)}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$$

For very weak electrolyte, $\alpha \ll 1$, then $(1 - \alpha) \simeq 1$

$$\therefore K_a = C\alpha^2 \text{ or } K_b = C\alpha^2$$

$$\therefore \alpha = \sqrt{\frac{K_a}{C}} \text{ or } \alpha = \sqrt{\frac{K_b}{C}}$$

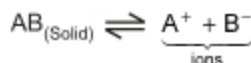
where K_a = Equilibrium constant for acid.

K_b = Equilibrium constant for base.

4. Solubility Product : K_{sp}

Solubility product is calculated for sparingly soluble salt in its saturated solution.

The solution remains in equilibrium with undissolved solute.



Since the solution is saturated, the concentration of unionised molecules of the electrolyte is constant at a particular temperature i.e. $[AB]$ is constant.

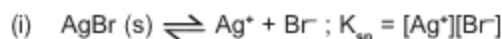
$$\therefore K_{sp} = [A^+][B^-]$$

where K_{sp} = solubility product.

For general electrolyte A_xB_y which is dissociated as

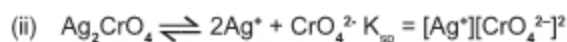


$$\therefore K_{sp} = [A^+]^x [B^-]^y$$



$$K_{sp} = s \times s = s^2 \text{ therefore } s = \sqrt{K_{sp}}$$

where 's' is solubility in mol L^{-1} .



$$K_{sp} = (2s)^2 (s) = 4s^3 \text{ therefore } s = \sqrt[3]{\frac{K_{sp}}{4}}$$



$$K_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3$$

$$K_{sp} = s(3s)^3 = 27s^4 \text{ therefore } s = \sqrt[4]{\frac{K_{sp}}{27}}$$



$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (3s)^3 (2s)^2 = 108s^5 \text{ therefore } s = \sqrt[5]{\frac{K_{sp}}{108}}$$

5. Criteria of Precipitation of an Electrolyte

- (i) When $K_{IP} < K_{SP}$ then solution is unsaturated in which more solute can be dissolved.
- (ii) When $K_{IP} = K_{SP}$ then solution is saturated in which no more solute can be dissolved.
- (iii) When $K_{IP} > K_{SP}$ then solution is supersaturated and precipitation takes place.

[K_{IP} = Ionic product; K_{sp} = Solubility product]

6. Buffer Solution

(a) Acidic Buffer : e.g., CH_3COOH and CH_3COONa .

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

(b) Basic Buffers : e.g., NH_4OH and NH_4Cl

$$\text{pH} = 14 - \text{pK}_b - \log \frac{[\text{Salt}]}{[\text{Base}]}$$

(c) Buffer capacity (ϕ) = $\frac{\text{Number of moles of H}^+ \text{ or OH}^- \text{ added per lit.}}{\Delta \text{pH}}$

Note : Addition of small amount of acid or base will almost does not change the pH of buffer solution.

7. Salt Hydrolysis

Consider the salt BA, which on hydrolysis will give acid and base inside the aqueous solution.



- (a) Salt made up of strong acid and strong base will not hydrolyse, it will simply ionise. And pH of aqueous solution will be neutral. The pH of aqueous solution is independent with dilution i.e., pH = 7. e.g., NaCl, Na_2SO_4 .
- (b) Salt made up strong acid and weak base will hydrolyse. e.g., NH_4Cl .

$$\text{Degree of hydrolysis (h)} = \sqrt{\frac{K_H}{C}}$$

$$\boxed{K_H = \frac{K_w}{K_b}} \quad \text{pH} = \frac{1}{2} [\text{pK}_w - \text{pK}_b - \log C]$$

- (c) Salt made up of weak acid and strong base. *e.g.*, CH_3COONa .

$$h = \sqrt{\frac{K_H}{C}}$$

$$\boxed{K_H = \frac{K_w}{K_a}} \quad \text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$$

- (d) Salt made up of weak acid and weak base. The pH of these salt solution depends on K_a and K_b but independent with concentration. *e.g.*, $\text{CH}_3\text{COONH}_4$.

$$\text{Degree of hydrolysis } (h) = \sqrt{K_H}$$

$$\boxed{K_H = \frac{K_w}{K_a K_b}} \quad \text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b + \text{p}K_a]$$



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Try Yourself

SECTION - A

Objective Type Questions

- In a chemical equilibrium the rate constant of the backward reaction is 7.5×10^{-4} and the equilibrium constant is 1.5. So the rate constant of the forward reaction is
 (1) 2×10^{-3} (2) 15×10^{-4}
 (3) 1.125×10^{-3} (4) 9.0×10^{-4}
- In which of the following equilibrium K_c and K_p are not equal?
 (1) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$
 (2) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
 (3) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
 (4) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- For a gaseous reaction, $pA + qB \rightleftharpoons qC + pD$, which of the following relationship is true?
 (1) $K_p = K_c$ (2) $K_p = K_c(RT)^{p+q}$
 (3) $K_p = K_c(RT)^{p-q}$ (4) $K_p = K_c = (RT)^{\frac{1}{p+q}}$
- Select the reaction for which the equilibrium equation is written as

$$[MA_2]^2[A_2] = \frac{[MA_3]^2}{K}$$
 (1) $MA_3 \rightleftharpoons MA_2 + \frac{1}{2}A_2$
 (2) $2MA_3 \rightleftharpoons 2MA_2 + A_2$
 (3) $2MA_2 + A_2 \rightleftharpoons 2MA_3$
 (4) $MA_2 + \frac{1}{2}A_2 \rightleftharpoons MA_3$
- For which of the following reaction, the degree of dissociation (α) and equilibrium constant (K_p) are related as $K_p = \frac{4\alpha^2 P}{(1-\alpha^2)}$?
 (1) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
 (2) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
 (3) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 (4) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
- At 700 K, the equilibrium constant, K_p , for the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ is 1.8×10^{-3} kPa. The value of K_c for the above reaction at the same temperature in moles per litre would be
 (1) $1.1 \times 10^{-7} \text{ mole}^{-1}$
 (2) $3.1 \times 10^{-7} \text{ mol L}^{-1}$
 (3) $6.2 \times 10^{-7} \text{ mole}^{-1}$
 (4) $9.3 \times 10^{-7} \text{ mol L}^{-1}$
- For the equilibrium $AB(g) \rightleftharpoons A(g) + B(g)$, K_p is equal to four times the total pressure. The number of moles of 'A' formed is
 (1) $\frac{\sqrt{5}}{2}$ (2) 2
 (3) $\sqrt{5}$ (4) $\frac{2}{\sqrt{5}}$
- K_p is how many times equal to K_c for the given reaction?
 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 (1) $\frac{1}{R^2 T^2}$ (2) $R^2 T^2$
 (3) $\frac{R}{T}$ (4) RT
- 4 gm H_2 , 32 gm O_2 , 14 gm N_2 and 11gm CO_2 are taken in a bulb of 500 ml. Which one of these has maximum active mass?
 (1) H_2 (2) O_2
 (3) N_2 (4) CO_2

10. XY_2 dissociates as,
 $XY_2(g) \rightleftharpoons XY(g) + Y(g)$
 Initial pressure of XY_2 is 600 mm Hg. The total pressure at equilibrium is 800 mm Hg. Assuming volume of system to remain constant, the value of K_p is
 (1) 50 (2) 100
 (3) 20 (4) 400
11. The initial pressure of $COCl_2$ is 1000 torr. The total pressure of the system becomes 1500 torr, when the equilibrium $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ is attained at constant temperature. The value of K_p of the reaction is
 (1) 1500 (2) 1000
 (3) 2500 (4) 500
12. Hydrogen (a moles) and iodine (b moles) react to give $2x$ moles of the HI at equilibrium. The total number of moles at equilibrium is
 (1) $a + b + 2x$ (2) $(a - b) + (b - 2x)$
 (3) $(a + b)$ (4) $a + b - x$
13. The decomposition of $N_2O_4 \rightleftharpoons 2NO_2$ is carried out at 573 K. When equilibrium is reached 0.2 mol of N_2O_4 and 2×10^{-3} mole of NO_2 are present in 2 litre solution. The equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is
 (1) 1×10^{-3} (2) 3×10^{-3}
 (3) 1×10^{-5} (4) 4×10^{-5}
14. When 1 mole of N_2 and 1 mole of H_2 is enclosed in a 3 L vessel and the reaction is allowed to attain equilibrium, it is found that at equilibrium there is 'x' mole of H_2 . The molar concentration of NH_3 formed would be
 (1) $\frac{2x}{3}$ (2) $\frac{2(1-x)}{9}$
 (3) $\frac{2(1-x)}{3}$ (4) $\frac{(1-x)}{2}$
15. In the reaction
 $A(s) + B(g) + \text{Heat} \rightleftharpoons 2C(s) + 2D(g)$
 equilibrium is established. The pressure of B is quadrupled in the other equilibrium. The factor by which D is changed is
 (1) $\sqrt{2}$ (2) 2
 (3) 4 (4) Can't be predicted
16. When 3.00 mole of A and 1.00 mole of B are mixed in a 1.00 litre vessel the following reaction takes place
 $A(g) + B(g) \rightleftharpoons 2C(g)$
 The equilibrium mixture contains 0.5 mole of C. What is the value of equilibrium constant for the reaction?
 (1) 0.12 (2) 6
 (3) 1.5 (4) 0.5
17. Given the reaction
 $2X(g) + Y(g) \rightleftharpoons Z(g) + 80 \text{ kcal}$
 Which combination of pressure and temperature gives the highest yield of Z at equilibrium?
 (1) 1000 atm and 500°C (2) 500 atm and 500°C
 (3) 1000 atm and 100°C (4) 500 atm and 100°C
18. Consider the water gas equilibrium reaction
 $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
 Which of the following is true at equilibrium?
 (1) If the amount of C(s) is increased, less water would be formed
 (2) If the amount of C(s) is increased, more CO and H_2 would be formed
 (3) If the pressure on the system is increased by halving the volume, more water would be formed
 (4) If the pressure on the system is increased by halving the volume, more CO and H_2 would be formed
19. Consider the given reaction
 $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
 In a closed container at equilibrium. What would be the effect of addition of $CaCO_3$ on the equilibrium constant?
 (1) Increases (2) Unpredictable
 (3) Decreases (4) Remains unchanged
20. Which of the following statement is correct?
 (1) At equilibrium concentration of reactants and products become constant because the reaction stops
 (2) Addition of catalyst speeds up forward reaction more than backward reaction
 (3) Equilibrium constant of an exothermic reaction decreases with increase of temperature
 (4) K_p is always greater than K_c

21. If a system contains SO_2 , O_2 and SO_3 gases at equilibrium, $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$, an increase in the partial pressure of SO_3 brought about by the addition of more SO_2 to the system will result in
- (1) A reaction in which amount of SO_3 remains same
 - (2) A reaction in which some of the added SO_2 is consumed
 - (3) A reaction in which no SO_2 is consumed
 - (4) A reaction in which some of the SO_3 is consumed
22. MgCO_3 dissociates as
- $$\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g}) - 100 \text{ kJ}$$
- in a closed container. The pressure of carbon dioxide
- (1) Increases if temperature is raised
 - (2) Increases on adding a catalyst
 - (3) Decreases if temperature is raised
 - (4) Increases if an inert gas is pumped keeping the volume constant
23. The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2 . The approximate percentage dissociation of N_2O_4 is
- (1) 40
 - (2) 57
 - (3) 67
 - (4) 87
24. Ostwald dilution law can be written as
- (1) $K_a = C \times V$
 - (2) $K_a = (1 + \alpha)/V$
 - (3) $K_a = \alpha^2 V$
 - (4) $K_a = \alpha^2/(1 - \alpha)V$
25. The pH of H_2O at 373 K is equal to [If $K_w = 10^{-12}$ at 373 K]
- (1) 6
 - (2) 7
 - (3) 9
 - (4) 7.5
26. When 4 gm of NaOH is dissolved in 10 litre of solution, the pH is
- (1) 6
 - (2) 12
 - (3) 0
 - (4) 14
27. An acidic solution of pH 6 is diluted thousand times. The pH of solution becomes approx.
- (1) 9
 - (2) 6
 - (3) 3
 - (4) 6.96
28. What will be the pH of a solution formed by mixing 40 ml of 0.10M HCl with 10 ml of 0.45 M NaOH?
- (1) 12
 - (2) 10
 - (3) 8
 - (4) 6
29. At 90°C pure water has $[\text{H}_3\text{O}^+] = 10^{-6}$ M. What is the value of K_w at this temperature?
- (1) 10^{-6}
 - (2) 10^{-12}
 - (3) 10^{-13}
 - (4) 10^{-14}
30. A solution of pH = 2 is more acidic than that of pH = 6 by a factor of
- (1) 4
 - (2) 12
 - (3) 400
 - (4) 10,000
31. When 75.00 ml of 0.100 M HNO_3 have been added to 25.00 ml of 0.100 M NaOH, the nature of the resulting solution is
- (1) Basic
 - (2) Neutral
 - (3) Acidic
 - (4) Can't predict
32. The conjugate base of HPO_4^{2-} is
- (1) PO_4^{3-}
 - (2) H_2PO_4^-
 - (3) H_3PO_4
 - (4) H_3PO_3
33. Decinormal solution of CH_3COOH ionises to an extent of 1.35%, its pH will be ($\log 1.3 = 0.11$)
- (1) 11.11
 - (2) 12
 - (3) 8
 - (4) 2.89
34. If dissociation constant of acetic acid is 1.6×10^{-5} , the hydrolysis constant of sodium acetate is
- (1) 6.25×10^{-9}
 - (2) 6.25×10^{-19}
 - (3) 0.625×10^{-5}
 - (4) 0.625×10^{-9}
35. In a buffer solution containing equal concentration of B^- and HB, the K_b for B^- is 10^{-10} . The pH of buffer solution is
- (1) 4
 - (2) 10
 - (3) 7
 - (4) 6
36. For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of the concentration of salt and acid should be ($K_a = 10^{-5}$)
- (1) 1 : 10
 - (2) 10 : 1
 - (3) 100 : 1
 - (4) 1 : 100
37. When 100 mL of 0.1 M solution of acetic acid is mixed with 100 mL of 0.1 M solution of NaOH, the resulting solution will have pH
- (1) Zero
 - (2) 7
 - (3) More than 7
 - (4) Less than 7
38. The salt whose aqueous solution has the highest pH is
- (1) KCl
 - (2) NH_4Cl
 - (3) $(\text{NH}_4)_2\text{CO}_3$
 - (4) Na_2CO_3

39. Consider the following

- (a) FeCl_3 in water - basic
- (b) Na_2CO_3 in water - basic
- (c) NH_4Cl in water - acidic
- (d) KCN in water - acidic

Which is not correctly matched?

- (1) (b) and (c) (2) (a) and (d)
- (3) Only (a) (4) Only (d)

40. The dissociation constant for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium



- (1) 3.0×10^{-4} (2) 3.0×10^4
- (3) 3.0×10^5 (4) 3.0×10^{-5}

41. If solubility of $\text{Ca}_3(\text{PO}_4)_2$ is 'x' mole/litre, its solubility product would be

- (1) $4x^3$ (2) x^2
- (3) $27x^4$ (4) $108x^5$

42. If the solubility of PbBr_2 is 'S' gm molecule per litre, its solubility product is

- (1) $2S^3$ (2) $4S^2$
- (3) $4S^3$ (4) $2S^4$

43. Among the following hydroxides the one which has the lowest value of K_{sp} at ordinary temperature at about 25°C is

- (1) $\text{Mg}(\text{OH})_2$ (2) $\text{Ca}(\text{OH})_2$
- (3) $\text{Ba}(\text{OH})_2$ (4) $\text{Be}(\text{OH})_2$

44. Solubility products of

- (a) MnS is 1.4×10^{-10} (b) ZnS is 1.2×10^{-28}
- (c) CdS is 3.6×10^{-28} (d) CuS is 8.5×10^{-36}

Which one of these salts has maximum solubility?

- (1) a (2) b
- (3) c (4) d

45. Let the solubilities of AgCl in H_2O , 0.01 M CaCl_2 , 0.01 M NaCl and 0.05 M AgNO_3 be S_1 , S_2 , S_3 , S_4 respectively. What is the correct relationship between these quantities?

- (1) $S_1 > S_3 > S_2 > S_4$
- (2) $S_1 > S_2 = S_3 > S_4$
- (3) $S_1 > S_2 > S_3 > S_4$
- (4) $S_4 > S_3 > S_2 > S_1$

SECTION - B

Previous Years Questions

1. Buffer solutions have constant acidity and alkalinity because [AIPMT 2012]

- (1) They have large excess of H^+ or OH^- ions
- (2) They have fixed value of pH
- (3) These give unionised acid or base on reaction with added acid or alkali
- (4) Acids and alkalies in these solutions are shielded from attack by other ions

2. pH of a saturated solution of $\text{Ba}(\text{OH})_2$ is 12. The value of solubility product (K_{sp}) of $\text{Ba}(\text{OH})_2$ is

[AIPMT 2012]

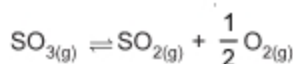
- (1) 4.0×10^{-6} (2) 5.0×10^{-6}
- (3) 3.3×10^{-7} (4) 5.0×10^{-7}

3. Equimolar solutions of the following substances were prepared separately. Which one of these will record the highest pH value? [AIPMT 2012]

- (1) LiCl (2) BeCl_2
- (3) BaCl_2 (4) AlCl_3

4. Given that the equilibrium constant for the reaction $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$ has a value of 278 at a particular temperature. What is the value of the equilibrium constant for the following reaction at the same temperature?

[AIPMT 2012]



- (1) 1.8×10^{-3} (2) 3.6×10^{-3}
- (3) 6.0×10^{-2} (4) 1.3×10^{-5}

5. Given the reaction between 2 gases represented by A_2 and B_2 to give the compound $\text{AB}_{(g)}$.



At equilibrium, the concentration

of $\text{A}_2 = 3.0 \times 10^{-3} \text{ M}$

of $\text{B}_2 = 4.2 \times 10^{-3} \text{ M}$

of $\text{AB} = 2.8 \times 10^{-3} \text{ M}$

If the reaction takes place in a sealed vessel at 527°C , then the value of K_c will be: [AIPMT 2012]

- (1) 2.0 (2) 1.9
- (3) 0.62 (4) 4.5

6. Which of these is least likely to act as a Lewis base? [NEET 2013]
 (1) F^- (2) BF_3
 (3) PF_3 (4) CO
7. For the reversible reaction, [AIPMT 2014]

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$$

 The equilibrium shifts in forward direction
 (1) By increasing the concentration of $NH_3(g)$
 (2) By decreasing the pressure
 (3) By decreasing the concentrations of $N_2(g)$ and $H_2(g)$
 (4) By increasing pressure and decreasing temperature
8. For a given exothermic reaction, K_p and K'_p are the equilibrium constants at temperatures T_1 and T_2 , respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2 , it is readily observed that [AIPMT 2014]
 (1) $K_p > K'_p$ (2) $K_p < K'_p$
 (3) $K_p = K'_p$ (4) $K_p = \frac{1}{K'_p}$
9. Which of the following salts will give highest pH in water? [AIPMT 2014]
 (1) KCl (2) $NaCl$
 (3) Na_2CO_3 (4) $CuSO_4$
10. Using the Gibbs energy change, $\Delta G^\circ = +63.3 \text{ kJ}$, for the following reaction,

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

 the K_{sp} of $Ag_2CO_3(s)$ in water at $25^\circ C$ is
 ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) [AIPMT 2014]
 (1) 3.2×10^{-26}
 (2) 8.0×10^{-12}
 (3) 2.9×10^{-3}
 (4) 7.9×10^{-2}
11. Which of the following statements is correct for a reversible process in a state of equilibrium? [AIPMT-2015]
 (1) $\Delta G^\circ = 2.30 RT \log K$
 (2) $\Delta G = -2.30 RT \log K$
 (3) $\Delta G = 2.30 RT \log K$
 (4) $\Delta G^\circ = -2.30 RT \log K$
12. The K_{sp} of Ag_2CrO_4 , $AgCl$, $AgBr$ and AgI are respectively, 1.1×10^{-12} , 1.8×10^{-10} , 5.0×10^{-13} , 8.3×10^{-17} . Which one of the following salts will precipitate last if $AgNO_3$ solution is added to the solution containing equal moles of $NaCl$, $NaBr$, NaI and Na_2CrO_4 ? [AIPMT-2015]
 (1) Ag_2CrO_4 (2) AgI
 (3) $AgCl$ (4) $AgBr$
13. If the value of an equilibrium constant for a particular reaction is 1.6×10^{12} , then at equilibrium the system will contain [AIPMT-2015]
 (1) Similar amounts of reactants and products
 (2) All reactants
 (3) Mostly reactants
 (4) Mostly products
14. If the equilibrium constant for

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
 is K , the equilibrium constant for $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$ will be [Re-AIPMT-2015]
 (1) K (2) K^2
 (3) $K^{1/2}$ (4) $\frac{1}{2}K$
15. Which one of the following pairs of solution is not an acidic buffer? [Re-AIPMT-2015]
 (1) H_2CO_3 and Na_2CO_3
 (2) H_3PO_4 and Na_3PO_4
 (3) $HClO_4$ and $NaClO_4$
 (4) CH_3COOH and CH_3COONa
16. What is the pH of the resulting solution when equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed? [Re-AIPMT-2015]
 (1) 7.0 (2) 1.04
 (3) 12.65 (4) 2.0
17. MY and NY_3 , two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3 ? [NEET-2016]
 (1) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities
 (2) The molar solubilities of MY and NY_3 in water are identical
 (3) The molar solubility of MY in water is less than that of NY_3
 (4) The salts MY and NY_3 are more soluble in 0.5 M KY than in pure water

18. Consider the following liquid-vapour equilibrium.



Which of the following relations is correct?

