CHEMISTRY
MODULE-I

PHYSICAL CHEMISTRY-I
for
JEE
(MAIN & ADVANCED)

Fully Solved

Ranveer Singh

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MODULE-I

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for

JEE

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About the Author

Ranveer Singh has an M.Sc. in Chemistry and has been mentoring and teaching Chemistry to JEE aspirants for more than 15 years. He aims for perfection and has an enormous passion when it comes to applying new methods to create solutions. These are the qualities that make him stand out from the crowd as a teacher and instructor.

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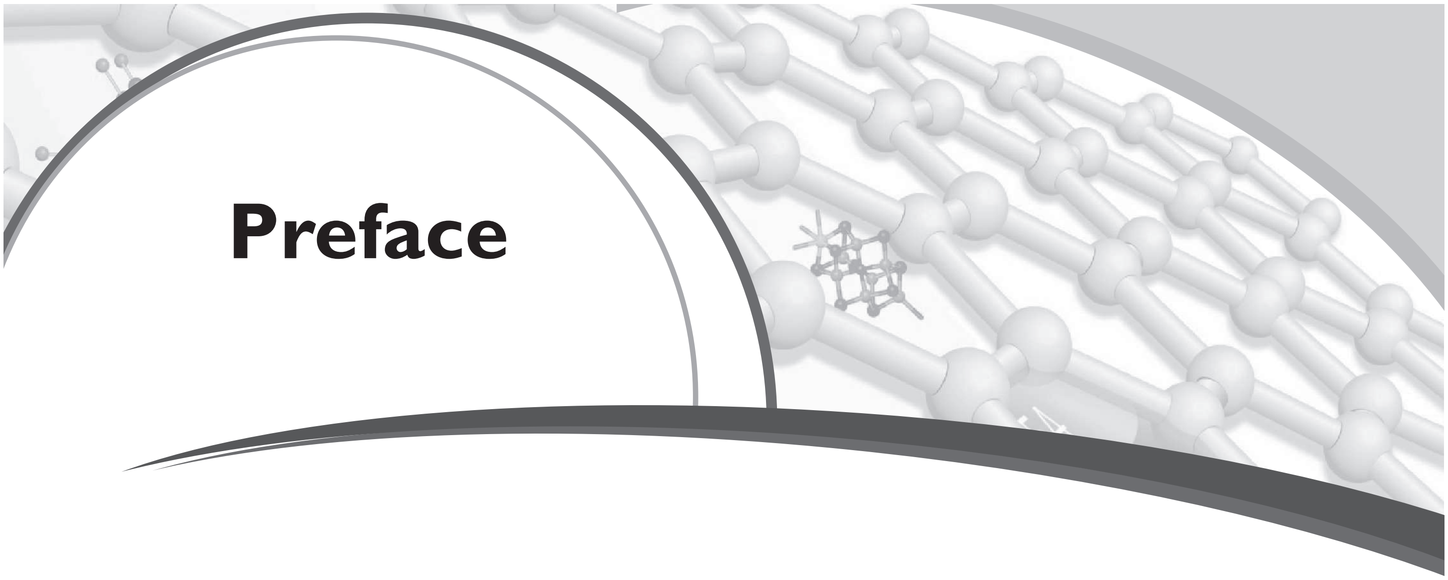
Dedicated
to
Shri Amar Chand Ji Maharaj



Preface

Chemistry forms an important part of all entrance tests. In my teaching career, spanning over a decade and half, I have felt that a chemistry book based on the changing perceptions, needs, feedback and the experiences of the students and educators is needed by the engineering aspirants. It is with this vision that the present book has been written.