[NEET-2016]

$$\begin{aligned} (1) \quad \frac{d \ln P}{dT} &= \frac{\Delta H_v}{RT^2} & (2) \quad \frac{d \ln G}{dT^2} &= \frac{\Delta H_v}{RT^2} \\ (3) \quad \frac{d \ln P}{dT} &= \frac{-\Delta H_v}{RT} & (4) \quad \frac{d \ln P}{dT^2} &= \frac{-\Delta H_v}{T^2} \end{aligned}$$

19. The percentage of pyridine ($\text{C}_5\text{H}_5\text{N}$) that forms pyridinium ion ($\text{C}_5\text{H}_5\text{N}^+\text{H}$) in a 0.10 M aqueous pyridine solution (K_b for $\text{C}_5\text{H}_5\text{N} = 1.7 \times 10^{-9}$) is

[NEET (Phase-2) 2016]

- (1) 0.0060% (2) 0.013%
(3) 0.77% (4) 1.6%

20. If the E°_{cell} for a given reaction has a negative value, which of the following gives the correct relationships for the values of ΔG° and K_{eq} ?

[NEET (Phase-2) 2016]

- (1) $\Delta G^\circ > 0$; $K_{\text{eq}} < 1$ (2) $\Delta G^\circ > 0$; $K_{\text{eq}} > 1$
(3) $\Delta G^\circ < 0$; $K_{\text{eq}} > 1$ (4) $\Delta G^\circ < 0$; $K_{\text{eq}} < 1$

21. The solubility of AgCl(s) with solubility product 1.6×10^{-10} in 0.1 M NaCl solution would be

[NEET (Phase-2) 2016]

- (1) $1.26 \times 10^{-5} \text{ M}$ (2) $1.6 \times 10^{-9} \text{ M}$
(3) $1.6 \times 10^{-11} \text{ M}$ (4) Zero

22. Boric acid is an acid because its molecule

[NEET (Phase-2) 2016]

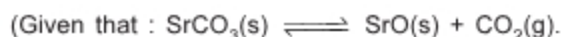
- (1) Contains replaceable H^+ ion
(2) Gives up a proton
(3) Accepts OH^- from water releasing proton
(4) Combines with proton from water molecule

23. Which of the following fluoro-compounds is most likely to behave as a Lewis base?

[NEET (Phase-2) 2016]

- (1) BF_3 (2) PF_3
(3) CF_4 (4) SiF_4

24. A 20 litre container at 400 K contains $\text{CO}_2(\text{g})$ at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the containers is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be



$$K_p = 1.6 \text{ atm}$$

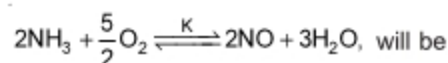
[NEET-2017]

- (1) 5 litre (2) 10 litre
(3) 4 litre (4) 2 litre

25. The equilibrium constants of the following are.



The equilibrium constant (K) of the reaction:



[NEET-2017]

$$(1) K_1 K_3^3 / K_2$$

$$(2) K_2 K_3^3 / K_1$$

$$(3) K_2 K_3 / K_1$$

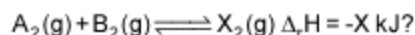
$$(4) K_2^3 K_3 / K_1$$

26. Concentration of the Ag^+ ions in a saturated solution of $\text{Ag}_2\text{C}_2\text{O}_4$ is $2.2 \times 10^{-4} \text{ mol L}^{-1}$. Solubility product of $\text{Ag}_2\text{C}_2\text{O}_4$ is

[NEET-2017]

- (1) 2.42×10^{-8} (2) 2.66×10^{-12}
(3) 4.5×10^{-11} (4) 5.3×10^{-12}

27. Which one of the following conditions will favour maximum formation of the product in the reaction,



[NEET-2018]

- (1) Low temperature and high pressure
(2) Low temperature and low pressure
(3) High temperature and low pressure
(4) High temperature and high pressure

28. The solubility of BaSO_4 in water is $2.42 \times 10^{-3} \text{ g L}^{-1}$ at 298 K. The value of its solubility product (K_{sp}) will be

(Given molar mass of $\text{BaSO}_4 = 233 \text{ g mol}^{-1}$)

[NEET-2018]

- (1) $1.08 \times 10^{-10} \text{ mol}^2 \text{L}^{-2}$
(2) $1.08 \times 10^{-12} \text{ mol}^2 \text{L}^{-2}$
(3) $1.08 \times 10^{-8} \text{ mol}^2 \text{L}^{-2}$
(4) $1.08 \times 10^{-14} \text{ mol}^2 \text{L}^{-2}$

29. Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations :
- a. $60 \text{ mL } \frac{M}{10} \text{ HCl} + 40 \text{ mL } \frac{M}{10} \text{ NaOH}$
- b. $55 \text{ mL } \frac{M}{10} \text{ HCl} + 45 \text{ mL } \frac{M}{10} \text{ NaOH}$
- c. $75 \text{ mL } \frac{M}{5} \text{ HCl} + 25 \text{ mL } \frac{M}{5} \text{ NaOH}$
- d. $100 \text{ mL } \frac{M}{10} \text{ HCl} + 100 \text{ mL } \frac{M}{10} \text{ NaOH}$
- pH of which one of them will be equal to 1?
- [NEET-2018]
- (1) b (2) a
(3) c (4) d
30. pH of a saturated solution of Ca(OH)_2 is 9. The solubility product (K_{sp}) of Ca(OH)_2 is:
- [NEET-2019]
- (1) 0.5×10^{-15} (2) 0.25×10^{-10}
(3) 0.125×10^{-15} (4) 0.5×10^{-10}
31. Conjugate base for Brönsted acids H_2O and HF are :
- [NEET-2019]
- (1) OH^- and H_2F^+ , respectively
(2) H_3O^+ and F^- , respectively
(3) OH^- and F^- , respectively
(4) H_3O^+ and H_2F^+ , respectively
32. Which will make basic buffer? [NEET-2019]
- (1) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH
(2) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH
(3) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH
(4) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH
33. The pH of 0.01 M NaOH (aq) solution will be [NEET-2019 (Odisha)]
- (1) 9 (2) 7.01
(3) 2 (4) 12
34. Which of the following **cannot** act both as Bronsted acid and as Bronsted base? [NEET-2019 (Odisha)]
- (1) HSO_4^-
(2) HCO_3^-
(3) NH_3
(4) HCl
35. The molar solubility of CaF_2 ($K_{sp} = 5.3 \times 10^{-11}$) in 0.1 M solution of NaF will be [NEET-2019 (Odisha)]
- (1) $5.3 \times 10^{-10} \text{ mol L}^{-1}$
(2) $5.3 \times 10^{-11} \text{ mol L}^{-1}$
(3) $5.3 \times 10^{-8} \text{ mol L}^{-1}$
(4) $5.3 \times 10^{-9} \text{ mol L}^{-1}$



Chapter 8

Redox Reactions and Electrochemistry

Sub-topics

Concept of oxidation and reduction, redox reactions, oxidation number, balancing of redox reactions in terms of loss and gain of electron and change in oxidation numbers. Conductance in electrolytic solutions, specific and molar conductivity variation of conductivity with concentration, Kohlrausch's Law, electrolysis and Laws of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells; lead accumulator, EMF of a cell, standard electrode potential, Relation between Gibbs energy change and EMF of a cell, fuel cells; corrosion.

Oxidation and Reduction

Oxidation	Reduction
(i) Loss of electron	(i) Gain of electron
(ii) Loss of hydrogen	(ii) Gain of hydrogen
(iii) Gain of oxygen	(iii) Loss of oxygen
(iv) Gain of electronegative element	(iv) Loss of electronegative element
(v) Loss of electropositive element	(v) Gain of electropositive element
e.g., $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + \text{e}^-$	e.g., $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$
(vi) Increase in oxidation number	(vi) Decrease in oxidation number

Redox Reaction

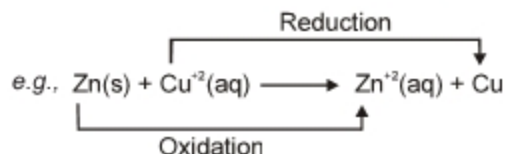
The reaction in which oxidation as well as reduction takes place together is known as **redox reaction**.

Oxidising Agent or Oxidant

The substance which oxidises others and itself get reduced.

Reducing Agent or Reductant

The substance which reduces others and itself get oxidised.



In the above redox reaction Zn is acting as reducing agent and Cu^{+2} as oxidising agent.

Rules to Determine Oxidation State

- A. In uncombined state or free state, oxidation number of an element is zero (H_2 , O_2 , Cu, Zn, S).
- B. In combined state, oxidation number of
- F is always -1 .
 - O is -2 , in peroxide ($-O-O-$) it is -1 , in superoxide it is $-\frac{1}{2}$. However in OF_2 it is $+2$ and in O_2F_2 it is $+1$.
 - H is $+1$, in metallic hydrides it is -1 .
 - Metal is always positive.
 - Alkali metal (Li, Na, K) is always $+1$.
 - Alkaline earth metal (Be, Mg, Ca, Sr) is always $+2$.
 - Halogen in halide is -1 . In oxy acids and oxides, halogen shows positive oxidation state except fluorine. Sulphur in sulphides is -2 .
 - The sum of oxidation number of all the elements is equal to zero in a molecule.
 - For ionic species sum is equal to total cationic or anion charge.
 - Molecules have zero oxidation state.

Note : Oxidation state of some of the compounds is to be determined by their structure.

e.g.,	Compound	Structure	Oxidation state
(i)	CrO_5		$+6$
(ii)	H_2SO_5		$+6$
(iii)	$H_2S_2O_8$		$+6$
(iv)	$CaOCl_2$		$+1$ and -1
(v)	$NOCl$	NO^+Cl^-	$+3$
(vi)	$Na_2S_4O_6$		Two S with zero O.N. and two with $+5$ O.N.

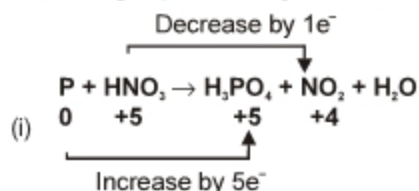
Balancing of Redox Reaction

- A. Oxidation number method
 B. Ion electron method

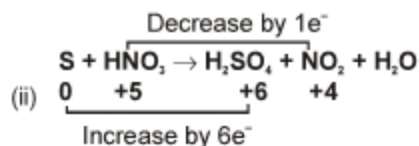
Oxidation Number Method	Ion Electron Method
1. Write the skeleton equation representing chemical change.	1. Write down the redox reaction in ionic form.
2. Assign oxidation numbers to find out which atoms are undergoing oxidation and reduction write separate equation for the atoms undergoing oxidation and reduction	2. Split the redox reaction into two half reactions, one for oxidation and other for reduction
3. Find the change in oxidation number in each equation. Make the change equal in both the equation by multiplying with suitable integers. Add both the equations.	3. Balance the number of atoms of ions undergoing reduction and oxidation.
4. Now balance those elements which are not undergoing oxidation or reduction except H and O. Then balancing H and O with the help of H_2O .	4. Now add electrons on that side of reaction where they are deficient to equalise the charge on both sides. Multiply if required by suitable number to balance electron on both sides of reaction.
	5. Now add both the half reactions and now balance atoms not undergoing reduction and oxidation (except H and O). Now balance H and O with help of water.

Balancing of H_2O can also be done as per the medium given

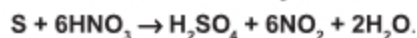
- (1) **Acidic Medium** : Add H_2O on that side of reaction where oxygen are deficient and double number of H^+ on opposite side of reaction.
 (2) **Basic Medium** : Add H_2O on that side of reaction where oxygen are excess and double number of OH^- on opposite side of reaction.

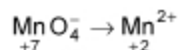
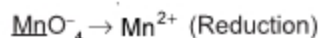
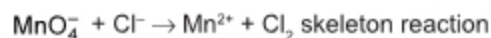
A. Balancing equations by oxidation number method

Multiply P by 1 and HNO_3 by 5 we get

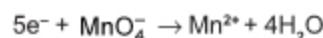


Multiply S by 1 and HNO_3 by 6 and balancing RHS we get

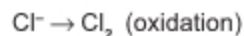
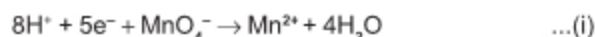


B. Ion electron method**(i) Acidic medium**

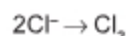
Add $5e^-$ on LHS to balance charge and $4\text{H}_2\text{O}$ to balance oxygen atoms



Add 8H^+ to balance hydrogen atoms



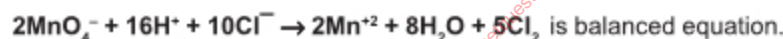
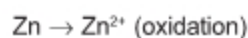
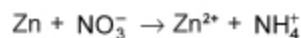
Multiply Cl^- by 2 to balance chlorine



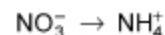
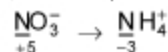
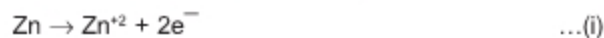
Add $2e^-$ on RHS to balance charge



Multiply (i) by 2 & (ii) by 5 to equalize number of electrons lost and gained and then adding, we get.

**(ii) Basic medium**

Add $2e^-$ on RHS to balance charge



Add $8e^-$ on LHS to balance the oxidation number

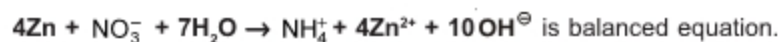


Add 10OH^- on RHS to balance charge on both side, $8e^- + \text{NO}_3^- \rightarrow \text{NH}_4^+ + 10\text{OH}^-$

Add $7\text{H}_2\text{O}$ on LHS to balance oxygen atoms.



Multiply equation (i) by 4 and adding (i) & (ii), we get

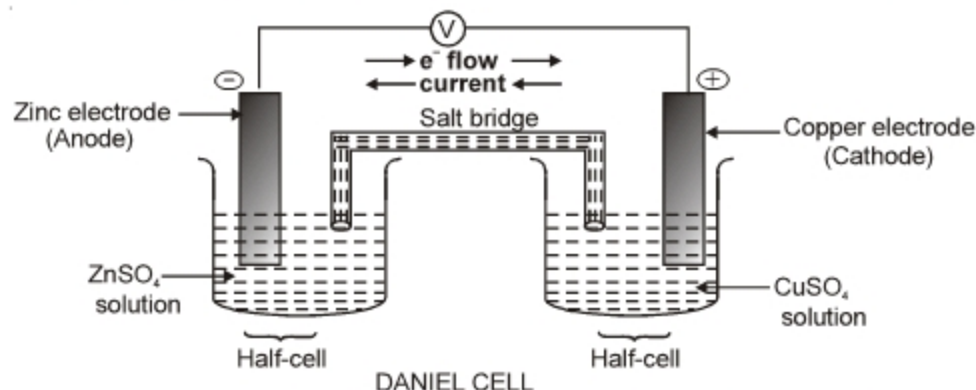


Electrochemistry

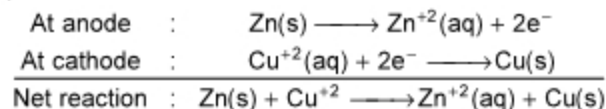
Branch of chemistry which deals with energy changes from electrical to chemical or chemical energy to electrical energy

Electrochemical Cell

- (a) **Electrolytic cell** - Cell in which electrical energy changes into chemical energy.
 (b) **Galvanic cell or Voltaic cell** - Cell in which chemical energy changes into electrical energy.



- (i) Voltaic or galvanic cell consists of two half-cells. The half-cell in which oxidation occurs is called oxidation half cell and half cell in which reduction occurs is called reduction half cell.
- (ii) The electrode where oxidation occurs is called **anode** and the electrode where reduction occurs is termed as **cathode**.
- (iii) Electrons flow from anode to cathode.
- (iv) Chemical energy is converted into electrical energy.
- (v) The net reaction is the sum of two half-cell reactions.



Schematic Representation : $\text{Zn} \mid \text{Zn}^{+2} \parallel \text{Cu}^{+2} \mid \text{Cu}$

Electrode Potential : The potential difference developed between the metal and the solution is known as electrode potential.

Oxidation Potential : When electrode is negatively charged with respect to solution *i.e.* it acts as anode. Oxidation occurs ($\text{M} \rightarrow \text{M}^{n+} + \text{ne}^{-}$) and the potential developed is oxidation potential.

Reduction Potential : When electrode is positively charged with respect to solution *i.e.* acts as cathode. Reduction occurs ($\text{M}^{n+} + \text{ne}^{-} \rightarrow \text{M}$). And the potential developed is known as reduction potential.

$$\begin{aligned}
 \text{EMF of the cell} &= E_{\text{anode}} + E_{\text{cathode}} \\
 &= \text{Oxidation potential of anode} + \text{Reduction potential of cathode.} \\
 &= \text{Reduction Potential of cathode} - \text{Reduction potential of anode.}
 \end{aligned}$$

Standard Electrode Potential : The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 298 K is called standard electrode potential.

Note : Standard reduction potential = – (Standard oxidation potential)
 or Standard oxidation potential = – (Standard reduction potential)

Standard Hydrogen Electrode – (SHE)

SHE Half Reaction	Electrode Potential
$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	0.0 V (anode)
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.0 V (cathode)

With the help of SHE - the SRP values of all the electrodes has been determined and are placed in electrochemical series.

Note : $E_{\text{Cell}}^\circ = \text{O.P. of anode} + \text{R.P. of cathode}$.

or $E_{\text{Cell}}^\circ = \text{R.P. of cathode} - \text{R.P. of anode}$.

Applications of electrochemical series : The important applications of electrochemical series are:

1. Relative strength of oxidising and reducing agents. In the series, the metals are arranged in the increasing order of reduction potentials or increasing order of oxidation potential. Therefore, the elements at the top are good reducing agents while those at the bottom are good oxidising agents.
2. **Calculating e.m.f. of the cell :** The e.m.f. of the cell can be determined by knowing the standard electrode potentials from the series as:

$$E^\circ_{\text{cell}} = E^\circ(\text{right}) - E^\circ(\text{left}) \text{ (If standard reduction potential are given)}$$

3. Predicting feasibility of a redox reaction. In general, a redox reaction is feasible only if the species which has higher reduction potential is reduced *i.e.*, accepts the electrons and the species which has lower reduction potential is oxidised *i.e.* loses the electrons. Otherwise, a redox reaction is not feasible. In other words, the species to release electrons must have lesser reduction potential as compared to the species which is to accept electrons. Simple redox reaction is feasible when $E^\circ_{\text{cell}} > 0$.
4. To predict whether a metal can liberate hydrogen from acid or not only the metals which have negative reduction potentials, can liberate hydrogen from the acids.

Nernst Equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log \frac{[\text{Prod.}]}{[\text{React.]}}$$

$$\text{or } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Prod.}]}{[\text{React.}]} \text{ [when } T = 298 \text{ K]}$$

e.g. E_{cell} for $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq.}) \rightleftharpoons \text{Zn}^{2+}(\text{aq.}) + \text{Cu(s)}$.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Concentration cell: Concentration cells are made up of same electrodes dipped in different concentration of its own ion.

e.g., $\text{Cu} | \text{Cu}^{2+}_{(0.01\text{M})} || \text{Cu}^{2+}_{(0.2\text{M})} | \text{Cu}$

Note : Both E_{cell} and E_{cell}° are intensive properties

Conductors and Conductance

Substance which allow the passage of electric current through them are called **electrical conductors**.

- (i) **Metallic or electronic conductors** : Conductors which transfer electric current by transfer of electrons, without transfer of any matter are known as metallic or electronic conductors.
e.g., Ag, Al.
- (ii) **Electrolytic conductors** : Conductors like aqueous solution of acids, bases and salt in which flow of electric current is accompanied by chemical decomposition are known as electrolytic conductors.

Electrolytic conductance : The conductance is the property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it.

$$\text{Conductance} = \frac{1}{\text{Resistance}}$$

Equivalent conductance (Λ_{eq}) : Conductance of all the ions produced by one gram equivalent of an electrolyte in given solution.

$$\Lambda = K \times V$$

$$\Lambda_{eq} = K \times \frac{1000}{N}$$

K = specific conductance

N = normality

Molar conductance (Λ_m) : Conductance of all ions produced by ionisation 1 gm mole of an electrolyte when present in V ml of solution. It is denoted by Λ_m or μ .

$$\Lambda_m = K \times \frac{1000}{M}$$

Note : $\text{Equivalent conductance} = \frac{\text{Molar conductance}}{n}$

n = charge on the ion.

Λ_m and Λ_{eq} increases with increase in dilution but specific conductivity (K) decreases with increase in dilution.