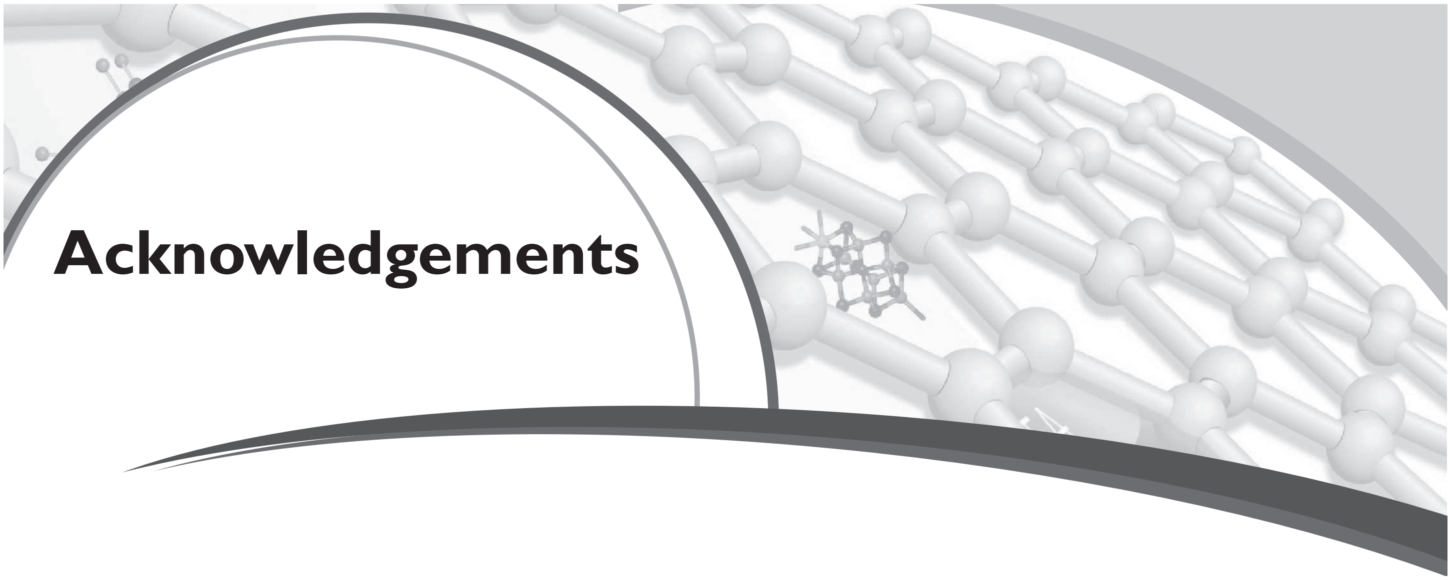
This book is not a textbook. It is a refresher text to help students revise their lessons in the quickest possible way and in the most effective manner. It does not over emphasise theories, as has been done in several other competitive books available in the market. However, every care has been taken to ensure that no important theory is left out. This book has several new features: coverage of the syllabus of JEE (Main + Advanced); a great number of solved numerical examples to acquaint students with the application of several theories, solution at the end of each exercise and two levels of questions at the end of the chapters to give readers an opportunity to assess their understanding of the chapters. The use of easily understandable language is at the core of the author's efforts.

The exercises given at the end of every chapter is further categorised into three difficulty level of questions and their patterns asked in JEE along with the previous year questions with solutions.

- Level-I has the questions mainly suitable for JEE Main exam.
- Level-II contains slightly difficult questions suitable for JEE Advanced.
- Level-III has the highest questions of various patterns asked in JEEAdvanced (such as more than one correct answer, comprehension, match the column and single digit integer).

I hope this book will help in motivating and encouraging the students towards the preparation forthe Chemistry portion of the examinations. Every care has been taken to make the book error-free. However, some mistakes may have been crept in inadvertently. Constructive suggestions and comments from students and teachers would encourage me to make the book more authentic and acceptable in the next edition. We wish our young readers a great success at the engineering entrance examinations.

Ranveer Singh



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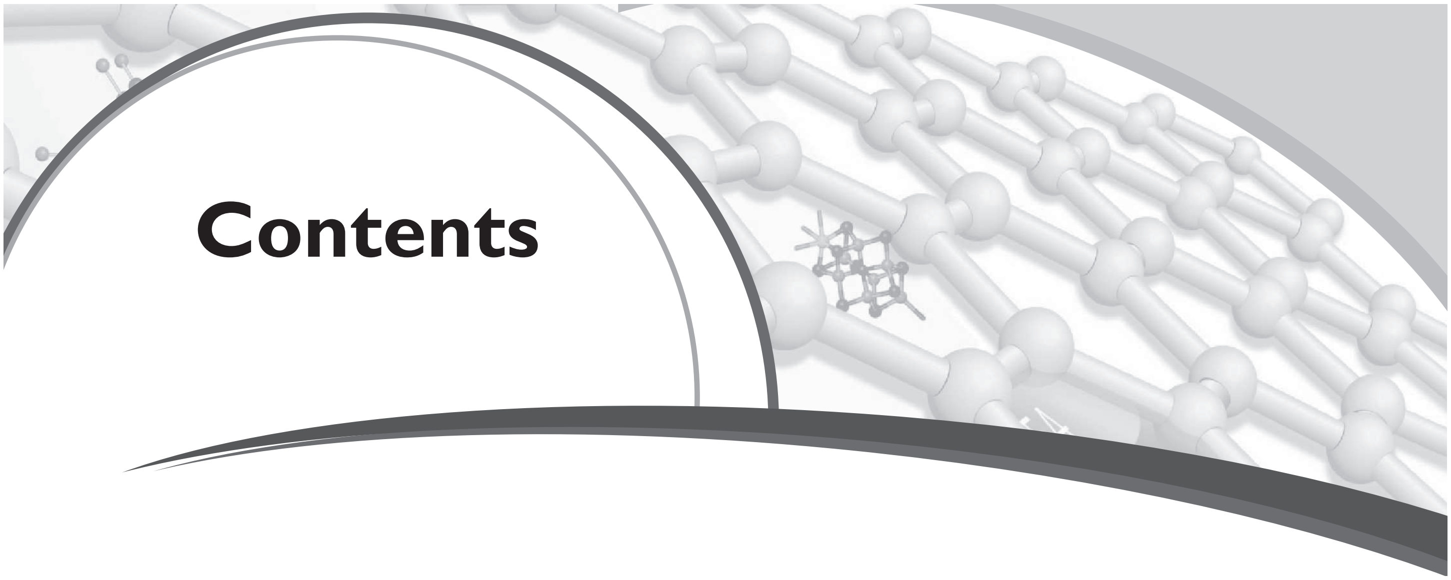