Kohlrausch's Law

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its ions.

$$\text{e.g., Equivalent conductance } \left(\Lambda^\infty = \frac{1}{Z^+} \lambda_+^\infty + \frac{1}{Z^-} \lambda_-^\infty \right)$$

λ_+^∞ and λ_-^∞ are molar conductance of cation and anion at infinite dilution and Z^+ and Z^- are charges of cation and anion.

$$\Lambda_{BaCl_2}^\infty = \frac{1}{2} \lambda_{Ba^{+2}}^\infty + \lambda_{Cl^-}^\infty$$

$$\Lambda_{AlCl_3}^\infty = \frac{1}{3} \lambda_{Al^{+3}}^\infty + \lambda_{Cl^-}^\infty$$

Molar conductance at infinite dilution

$$\Lambda_m^\infty = m \lambda_+^\infty + n \lambda_-^\infty, \quad \text{where } m \text{ and } n \text{ are number of ions.}$$

$$\text{e.g., } \Lambda_{BaCl_2}^\infty = \lambda_{Ba^{+2}}^\infty + 2 \lambda_{Cl^-}^\infty$$

Molar conductance = (equivalent conductance) \times n -factor.

Faraday's Laws of Electrolysis(i) **Faraday's First Law :** $w \propto Q$ w = wt. of substance deposited by passing Q coulomb of charge.

$$w \propto It \quad (\because Q = It)$$

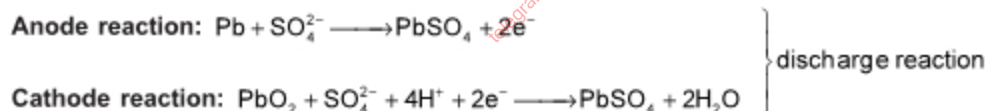
$$\therefore \boxed{w = Z \times I \times t} \quad \text{where } Z = \text{Electrochemical equivalent} = \frac{\text{Equivalent wt.}}{96500}$$

(ii) **Faraday's Second Law :**

$$\frac{\text{wt. of electrolyte (A)}}{\text{Eq. wt. of (A)}} = \frac{\text{wt. of electrolyte (B)}}{\text{Eq. wt. of (B)}}$$

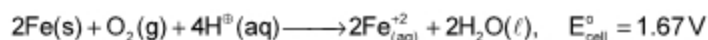
Relation between Gibb's energy change and EMF of a cell

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

For spontaneity of reaction, $E_{\text{cell}} > 0$ i.e., $\Delta G < 0$.**Different types of Cell:****Primary Batteries:** The reaction occurs only once and after use over a period of time battery becomes dead e.g., Dry cell, Mercury cell.**Secondary Batteries:** The cells after use can be recharged by passing current through it in opposite direction.**Lead Storage Battery:** It is secondary cell and used in automobile and invertors. Electrolyte is 38% H_2SO_4 solution. The reaction in recharging is reverse of discharge reaction.**Fuel Cell:** Galvanic cells which convert the energy of combustion of fuels directly into electrical energy are called fuel cells.**Rusting of iron**

Rusting of iron is an example of corrosion. Corrosion is a slow electrochemical process, and it occurs in the presence of water and air.

The overall reaction involved in the rusting of iron is





Try Yourself

SECTION - A

Objective Type Questions

- In a reaction,

$$\text{H}_2\text{O (Steam)} + \text{C}_{(s)} \longrightarrow \text{CO}_{(g)} + \text{H}_{2(g)}$$
 - H_2O is the reducing agent
 - H_2O is the oxidising agent
 - Carbon is the oxidising agent
 - It is not a redox reaction
- The strongest reducing agent is
 - K
 - Ca
 - Al
 - Zn
- In which of the following reactions the underlined substance is oxidised?
 - $3\text{Mg} + \underline{\text{N}_2} \longrightarrow \text{Mg}_3\text{N}_2$
 - $2\text{KI} + \underline{\text{Br}_2} \longrightarrow 2\text{KBr} + \text{I}_2$
 - $\underline{\text{CuO}} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$
 - $\underline{\text{Co}} + \text{Cl}_2 \longrightarrow \text{CoCl}_2$
- In which of the following reactions there is no change in oxidation state?
 - $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 3\text{S} + \text{H}_2\text{O}$
 - $2\text{Na} + \text{O}_2 \longrightarrow \text{Na}_2\text{O}_2$
 - $\text{Cl}_2 + \text{NaOH} \longrightarrow \text{NaClO} + \text{NaCl} + \text{H}_2\text{O}$
 - $\text{AgNO}_3 + \text{KCl} \longrightarrow \text{AgCl} + \text{KNO}_3$
- The conversion of $\text{K}_2\text{Cr}_2\text{O}_7$ into $\text{Cr}_2(\text{SO}_4)_3$ is a process of
 - Oxidation
 - Reduction
 - Decomposition
 - Substitution
- The oxidation number of Fe in Fe_3O_4 is
 - $\frac{1}{2}, \frac{1}{2}$
 - +2, +3
 - +2
 - +4, +2
- Each chromium in $\text{K}_2\text{Cr}_2\text{O}_7 \longrightarrow \text{Cr}_2\text{O}_3$ is changing from
 - +6 to +12 oxidation state
 - +12 to +6 oxidation state
 - +6 to +3 oxidation state
 - No change in oxidation state
- Oxidation state of each nitrogen in $\text{NH}_2\text{—NH}_2$ is
 - 2, – 2
 - + 2, – 2
 - 3, – 3
 - 4, + 4
- In the given reaction,

$$\text{Cl}_2 + \text{IO}_3^- \xrightarrow{\text{OH}^-} \text{IO}_4^- + 2\text{Cl}^-$$
 The oxidising and reducing agent respectively are
 - Cl^- , IO_3^-
 - Cl_2 , IO_3^-
 - Cl^- , IO_4^-
 - Cl_2 , IO_4^-
- If Cl_2 is changing to ClO_3^- and Cl^- , then this reaction is known as
 - Hydrolysis
 - Disproportionation reaction
 - Redox reaction
 - Reduction process
- For the reaction,

$$x\text{MnO}_4^- + y\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \longrightarrow \text{Mn}^{+2} + z\text{CO}_2 + 8\text{H}_2\text{O}$$
 The x, y, z are
 - 2, 5, 10
 - 2, 5, 16
 - 1, 2, 5
 - 2, 5, 5
- The emf of the cell, $\text{Ni} | \text{Ni}^{+2} (1.0\text{M}) || \text{Ag}^+ (1.0\text{M}) | \text{Ag}$ (E° for $\text{Ni}^{+2}/\text{Ni} = -0.25$ volt, E° for $\text{Ag}^+/\text{Ag} = 0.80$ volt) is given by
 - $-0.25 + 0.80 = 0.55$ volt
 - $-0.25 - (+0.80) = -1.05$ volt
 - $+0.80 - (-0.25) = +1.05$ volt
 - $-0.80 - (-0.25) = -0.55$ volt

13. The strong oxidising agent has
 (1) High value of reduction potential
 (2) High value of oxidation potential
 (3) Low value of reduction potential
 (4) High tendency to lose electrons
14. The oxidation potentials of Zn, Cu, Ag, H₂ and Ni are 0.76, -0.34, -0.80, 0V, 0.55 volt respectively. Which of the following reactions will provide maximum voltage?
 (1) $\text{Zn} + \text{Cu}^{+2} \longrightarrow \text{Cu} + \text{Zn}^{+2}$
 (2) $\text{Zn} + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Zn}^{+2}$
 (3) $\text{H}_2 + \text{Cu}^{+2} \longrightarrow 2\text{H}^+ + \text{Cu}$
 (4) $\text{H}_2 + \text{Ni}^{+2} \longrightarrow 2\text{H}^+ + \text{Ni}$
15. For the cell reaction,

$$2\text{Ce}^{+4} + \text{Co} \longrightarrow 2\text{Ce}^{+3} + \text{Co}^{+2}$$
 E°_{cell} is 1.89 V. If $E^\circ_{\text{Co}^{+2}|\text{Co}}$ is -0.28V, what is the value of $E^\circ_{\text{Ce}^{+4}|\text{Ce}^{+3}}$?
 (1) 1.61 V (2) -1.61 V
 (3) 1.89 V (4) 2.17 V
16. The emf of the following cell at 25°C is

$$\text{Pt}, \text{H}_2 / \text{HCl}(C_1) // \text{HCl}(C_2) / \text{H}_2, \text{Pt}$$
 (2 atm) (10 atm)
 (1) -2 V (2) 0 V
 (3) -0.02 V (4) 0.03 V
17. Which one of the following will increase standard electrode potential of the cell?
 $\text{Sn} + 2\text{Ag}^+ \rightarrow \text{Sn}^{+2} + 2\text{Ag}$
 (1) Increase in the size of silver rod
 (2) Increase in the concentration of Sn^{+2} ions
 (3) Increase in the concentration of Ag^+ ions
 (4) None of these
18. The standard reduction potential for $\text{A}^+ / \text{A} = 0.3 \text{ V}$ and for $\text{H}^+ / \text{H}_2 = 0 \text{ V}$. Then which of the following is correct if the cell is formed by the two half cells?
 (1) H₂ gas will be evolved
 (2) H₂ gas will be oxidised
 (3) In electrochemical cell hydrogen electrode will act as cathode
 (4) In electrochemical cell A^+ / A will act as anode
19. Specific conductance of a salt of 0.01M concentration is $1.061 \times 10^{-4} \text{ S.cm}^{-1}$. Molar conductance of the same solution will be
 (1) 1.061×10^{-4} (2) 1.061×10^{-5}
 (3) 10.61 (4) 106.1
20. If the specific conductance is $\frac{1}{x}$ and normality is 0.2 N H₂SO₄. Then molar conductance is
 (1) $\Lambda_m = \frac{1000}{x \times 0.1}$ (2) $\Lambda_m = \frac{x \times 1000}{0.1}$
 (3) $\Lambda_m = \frac{1000}{0.2x}$ (4) $\Lambda_m = \frac{0.1x}{1000}$
21. For electrolyte Al₂(SO₄)₃. The molar conductance is given by
 (1) $\Lambda_m^\infty = 2\lambda_{\text{Al}^{+3}}^\infty + 3\lambda_{\text{SO}_4^{2-}}^\infty$
 (2) $\Lambda_m^\infty = \frac{1}{2}\lambda_{\text{Al}^{+3}}^\infty + \frac{1}{3}\lambda_{\text{SO}_4^{2-}}^\infty$
 (3) $\Lambda_m^\infty = \frac{1}{3}\lambda_{\text{Al}^{+3}}^\infty + \frac{1}{2}\lambda_{\text{SO}_4^{2-}}^\infty$
 (4) $\Lambda_m^\infty = 3\lambda_{\text{Al}^{+3}}^\infty + 2\lambda_{\text{SO}_4^{2-}}^\infty$
22. Which of the following aqueous solution will show maximum pH after electrolysis?
 (1) CuCl₂ (2) CuSO₄
 (3) Cu(NO₃)₂ (4) KCl
23. The amount of charge required to deposit one gm equivalent of Al is
 (1) 96500C (2) $3 \times 96500\text{C}$
 (3) $2 \times 96500\text{C}$ (4) 9650C
24. For two reactions,
 (i) $\text{Na}^+ \longrightarrow \text{Na}$ (ii) $\text{Ca}^{+2} \longrightarrow \text{Ca}$
 If one faraday of charge is flowing individually then amount of Na and Ca deposited respectively is
 (1) 23g, 40g (2) 40g, 23g
 (3) 23g, 20g (4) 23g, 4g
25. Three faradays of electricity was passed through molten iron (II) bromide. The mass of iron metal (atomic mass 56) deposited at the cathode is
 (1) 56 g (2) 84 g
 (3) 112 g (4) 168 g
26. For given electrodes
 (a) A^+ / A $E^\circ = 0.6 \text{ V}$
 (b) B^+ / B $E^\circ = 0.3 \text{ V}$
 (c) C^+ / C $E^\circ = 1.1 \text{ V}$
 (d) D^+ / D $E^\circ = 2.1 \text{ V}$
 Then strongest and weakest oxidising agent respectively are
 (1) b, c (2) a, d
 (3) b, d (4) d, b

27. What weight of substance is deposited if x ampere of current is flown through its salt solution for 10 s? (The equivalent weight of the substance is M/y)
- (1) $w = \frac{My}{10x}$ (2) $w = \frac{10Mx}{yF}$
 (3) $w = \frac{yF}{10Mx}$ (4) $w = \frac{yF10x}{M}$
28. For electrodes, $P^{+2} | P$, $E_{RP} = 0.8$ V and for $R^{+2} | R$, $E_{RP} = 1.2$ V. Then, the correct schematic representation is
- (1) $P^{+2} | P || R^{+2} | R$ (2) $P^{+2} | P || R | R^{+2}$
 (3) $P | P^{+2} || R^{+2} | R$ (4) $P | P^{+2} || R | R^{+2}$
29. For $\frac{1}{2} H_2 \rightleftharpoons H^+$, the electrode potential value will increase if
- (1) H^+ ion concentration is decreased
 (2) pH is increased
 (3) Both (1) & (2)
 (4) For hydrogen electrode, potential value always remains same
30. For a redox reaction, $R + ne^- \longrightarrow P$, the Nernst equation is given as
- (1) $E = E^\circ + \frac{RT}{nF} \ln \frac{[P]}{[R]}$ (2) $E = E^\circ - \frac{RT}{nF} \ln \frac{[P]}{[R]}$
 (3) $E = E^\circ - \frac{RT}{nF} \ln \frac{[R]}{[P]}$ (4) $E = E^\circ - \frac{RT}{nF} \ln \frac{[P]}{[R]}$
3. Standard reduction potentials of the half reactions are given below [AIPMT 2012]
- $F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}$; $E^\circ = +2.85$ V
 $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$; $E^\circ = +1.36$ V
 $Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$; $E^\circ = +1.06$ V
 $I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$; $E^\circ = +0.53$ V
- The strongest oxidising and reducing agents respectively are
- (1) F_2 and I^- (2) Br_2 and Cl^-
 (3) Cl_2 and Br^- (4) Cl_2 and I_2
4. A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode would be [NEET 2013]
- (1) 0.59 V (2) 0.118 V
 (3) 1.18 V (4) 0.059 V
5. A button cell used in watches functions as following
- $Zn(s) + Ag_2O(s) + H_2O(l) \rightleftharpoons 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq)$
- If half cell potentials are
- $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$; $E^\circ = -0.76$ V
 $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$, $E^\circ = 0.34$ V
- The cell potential will be [NEET 2013]
- (1) 0.42 V (2) 0.84 V
 (3) 1.34 V (4) 1.10 V

SECTION - B

Previous Years Questions

1. When Cl_2 gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from [AIPMT 2012]
- (1) Zero to -1 and zero to +3
 (2) Zero to +1 and zero to -3
 (3) Zero to +1 and zero to -5
 (4) Zero to -1 and zero to +5
2. Limiting molar conductivity of NH_4OH (i.e. $\Lambda_m(NH_4OH)$) is equal to [AIPMT 2012]
- (1) $\Lambda_m(NH_4OH) + \Lambda_m(NH_4Cl) - \Lambda_m(HCl)$
 (2) $\Lambda_m(NH_4Cl) + \Lambda_m(NaOH) - \Lambda_m(NaCl)$
 (3) $\Lambda_m(NH_4Cl) + \Lambda_m(NaCl) - \Lambda_m(NaOH)$
 (4) $\Lambda_m(NaOH) + \Lambda_m(NaCl) - \Lambda_m(NH_4Cl)$
6. At 25°C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is $9.54 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and at infinite dilution its molar conductance is $238 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is [NEET 2013]
- (1) 20.800% (2) 4.008%
 (3) 40.800% (4) 2.080%
7. (a) $H_2O_2 + O_3 \rightarrow H_2O + 2O_2$
 (b) $H_2O_2 + Ag_2O \rightarrow 2Ag + H_2O + O_2$
- Role of hydrogen peroxide in the above reactions is respectively [AIPMT 2014]
- (1) Oxidizing in (a) and reducing in (b)
 (2) Reducing in (a) and oxidizing in (b)
 (3) Reducing in (a) and (b)
 (4) Oxidizing in (a) and (b)

8. In acidic medium, H_2O_2 changes $\text{Cr}_2\text{O}_7^{2-}$ to CrO_5 which has two ($-\text{O}-\text{O}-$) bonds. Oxidation state of Cr in CrO_5 is [AIPMT 2014]
- (1) +5 (2) +3
(3) +6 (4) -10
9. When 0.1 mol MnO_4^{2-} is oxidised the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is [AIPMT 2014]
- (1) 96500 C
(2) 2×96500 C
(3) 9650 C
(4) 96.50 C
10. The weight of silver (at. wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be [AIPMT 2014]
- (1) 5.4 g (2) 10.8 g
(3) 54.0 g (4) 108.0 g
11. Molar conductivities (Λ_m°) at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 425.9 and $91.0 \text{ S cm}^2 \text{ mol}^{-1}$ respectively Λ_m° for CH_3COOH will be [AIPMT 2014]
- (1) $425.5 \text{ S cm}^2 \text{ mol}^{-1}$
(2) $180.5 \text{ S cm}^2 \text{ mol}^{-1}$
(3) $290.8 \text{ S cm}^2 \text{ mol}^{-1}$
(4) $390.5 \text{ S cm}^2 \text{ mol}^{-1}$
12. The Gibb's energy for the decomposition of Al_2O_3 at 500°C is as follows :
- $$\frac{2}{3} \text{Al}_2\text{O}_3 \longrightarrow \frac{4}{3} \text{Al} + \text{O}_2; \Delta_r G = + 960 \text{ kJ mol}^{-1}$$
- The potential difference needed for the electrolytic reduction of aluminium oxide (Al_2O_3) at 500°C is at least: [AIPMT 2014]
- (1) 4.5 V (2) 3.0 V
(3) 2.5 V (4) 5.0 V
13. Which of the following processes does not involve oxidation of iron? [AIPMT-2015]
- (1) Liberation of H_2 from steam by iron at high temperature
(2) Rusting of iron sheets
(3) Decolourization of blue CuSO_4 solution by iron
(4) Formation of $\text{Fe}(\text{CO})_5$ from Fe
14. Aqueous solution of which of the following compounds is the best conductor of electric current? [Re-AIPMT-2015]
- (1) Ammonia, NH_3
(2) Fructose, $\text{C}_6\text{H}_{12}\text{O}_6$
(3) Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$
(4) Hydrochloric acid, HCl
15. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as [AIPMT-2015]
- (1) Ni-Cd cell
(2) Fuel cell
(3) Electrolytic cell
(4) Dynamo
16. Assuming complete ionization, same moles of which of the following compounds will require the least amount of acidified KMnO_4 for complete oxidation?
- (1) FeC_2O_4
(2) $\text{Fe}(\text{NO}_2)_2$
(3) FeSO_4
(4) FeSO_3
17. The pressure of H_2 required to make the potential of H_2 - electrode zero in pure water at 298 K is [NEET-2016]
- (1) 10^{-4} atm (2) 10^{-14} atm
(3) 10^{-12} atm (4) 10^{-10} atm
18. The molar conductivity of a 0.5 mol/dm^3 solution of AgNO_3 with electrolytic conductivity of $5.76 \times 10^{-3} \text{ S cm}^{-1}$ at 298 K [NEET (Phase-2) 2016]
- (1) $2.88 \text{ S cm}^2/\text{mol}$
(2) $11.52 \text{ S cm}^2/\text{mol}$
(3) $0.086 \text{ S cm}^2/\text{mol}$
(4) $28.8 \text{ S cm}^2/\text{mol}$
19. During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is [NEET (Phase-2) 2016]
- (1) 55 minutes (2) 110 minutes
(3) 220 minutes (4) 330 minutes

20. The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is (charge on electron = 1.60×10^{-19} C)

[NEET (Phase-2) 2016]

- (1) 6×10^{23}
 (2) 6×10^{20}
 (3) 3.75×10^{20}
 (4) 7.48×10^{23}

21. Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because

[NEET (Phase-2) 2016]

- (1) Zinc is lighter than iron
 (2) Zinc has lower melting point than iron
 (3) Zinc has lower negative electrode potential than iron
 (4) Zinc has higher negative electrode potential than iron

22. Hot concentrated sulphuric acid is a moderately strong oxidizing agent. Which of the following reactions does not show oxidizing behaviour?

[NEET (Phase-2) 2016]

- (1) $\text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
 (2) $3\text{S} + 2\text{H}_2\text{SO}_4 \rightarrow 3\text{SO}_2 + 2\text{H}_2\text{O}$
 (3) $\text{C} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O}$
 (4) $\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{HF}$

23. In the electrochemical cell :

$\text{Zn}|\text{ZnSO}_4(0.01\text{M})||\text{CuSO}_4(1.0\text{M})|\text{Cu}$, the emf of this Daniel cell is E_1 . When the concentration of ZnSO_4 is changed to 1.0 M and that of CuSO_4 changed to 0.01 M, the emf changes to E_2 . From the following, which one is the relationship between E_1 and E_2 ?

(Given, $\frac{RT}{F} = 0.059$) [NEET-2017]

- (1) $E_1 = E_2$ (2) $E_1 < E_2$
 (3) $E_1 > E_2$ (4) $E_2 = 0 \neq E_1$

24. The correct order of N-compounds in its decreasing order of oxidation states is [NEET-2018]

- (1) HNO_3 , NO, N_2 , NH_4Cl
 (2) HNO_3 , NO, NH_4Cl , N_2
 (3) NH_4Cl , N_2 , NO, HNO_3
 (4) HNO_3 , NH_4Cl , NO, N_2

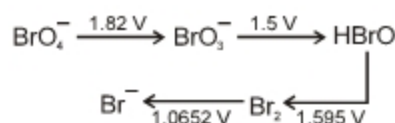
25. For the redox reaction



The correct coefficients of the reactants for the balanced equation are [NEET-2018]

MnO_4^-	$\text{C}_2\text{O}_4^{2-}$	H^+
(1) 16	5	2
(2) 2	5	16
(3) 5	16	2
(4) 2	16	5

26. Consider the change in oxidation state of Bromine corresponding to different emf values as shown in the diagram below :



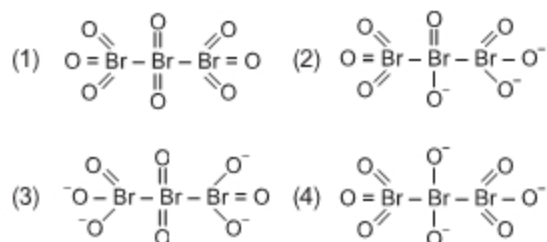
Then the species undergoing disproportionation is

[NEET-2018]

- (1) BrO_3^- (2) BrO_4^-
 (3) HBrO (4) Br_2

27. The correct structure of tribromooxaoxide is

[NEET-2019]



28. Which of the following reactions are disproportionation reaction? [NEET-2019]

- (a) $2\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{Cu}^0$
 (b) $3\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
 (c) $2\text{KMnO}_4 \xrightarrow{\Delta} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
 (d) $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^+$

Select the correct option from the following

- (1) (a) and (b) only (2) (a), (b) and (c)
 (3) (a), (c) and (d) (4) (a) and (d) only

29. For a cell involving one electron $E^\circ_{\text{cell}} = 0.59 \text{ V}$ at 298 K, the equilibrium constant for the cell reaction is :

$$\left[\text{Given that } \frac{2.303 RT}{F} = 0.059 \text{ V at } T = 298 \text{ K} \right]$$

[NEET-2019]

- (1) 1.0×10^2
(2) 1.0×10^5
(3) 1.0×10^{10}
(4) 1.0×10^{30}
30. The oxidation state of Cr in CrO_6 is

[NEET-2019 (Odisha)]

- (1) +4
(2) -6
(3) +12
(4) +6

31. Following limiting molar conductivities are given as

$$\lambda_m^\circ(\text{H}_2\text{SO}_4) = x \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_m^\circ(\text{K}_2\text{SO}_4) = y \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_m^\circ(\text{CH}_3\text{COOK}) = z \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_m^\circ(\text{in S cm}^2 \text{ mol}^{-1}) \text{ for } \text{CH}_3\text{COOH} \text{ will be}$$

[NEET-2019 (Odisha)]

- (1) $\frac{(x-y)}{2} + z$ (2) $x - y + 2z$
(3) $x + y + z$ (4) $x - y + z$

32. The standard electrode potential (E^\ominus) values of Al^{3+}/Al , Ag^+/Ag , K^+/K and Cr^{3+}/Cr are -1.66 V , 0.80 V , -2.93 V and -0.74 V , respectively. The correct decreasing order of reducing power of the metal is

[NEET-2019 (Odisha)]

- (1) $\text{Al} > \text{K} > \text{Ag} > \text{Cr}$ (2) $\text{Ag} > \text{Cr} > \text{Al} > \text{K}$
(3) $\text{K} > \text{Al} > \text{Cr} > \text{Ag}$ (4) $\text{K} > \text{Al} > \text{Ag} > \text{Cr}$



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Chapter 9

Solid State

Sub-topics

Classification of solids based on different binding forces; molecular, ionic covalent and metallic solids, amorphous and crystalline solids (elementary idea), unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects, electrical and magnetic properties, Band theory of metals, conductors, semiconductors and insulators.

In solid state, the particles are closely packed and are held together by strong intermolecular attractive forces.

Solids are with

- (1) Definite shape and volume
- (2) High density and low compressibility
- (3) With less vapour pressure

Types of Solids

- (1) Depending on three dimension-arrangement.
 - (i) **Amorphous Solids** : Amorphous (mean-amorphe-shapeless) solids are with irregular arrangement without any shape or geometry.
 - (ii) **Crystalline Solids** : Solids with ordered arrangement of constituent particles in three dimension.
- (2) Depending on bonding

Type of solid	Particles	Bonding/Attractive forces	Example
Ionic	Ions	Coulombic or electrostatic	NaCl, MgO, KCl
Covalent	Atoms	Covalent bonding	SiC, SiO ₂ , Diamond
Metallic	Positive ions in a sea of delocalised electrons	Metallic bonding	Ag, Cu, Mg
Molecular	Molecules	1. Dispersion 2. Dipole interaction 3. Hydrogen bonding	Argon HCl H ₂ O(ice)

Space Lattice : A regular three dimensional arrangement of points in space is called space lattice.

Crystal System

On basis of geometrical consideration, main seven crystal system are present also known as seven primitive unit cells, which differ three-dimensionally in axial edge length (a , b and c) and axial angles (α , β , γ).

Crystal System	Axial distance or Edge lengths	Axial angles	Example
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	KCl, ZnS
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	HgS
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SnO_2 , TiO_2
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO_3
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	Monoclinic sulphur
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	ZnO
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$

Note : (i) Triclinic is most unsymmetric crystal system.

(ii) Out of all crystal system, we have to study cubic crystal system in detail.

Cubic Crystal System

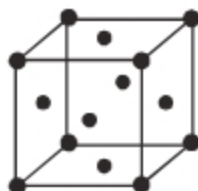
For cubic crystal system total three variations are there. i.e., FCC, SC and BCC.

Number of atoms per unit cell of cubic crystal system

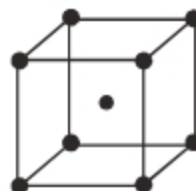
Type of Cell	Number of atoms at corner	Number of atom at faces	Number of atoms in centre of cube	Total atoms
Primitive cubic (SC)	$\frac{1}{8} \times 8 = 1$	—	—	1
Body centred cubic (BCC)	$\frac{1}{8} \times 8 = 1$	—	1	2
Face centred cubic (FCC)	$\frac{1}{8} \times 8 = 1$	$\frac{1}{2} \times 6 = 3$	—	4



Simple cubic



Face centred cubic



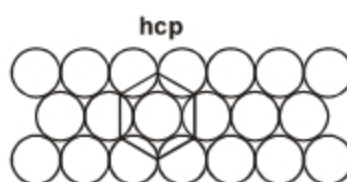
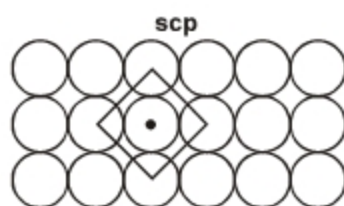
Body centred cubic

Types of cubic units cells

Packing in Crystal

Two-dimensional packing

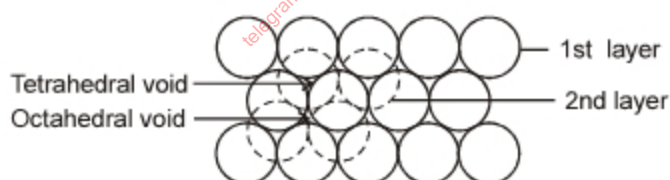
- (a) Square close packing (scp)
 (b) Hexagonal close packing (hcp)



Voids : In close packed arrangement, some space or holes are created amongst the sphere/atom.

Two types of voids present in ccp and hcp in 3D are :-

- (1) Octahedral void
 (2) Tetrahedral void



Radius of octahedral void (R_o).

$$\text{i.e. } R_o = 0.414 R_{\text{atom}}$$

Radius of tetrahedral void (R_t)

$$\text{i.e. } R_t = 0.225 R_{\text{atom}}$$

Note : For 'N' atoms per unit cell 'N' will be the octahedral voids and '2N' will be tetrahedral voids.

Number of voids of FCC : As number of atoms in fcc per unit cell are 4. It will have 4 octahedral voids and 8 are tetrahedral voids.

Number of octahedral void per unit cell : In fcc, octahedral voids are located at the centre of edges (3) and one at the body centre of unit cell.

Number of tetrahedral voids per unit cell : In fcc, all tetrahedral voids are within the unit cell, two on each body diagonal, each tetrahedral void is at a distance of $\frac{\sqrt{3}a}{4}$ from the corner, where a is the edge of the cube.

Hence, number of tetrahedral voids per unit cell = 8.

Relation between edge length (a), radius (r) and interionic distance (d).

$$\text{SC} \quad r = \frac{a}{2} \quad d = a$$

$$\text{FCC} \quad r = \frac{a}{2\sqrt{2}} \quad d = \frac{a}{\sqrt{2}}$$

$$\text{BCC} \quad r = \frac{\sqrt{3}a}{4} \quad d = \frac{\sqrt{3}a}{2}$$

Packing fraction for cubic crystal system.

$$\text{P.F} = \frac{Z \times \text{Volume of sphere}}{\text{Volume of the unit cell}}$$

where Z = number of atoms per unit cell

$$\text{Volume of cube} = a^3$$

$$\text{Volume of sphere} = \frac{4}{3}\pi r^3$$

Thus P.F for SC, FCC and BCC respectively are 52.4%, 74% and 68%.

Note : Higher the packing fraction higher is the stability of the crystal.

Density of crystal

$$\text{Density} = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

$$\text{i.e., } d = \frac{Z \times M}{a^3 \times N_A}$$

where Z = number of atoms per unit cells.

M = Molar mass

N_A = Avogadro's number

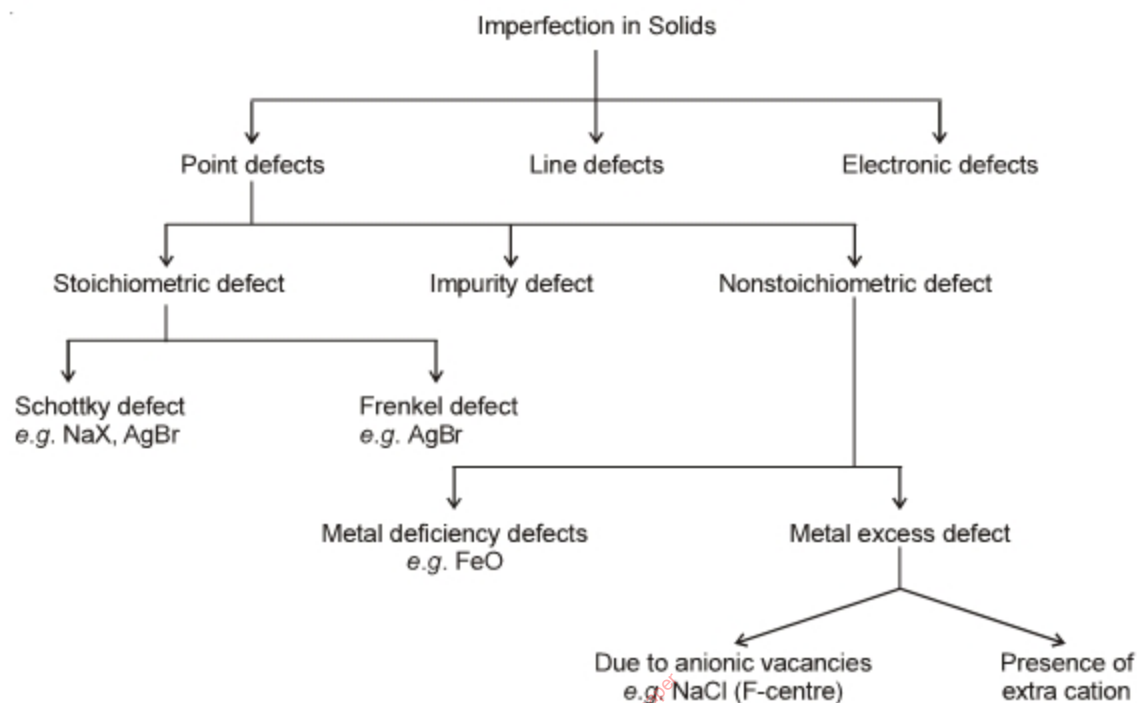
a = Edge length (in cm)

Radius ratio

r_+/r_-	Geometry	Co-ordination number	Example
0.155 – 0.225	Triangular planar	3	B_2O_3
0.255 – 0.414	Tetrahedral	4	ZnS
0.414 – 0.732	Octahedral	6	NaCl
0.732 – 1	Cubic	8	CsCl

Imperfection in solids

Deviation from ideal arrangement of particles is known as imperfection.



Note : AgBr shows both Schottky and Frenkel defects

Properties of Solids:

Electrical properties: On the basis of conductivity, solids are classified as conductors, semiconductors and insulators.

Mechanism of electrical conduction: The atomic orbitals of metal atoms form molecular orbitals which together forms a band. Outermost filled energy band is valence band and next empty band in which electrons can move is called conduction band.

When some impurity is added to Si and Ge they can be converted to semiconductors. This doping may generate two types of semiconductors.

(i) n-type semiconductors : Si + group 15 element.

(ii) p-type semiconductors : Si + group 13 element.

(a) **Magnetic properties :** Solids show magnetic properties due to magnetic moment (orbital and spin) of electron.

Ferromagnetic	: $\uparrow\uparrow\uparrow\uparrow$	} alignment of magnetic moment.
Antiferromagnetic	: $\uparrow\downarrow\uparrow\downarrow$	
Ferrimagnetic	: $\uparrow\uparrow\downarrow\uparrow$	

(b) **Dielectric properties :** Crystal with net dipole moment exhibit **piezoelectricity** when these crystals are deformed by mechanical stress, where electricity is produced due to displacement of ion. Some piezoelectric crystals when heated produce small electric potential i.e. **pyroelectricity**.





Try Yourself

SECTION - A

Objective Type Questions

- The structure of NaCl crystal is
 - Body centred cubic lattice
 - Face centred cubic lattice
 - Octahedral
 - Simple cubic lattice
- The co-ordination number of a body centred atom is
 - 4
 - 6
 - 8
 - 12
- What is the probable co-ordination number of X^+ ion in XY if radii of X^+ and Y^- ions are 147 pm and 216 pm respectively?
 - 6
 - 8
 - 4
 - 2
- In a compound, atoms of element y form ccp lattice and those of element x occupy $\frac{2}{3}$ rd of tetrahedral voids. The formula of compound will be
 - x_3y_4
 - x_4y_3
 - x_2y_3
 - x_2y
- If one cation and one anion are lost simultaneously from the crystal lattice, the defect is called as
 - Schottky defect
 - Frenkel defect
 - Crystal defect
 - Ionic defect
- The displacement of a cation into the interstitial site of a crystal is found in
 - Schottky defect
 - Frenkel defect
 - Ionic defect
 - Non-ionic defect
- Lithium metal has a body centred cubic structure. Its density is 0.53 g cm^{-3} and its molar mass is 6.94 g mol^{-1} . Calculate the edge length of a unit cell of Lithium metal
 - 153.6 pm
 - 351.6 pm
 - 527.4 pm
 - 263.7 pm
- A compound formed by elements A and B form cubic structure in which 'A' atoms are at the corners of a cube and 'B' atoms are at the face centre. The formula of the compound is
 - AB_3
 - AB_2
 - A_2B
 - AB
- Zinc oxide on heating changes to yellow. This is because
 - Zinc oxide is a stoichiometric compound
 - Zinc oxide is a covalent compound
 - Zinc oxide shows metal excessive defect
 - All of these
- If a is the length of unit cell, then which one is correct relationship?
 - For simple cubic lattice,
Radius of metal atom = $\frac{a}{2}$
 - For bcc lattice,
Radius of metal atom = $\frac{\sqrt{3}a}{4}$
 - For fcc lattice,
Radius of metal atom = $\frac{a}{2\sqrt{2}}$
 - All of these
- Fraction of the total volume occupied by atoms in a simple cube is
 - $\frac{\pi}{2}$
 - $\frac{\sqrt{3}\pi}{8}$
 - $\frac{\sqrt{2}\pi}{6}$
 - $\frac{\pi}{6}$
- The number of octahedral sites in a cubical close pack array of N spheres is
 - $\frac{N}{2}$
 - 2N
 - 4N
 - N
- The radius of Ag^+ ion is 126 pm while that of I^- ion is 216 pm. The co-ordination number of Ag in AgI is
 - 2
 - 4
 - 6
 - 8

14. ABC...ABC... type close packing results in the formation of
 (1) Simple cubic unit cell
 (2) Face centred cubic unit cell
 (3) Body centred cubic unit cell
 (4) End centred cubic unit cell
15. Doping of Arsenic in Germanium produces
 (1) n-type semiconductor
 (2) p-type semiconductor
 (3) Metal excess defect
 (4) Cation vacancy defect
16. Which of the following is an example of molecular solid?
 (1) ZnS (2) MgO
 (3) Ice (4) Graphite
17. A unit cell having $a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$ is known as
 (1) Cubic (2) Tetragonal
 (3) Orthorhombic (4) Rhombohedral
18. How many atoms are there in a cubic unit cell having one atom on each corner and two atoms on each body diagonal of the cube?
 (1) 8 (2) 6
 (3) 12 (4) 9
19. What is the contribution of the atom present at edge centre to the cubical unit cell?
 (1) $\frac{\pi}{6}$ (2) $\frac{1}{4}$
 (3) $\frac{1}{8}$ (4) 1
20. The radius ratio of any ionic compound is 0.95. The structure of AB is similar to
 (1) NaCl (2) CsCl
 (3) ZnS (4) MgCl_2
21. Packing fraction of BCC unit cell
 (1) 52% (2) 68%
 (3) 74% (4) 46%
22. Anti ferromagnetic substances possess
 (1) Low magnetic moment
 (2) Zero magnetic moment
 (3) High magnetic moment
 (4) All of these
23. In a sodium chloride type structure of A and B, 4 atoms of 'A' are removed from the edges and 4 atoms of 'B' are removed from corners. The formula of the new compound will be
 (1) AB (2) AB_2
 (3) A_3B (4) A_6B_7
24. If radius ratio of constituent particle is 0.732 to 1 then coordination number of each sphere is
 (1) 4 (2) 6
 (3) 8 (4) 12
25. AB is rock salt type crystal. If radius of A^+ is 75 pm then radius of B^- will be
 (1) 181.2 pm (2) 333.3 pm
 (3) 102.5 pm (4) 323.5 pm

SECTION - B

Previous Years Questions

1. The number of octahedral void(s) per atom present in a cubic close-packed structure is
 [AIPMT 2012]
 (1) 2 (2) 4
 (3) 1 (4) 3
2. A metal crystallizes with a face-centered cubic lattice. The edge of the unit cell is 408 pm. The diameter of the metal atom is [AIPMT 2012]
 (1) 144 pm
 (2) 204 pm
 (3) 288 pm
 (4) 408 pm
3. Structure of a mixed oxide is cubic close packed (c.c.p.). The cubic unit cell of mixed oxide is composed of oxide ions. One fourth of the tetrahedral voids are occupied by divalent metal A and the octahedral voids are occupied by a monovalent metal B. The formula of the oxide is :
 [AIPMT 2012]
 (1) ABO_2 (2) A_2BO_2
 (3) $\text{A}_2\text{B}_3\text{O}_4$ (4) AB_2O_2
4. A metal has a fcc lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72 g cm^{-3} . The molar mass of the metal is (N_A = Avogadro's constant = $6.02 \times 10^{23} \text{ mol}^{-1}$)
 [NEET 2013]
 (1) 30 g mol^{-1}
 (2) 27 g mol^{-1}
 (3) 20 g mol^{-1}
 (4) 40 g mol^{-1}
5. The number of carbon atoms per unit cell of diamond unit cell is [NEET 2013]
 (1) 8 (2) 6
 (3) 1 (4) 4

6. If a is the length of the side of a cube, the distance between the body centered atom and one corner atom in the cube will be [AIPMT 2014]
- (1) $\frac{2}{\sqrt{3}}a$ (2) $\frac{4}{\sqrt{3}}a$
 (3) $\frac{\sqrt{3}}{4}a$ (4) $\frac{\sqrt{3}}{2}a$
7. The vacant space in bcc lattice unit cell is [Re-AIPMT-2015]
- (1) 23% (2) 32%
 (3) 26% (4) 48%
8. The correct statement regarding defects in crystalline solids is [Re-AIPMT-2015]
- (1) Frenkel defect is a dislocation defect
 (2) Frenkel defect is found in halides of alkaline metals
 (3) Schottky defects have no effect on the density of crystalline solids
 (4) Frenkel defects decrease the density of crystalline solids
9. A given metal crystallizes out with a cubic structure having edge length of 361 pm. If there are four metal atoms in one unit cell, what is the radius of one atom? [AIPMT-2015]
- (1) 108 pm (2) 40 pm
 (3) 127 pm (4) 80 pm
10. Lithium has a bcc structure. Its density is 530 kg m^{-3} and its atomic mass is 6.94 g mol^{-1} . Calculate the edge length of a unit cell of Lithium metal ($N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$) [NEET-2016]
- (1) 264 pm (2) 154 pm
 (3) 352 pm (4) 527 pm
11. The ionic radii of A^+ and B^- ions are $0.98 \times 10^{-10} \text{ m}$ and $1.81 \times 10^{-10} \text{ m}$. The coordination number of each ion in AB is [NEET-2016]
- (1) 2 (2) 6
 (3) 4 (4) 8
12. In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca^{2+}) and fluoride ion (F^-) are [NEET (Phase-2) 2016]
- (1) 4 and 2 (2) 6 and 6
 (3) 8 and 4 (4) 4 and 8
13. Which is the incorrect statement? [NEET-2017]
- (1) $\text{FeO}_{0.98}$ has non stoichiometric metal deficiency defect
 (2) Density decreases in case of crystals with Schottky's defect
 (3) NaCl(s) is insulator, silicon is semiconductor, silver is conductor, quartz is piezo electric crystal
 (4) Frenkel defect is favoured in those ionic compounds in which sizes of cation and anions are almost equal
14. Iron exhibits bcc structure at room temperature. Above 900°C , it transforms to fcc structure. The ratio of density of iron at room temperature to that at 900°C (assuming molar mass and atomic radii of iron remains constant with temperature) is [NEET-2018]
- (1) $\frac{\sqrt{3}}{\sqrt{2}}$ (2) $\frac{4\sqrt{3}}{3\sqrt{2}}$
 (3) $\frac{1}{2}$ (4) $\frac{3\sqrt{3}}{4\sqrt{2}}$
15. A compound is formed by cation C and anion A. The anions form hexagonal close packed (hcp) lattice and the cations occupy 75% of octahedral voids. The formula of the compound is: [NEET-2019]
- (1) C_2A_3 (2) C_3A_2
 (3) C_3A_4 (4) C_4A_3
16. Formula of nickel oxide with metal deficiency defect in its crystal is $\text{Ni}_{0.98}\text{O}$. The crystal contains Ni^{2+} and Ni^{3+} ions. The fraction of nickel existing as Ni^{2+} ions in the crystal is [NEET-2019 (Odisha)]
- (1) 0.31 (2) 0.96
 (3) 0.04 (4) 0.50



Chapter 10

Solutions

Sub-topics

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, colligative properties- relative lowering of vapour pressure, Raoult's law, elevation in boiling point, depression in freezing point, osmotic pressure, determination of molecular masses using colligative properties abnormal molecular mass. Van't Hoff factor.