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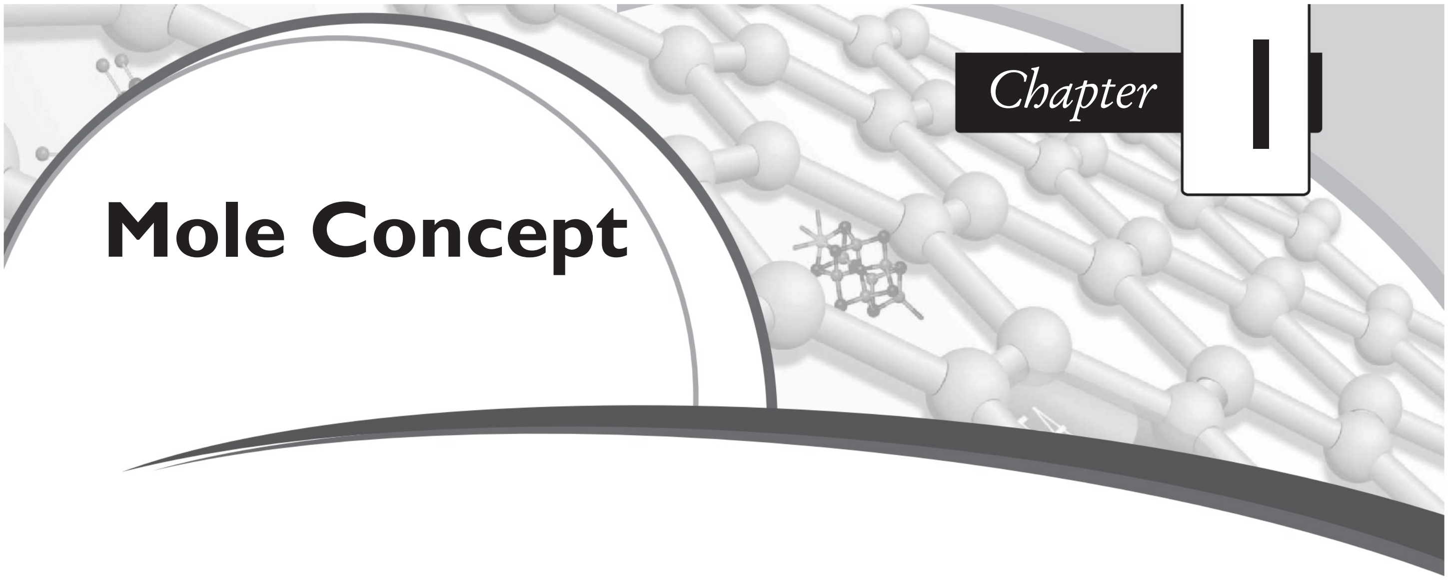


Chapter 1

Mole Concept

Key Concepts

Mole in Latin means 'heap' or 'mass' or 'pile'. A mole of atoms is a collection of atoms whose total weight is the number of grams equal to the atomic weight.

The mole is defined as the amount of a substance containing as many atoms, molecules, ions, electrons or other elementary entities as there are carbon atoms in exactly 12 g of C^{12}. Hence, 1 mole is a collection of 6.022×10^{23} particles which is known as the Avogadro Number

$$1\ N_A = 6.022 \times 10^{23}$$

METHOD OF CALCULATION OF MOLE

(i) If the number of species is given then

$$\text{Number of moles} = \frac{\text{Number of atom}}{6.022 \times 10^{23}}$$

(ii) If the weight of an element is given then

$$\text{Number of moles} = \frac{\text{Weight in gram}}{\text{Atomic weight}}$$

(iii) If the weight of a molecule is given

$$\text{Number of moles} = \frac{\text{Weight in gram}}{\text{Molecular weight}}$$

(iv) Calculation of moles for ideal gases. We know

$$PV = nRT$$

$$\therefore \quad n = \frac{P_{\text{atm}} \times V_{\text{liter}}}{0.0821 \times T_{\text{Kelvin}}}$$

P = Pressure exerted by gas (no force of attraction between them)

1 atm = 760 mm Hg or 76 cm Hg

V = Volume of gas (free volume available for the motion of gas molecule

1 Liter = 10^{-3} m^3

T = Temperature in Kelvin

R = Universal gas constant

= 0.0821 L atom K^{-1} mol^{-1}

= 8.314 J K^{-1} mol^{-1}

= 1.987 cal K^{-1} mol^{-1}

STP or NTP ⇒ Temperature 273 k and P = 1 atm but in thermodynamics, T = 298 k.

⇒ Volume of 1 mole of gas at STP is 22.4 L

⇒ Volume of 1 mole of gas at 300 k is 24.63 L

⇒ Number of moles of solute = Molarity × Volume of solution in Liter

AVERAGE ATOMIC MASS

It is defined as the mass of all atoms divided by number of atoms.

AVERAGE MOLECULAR MASS

It is defined as the total mass of molecules divided by number of molecules

$$\text{Average molecular mass} = \frac{x_1M_1 + x_2M_2 + x_3M_3 \ldots}{x_1 + x_2 + x_3 + \ldots}$$

where M_1, M_2, M_3 are the molecular masses of compound whose abundance x_1, x_2, x_3 ….

⇒ It is in terms of number of moles or in terms of molecules

⇒ If $x_1 + x_2 + x_3 + \ldots = 100$ then it is called percentage abundance

MOLECULAR FORMULAE AND EMPIRICAL FORMULAE

Molecular formulae: The actual number of atoms of various elements present in the compound, e.g., $C_6H_{12}O_6$.

Empirical formulae: The simplest whole number ratio of atom in element present in compound, e.g., E.F. of glucose ($C_6H_{12}O_6$) is CH_2O which shows that carbon, hydrogen and oxygen combined in simple ratio 1 : 2 : 1.

Relation between M.F. and E.F.

Molecular Formula = n[Empirical formula]

$$n = 1, 2, 3, \ldots..$$

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

Step for Determination of Empirical Formulae

(i) Divide % of atom by its atomic mass. It gives relative number of moles of various elements present in the compound.

(ii) Divide relative number of moles obtained in Step (i) by the smallest mole so as to get simple ratio of moles of various elements present in compound.

(iii) If simple ratio of mole is a fractional value, then the value of simple ratio of moles of each element is multiplied by smallest integer so as to get simplest whole number ratio of each element present in the compound.

Determination of Molecular Formulae

(i) When the molecular mass is given

Suppose Empirical formula = C_3H_6O and

Molecular mass = 174

$$n = \frac{174}{58} = 3$$

then M.M. = $3[C_3H_6O] = C_9H_{18}O_3$

(ii) When number of any atom is given

Suppose EF is C_3H_6O and given that number of oxygen atom is 2.

then MF = $[C_3H_6O] \times 2 = C_6H_{12}O_6$

(iii) When the vapour density is given

(only for gas and vapour)

$$n = \frac{2 \times \text{VD}}{\text{Molecular weight}}$$

STOICHIOMETRY

It deals with the calculation of quantities of various reactants and products in a chemical reaction.

The numerical used to balance a chemical reaction is known as *stoichiometric coefficient*.

Balanced equations gives the qualitative and quantitative information.

N_2	+	$3H_2$	→	$2\,NH_3$
Nitrogen		Hydrogen		Ammonia
1 mole		3 mole		2 mole
28 gram		6 gram		34 gram
N_A molecules		$3\,N_A$		$2\,N_A$
22.4 litre		3 × 22.4 litre		2 × 22.4 litre

Steps for Using Mole Method in Problem

(i) Write down a balanced chemical reaction.

(ii) Calculate the number of moles known substance.

(iii) Write down the number of moles of known substance under the chemical reaction and relate them.

SOLUTION AND CONCENTRATION TERM

Solution is defined at a homogenous mixture of more than one substance in which one is solvent and rest solute.

Which substance is solute or solvent is controversial and can be concluded in the following cases:

Case I: When substances forming solution are in different states, the final state of solution will be solvent irrespective of substances.

Case II: When substances forming solution are in the same state, then the solvent is one which is present in large amount.

Amounts compared should be in mass and mole.

Some hints are given in the question like A in B. Then A is solute and B is solvent.

All the concentrated terms defined are applicable only for homogenous mixture and not for heterogeneous mixture.

1. Density = $\dfrac{\text{Weight of solute}}{\text{Volume of solution}}$

Unit is either in g/mL or g/litre

Temperature is dependent because Mass $\not\propto T$ but volume is depend upon temperature ($T \propto V$).

$\therefore$ T inversily proportional to

$$\frac{\text{Weight of solute}}{\text{Volume of solution}}(\text{density}) \text{ except water}$$

2. Mass percentage or percentage mass $\dfrac{\text{W}}{\text{W}}\%$

$$\frac{\text{W}}{\text{W}}\% = \frac{\text{Weight of Solute}}{\text{Weight of solution}} \times 100$$

Temperature independent

For example, 20% mass of NaOH solution means 100 g of solution contains 20 g of NaOH and mass of solvent is 80 g.

3. % weight by volume or $\dfrac{\text{W}}{\text{V}}\%$ or % by volume.

$$\frac{\text{W}}{\text{V}}\% = \frac{\text{Weight of Solute}}{\text{Volume of solution}} \times 100$$

4. % volume by volume or $\dfrac{V}{V}\%$ or % by volume.

$$\frac{\text{V}}{\text{V}}\% = \frac{\text{Volume of Solute}}{\text{Volume of solution}} \times 100$$

Molarity

$$M = \frac{\text{Moles of solute}}{\text{Volume in liter}}$$

Temperature dependent

For example, 2 M NaCl solution means 1 L solution contains 2 moles of NaCl.

MOLARITY OF PURE SUBSTANCE

1 mL = 1 g

1000 mL = 1000 g = 55.56 moles

$\therefore$ moles in 1 L pure solution

$$= \frac{\frac{\text{weight}}{\text{Molar mass}}}{\text{Volume in liter}} = \frac{55.56 \text{ mole}}{1 \text{ liter}} = \text{Molarity} = 55.56 \text{ M}$$

MOLALITY [m]

Number of moles of solute in 1 kg solvent.
So temperature is independent.
For example, 2 m solution of NaCl means 2 moles of NaCl present in 1000 g of solvent.