A homogeneous mixture whose composition can be varied within certain limits is termed a true solution. Majority ingredient as **solvent** and minority ingredient as **solute**.

Concentration of Solution

1. Mole fraction = $\frac{\text{Mole of component}}{\text{Total moles}}$
2. Molality = $\frac{\text{wt. of solute} \times 1000}{\text{mol wt. of solute} \times \text{wt. of solvent in g}}$
3. Molarity = $\frac{W_{\text{solute}} \times 1000}{\text{Mol wt.} \times \text{volume in ml}}$
4. % weight by volume
5. % weight by mass
6. Normality = $\frac{\text{Equivalent of solute}}{\text{Volume of solution in litre}}$

Note : Molarity, normality etc. are temperature dependent while molality, mole fraction etc. are temperature independent.

Solubility of gases in liquids (Henry law): Solubility of a gas in liquid is directly proportional to the pressure of the gas at the surface of the liquid. Easily liquefiable gases i.e., gases having higher value for critical temperature, have more solubility.

Henry's law : Mole fraction of the gas in a solution is proportional to the partial pressure of the gas.

$$x \propto P \quad \text{or} \quad P = k_H x; \quad k_H = \text{Henry's constant}$$

The value of Henry constant depends upon nature of the gas and temperature.

Note : More the value of Henry law constant for a gas lesser is the solubility of the gas in liquid.

Vapour Pressure of Solutions of Solid in Liquids

Vapour pressure is the pressure exerted by the vapours on the surface of liquid when vapours and liquid is in equilibrium.

Effect on vapour pressure when

- (a) Non-volatile solute is added in volatile solvent.
- (b) Less volatile solute is added in more volatile solvent.

In both the cases there is the lowering of vapour pressure of the volatile solvent.

Raoult's Law

- (a) **Non Volatile Solute in Volatile Solvent :** Raoult's law states that relative decrease in vapour pressure when a non-volatile solute is added to a solvent is equal to mole fraction of solute

$$\frac{p^\circ - p_s}{p^\circ} = \chi_{\text{solute}}$$

where p° = vapour pressure of pure solvent

p_s = vapour pressure of solution

χ_{solute} = mole fraction of solute

- (b) **Volatile Solute in Volatile Solvent :** "The partial pressure of any volatile component of an ideal solution is directly proportional to its mole fraction in the solution".

$$p_A = \chi_A p_A^\circ$$

$$p_B = \chi_B p_B^\circ$$

$$P_{\text{total}} = p_A + p_B$$

where p_A = vapour pressure of A (Solvent)

p_B = vapour pressure of B (Solute)

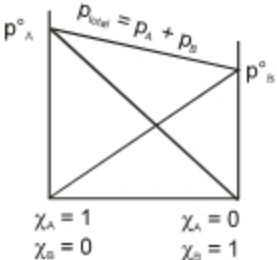
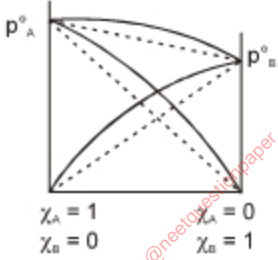
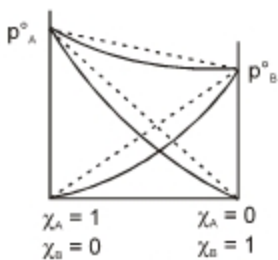
p_A° = vapour pressure of pure A

p_B° = vapour pressure of pure B

χ_A and χ_B = mole fraction of A and B in solution

Ideal and Non-Ideal Solutions

The solutions which obey Raoult's law are ideal solutions and those which do not obey Raoult's law form non-ideal solutions.

Ideal Solution	Non-Ideal Solution	
	Positive Deviation	Negative Deviation
1. Obey's Raoult's law	1. Disobey's Raoult's law	1. Disobey's Raoult's law
2. $p_A = p_A^\circ \chi_A$ $p_B = p_B^\circ \chi_B$ $p_{\text{total}} = p_A + p_B$	2. $p_A \neq p_A^\circ \chi_A$ $p_B \neq p_B^\circ \chi_B$ $p_{\text{total}} \neq p_A + p_B$ [$P_{\text{total}} > P_A + P_B$]	2. $p_A \neq p_A^\circ \chi_A$ $p_B \neq p_B^\circ \chi_B$ $p_{\text{total}} \neq p_A + p_B$ [$P_{\text{total}} < P_A + P_B$]
3. $\Delta H_{\text{mix}} = 0$ $\Delta V_{\text{mix}} = 0$	3. $\Delta H_{\text{mix}} = +ve$ $\Delta V_{\text{mix}} = +ve$	3. $\Delta H_{\text{mix}} = -ve$ $\Delta V_{\text{mix}} = -ve$
4. Interaction $A-B \approx A-A/B-B$ e.g. Chlorobenzene + Bromobenzene	4. Interaction $A-B < A-A/B-B$ e.g. $\text{CH}_3\text{OH} - \text{H}_2\text{O}$	4. Interaction $A-B > A-A/B-B$ e.g. $\text{CH}_3\text{COCH}_3 + \text{CHCl}_3$
 <p>(I)</p>	 <p>(II)</p>	 <p>(III)</p>

* Dotted lines for ideal solution in graph II and III

Colligative Properties

A colligative property of a solution is one that depends on the number of solute particles dissolved in it.

(a) Relative lowering of vapour pressure, $\frac{p^\circ - p_s}{p^\circ} = \chi_{\text{solute}}$

(b) Osmotic pressure, $\pi = CRT$.

(c) Elevation in boiling point, $\Delta T_b = k_b m$.

(d) Depression in freezing point, $\Delta T_f = k_f m$.

(a) **Relative lowering of V.P. :** The relative lowering in V.P. of an ideal solution is equal to the mole fraction of solute at that temperature.

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \chi_B = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1} = \frac{w_2}{M_2} \times \frac{M_1}{w_1}$$

Determination of molecular masses by relative lowering in vapour pressure.

$$\frac{p^\circ - p_A}{p_A} = \frac{w}{m} \times \frac{M}{W} \quad (\text{For dilute and concentrated solution})$$

w = wt. of solute

m = Mol. wt. of solute

W = wt. of solvent

M = Mol. wt. of solvent

- (b) **Osmotic pressure:** The excess pressure which must be applied on a solution to prevent the passage of solvent into it through a semipermeable membrane.

Determination: Berkley–Hartley method:

Semipermeable membrane \rightarrow egg membrane;

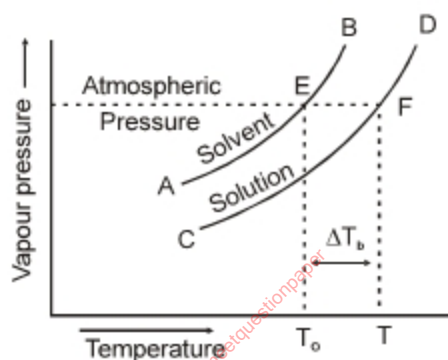
Chemical Semipermeable membrane \rightarrow cupric ferrocyanide.

$$\pi = CRT = n/V \cdot RT; \pi V = nRT \text{ (van't Hoff equation for dilution solutions)}$$

$$n = \frac{w_2}{M_2}; M_2 = \frac{w_2 \cdot RT}{\pi V}$$

- (c) **Elevation in boiling point:** The property of rise in boiling point when some non volatile solute is added.

We know that the vapour pressure of the solution is lower than that of the pure solvent and vapour pressure increases with increase in temperature. Hence the solution has to be heated more to make the vapour pressure equal to the atmospheric pressure.



Elevation in boiling point

Alternatively, the elevation in boiling point may be explained on the basis of plots of vapour pressure versus temperature as follows :

Vapour pressure of the solvent increases with increase in temperature as shown by the curve AB. As at any temperature, vapour pressure of the solution is less than that of the solvent, the curve for the solution lies below that of the solvent, as shown by the curve CD. The temperatures at which the vapour pressure of the solvent and the solution become equal to the atmospheric pressure are T_0 and T respectively. Obviously $T > T_0$. The difference, called the elevation in boiling point, ΔT_b , is given by

$$\Delta T_b = T - T_0$$

Molal elevation constant or ebullioscopic constant, k_b . It is the increase in boiling point when the molality of the solution is unity.

$$\Delta T_b = k_b m \text{ when } m = 1, \Delta T_b = k_b$$

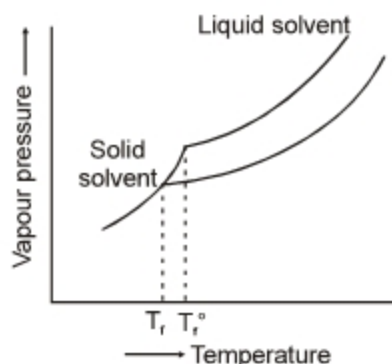
$$M_b = \frac{W_B \times 1000}{\Delta T_b \times W_A} \times k_b$$

- (d) **Depression in freezing point :** The property of decrease in freezing point when some non-volatile solute is dissolved. The depression in freezing point is given by ΔT_f

Freezing point : Temperature at which the liquid and the solid forms of the same substance are in equilibrium and hence have same vapour pressure.

We know that vapour pressure of the solution is less than that of the pure solvent. As freezing point is the temperature at which the vapour pressure of the liquid and the solid phase are equal, therefore for the solution, this will occur at lower temperature (lower the temperature lower the vapour pressure).

The graph explains this.



$$\Delta T_f = T_f^0 - T_f$$

Molal depression constant, or cryoscopic constant (k_f). It is the decrease in f.pt. when the molality of solution is unity

$$\Delta T_f = k_f \cdot m$$

when $m = 1$, $\Delta T_f = k_f$

$$M_B = \frac{W_B}{\Delta T_f \times W_A} \times 1000 \times k_f$$

K_b and K_f are intensive properties of solvent and do not depend upon solute or solution.

Van't Hoff Factor (i)

The solute which is added in solvent may be electrolytic or non-electrolytic in nature. Electrolytes may undergo association and dissociation due to which there is difference in observed colligative property and calculated colligative property. (by a factor 'i' known as Van't Hoff factor)

$$i = \frac{\text{Observed value of colligative property}}{\text{Theoretical value of colligative property}}$$

$$i = \frac{\text{number of moles after dissociation}}{\text{number of moles before dissociation}}$$

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property i.e.

$$\begin{aligned} \text{van't Hoff factor} &= \frac{\text{Experimental value of the colligative property}}{\text{Calculated value of the colligative property when the solution behaves ideally}} \\ &= \frac{\text{Observed value of the colligative property}}{\text{Normal value of the same property}} \end{aligned}$$

$$i = \Delta T (\text{obs}) / \Delta T (\text{cal}) = \pi (\text{obs}) / \pi (\text{cal})$$

$$= \Delta p (\text{obs}) / \Delta p (\text{cal}) = M (\text{cal}) / M (\text{obs})$$

Elevation in boiling point, $\Delta T_b = i k_b m$

Depression in freezing point, $\Delta T_f = i k_f m$

$$\text{Osmotic pressure, } P \text{ (or } \pi) = i \frac{n}{V} RT$$

When $i = 1$ then solution is ideal

$i > 1$ Dissociation

$i < 1$ Association

Degree of association : Degree of association is defined as the fraction of the total substance which exists in the form of associated molecules i.e.

$$\text{Degree of association } (\alpha) = \frac{\text{No. of moles associated}}{\text{Total number of moles taken}}$$

Suppose n simple molecules of the solute A associate to form the associated molecule A_n so that we have the equilibrium.



If α is the degree of association and we start with one mole of A , then at equilibrium

$$\text{Number of moles of } A = 1 - \alpha$$

$$\text{Number of moles of } A_n = \alpha/n$$

$$\therefore \text{The total number of moles} = 1 - \alpha + \alpha/n.$$

Since the colligative property is proportional to the number of moles of the solute present in solution, therefore,

$$\text{van't Hoff factor } i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$$

$$\Rightarrow i = 1 + \left(\frac{1}{n} - 1 \right) \alpha, \quad \alpha = \frac{i - 1}{\frac{1}{n} - 1}$$

Degree of dissociation : The degree of dissociation is defined as the fraction of the total substance that undergoes dissociation i.e.,

$$\text{Degree of dissociation } (\alpha) = \frac{\text{No. of moles dissociated}}{\text{Total number of moles taken}}$$

$$\therefore \text{van't Hoff factor } i = \frac{1 + (n-1)\alpha}{1} \text{ or } \alpha = \frac{i - 1}{n - 1}$$

$$\Rightarrow i = 1 + (n - 1)\alpha$$

where n is the total number of ions produced per molecules of electrolyte.





Try Yourself

SECTION - A

Objective Type Questions

- The boiling points of C_6H_6 , CH_3OH , $C_6H_5NH_2$ and $C_6H_5NO_2$ are $80^\circ C$, $65^\circ C$, $184^\circ C$ and $212^\circ C$ respectively. Which of the following will have highest vapour pressure at room temperature?
(1) C_6H_6
(2) CH_3OH
(3) $C_6H_5NH_2$
(4) $C_6H_5NO_2$
- The mole fraction of oxygen in a mixture of 7 g of nitrogen and 8 g of oxygen is
(1) $8/15$ (2) 0.5
(3) 0.25 (4) 1.0
- At $40^\circ C$ the vapour pressure (in torr) of mixture of methyl alcohol and ethyl alcohol is represented by $P = 199x + 135$
(where x is the mole fraction of methyl alcohol.)
What are the vapour pressures of pure methyl alcohol and pure ethyl alcohol at $40^\circ C$?
(1) 135 and 254 torr
(2) 119 and 135 torr
(3) 119 and 254 torr
(4) 334 and 135 torr
- Calculate the mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.5. (The vapour pressure of pure benzene is 119 torr and that of toluene is 37 torr at the same temperature)
(1) 0.5 (2) 0.75
(3) 0.625 (4) 0.237
- An ideal solution was obtained by mixing methanol and ethanol. If the partial vapour pressure of methanol and ethanol are 2.619 kPa and 4.556 kPa respectively, the composition of vapour (in terms of mole fraction) will be
(1) 0.635 MeOH, 0.365 EtOH
(2) 0.365 MeOH, 0.635 EtOH
(3) 0.574 MeOH, 0.326 EtOH
(4) 0.173 MeOH, 0.827 EtOH
- The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be the mole fraction of solvent if decrease in vapour pressure is 20 mm of Hg?
(1) 0.8
(2) 0.6
(3) 0.4
(4) 0.2
- At room temperature, the mole fraction of a solute is 0.2 and the vapour pressure of the pure solvent is 0.80 atm. Then the lowering of vapour pressure is
(1) 0.16 (2) 0.6
(3) 0.20 (4) 0.80
- A solution of A and B shows negative deviation from the ideal behaviour because
(1) $\Delta V_{mix} > 0$
(2) $\Delta H_{mix} > 0$
(3) A-B interaction is greater than average of A-A and B-B interaction
(4) $\Delta S_{mix} > 0$

9. Which pair from the following will not form an ideal solution?
- $\text{CCl}_4 + \text{SiCl}_4$
 - $\text{H}_2\text{O} + \text{C}_4\text{H}_9\text{OH}$
 - $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{I}$
 - $\text{C}_6\text{H}_{14} + \text{C}_7\text{H}_{16}$
10. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. 2g of a non volatile solid is added to 39g of benzene. The vapour pressure of the solution is 600 mm. The molecular weight of the substance is
- 30
 - 20
 - 60
 - 64
11. The vapour pressure of water at room temperature is equal to 23.8 mm Hg. the vapour pressure of an aqueous solution of sucrose with mole fraction 0.1 is equal to
- 23.9 mm Hg
 - 24.2 mm Hg
 - 2.38 mm Hg
 - 21.42 mm Hg
12. The osmotic pressure of a solution at 0°C containing 46.0g of glycerol in water per litre is
- 112 atm
 - 11.2 atm
 - 12.1 atm
 - 1.12 atm
13. A solution contains non-volatile solute of molecular mass M_2 which of the following can be used to calculate the molecular mass of solute in terms of osmotic pressure? (m_2 = mass of solute, V = volume of solution, π = osmotic pressure)
- $M_2 = \left(\frac{m_2}{\pi}\right) VRT$
 - $M_2 = \left(\frac{m_2}{V}\right) \frac{RT}{\pi}$
 - $M_2 = \left(\frac{m_2}{V}\right) \pi RT$
 - $M_2 = \left(\frac{m_2}{V}\right) \frac{\pi}{RT}$
14. The molal freezing point constant for water is 1.86. If 342 gm of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) are dissolved in 1000 gm water, the solution will freeze at
- -1.86°C
 - 1.86°C
 - 3.72°C
 - -3.42°C
15. Van't Hoff factor for $\text{Al}_2(\text{SO}_4)_3$ is (assume 100% dissociation)
- $i = 5$
 - $i = 2$
 - $i = 4$
 - $i = 1$
16. The Van't Hoff factor for 0.1M $\text{Ba}(\text{NO}_3)_2$ solution is 2.74. The degree of dissociation is
- 91.3%
 - 87%
 - 97%
 - 74%
17. When CuSO_4 is added to a solution of ammonia
- Freezing point is lowered
 - Freezing point is raised
 - Boiling point is raised
 - Both (1) & (3)
18. The degree of dissociation (α) of a weak electrolyte A_xB_y is related to Van't Hoff factor (i) by expression
- $\alpha = \frac{i - 1}{x + y + 1}$
 - $\alpha = \frac{i - 1}{x + y - 1}$
 - $\alpha = \frac{1 - i}{1 + x + y}$
 - $\alpha = \frac{1 - i}{x + y}$
19. Least osmotic pressure is of
- 0.1 M Hg_2Cl_2
 - 0.1 M $\text{Ca}_3(\text{PO}_4)_2$
 - 0.1 M $\text{K}_4[\text{Fe}(\text{CN})_6]$
 - 0.1 M AlCl_3

20. Assuming salts to be 90% dissociated, which of the following will have highest osmotic pressure?
- Decimolar $\text{Al}_2(\text{SO}_4)_3$
 - Decimolar BaCl_2
 - Decimolar Na_2SO_4
 - A solution obtained by mixing equal volumes of (2) and (3) and filtering
21. Which of the following aqueous solution has maximum freezing point?
- 0.01 M NaCl
 - 0.005 M $\text{C}_2\text{H}_5\text{OH}$
 - 0.005 M MgI_2
 - 0.01 M MgSO_4
22. The lowering of vapour pressure of 0.1 M aqueous solution of NaCl, CuSO_4 and K_2SO_4 are
- All equal
 - In the ratio of 1 : 1 : 1.5
 - In the ratio of 3 : 2 : 1
 - In the ratio of 1.5 : 1 : 2.5
23. An aqueous solution of KCl freezes at -0.186°C ($K_f = 1.86$, $K_b = 0.512$). What is the elevation in boiling point? (Assume complete dissociation)
- 0.512
 - 0.0512
 - 1.024
 - 0.05×10^{-1}
24. The molal boiling point elevation of water is 0.512°C/m , therefore the boiling point of 0.1m CaCl_2 solution in water is expected to be
- 0.1536°C
 - 99.8464°C
 - 100.0512°C
 - 100.1536°C
25. 0.1M NaCl and 0.1M CH_3COOH are kept in separate containers. If their osmotic pressures are π_1 and π_2 respectively then what is the correct statement?
- $\pi_1 > \pi_2$
 - $\pi_1 = \pi_2$
 - $\pi_1 < \pi_2$
 - $\pi_1 = \pi_2 = 0 \text{ atm}$