MOLE FRACTION

Ratio of moles of one component to the total number of moles of solution.

A	B	C	
n_A	n_B	n_C	Number of moles
X_A	X_B	X_C	mole fraction

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

and $\Sigma x = 1$

or $x_A + x_B + x_C = 1$

For binary solution $x_A + x_B = 1$

$$X_B = 1 - x_A$$

$\text{Log}_{10}[x_A + x_B + x_C] = \log_{10} 1 = 0$

If $\Sigma n = 1$

$$X_A = n_A$$

It means MF of A = mole of A.

PPM and PPB (Parts per million and Parts per billion)

$$\textbf{PPM} = \frac{\text{Parts of solute}}{\text{Parts of solution}} \times 10^6$$

$$\textbf{PPB} = \frac{\text{Parts of solute}}{\text{Parts of solution}} \times 10^9$$

For gases

$$\textbf{PPM} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 10^6$$

$$\textbf{PPB} = \frac{\text{Moles of solute}}{\text{Moles of solution}} \times 10^9$$

→ For gases parts = volume = moles

→ For solid/liquid parts = weight

For solid/liquid

$$\textbf{PPM} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 10^6$$

$$\textbf{PPB} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 10^9$$

→ For dilute solution
(Weight of Solute ≃ Weight of Solution)

$$\textbf{PPM} = \frac{\text{weight of solute}}{\text{weight of solvent}} \times 10^6$$

TYPICAL CONCENTRATION TERMS

These concentrated terms are typical because they are defined exclusively for the substance concerned depending on what purpose those substances are used.

Concentration of H_2O_2: H_2O_2 is used as a source of oxygen gas and hence the typical concentration of H_2O_2 gives the value of oxygen obtained from the given solution. Since it decomposes according to following reaction:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Definition of concentration term of H_2O_2: "x volume H_2O_2" means 1 L of H_2O_2 gives x L of O_2 gas at STP.

For example, 20 volume H_2O_2 means 1 L of H_2O_2 gives 20 L of O_2 at STP. It can be converted to normal concentration.

CONCENTRATION OF OLEUM

Oleum is considered as a solution of SO_3 gas dissolved in H_2SO_4. $H_2S_2O_7$ is a type of oleum and 1 mole of SO_3 and 1 mole of H_2SO_4.

H_2SO_4	SO_3	$H_2S_2O_7$
Liquid	Gas	
Solvent	solute	solution

Concentration of oleum is defined in such a way that it gives an idea of amount of H_2SO_4 it can give.

Concentration of oleum is given by x % oleum. It means 100 g of oleum sample can maxima give x g of H_2SO_4 by the addition of (x – 100) g of water.

For example, **109 % oleum** means 100 g oleum is capable of giving 109 g H_2SO_4 by adding 9 g of H_2O in 100 g of oleum.

An oleum sample labelled as x % implies the (x – 100) g of H_2O will be required to react with all the SO_3 present in 100 g of oleum according to the following reaction:

$$H_2O + SO_3 \rightarrow H_2SO_4 \text{ in 100 g oleum}$$

So, number of mole of water required = number of moles of SO_3 gas present in Oleum

x % Oleum	**Max. H_2SO_4**	w_{H_2O}	$n_{H_2O} = n_{SO_3}$	w_{SO_3}	$w_{H_2SO_4}$
104.5%	104.5	4.5	0.25	$0.25 \times 80 = 20$	$100 - 20 = 80$
109%	109	9	0.5	$0.5 \times 80 = 40$	60
118%	118	18	1	$1 \times 80 = 80$	20

ANALYSIS OF GASEOUS REACTION [EUDIOMETRY]

This method is used to determine the composition of gaseous mixture or to find out the M.F. of an unknown compound.

It is based on 'Gay Lussac Law of combining volume'.

This law states that gaseous reaction volume of reactant consumed and volume of product obtained [at fixed T and P] are in a simple whole number ratio [which is same as the ratio of Stoichiometric coefficient of balanced reaction].

For example, from experiment it was found that 10 L of N_2 require 30 L of H_2 to produce 20 L NH_3.

$\therefore$ volume ratio = 1 : 3 : 2 [Stoichiometric coefficient]

Since the reaction is carried out at constant T and P, then, volume of gaseous mixture is directly proportional to number of moles of gases and change in volume is proportional to change in number of moles of gases.

$$V \propto n$$

$$\therefore \quad \Delta V \propto \Delta n$$

This expression can be used if pressure of individual species used [at constant T and V]

$$P \propto n$$

$$\Delta P \propto \Delta n$$

$$\begin{array}{lllll} \text{Hence, for} & N_2 & + \quad 3H_2 & \rightarrow & 2NH_3 \\ & 1 \text{ mole} & \quad\;\; 3 \text{ mole} & & 2 \text{ mole} \\ & 1 \text{ atm of } N_2 & \quad\;\; 3 \text{ atm of } N_2 & & 2 \text{ atm of } NH_3 \end{array}$$

So $\quad V \propto n \quad$ [at constant T and P]

$\quad\;\; P \propto n \quad$ [at constant T and V]

Example: 10 mL of alkane on complete combustion gives 30 mL of CO_2. Calculate molecular formula?

$$\begin{array}{lllll} C_xH_y & + \left[x + \dfrac{y}{4}\right] O_2 & \rightarrow & xCO_2 & + \quad \dfrac{y}{2} H_2O \\ 1 \text{ mole} & \text{gives} & & x \text{ mole} & \\ 1 \text{ mL} & \text{give} & & x \text{ mL} & \\ 10 \text{ mL} & & & 10 \times x \text{ mL} = 30 \text{ mL given} & \\ \text{and} & & & x = 3 & \\ 10 \text{ mL} & 10\left[x + \dfrac{y}{2}\right] \text{ml} & & 10x \text{ mL} & 10 \times \dfrac{y}{2} \text{ mL} \end{array}$$

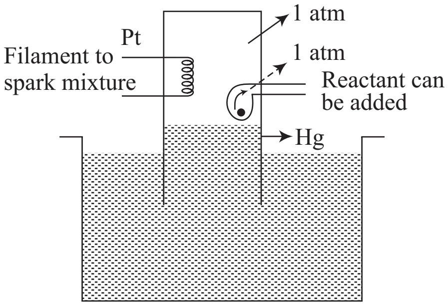
Since, molecular formula of alkane $C_xH_{2x+2} = C_x H_y$

So, $\quad y = 8$

Therefore, molecular formula = C_3H_8

ANALYSIS OF GASEOUS SUBSTANCES IN EUDIOMETRIC TUBES

Gaseous reactions are studied in this tube. After the completion of reaction, the reaction is brought back to original temperature.



Eudiometric Tube

Fig. 1.1

To estimate the volume of each gas, certain solvents are used.

	Solvent	**Gases absorbed**
1.	KOH	CO_2, SO_2, Cl_2
2.	$CuSO_4/CaCl_2$	H_2O (g)
3.	H_2O	NH_3, HCl
4.	Terpentine oil	O_3
5.	Alk. Pyrogallol	O_2
6.	Ammonical Cu_2Cl_2	CO

We will consider only the volume of gases and not of solid and liquid as they have very less volume compared to gas. Hence, the volume of solids and liquids is neglected with respect to gases.

Whenever water is formed inside the eudiometric tube, it is always assumed to be liquid until a minimum temperature of 100°C.

It is used in the following combinations:

(i) Combustion of all organic compound.
(ii) Reaction of H_2 with O_2.
(iii) Dissociation or formation of NH_3.
(iv) Reaction between N_2 and O_2 never occur inside the eudiometric tube as it requires very high temperature.
(v) H_2 when reacts with certain oxide gives H_2O.
(vi) Whenever a substance is added in eudiometric tube for a particular reaction, it is always assumed to be taken in excess.

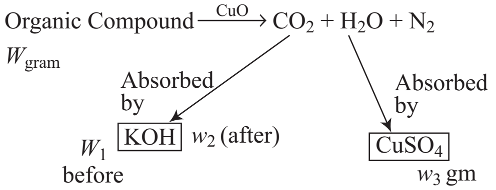
EXPERIMENTAL METHODS FOR DETERMINATION OF ELEMENTS IN ORGANIC COMPOUND

A sample of organic compound on qualitative analysis (with elements present) was found to contain C S H N P O X. The following experiment were performed. Calculate % composition of each element.

A w g sample was burned in the presence of CuO to cause oxidation of C, H and N only (CO_2, H_2O, N_2). The gaseous mixture was passed through a solution of KOH weighing w_1 g. The final weight after passing the gases was w_2. The remaining gases on passing through white $CuSO_4$ crystal to convert into blue crystal (hydrated $CuSO_4$) caused a weight rise of w_3 g.

The remaining gas was collected over H_2O at T Kelvin. [Any gas collected over H_2O is present with some water vapour]. Total pressure observed was ‘P atm’. Value of displaced liquid was V mL and T. If aq. tension of H_2O at T is P_1 atm [aq. tension at any temperature is defined as maximum pressure which can be exerted by water vapour in equilibrium with water in liquid form], calculate the composition of each element. From first experiment

[Liebig Method]



Weight rise in KOH = $w_2 - w_1 = w_{CO_2}$

Since all CO_2 obtain from Organic Compound

$$\therefore \quad n_C = n_{CO_2} \Rightarrow \frac{w_2 - w_1}{44}$$

$\therefore$ % of Carbon in Organic Compound

$$= \frac{1}{44}\ \frac{w_2 - w_1}{W} \times 12 \times 100$$

$$\text{Moles of } H_2O = \frac{w_3}{18} = n_{H_2O} = n_{H_2}$$

$$\therefore \quad \text{moles of } H_2 = \frac{w_3}{18}$$

$$\therefore \quad \text{weight of } H_2 = \frac{w_3}{18} \times 2$$

$$\therefore \quad \text{\% of H in Organic Compound} = \frac{w_3}{18} \times \frac{2}{W} \times 100$$