SECTION - B

Previous Years Questions

- p_A and p_B are the vapour pressure of pure liquid components, A and B, respectively of an ideal binary solution. If x_A represents the mole fraction of component A, the total pressure of the solution will be [AIPMT 2012]
 - $p_B + x_A (p_B - p_A)$
 - $p_B + x_A (p_A - p_B)$
 - $p_A + x_A (p_B - p_A)$
 - $p_A + x_A (p_A - p_B)$
- Which of the following compounds can be used as antifreeze in automobile radiators? [AIPMT 2012]
 - Methyl alcohol
 - Glycol
 - Nitrophenol
 - Ethyl alcohol
- Of the following 0.10 m aqueous solutions, which one will exhibit the largest freezing point depression? [AIPMT 2014]
 - KCl
 - $\text{C}_6\text{H}_{12}\text{O}_6$
 - $\text{Al}_2(\text{SO}_4)_3$
 - K_2SO_4
- What is the mole fraction of the solute in a 1.00 m aqueous solution? [Re-AIPMT-2015]
 - 0.0354
 - 0.0177
 - 0.177
 - 1.770
- Which one is not equal to zero for an ideal solution? [AIPMT-2015]
 - $\Delta P = P_{\text{observed}} - P_{\text{Raoult}}$
 - ΔH_{mix}
 - ΔS_{mix}
 - ΔV_{mix}
- The boiling point of 0.2 mol kg^{-1} solution of X in water is greater than equimolal solution of Y in water. Which one of the following statements is true in this case? [AIPMT-2015]
 - Y is undergoing dissociation in water while X undergoes no change
 - X is undergoing dissociation in water
 - Molecular mass of X is greater than the molecular mass of Y
 - Molecular mass of X is less than the molecular mass of Y

7. Which one of the following electrolytes has the same value of van't Hoff's factor (i) as that of $Al_2(SO_4)_3$ (if all are 100% ionised)? [AIPMT-2015]
- (1) $K_4[Fe(CN)_6]$ (2) K_2SO_4
(3) $K_3[Fe(CN)_6]$ (4) $Al(NO_3)_3$
8. At $100^\circ C$ the vapour pressure of a solution of 6.5 g of a solute in 100 g water is 732 mm. If $K_b = 0.52$, the boiling point of this solution will be [NEET-2016]
- (1) $103^\circ C$ (2) $101^\circ C$
(3) $100^\circ C$ (4) $102^\circ C$
9. Which of the following statements about the composition of the vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at $25^\circ C$. (Given, Vapour Pressure Data at $25^\circ C$, benzene = 12.8 kPa, toluene = 3.85 kPa) [NEET-2016]
- (1) Not enough information is given to make a prediction
(2) The vapour will contain a higher percentage of benzene
(3) The vapour will contain a higher percentage of toluene
(4) The vapour will contain equal amounts of benzene and toluene
10. The van't Hoff factor (i) for a dilute aqueous solution of the strong electrolyte barium hydroxide is [NEET (Phase-2) 2016]
- (1) 0 (2) 1
(3) 2 (4) 3
11. Which one of the following is **incorrect** for ideal solution? [NEET (Phase-2) 2016]
- (1) $\Delta H_{mix} = 0$
(2) $\Delta U_{mix} = 0$
(3) $\Delta P = P_{obs} - P_{calculated \text{ by Raoult's law}} = 0$
(4) $\Delta G_{mix} = 0$
12. Which of the following is dependent on temperature? [NEET-2017]
- (1) Molality (2) Molarity
(3) Mole fraction (4) Weight percentage
13. If molality of the dilute solution is doubled, the value of molal depression constant (K_f) will be [NEET-2017]
- (1) Doubled (2) Halved
(3) Tripled (4) Unchanged
14. The mixture that forms maximum boiling azeotrope is [NEET-2019]
- (1) Water + Nitric acid
(2) Ethanol + Water
(3) Acetone + Carbon disulphide
(4) Heptane + Octane
15. For an ideal solution, the **correct** option is [NEET-2019]
- (1) $\Delta_{mix} S = 0$ at constant T and P
(2) $\Delta_{mix} V \neq 0$ at constant T and P
(3) $\Delta_{mix} H = 0$ at constant T and P
(4) $\Delta_{mix} G = 0$ at constant T and P
16. Which of the following statements is correct regarding a solution of two components A and B exhibiting positive deviation from ideal behaviour? [NEET-2019 (Odisha)]
- (1) Intermolecular attractive forces between A-A and B-B are equal to those between A-B.
(2) Intermolecular attractive forces between A-A and B-B are stronger than those between A-B.
(3) $\Delta_{mix} H = 0$ at constant T and P.
(4) $\Delta_{mix} V = 0$ at constant T and P.



Chapter 11

Chemical Kinetics

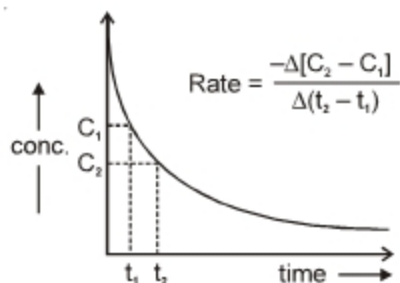
Sub-topics

Rate of a reaction (average and instantaneous), factors affecting rates of reaction; concentration, temperature, catalyst; order and molecularity of a reaction; rate law and specific rate constant, integrated rate equations and half life (only for zero and first order reactions); concept of collision theory (elementary idea, no mathematical treatment). Activation energy, Arrhenius equation.

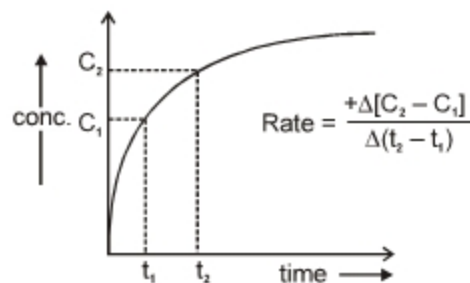
Chemical kinetics is the branch of science which deals with the rate and mechanism of reactions and the factors that influence the rate of a reaction.

Rate of Chemical Reaction

The rate of a reaction is defined as the rate of change of concentration of any of the reactants or the products in a given time.



Rate w.r.t. reactant concentration



Rate w.r.t. product concentration

$$\text{Reaction rate} = \frac{\text{change in conc. of reactant}}{\text{change in time}}$$

$$\text{Reaction rate w.r.t. disappearance of reactant} = \frac{-d[A]}{dt}$$

$$\text{Reaction rate w.r.t. appearance of product} = \frac{d[B]}{dt}$$

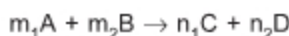


$$\text{rate} = \frac{-d[\text{PCl}_5]}{dt} = \frac{+d[\text{PCl}_3]}{dt} = \frac{+d[\text{Cl}_2]}{dt}$$



$$\text{rate} = \frac{-d[\text{H}_2]}{dt} = \frac{-d[\text{I}_2]}{dt} = +\frac{1}{2} \frac{d[\text{HI}]}{dt}$$

In general,



$$\therefore \text{Rate} = \frac{1}{m_1} \times \frac{-d[\text{A}]}{dt} = \frac{1}{m_2} \times \frac{-d[\text{B}]}{dt} = \frac{1}{n_1} \times \frac{d[\text{C}]}{dt} = \frac{1}{n_2} \times \frac{d[\text{D}]}{dt}$$

Factors Influencing the Rate of Reaction

- (a) **Temperature** : The rate constant increases with increase in temperature and hence rate of reaction also increases.
- (b) **Concentration** : According to law of mass action, the rate of reaction may increase with increase in concentration of reactants.
- (c) **Pressure** : In gaseous reaction, on increasing the pressure, volume decreases hence conc. increases which increases rate.
- (d) **Catalyst** : Positive catalyst increases the rate of reaction.

Order of the Reaction

The order of the reaction w.r.t. some component is the power to which the concentration of the components is raised in the rate law. The over all order of a reaction is the sum of the orders of all components. Order is found by experiment only it can't be deduced from the equation for a given reaction.

For reaction $a\text{A} + b\text{B} \rightarrow \text{Product}$

The rate law can be written as

$$\text{Rate of reaction} = k [\text{A}]^m [\text{B}]^n$$

$$\text{order of overall reaction} = m + n$$

Note : (a) $m + n$ may or may not be equal to $a + b$.

- (i) e.g. : $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$, the order of reaction is not two but it is zero order reaction, as rate of the reaction remains unaltered though the conc. of H_2 and Cl_2 are changed, hence $\text{rate} = k [\text{H}_2]^0 [\text{Cl}_2]^0$. Zero order means rate of reaction is independent of conc.
- (ii) e.g. : $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$, the order of reaction is not 2 (as per stoichiometry), but it is first order reaction, since rate of the reaction gets doubled when conc. of H_2O_2 is doubled.
- (b) For complex reaction (multistep) the order reaction is determined by slowest step.
- (c) If rate of reaction gets doubled and quadrupled by doubling the conc. of reactants then the respective order of reactions are first order and second order respectively
- (d) Order can be zero, negative, positive or fraction also.

Molecularity of reaction: The number of reacting molecules colliding together simultaneously to give the product is called molecularity of reaction. It is theoretical and its value cannot be more than 3 but whole number (1, 2, 3).

Rate constant for different order of reaction.

Reaction	Order	Rate law eqn.	Rate constant
$A \rightarrow \text{product}$	0	Rate = k	$k = \frac{1}{t}([A_0] - [A])$
$A \rightarrow \text{product}$	1	Rate = k[A]	$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$
$2A \rightarrow \text{product}$	2	Rate = k[A] ²	$k = \frac{1}{t} \left[\frac{1}{[A]} - \frac{1}{[A_0]} \right]$

The units for k for different order of reaction is $(\text{mol litre}^{-1})^{(1-n)} \cdot \text{time}^{-1}$, where n is order of reaction.

Order	unit of k
Zero	$\text{mol L}^{-1} \text{time}^{-1}$
First	time^{-1}
Second	$\text{L mol}^{-1} \text{time}^{-1}$
Third	$\text{L}^2 \text{mol}^{-2} \text{time}^{-1}$

Methods to Determine Order of Reaction**(a) Initial Rate Method**

In this method, the initial rate of a reaction is determined by varying the concentration of one of the reactants while others are kept constant.

(b) Integrated Rate Law Method

In this method, the rate constant is determined at different intervals of time, if rate constant is same at different interval of time then it predicts the order of reaction.

For e.g., rate constant k for first order is

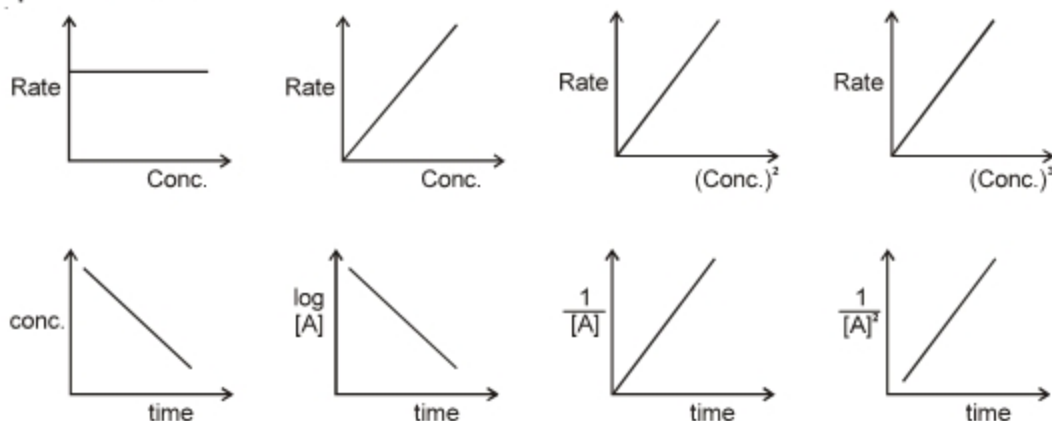
$$k = \frac{2.303}{t} \log \frac{[\text{Int. conc.}]}{[\text{conc. after time } t]} \quad \text{For 1st order}$$

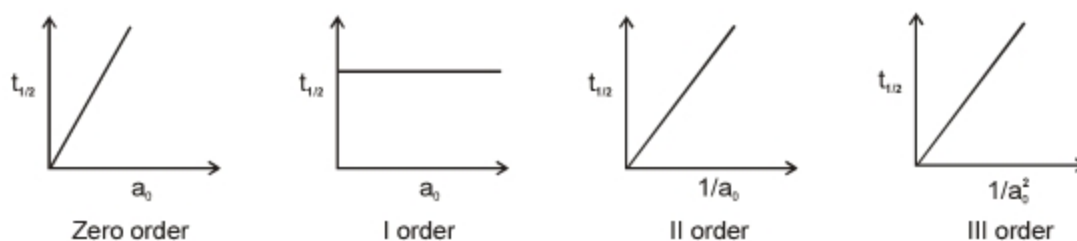
For e.g., decomposition of hydrogen peroxide; $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$.

The concentration of H_2O_2 at different interval of time is determined, if it is a first order reaction then the rate constant (k of first order) at different interval of time (k_1, k_2, k_3, \dots for C_1, C_2, C_3, \dots) should be same.

$$\text{Also, } k = \frac{2.303}{t} \log \frac{N_0}{N_t} \quad \dots \text{as per given data}$$

$$[\text{For hydrolysis of ester; } \frac{N_0}{N_t} = \frac{V_\infty - V_0}{V_\infty - V_t}] \quad [\text{For hydrolysis of sucrose; } \frac{N_0}{N_t} = \frac{r_0 - r_\infty}{r_t - r_\infty}]$$

(c) Graphical Method

(d) **Half-life Method**

Using expression $t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$, order (n) can be calculated if $t_{1/2}$ for two different values of $[A_0]$ is known

$$n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log C_2 - \log C_1}$$

(e) **Ostwald's Isolation Method**

For reaction, $aA + bB + cC \rightarrow \text{Product}$, taking all except one in excess one by one, order with respect to that reactant is determined because concentrations of those taken in excess almost do not change.

rate = $k[A]^\alpha$ if [B] and [C] are taken in excess

rate = $k[B]^\beta$ if [A] and [C] are taken in excess

rate = $k[C]^\gamma$ if [B] and [A] are taken in excess

Integrated rate equations

- For zero order reaction

$$k = \frac{[A_0] - [A]}{t}$$

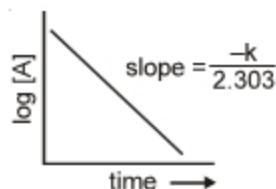
$$t_{1/2} = \frac{[A_0]}{2k}$$

- For first order reaction

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

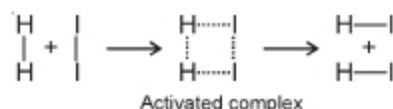
$$\text{or } \log[A] = \frac{-kt}{2.303} + \log[A_0]$$

When a graph is plotted between $\log [A]$ Vs t , a straight line is obtained with slope = $-\frac{k}{2.303}$ and intercept is $\log [A_0]$.

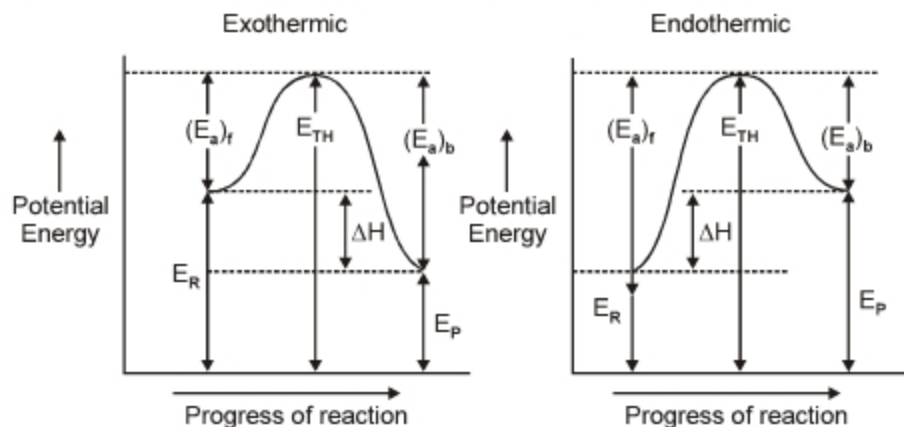


$$t_{1/2} = \frac{0.693}{k}$$

Collision Theory: Reactant molecules collide with each other to form transition state or activated state and immediately give product.



Activation energy : The minimum energy required by molecules of reactants to cross the energy barrier.



E_{TH} = Threshold Energy

E_R = Potential energy of reactants.

E_P = Potential energy of product.

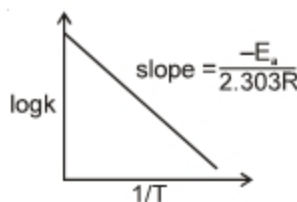
$(E_a)_f$ = Activation energy for forward reaction.

$(E_a)_b$ = Activation energy for backward reaction.

Note : $\Delta H = H_P - H_R$, $\Delta H = (E_a)_f - (E_a)_b$, $E_{TH} = E_R + (E_a)_f$ or $E_{TH} = E_P + (E_a)_b$.

Arrhenius equation: The rate constant for most of the reactions increase with the increase of temperature

as related by **Arrhenius equation**, $k = Ae^{\frac{-E_a}{RT}}$ i.e., $\ln k = \ln A - E_a/RT$.



By plotting graph $\ln k$ vs $\frac{1}{T}$ activation energy can be determined.

Temperature co-efficient : With every 10°C rise in temperature the rate of reaction either gets doubled or

tripled or between them i.e., $2 \leq \frac{r_{t+10}}{r_t} \leq 3$.





Try Yourself

SECTION - A

Objective Type Questions

- For the hypothetical reaction $2A \rightarrow 3C$, the reaction rate 'r' in terms of the rate of change of the concentration of reactant is given by
 - $r = -\frac{d[A]}{dt}$
 - $r = -\frac{1}{2} \frac{d[A]}{dt}$
 - $r = \frac{1}{3} \frac{d[A]}{dt}$
 - $r = \frac{d[A]}{dt}$
- In a reaction $2A \rightarrow \text{Products}$; the concentration of A decreases from $0.5 \text{ mol litre}^{-1}$ to $0.4 \text{ mol litre}^{-1}$ in 10 minutes. The rate of reaction during this interval is
 - 0.05 M min^{-1}
 - 0.005 M min^{-1}
 - 0.5 M min^{-1}
 - 5 M min^{-1}
- For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of change of concentration for hydrogen is $3.0 \times 10^{-3} \text{ Ms}^{-1}$. The rate of change of concentration of ammonia is
 - -2.0×10^3
 - 2.0×10^{-3}
 - 1.0×10^{-3}
 - 3.0×10^{-3}
- For the reaction,

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$
 Given,

$$-\frac{d[N_2O_5]}{dt} = K_1 [N_2O_5]$$

$$\frac{d[NO_2]}{dt} = K_2 [N_2O_5]$$
 and

$$\frac{d[O_2]}{dt} = K_3 [N_2O_5]$$
 The relation between K_1 , K_2 and K_3 is
 - $2K_1 = K_2 = 4K_3$
 - $K_1 = K_2 = K_3$
 - $2K_1 = 4K_2 = K_3$
 - None of these
- The unit of rate constant for the following reaction is $PCl_5 \rightarrow PCl_3 + Cl_2$ (Assuming it is elementary reaction)
 - s^{-1}
 - $L \text{ mol}^{-1}s^{-1}$
 - $\text{mol}^{-1} s^{-1}$
 - mol s^{-1}
- If the volume of closed vessel in which the following simple reaction is carried out is reduced to one third of original volume, the rate of reaction becomes

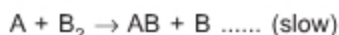
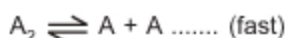
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
 - One third
 - Three times
 - Nine times
 - Twenty seven times
- The order of reaction can be determined from
 - Chemical equation
 - Experiment
 - Rate of disappearance of reactants
 - Thermochemical equation
- The inversion of cane sugar represented by $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_2H_{12}O_6$ is a reaction
 - Unimolecular
 - Second order
 - Pseudo bimolecular
 - Pseudo first order
- For the reaction, $A \rightarrow E$, it is found that the rate of the reaction doubles when the concentration of A is increased four times. The order of A in this is
 - 3
 - 1
 - 0
 - $\frac{1}{2}$
- For the reaction $A + B \rightarrow \text{products}$, it is found that order of A is 2 and the order of B is 3 in the rate expression. When the concentrations of both A and B are doubled the rate will increase by a factor
 - 10
 - 16
 - 32
 - 28
- For a reaction $A \rightarrow B$, the rate of reaction is quadrupled when the concentration is doubled. The rate expression of the reaction is $r = k[A]^n$ where the value of n is
 - 3
 - 2
 - 1
 - Zero

12. Consider the data below for a reaction
- $A \rightarrow B$

Time (sec)	0	10	20	30
Rate	1.60×10^{-2}	1.60×10^{-2}	1.60×10^{-2}	1.60×10^{-2}

From the above data the order of reaction is

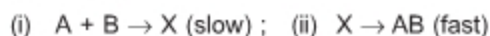
- (1) Zero (2) 1
(3) 2 (4) 3
13. Decomposition of H_2O_2 is _____ order reaction.
(1) First (2) Second
(3) Zero (4) Third
14. A reaction, $A_2 + B_2 \rightarrow 2AB$ occurs by the following mechanism;



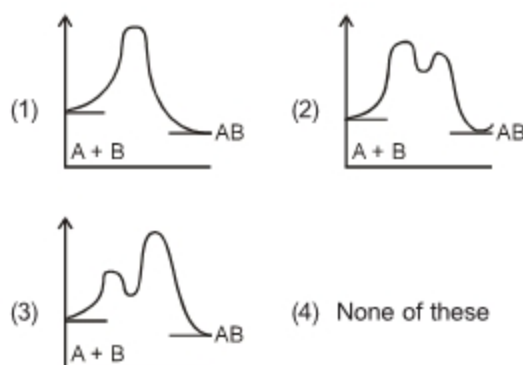
The order of reaction is

- (1) $\frac{3}{2}$ (2) 1
(3) Zero (4) 2
15. The rate constant is numerically the same for three reaction of first, second and third order respectively. Which one is true for rate of three reaction, if concentration of reactant is greater than 1M?
(1) $r_1 = r_2 = r_3$
(2) $r_1 > r_2 > r_3$
(3) $r_1 < r_2 < r_3$
(4) All of these
16. $t_{1/2}$ is directly proportional to initial concentration for
(1) Zero order (2) Second order
(3) First order (4) None of these
17. For a 1st order reaction, a straight line is obtained if you plot
(1) log concentration vs. time
(2) concentration vs. time
(3) 1/concentration vs. time
(4) log concentration vs. 1/time
18. Rate constant of a reaction is 0.0693 min^{-1} starting with 10 mole, rate of the reaction after 10 min is
(1) 0.693 mol/min
(2) $0.0693 \times 2 \text{ mol/min}$
(3) $0.0693 \times 5 \text{ mol/min}$
(4) $0.0693 \times (5)^2 \text{ mol/min}$

19. For an exothermic chemical process occurring in two steps as



The progress of the reaction can be best described by



SECTION - B

Previous Years Questions

1. In a hypothetical reaction $A \rightarrow B$, the activation energies for the forward and backward reactions are 15 and 9 kJ mol⁻¹ respectively. The potential energy of A is 10 kJ mol⁻¹, the correct statement regarding given reaction is [AIPMT 2012]
(1) The threshold energy of the reaction is 2 kJ
(2) The potential energy of B is 19 kJ
(3) Heat of the reaction is 25 kJ
(4) The reaction is endothermic
2. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become [AIPMT 2012]
(1) 64 times
(2) 128 times
(3) 256 times
(4) 512 times
3. In a reaction, $A + B \rightarrow \text{Product}$, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentrations of both the reactants (A and B) are doubled, rate law for the reaction can be written as [AIPMT 2012]
(1) Rate = $k[A][B]$
(2) Rate = $k[A]^2[B]$
(3) Rate = $k[A][B]^2$
(4) Rate = $k[A]^2[B]^2$

4. Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by

[AIPMT 2012]

$$(1) \ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$(2) \ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$(3) \ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} + \frac{1}{T_1} \right)$$

$$(4) \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

5. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C ? ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

[NEET 2013]

$$(1) 269 \text{ kJ mol}^{-1}$$

$$(2) 34.7 \text{ kJ mol}^{-1}$$

$$(3) 15.1 \text{ kJ mol}^{-1}$$

$$(4) 342 \text{ kJ mol}^{-1}$$

6. The rate constant of the reaction $A \longrightarrow B$ is 0.6×10^{-3} mole per second. If the concentration of A is 5 M, then concentration of B after 20 minutes is

[Re-AIPMT-2015]

$$(1) 0.36 \text{ M}$$

$$(2) 0.72 \text{ M}$$

$$(3) 1.08 \text{ M}$$

$$(4) 3.60 \text{ M}$$

7. The activation energy of a reaction can be determined from the slope of which of the following graphs?

[AIPMT-2015]

$$(1) \frac{T}{\ln K} \text{ vs } \frac{1}{T}$$

$$(2) \ln K \text{ vs } T$$

$$(3) \frac{\ln K}{T} \text{ vs } T$$

$$(4) \ln K \text{ vs } \frac{1}{T}$$

8. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is

[AIPMT-2015]

$$(1) \text{ More than zero but less than first}$$

$$(2) \text{ Zero}$$

$$(3) \text{ First}$$

$$(4) \text{ Second}$$

9. The addition of a catalyst during a chemical reaction alters which of the following quantities?

[NEET-2016]

$$(1) \text{ Activation energy}$$

$$(2) \text{ Entropy}$$

$$(3) \text{ Internal energy}$$

$$(4) \text{ Enthalpy}$$

10. The rate of a first-order reaction is $0.04 \text{ mol l}^{-1} \text{ s}^{-1}$ at 10 seconds and $0.03 \text{ mol l}^{-1} \text{ s}^{-1}$ at 20 seconds after initiation of the reaction. The half-life period of the reaction is

[NEET-2016]

$$(1) 54.1 \text{ s}$$

$$(2) 24.1 \text{ s}$$

$$(3) 34.1 \text{ s}$$

$$(4) 44.1 \text{ s}$$

11. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the

[NEET (Phase-2) 2016]

$$(1) \text{ Rate is proportional to the surface coverage}$$

$$(2) \text{ Rate is inversely proportional to the surface coverage}$$

$$(3) \text{ Rate is independent of the surface coverage}$$

$$(4) \text{ Rate of decomposition is very slow}$$

12. A first order reaction has a specific reaction rate of 10^{-2} s^{-1} . How much time will it take for 20 g of the reactant to reduce to 5 g?

[NEET-2017]

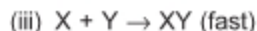
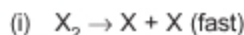
$$(1) 238.6 \text{ second}$$

$$(2) 138.6 \text{ second}$$

$$(3) 346.5 \text{ second}$$

$$(4) 693.0 \text{ second}$$

13. Mechanism of a hypothetical reaction $X_2 + Y_2 \rightarrow 2XY$ is given below :



The overall order of the reaction will be [NEET-2017]

$$(1) 1$$

$$(2) 2$$

$$(3) 0$$

$$(4) 1.5$$

14. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction

[NEET-2018]

$$(1) \text{ Is halved}$$

$$(2) \text{ Is doubled}$$

$$(3) \text{ Remains unchanged}$$

$$(4) \text{ Is tripled}$$

15. The correct difference between first and second order reactions is that **[NEET-2018]**
- The rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
 - The half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$
 - The rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations
 - A first-order reaction can be catalyzed; a second-order reaction cannot be catalyzed
16. If the rate constant for a first order reaction is k , the time (t) required for the completion of 99% of the reaction is given by: **[NEET-2019]**
- $t = 0.693/k$
 - $t = 6.909/k$
 - $t = 4.606/k$
 - $t = 2.303/k$
17. For the chemical reaction
- $$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- The correct option is: **[NEET-2019]**
- $-\frac{1}{3} \frac{d[\text{H}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
 - $-\frac{d[\text{N}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$
 - $-\frac{d[\text{N}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
 - $3 \frac{d[\text{H}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$
18. A first order reaction has a rate constant of $2.303 \times 10^{-3} \text{ s}^{-1}$. The time required for 40 g of this reactant to reduce to 10 g will be
[Given that $\log_{10} 2 = 0.3010$]
- [NEET-2019 (Odisha)]**
- | | |
|-----------|-------------|
| (1) 602 s | (2) 230.3 s |
| (3) 301 s | (4) 2000 s |



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Chapter 12

Surface Chemistry

Sub-topics

Adsorption-physisorption and chemisorption; factors affecting adsorption of gases on solids, catalysis homogeneous and heterogeneous, activity and selectivity: enzyme catalysis; colloidal state: distinction between true solutions, colloids and suspensions; lyophilic, lyophobic multimolecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation; emulsions- types of emulsions.

Surface chemistry is the chemistry at the boundary separating two bulk phases.

Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface. The substance on the surface of which adsorption takes place is called **adsorbent** and the substance adsorbed is known as **adsorbate**.

Types of Adsorption

- (i) Physisorption
- (ii) Chemisorption

Physisorption	Chemisorption
1. Adsorption by weak van der Waal's attraction.	1. Adsorption the binding is of chemical nature i.e., molecules form chemical bond.
2. Enthalpy of adsorption is of order of -20 to -40 kJ mol^{-1} .	2. Enthalpy of adsorption is of the order of -80 to -240 kJ mol^{-1} .
3. It usually takes place at low temperature.	3. It takes place relatively at high temperature.
4. It is reversible process.	4. It is irreversible process.
5. It may be multimolecular phenomenon.	5. It is unimolecular phenomenon.
6. It is non-specific e.g., gases adsorbed on charcoal surface.	6. It is specific. e.g., H_2 adsorbed on Pt surface.

Factors Affecting Adsorption

The amount of gas adsorbed by a solid depends on following

- (a) Nature of adsorbate
- (b) Nature of adsorbent

- (c) Pressure - Adsorption isotherm (Freundlich adsorption isotherm)
- (d) Temperature - Adsorption isobar
- (a) **Nature of adsorbent** : The adsorption tendency depends on surface area.
Colloidal solution > liquid > solid.
- (b) **Nature of adsorbate**: The easily liquefiable gases gets easily adsorbed.
- (c) **Freundlich Adsorption Isotherm** : At constant temperature, mass of the gas adsorbed by a solid adsorbent at various pressure is given by Freundlich equation.

$\frac{x}{m} = kp^{1/n}$ where x = mole of gas adsorbed on m gram of solid adsorbent at pressure (p) where k and n are constants at given temperature for a gas and solid adsorbent. ($n \geq 1$)

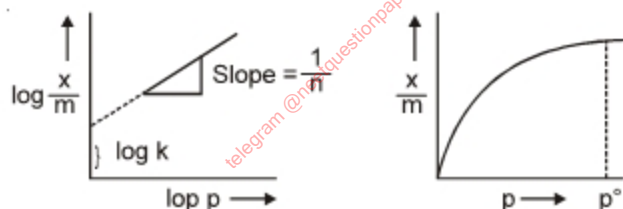
- (i) **At Low Pressure** : The graph of x/m versus p is nearly a straight line as gas molecules are being constantly adsorbed on solid surface.

$$\frac{x}{m} \propto p^{1/n} \text{ or } \frac{x}{m} = \text{constant} \times p$$

($n = 1$ at low pressure)

- (ii) **At High Pressure** : x/m becomes independent of the values of ' p ' as very few sites are left on the surface of the solid for adsorption and, therefore x/m reaches constant value and $\therefore x/m = \text{constant}$, or $x/m = \text{constant} \times p^0$.

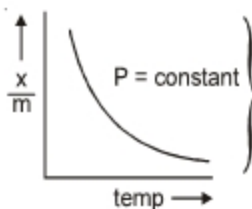
$$\therefore \frac{x}{m} = k$$



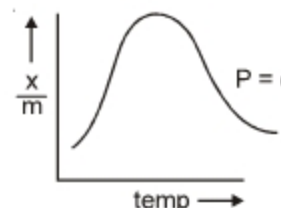
Note : Langmuir adsorption isotherm is given as $\frac{x}{m} = \frac{ap}{1 + bp}$, where a and b are Langmuir parameters.

(d) **Adsorption Isobar**

A plot of x/m versus temperature at a given pressure is called "adsorption isobar".



Physisorption \Rightarrow The amount of gas adsorbed/area of the surface of the solid adsorbent decreases with increase in temperature.



Chemisorption \Rightarrow The amount of adsorption first increases because of activation energy required reaches maximum value and then decreases.

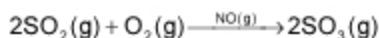
Both graphs are used to distinguish physisorption and chemisorption.

Catalysis

Substances which alter the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as catalysts, and the phenomenon is known as catalysis.

Promoters and poisons: Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst. For example, in Haber's process for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as a catalyst.

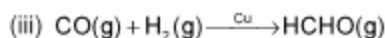
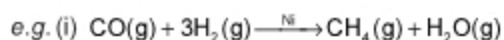
Homogeneous catalysis: The catalysis in which the reactants and the catalyst are in the same phase is said to be homogeneous catalysis.



Heterogeneous catalysis: The catalysis in which the reactants and the catalysts are in different phases is known as heterogeneous catalysis.



Activity and selectivity of a catalyst: The **activity** of a catalyst depends upon the strength of chemisorption to a large extent. The **selectivity** of a catalyst is its ability to direct a reaction to yield a particular product.



Colloids and Sols

- (a) **Colloidal Solution** : It is a heterogeneous mixture of a solid in a liquid in which the solids particles do not settle down under effect of gravity. For example – milk is a colloidal solution of proteins and fats in water.
- (b) A colloidal solution has two phases
- Dispersed phase → Phase constituting the colloidal particles.
 - Dispersion medium → The medium in which matter is dispersed.
- (c) **Colloidal State** : A solute that forms a colloidal solution when mixed with a solvent is said to be in the colloidal state.

Types of Solution	Particle size	Example
1. True molecular solution	(< 1 nm)	Glucose solution in water
2. Colloidal particles	(1 – 1000 nm)	Gold sol., Inks
3. Suspension	(> 1000 nm)	mixture of sand and water

Classification of Colloidal Solutions

Colloidal solutions can be classified

1. On the basis of the state of the dispersed phase or dispersion medium.
2. On the basis of the nature of dispersion medium.
3. On the basis of attraction between the dispersed phase and dispersion medium.
4. On the basis of the size of the particles.

Types of Colloidal Solutions : (Based on state)

Sr. No.	Dispersed Phase	Dispersion Medium	Types of Colloid	Examples
1.	Gas	Liquid	Foam	Soap, lather, froth
2.	Gas	Solid	Solid sol	Foam rubber
3.	Liquid	Gas	Aerosols of liquid	Fog, mist
4.	Liquid	Solid	Gels	Butter, cheese
5.	Liquid	Liquid	Emulsion	Milk
6.	Solid	Gas	Aerosols of solids	Dust, smoke
7.	Solid	Liquid	Sols	ink, gold sol
8.	Solid	Solid	Solid sols	Pearls, ruby glass

Gas-Gas colloidal solution is not possible. It always forms true solution.

Types of Colloids (Based on nature of dispersion medium)

1. Hydrosols : Dispersion medium is water e.g., gold sol.
2. Alcosols : Dispersion medium is alcohol.
3. Benzolsols : Dispersion medium is benzene.
4. Aerosols : Dispersion medium is gas e.g., smoke.

Types of Colloids (Based on the size of the particles)

- A. Multimolecular colloids : e.g., A gold sol, gold particles of various size.
- B. Macromolecular colloids : e.g., Proteins of high molecular mass in a suitable dispersion medium.
- C. Associated colloids : e.g., Soaps and detergents.

Types of Colloids (Based on attraction between the dispersed phase and dispersion medium)

- A. Lyophobic colloids (Solvent Repellent)
 - (a) Weak interaction between dispersed phase and dispersion medium.
 - (b) Lyophobic sols are readily precipitated by addition of small quantities of electrolytes, heating.
 - (c) e.g., Metallic sulphide and oxides and silver halides in aqueous solution, gold sol, arsenous sulphide sol, etc
- B. Lyophilic colloids (Solvent Attracting)
 - (a) They are surrounded by hydration layers.
 - (b) Strong attraction between dispersed phase and dispersion medium that makes lyophilic sols stable.
 - (c) e.g., gelatine, starch etc

Methods of Preparation of Sols

Preparation of lyophobic colloids

A. **Dispersion Methods** : The larger particles of solute are broken down to colloidal size e.g., Mechanical dispersion, peptization.

(a) **Peptization** : It is conversion of freshly prepared precipitate into colloidal state by adding appropriate electrolyte. It is the reverse of coagulation.

e.g.,

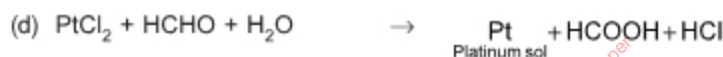
(i) A suspension of AgCl when shaken with an electrolyte (HCl) becomes colloidal.

(ii) A suspension of nickel sulphide when shaken with H_2S gives colloidal solution of nickel sulphide.

(b) **Bredig's Arc Method**: Metal sols (Pt, Au, Ag) are obtained by striking an electric arc between electrodes of relevant metal immersed in liquid medium.

B. **Chemical Methods** : Molecules and ions are united to form colloidal particles. e.g., reduction, hydrolysis, oxidation.

Some important preparations

**Properties of Colloids:**

(i) **Brownian movement** : The continuous zig-zag motion of particles of dispersed phase is called Brownian motion.

(ii) **Electrophoresis**: The movement of particles of dispersed phase towards one of the electrodes when placed in electric field is called electrophoresis.

(iii) **Tyndall effect**: The phenomenon of scattering of light by dispersed phase particles is known as Tyndall effect.

Charge on Colloidal Particles

Negatively Charged Sols	Positively Charged Sols
1. Metals Pt, Au, Ag, Cu	1. Ferric hydroxide $Fe(OH)_3 + Fe^{+3} \rightarrow \underbrace{Fe(OH)_2/Fe^{+3}}_{\text{positive charge}}$
2. Arsenous sulphide $(As_2S_3 + S^{2-}) \longrightarrow (As_2S_3/S^{2-})$	2. Aluminium hydroxide
3. Starch, gelatin	3. Basic dyes
4. Clay	4. Proteins in acid solution
5. Silicic acid	5. Haemoglobin
6. Acid dyes	

Coagulation

- (a) **Coagulation** is the process of converting the colloidal particles in the solution into the insoluble precipitate.
- (b) It is brought about by adding an electrolyte to a colloidal solution (sol).
- (c) When the colloid coagulates or ppt. by adding suitable electrolyte is called **flocculation**.

Hardy-Schulze Rule

A study of coagulation effects of various electrolytes on colloidal solutions give rise to two general rules together known as "**Hardy-Schulze Rule**".

Rule 1

- (a) A positively charged colloid is coagulated by a negative ion and a negatively charged colloid is coagulated by a positive ion.
- (b) The minimum amount of an electrolyte required to coagulate a colloid is called **coagulation value of the colloid**.
- (c) Coagulation value is expressed in millimoles/litre.
- (d) Lower the coagulation value, more efficient is the electrolyte in causing coagulation of a sol.

Rule 2

- (a) Increase in valence of an ion decreases coagulation value of the colloid.
e.g., Decreasing order of coagulating power of various cations and anions.
 $Al^{+3} > Mg^{+2} > Na^{+}$
 $PO_4^{3-} > SO_4^{2-} > Cl^{-}$
- (b) The coagulating powers of the electrolytes to coagulate the same colloidal solution can be calculated as

$$\frac{\text{Coagulating power of electrolyte A}}{\text{Coagulating power of electrolyte B}} = \frac{\text{Coagulating value of B}}{\text{Coagulating value of A}}$$

As_2S_3	$NaCl$	$MgCl_2$	$BaCl_2$	$AlCl_3$
	⁺	⁺²	⁺²	⁺³
C. value	52	0.72	0.69	0.093

Emulsions: Colloidal solution when both dispersed phase and dispersion medium are liquids.