From second experiment : [Duma Method]

$$\text{Organic Compound} \xrightarrow{CuO} H_2O + CO_2 + N_2$$

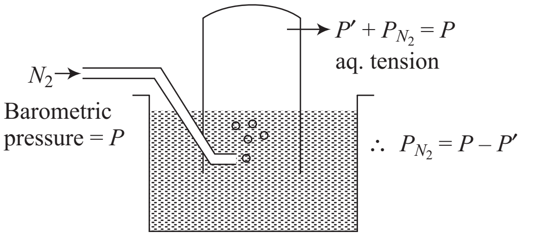


Fig. 1.2

$$n_{N_2} = \frac{P_{N_2}\cdot V_{N_2}}{R\cdot T_{N_2}} \quad \text{but} \quad \text{\% N in Organic Compound}$$

$$= \frac{w_{N_2}}{W} \times 100$$

$$\therefore \quad \%N = \frac{n_{N_2} \times 28 \times 100}{W}$$

$$\text{and} \quad n_{N_2} = \frac{[P-P']V\ \text{ml} \times 10^{-3}}{RT}$$

$$\therefore \quad \%\ N = \left[\frac{(P-P')V\ \text{ml} \times 10^{-3}}{RT}\right] \times \frac{28}{W} \times 100$$

ESTIMATION OF N_2 INFORM OF NH_3 IN SOLUTION KJELDOHL’S METHOD

W g sample was reacted with concentrated H_2SO_4 to cause conversion of all N_2 present in the compound. Ammonium sulphate $(NH_4)_2SO_4$ solution was then added with excess of NaOH and all NH_3 librated was reacted with H_2SO_4 solution having molarity M_1 and volume V_1 liter. The residual acid was reacted with NaOH solution and it was observed that V_2 liter of NaOH molarity M_2 was required to complete naturalization of residual acid. Calculate % composition of N_2 from above data?

Sol. $$\underset{W\text{ gram}}{\text{Organic Compound}} \xrightarrow[M_1V_1]{\text{con.}H_2SO_4} (NH_4)_2SO_4$$

$$\xrightarrow[M_2V_2]{\text{NaOH (for neutralisation of excess } H_2SO_4)} NH_3$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2\,SO_4$$

and

$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2H_2O$$

$$\frac{1}{2}M_2V_2\ M_2V_2$$

(i) $\underset{\text{(react with NaOH)}}{n_{H_2SO_4}} = \dfrac{M_2V_2}{2}$

(ii) $\underset{\text{react with } NH_3}{n_{H_2SO_4}} = \left[M_1V_1 - \dfrac{M_2V_2}{2}\right]$

(iii) $\therefore\ n_{NH_3} = 2\left[M_1V_1 - \dfrac{M_2V_2}{2}\right]$

(iv) % N in OC = $\left[\dfrac{1 \times n_{NH_3} \times 14}{W}\right] \times 100$

$$= \frac{\left\{2\left[M_1V_1 - \dfrac{M_2V_2}{2}\right] \times 14\right\}}{W} \times 100$$

CARIUS METHOD [IDENTIFICATION OF HALOGEN EXCEPT FLUORINE]

$$\text{Organic Compound } W_{\text{gram}} \xrightarrow{HNO_3} X^-$$

$$\text{ion in solution} \xrightarrow{AgNO_3} AgX$$

W Gram

W g of Organic Compound is reacted with concentrated HNO_3, then $AgNO_3$ solution is added in the remaining solution (containing halide ion solution which is obtained by reaction between Organic Compound and concentrated HNO_3). Weight of residue will be formed if w_1 g white precipitate, w_2 g of AgBr (pale yellow precipitate) and w_3 g of AgI (bright yellow precipitate) are formed. Then calculate % composition of Cl, Br and iodine.

$$\% W_{Cl} \text{ in Organic Compound} = \frac{w_{Cl}}{W} \times 100$$

$$= \frac{1 \times n[\text{AgCl}] \times 35.5 \times 100}{W} \text{ (using POAC)}$$

$$\% W_{Cl} \text{ in Organic Compound} = \frac{1 \times w_1 \times 35.5}{143.5 \times W} \times 100$$

as same

$$\% W_{Br} \text{ in Organic Compound} = \frac{1 \times w_2}{188} \times \frac{80}{W} \times 100$$

$$\% W_{I} \text{ in Organic Compound} = \frac{1 \times w_3}{235 \times W} \times 127 \times 100$$

ESTIMATION OF SULPHUR

W g sample of Organic Compound was reacted with concentrated HNO_3. The remaining solution containing H_2SO_4 (obtained after all the sulphure gets oxidised to SO_3 and then to H_2SO_4) was reacted with excess of $BaCl_2$ solution and w_1 g of white ppt of $BaSO_4$ was obtained. Calculate % composition of sulphur.

$$\% \text{ S} = \frac{w_S}{W} \times 100 = \frac{1 \times w_1 \times 32}{W \times 233} \times 100$$

ESTIMATION OF PHOSPHORUS

$$\text{Organic Compound} \xrightarrow{HNO_3} H_3PO_4 \xrightarrow[\text{[MgSO}_4 + \text{NH}_4\text{Cl]}]{\text{Magnesia mixture}}$$

$$\text{Mg(NH}_4\text{)PO}_4 \xrightarrow{\Delta} Mg_2P_2O_7 \text{ (white ppt)}$$