Try Yourself

SECTION - A

Objective Type Questions

- Which is/are correct about the role of a catalyst in a reaction?
 - (1) It is reactant in a rate determining step and then a product of some subsequent step
 - (2) It provides alternate path for the reaction and lowers the activation energy
 - (3) It cannot change the amount of product formed although changes the mechanism
 - (4) All of these
- The migration of positively charged colloidal particles, under an electrical field, towards the cathode is called
 - (1) Cataphoresis
 - (2) Electro-osmosis
 - (3) Sedimentation
 - (4) Electrodialysis
- Freundlich adsorption isotherm gives a straight line on plotting
 - (1) x/m vs P
 - (2) $\log x/m$ vs P
 - (3) $\log x/m$ vs $\log P$
 - (4) x/m vs $1/P$
- Point out the incorrect statement
 - (1) Adsorption may or may not involve the formation of chemical bond between adsorbent and adsorbate
 - (2) At high pressure the Freundlich isotherm acquires a form $x/m \propto p$
 - (3) Physisorption involves formation of multimolecular layers
 - (4) Adsorption involves increase in concentration of one substance over the surface of other
- Which one of the following is a property of physisorption?
 - (1) Non-specific nature
 - (2) High specificity
 - (3) Irreversibility
 - (4) Increases with increase in temperature
- Which can adsorb larger volume of hydrogen gas?
 - (1) Colloidal solution of palladium
 - (2) Finely divided nickel
 - (3) Finely divided platinum
 - (4) Colloidal $\text{Fe}(\text{OH})_3$
- In aerosol, the dispersion medium is
 - (1) Solid
 - (2) Liquid
 - (3) Gas
 - (4) Any of these
- Fog is an example of colloidal system of
 - (1) Liquid dispersed in gas
 - (2) Gas dispersed in gas
 - (3) Solid dispersed in gas
 - (4) Solid dispersed in liquid
- Lyophobic colloids are
 - (1) Reversible colloids
 - (2) Irreversible colloids
 - (3) Protective colloids
 - (4) Gum, proteins
- Above CMC, the surfactant molecule undergoes
 - (1) Association
 - (2) Aggregation
 - (3) Micelle formation
 - (4) All of these
- The critical micelle concentration (CMC) is
 - (1) The concentration above which micelle can be formed
 - (2) The concentration above which true solution is formed
 - (3) The concentration at which one molar electrolyte is present per 1000 gm of solution
 - (4) The concentration at which solute and solution form equilibrium
- The substances which readily form sol when brought in contact with water is called
 - (1) Hydrophobic
 - (2) Hydrophilic
 - (3) Crystalloid
 - (4) Suspension

13. Metals like silver and copper can be obtained in the colloidal state by
 (1) Peptization (2) Bredig's arc method
 (3) Dialysis (4) Coagulation
14. The migration of dispersion medium under the influence of electric current is known as
 (1) Dialysis (2) Electro-osmosis
 (3) Electrophoresis (4) Hydrolysis
15. The Tyndall effect is due to
 (1) Presence of electrical charge on colloidal particles
 (2) Scattering of light by colloidal particles
 (3) Total internal reflection of light
 (4) Total absorption of light
16. Which of the following method is not employed for the purification of colloids?
 (1) Electrodialysis (2) Dialysis
 (3) Ultracentrifugation (4) Peptisation
17. A sol has positively charged colloidal particles. Which of the following solutions is required in lowest concentration for coagulation?
 (1) NaCl (2) $K_4[Fe(CN)_6]$
 (3) $ZnCl_2$ (4) Na_2SO_4
18. The colloidal sol of $Fe(OH)_3$ is
 (1) Negatively charged (2) Positively charged
 (3) No charge (4) Unpredictable
19. When dilute aqueous solution of $AgNO_3$ (excess) is added to KI solution, positively charged sol particles of AgI are formed due to adsorption of ion
 (1) K^+ (2) Ag^+
 (3) I^- (4) NO_3^-
20. Coagulation of colloidal solutions takes place
 (1) By the action of atmospheric oxygen
 (2) By the use of electrolytes
 (3) By allowing it to stand for some time
 (4) By adding protective colloids
21. Which statement is incorrect?
 (1) Higher the gold number of a lyophilic substance better is its protective action
 (2) Lower the gold number of a lyophilic substance better is its protective action
 (3) Bredig's arc method is usually suitable for preparing sols of metals
 (4) The osmotic pressure method can be used to find the average molar mass of a polymer
22. When a few drops of dilute hydrochloric acid is added to freshly precipitated ferric hydroxide, a red coloured sol is obtained. The process is called
 (1) Dissolution (2) Dialysis
 (3) Osmosis (4) Peptization
23. Size of colloidal particle ranges between
 (1) 1 nm to 100 nm (2) 1 nm to 1000 nm
 (3) 10 nm to 1000 nm (4) 100 nm to 1000 nm
24. Which is not a colloidal solution?
 (1) Smoke (2) Ink
 (3) Air (4) Blood
25. Medicines are more effective if they are used in
 (1) Colloidal state (2) Solid state
 (3) Solution state (4) Both (1) & (3)

SECTION - B

Previous Years Questions

1. In Freundlich Adsorption isotherm, the value of $1/n$ is [AIPMT 2012]
 (1) 1 in case of physical adsorption
 (2) 1 in case of chemisorption
 (3) Between 0 and 1 in all cases
 (4) Between 2 and 4 in all cases
2. Which one of the following statement is **incorrect** about enzyme catalysis? [AIPMT 2012]
 (1) Enzymes are denaturated by ultraviolet rays and at high temperature
 (2) Enzymes are least reactive at optimum temperature
 (3) Enzymes are mostly proteinous in nature
 (4) Enzyme action is specific
3. The protecting power of lyophilic colloidal sol is expressed in terms of [AIPMT 2012]
 (1) Critical miscelle concentration
 (2) Oxidation number
 (3) Coagulation value
 (4) Gold number
4. Which property of colloids is not dependent on the charge on colloidal particles? [AIPMT 2012]
 (1) Coagulation (2) Electrophoresis
 (3) Electro-osmosis (4) Tyndall effect

5. Which of the following statements is correct for the spontaneous adsorption of a gas? [AIPMT 2012]
- ΔS is negative and, therefore, ΔH should be highly positive
 - ΔS is negative and therefore, ΔH should be highly negative
 - ΔS is positive and, therefore, ΔH should be negative
 - ΔS is positive and, therefore, ΔH should also be highly positive
6. Which property of colloidal solution is independent of charge on the colloidal particles? [AIPMT-2015]
- Tyndall effect
 - Coagulation
 - Electrophoresis
 - Electro-osmosis
7. Which one of the following characteristics is associated with adsorption? [NEET-2016]
- ΔG and ΔS are negative but ΔH is positive
 - ΔG is negative but ΔH and ΔS are positive
 - ΔG , ΔH and ΔS all are negative
 - ΔG and ΔH are negative but ΔS is positive
8. Fog is a colloidal solution of [NEET-2016]
- Gas in gas
 - Liquid in gas
 - Gas in liquid
 - Solid in gas
9. The coagulation values in millimoles per litre of the electrolytes used for the coagulation of As_2S_3 are given below :
- (NaCl) = 52
 - ($BaCl_2$) = 0.69
 - ($MgSO_4$) = 0.22
- The correct order of their coagulating power is [NEET (Phase-2) 2016]
- I > II > III
 - II > I > III
 - III > II > I
 - III > I > II
10. Which one of the following statements is not correct? [NEET-2017]
- Catalyst does not initiate any reaction
 - The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium
 - Enzymes catalyse mainly bio-chemical reactions
 - Coenzymes increase the catalytic activity of enzyme
11. On which of the following properties does the coagulating power of an ion depend? [NEET-2018]
- The magnitude of the charge on the ion alone
 - Size of the ion alone
 - The sign of charge on the ion alone
 - Both magnitude and sign of the charge on the ion
12. Which mixture of the solutions will lead to the formation of negatively charged colloidal $[AgI]^-$ sol? [NEET-2019]
- 50 mL of 1 M $AgNO_3$ + 50 mL of 1.5 M KI
 - 50 mL of 1 M $AgNO_3$ + 50 mL of 2 M KI
 - 50 mL of 2 M $AgNO_3$ + 50 mL of 1.5 M KI
 - 50 mL of 0.1 M $AgNO_3$ + 50 mL of 0.1 M KI
13. The correct option representing a Freundlich adsorption isotherm is [NEET-2019 (Odisha)]
- $\frac{x}{m} = kp^{-1}$
 - $\frac{x}{m} = kp^{0.3}$
 - $\frac{x}{m} = kp^{2.5}$
 - $\frac{x}{m} = kp^{-0.5}$
14. Match the catalyst with the process [NEET-2019 (Odisha)]
- | Catalyst | Process |
|----------------------------|---|
| (i) V_2O_5 | (a) The oxidation of ethyne to ethanal |
| (ii) $TiCl_4 + Al(CH_3)_3$ | (b) Polymerisation of alkynes |
| (iii) $PdCl_2$ | (c) Oxidation of SO_2 in the manufacture of H_2SO_4 |
| (iv) Nickel complexes | (d) Polymerisation of ethylene |
- Which of the following is the correct option?
- (i)-(c), (ii)-(a), (iii)-(d), (iv)-(b)
 - (i)-(c), (ii)-(d), (iii)-(a), (iv)-(b)
 - (i)-(a), (ii)-(b), (iii)-(c), (iv)-(d)
 - (i)-(a), (ii)-(c), (iii)-(b), (iv)-(d)



Sample Question Paper

Choose the correct answer :

- Distance between nearest opposite ions will be equal to, if edge length of a unit cell having Rock salt structure is 280 pm
 - 140
 - 197.4
 - 240.8
 - 394.8
- Which one of the following molecules is non-linear?
 - C_3O_2
 - CO_2
 - SO_2
 - NO_2^+
- Which one of the following compounds is planar?
 - $N(SiH_3)_3$
 - $N(CH_3)_3$
 - H_2O
 - NH_3
- $A \rightarrow B$ is reaction of 1st order if 750 mmol are consumed out of one mol of A within 462 minutes then specific reaction rate of this process will be
 - 0.003
 - 0.006
 - 0.03
 - 0.06
- If 0.50 mole of $BaCl_2$ is mixed with 0.20 mole of Na_3PO_4 , the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is
 - 0.70
 - 0.50
 - 0.20
 - 0.10
- Electronic configuration of element of least negative value of electron gain enthalpy
 - $3s^2 3p^5$
 - $3s^2 3p^4$
 - $2s^2 2p^4$
 - $4s^2 4p^4$
- The number of photons released when an electron jumps directly from 5th orbit to 2nd orbit in H-atom is
 - 12
 - 6
 - 3
 - 1
- Which one of the following has maximum number of atoms?
 - 200 mL of water at 4°C
 - 44.4 L of CO_2 gas at STP
 - 180 g of glucose
 - 10 g of H_2 gas
- The most electronegative and the most electropositive elements of the periodic table is
 - Li & F
 - F & Ce
 - F & Li
 - F & Cs
- Which one of the following has minimum boiling point?
 - Be
 - Mg
 - Ca
 - Sr
- At 90°C, K_w for water is $10^{-12} M^2$, choose the correct statement
 - pH = 6 and water is acidic
 - pH = 8 and water is basic
 - pH = 6 and water is neutral
 - pH = 8 and water is neutral
- When 25 g of $CaCO_3$ is allowed to dissociate in 1 L container heated to 727°C, 60% of $CaCO_3$ remains undissociated at equilibrium, then K_p is
 - 8.21
 - 82.1
 - 0.0821
 - 821.0

13. Which one of the following statements is true for an irreversible process?
- $\Delta S_{\text{system}} + \Delta S_{\text{surr}} = 0$
 - $\Delta S_{\text{system}} + \Delta S_{\text{surr}} = +ve$
 - $\Delta S_{\text{system}} + \Delta S_{\text{surr}} = -ve$
 - All of these
14. Given that
- $$S(s) + \frac{3}{2} O_2(g) \longrightarrow SO_3(g); \Delta H = -2x \text{ J}$$
- $$SO_2(g) + \frac{1}{2} O_2(g) \longrightarrow SO_3(g); \Delta H = -y \text{ J}$$
- What would be the enthalpy of formation of $SO_3(g)$?
- $-(2x - y) \text{ J}$
 - $(x + y) \text{ J}$
 - $-\left(x + \frac{y}{2}\right) \text{ J}$
 - $-2x \text{ J}$
15. The molecule having one unpaired electron is
- NO
 - CO
 - CN^-
 - O_2
16. In which one of the following reactions, H_2O_2 is a reducing agent?
- $H_2O_2 \longrightarrow H_2O + O_2$
 - $HI + H_2O_2 \longrightarrow H_2O + I_2$
 - $Cl_2 + H_2O_2 \longrightarrow HCl + O_2$
 - $Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + H_2O$
17. Which one of the following is the strongest oxidising agent?
- I_2
 - O_2
 - $KMnO_4$
 - F_2
18. The hydrogen bond is strongest in
- $O - H \cdots S$
 - $S - H \cdots O$
 - $F - H \cdots F$
 - $F - H \cdots O$
19. Which one of the following does not obey Dalton's law of partial pressures?
- $Cl_2 + SO_2$
 - $NH_3 + HCl$
 - $CaCO_3 + CaO$
 - All of these
20. Consider the following chemical species
- $NO_2^{(-)}$
 - $NO_2^{(+)}$
 - NO_2
- The correct increasing bond length of N – O is
- III > II > I
 - II > III > I
 - I > II > III
 - I > III > II
21. Which of the following is not a proper set of Lewis bases?
- $:CCl_2, BeF_3^-, :NH_3$
 - $:CCl_2, B_2H_6, H_2\ddot{O}:$
 - $:NH_3, :\ddot{O} \begin{smallmatrix} R \\ \diagup \end{smallmatrix} \begin{smallmatrix} R \\ \diagdown \end{smallmatrix}, R - \ddot{N}H_2$
 - Both (1) & (2)
22. The principal quantum number of an atom is related to
- Size of orbital
 - Spin angular momentum
 - Orbital angular momentum
 - Orientation of the orbital in space
23. What is the maximum number of orbitals that can be identified with the following quantum numbers?
 $n = 3, l = 1$ and $m_l = 0$
- 2
 - 3
 - 4
 - 1
24. Ionization enthalpy of gaseous Na atom is $495.5 \text{ kJ mol}^{-1}$. The lowest possible frequency of light that ionizes a sodium atom is
- $1.24 \times 10^{15} \text{ s}^{-1}$
 - $3.15 \times 10^{15} \text{ s}^{-1}$
 - $4.76 \times 10^{15} \text{ s}^{-1}$
 - $7.50 \times 10^{15} \text{ s}^{-1}$
25. The normality of 0.3 M phosphorous acid (H_3PO_3) is
- 0.1
 - 0.9
 - 0.3
 - 0.6
26. According to Bohr's theory, $\frac{\text{potential energy}}{\text{kinetic energy}} = x$, then x will be
- 1
 - 1
 - 2
 - $-\frac{1}{2}$

27. If the carbon atom had electronic configuration $1s^6$, then it is violation of
 (1) Hund's rule
 (2) Pauli's exclusion principle
 (3) de Broglie's dual nature
 (4) Heisenberg's uncertainty principle
28. M is molecular weight of $KMnO_4$. The eq. wt. of $KMnO_4$ when it is converted into K_2MnO_4 is
 (1) M (2) $\frac{M}{3}$
 (3) $\frac{M}{5}$ (4) $\frac{M}{7}$
29. The number of radial nodes in $3s$ and $4p$ respectively are
 (1) 2 and 0 (2) 2 and 2
 (3) 2 and 3 (4) 3 and 4
30. Equimolar solutions in the same solvent have
 (1) Same B.P. but different F.P.
 (2) Same concentration
 (3) Same osmotic pressure
 (4) All of these
31. In a lattice cation is shifted to interstitial position, the lattice defect is
 (1) Interstitial defect (2) Vacancy defect
 (3) Frenkel defect (4) Schottky defect
32. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc, then radius of atom is (in pm)
 (1) 100
 (2) 186
 (3) 216
 (4) 294
33. Which statement is correct for E_a ?
 (1) It is less than ΔH for exothermic reaction
 (2) Energy is given or taken from system
 (3) E_a depends on rate constant at constant temperature
 (4) E_a depends on catalyst (positive or negative)
34. Which of the following compounds has to bear highest osmotic pressure if solution is kept with H_2O ?
 (1) 1 M $C_6H_{12}O_6$
 (2) 40 g NaCl in 1 litre
 (3) 0.5 M Hg_2Cl_2
 (4) 60 g urea in 1 litre
35. The rate of reaction between two reactants (A) and (B) decreases by a factor of 4 if the concentration of reactant (B) is reduced to $\frac{1}{4}$. The order of reaction with respect to B is
 (1) 1 (2) 2
 (3) $\frac{1}{2}$ (4) $\frac{1}{4}$
36. If 965 ampere current is flown for 5 minute, then the volume of O_2 evolved during electrolysis of H_2O , at S.T.P. is
 (1) 5.6 L (2) 16.8 L
 (3) 22.4 L (4) 11.2 L
37. Which gas does not form clathrates?
 (1) Xe (2) Kr
 (3) He (4) Ar
38. Which allotrope of S is thermodynamically most stable?
 (1) Plastic 'S' (2) Rhombic 'S'
 (3) Monoclinic 'S' (4) Amorphous 'S'
39. For complete oxidation of 4 L of CO at NTP, the required volume of O_2 at NTP is
 (1) 4 L (2) 8 L
 (3) 2 L (4) 1 L
40. Rate constant of a reaction depends upon
 (1) Concentration (2) Pressure
 (3) Number of moles (4) Catalyst
41. What is the distance between tetrahedral void and octahedral void? (if edge length is a)
 (1) $\frac{a}{\sqrt{2}}$ (2) $\sqrt{2}a$
 (3) $\frac{\sqrt{3}a}{4}$ (4) $\frac{\sqrt{3}a}{2}$

42. At the same temperature which pair of the following solutions are isotonic?
- (1) 0.2 M BaCl_2 and 0.2 M urea
 - (2) 0.1 M urea and 0.1 M NaCl
 - (3) 0.1 M NaCl and 0.1 M K_2SO_4
 - (4) 0.1 M $\text{Ba}(\text{NO}_3)_2$ and 0.1 M Na_2SO_4
43. Kinetic energy of photoelectrons in two different experiments of photoelectric effect were found in the ratio of 2 : 1. If frequencies of these radiations were ν_1 and ν_2 , then what should be threshold frequency?
- (1) $2\nu_2 - \nu_1$
 - (2) $\nu_2 - \nu_1$
 - (3) $\nu_2 - 2\nu_1$
 - (4) $\nu_1 - 3\nu_2$
44. Maximum number of electrons having $m = 0$ in Ar (per atom)
- (1) 8
 - (2) 10
 - (3) 0
 - (4) 2
45. Among the following, the minimum packing efficiency is of
- (1) BCC
 - (2) SCC
 - (3) FCC
 - (4) HCP



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ANSWERS

Chapter 1 : Some Basic Concepts of Chemistry

Section A : Objective Type Questions

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|---------|---------|---------|---------|---------|---------|---------|
| 1. (2) | 2. (3) | 3. (2) | 4. (1) | 5. (1) | 6. (1) | 7. (2) |
| 8. (2) | 9. (1) | 10. (2) | 11. (4) | 12. (2) | 13. (1) | 14. (2) |
| 15. (3) | 16. (4) | 17. (3) | 18. (1) | 19. (4) | 20. (4) | |

Section - B : Previous Years Questions

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

Chapter 2 : Structure of Atom

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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

Chapter 3 : Classification of Elements and Periodicity in Properties

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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|--------|--------|--------|------------|--------|--------|--------|
| 1. (3) | 2. (2) | 3. (4) | 4. (3 & 4) | 5. (2) | 6. (2) | 7. (1) |
|--------|--------|--------|------------|--------|--------|--------|

Chapter 4 : Chemical Bonding and Molecular Structure

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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|---------|---------|---------|---------|---------|-------------|---------|
| 1. (2) | 2. (2) | 3. (3) | 4. (4) | 5. (1) | 6. (4) | 7. (2) |
| 8. (1) | 9. (1) | 10. (1) | 11. (3) | 12. (2) | 13. (2) | 14. (4) |
| 15. (2) | 16. (3) | 17. (1) | 18. (1) | 19. (3) | 20. (3) | 21. (3) |
| 22. (2) | 23. (2) | 24. (3) | 25. (3) | 26. (3) | 27. (1 & 4) | 28. (1) |
| 29. (3) | 30. (3) | 31. (4) | 32. (3) | 33. (2) | 34. (3) | 35. (2) |
| 36. (3) | 37. (2) | 38. (1) | 39. (3) | 40. (3) | | |

Chapter 5 : States of Matter

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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|--------|--------|---------|---------|---------|--------|--------|
| 1. (2) | 2. (3) | 3. (3) | 4. (2) | 5. (3) | 6. (3) | 7. (2) |
| 8. (3) | 9. (1) | 10. (3) | 11. (1) | 12. (4) | | |

Chapter 6 : Thermodynamics

Section A : Objective Type Questions

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|---------|---------|---------|---------|---------|---------|---------|
| 1. (3) | 2. (2) | 3. (3) | 4. (3) | 5. (3) | 6. (2) | 7. (2) |
| 8. (2) | 9. (3) | 10. (1) | 11. (3) | 12. (3) | 13. (3) | 14. (4) |
| 15. (1) | 16. (2) | 17. (1) | 18. (2) | 19. (3) | 20. (3) | 21. (4) |
| 22. (2) | 23. (1) | 24. (2) | 25. (1) | 26. (2) | 27. (1) | 28. (2) |
| 29. (2) | 30. (1) | 31. (2) | 32. (2) | 33. (1) | 34. (3) | 35. (2) |

Section - B : Previous Years Questions

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|------------|---------|---------|---------|---------|---------|---------|
| 1. (3) | 2. (3) | 3. (1) | 4. (4) | 5. (2) | 6. (2) | 7. (3) |
| 8. (2 & 4) | 9. (2) | 10. (3) | 11. (2) | 12. (4) | 13. (1) | 14. (4) |
| 15. (3) | 16. (1) | | | | | |

Chapter 7 : Equilibrium

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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|---------|---------|---------|---------|---------|---------|---------|
| 1. (3) | 2. (4) | 3. (3) | 4. (3) | 5. (3) | 6. (2) | 7. (4) |
| 8. (1) | 9. (3) | 10. (2) | 11. (4) | 12. (1) | 13. (4) | 14. (3) |
| 15. (3) | 16. (3) | 17. (3) | 18. (1) | 19. (2) | 20. (1) | 21. (2) |
| 22. (3) | 23. (2) | 24. (1) | 25. (2) | 26. (4) | 27. (1) | 28. (1) |
| 29. (3) | 30. (1) | 31. (3) | 32. (3) | 33. (4) | 34. (4) | 35. (4) |

Chapter 8 : Redox Reactions and Electrochemistry

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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

Chapter 9 : Solid State

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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

Chapter 10 : Solutions

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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|---------|---------|---------|---------|---------|---------|---------|
| 1. (2) | 2. (2) | 3. (3) | 4. (2) | 5. (3) | 6. (2) | 7. (1) |
| 8. (2) | 9. (2) | 10. (4) | 11. (4) | 12. (2) | 13. (4) | 14. (1) |
| 15. (3) | 16. (2) | | | | | |

Chapter 11 : Chemical Kinetics

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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

Chapter 12 : Surface Chemistry

Section A : Objective Type Questions

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

Section - B : Previous Years Questions

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

Sample Question Paper

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