W g sample of Organic Compound was reacted with HNO_3. All phosphorous after being oxidised to H_3PO_4 was reacted with magnesia mixture and a yellow precipitate was obtained, which on heating gives w_1 g of white precipitate of $Mg_2P_2O_7$. Calculate % of P in Organic Compound.

$$\% \text{ of } P \text{ in Organic Compound} = \frac{w_P}{W} \times 100$$

$$= \frac{2 \times w_1}{222} \times \frac{31}{W} \times 100$$

From

$$\frac{2[n_{Mg_2P_2O_7}]}{W} \times 31 \times 100$$

ESTIMATION OF OXYGEN

Weight of oxygen in Organic Compound

= Weight of organic compound – W'

[sum of weight of all element]

EXPERIMENTAL METHODS FOR DETERMINATION OF ATOMIC MASS OF METALS

Dulong Petit's law

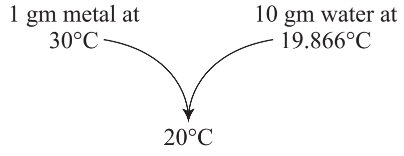
Atomic weight × Specific heat of compound ≥ 6.4

(i) This is experimental law.

(ii) Specific heat should be measured in calorie/gram.

(iii) The above expression given is approximately Atomic weight.

1 g of metal at 30º was immersed in 10 g of water at 19.886 ºC. If the final temperature is 20ºC then predict that metal could be iron (Specific heat of H_2O = 1 cal/g).



Heat lost by metal = Heat gained by water

$$m_1 C_1 \Delta t_1 = m_2 C_2 \, \Delta t_2$$

$$1 \times C_1 \times [30 - 20] = 10 \times 1[20 - 19.886]$$

$$\therefore \quad C_1 = 0.114$$

$$\therefore \quad \text{Atomic mass} = \frac{6.4}{0.114} = 56.2$$

DETERMINATION OF MOLECULAR MASS [VICTOR MAYER METHOD]

$$PV = nRT = \frac{\text{Weight}}{\text{Molar Mass}} \times RT$$

$$M \text{ Mass} = \frac{W\,RT}{(P - P')V}$$

$$V_{air} \text{ displaced} = V_{vapour}$$

and $$P_{air} \text{ displaced} = P_{vapour}$$

and $$\frac{w}{\text{Molar mass}} = \frac{(P - P')V}{RT}$$

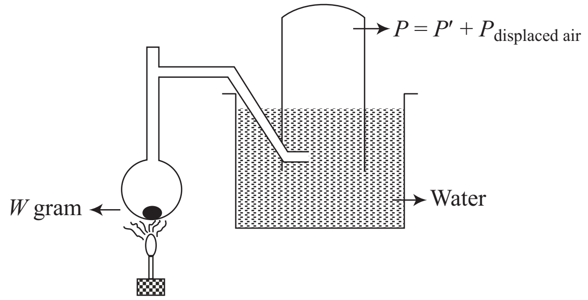


Fig. 1.3

$$\therefore \quad P_{displaced\ air} = (P - P')$$

Vapour of volatile substance are collected over water and measured by the method as Duma's method.

DETERMINATION OF MOLECULAR MASS OF ORGANIC ACID SILVER SALT METHOD

Hydrogen connected to a more electronegative atom is acidic.

Basicity is defined as the number moles of hydrogen ion in 1 mole of given acid.

$$\text{Organic Acid} \xrightarrow{AgNO_3 \text{ soluton}} \text{Silver salt} \xrightarrow{\Delta} Ag$$

For monobasic Acid (CH_3COOH)

$$\begin{array}{lll} HX \xrightarrow{AgNO_3} & AgX \xrightarrow{\Delta} & Ag \\ CH_3COOH & w_1 & w_2 \end{array}$$

Applying POAC on Ag Atom

$$\frac{w_1}{\text{Molar Mass of AgX}} = \frac{w_2}{\text{Atomic Mass of Ag}}$$

$$\therefore \quad \text{Molar Mass of AgX} = \frac{w_1}{w_2} \times \text{Atomic Mass of Ag}$$

$$= \frac{w_1}{w_2} \times 108$$

and Molar Mass of AgX = Atomic Mass of Ag + Molecular Mass of X

$$\frac{w_1}{w_2} \times 108 = 108 + \text{Molecular Mass of X}$$

$$\text{Molecular mass of X} = \left[\frac{w_1}{w_2} \times 108 - 108\right]$$

$$\text{Molecular mass of HX} = \text{Atomic Mass of H} + \text{Molecular Mass of X}$$

$$= 1 + \text{M.M. of X}$$

Molecular mass of HX or Organic Acid = 1 + Molar Mass of X

For dibasic Acid H_2X

$$\text{Molecular mass of } H_2X = 2 + \left\{\left[\frac{w_1}{w_2} \times 108 - 108\right]\right\} \times 2$$

$$\textit{For tribasic Acid } H_3X = 3 + \left\{\left[\frac{w_1}{w_2} \times 108 - 108\right]\right\} \times 3$$

$$= \left[\frac{w}{w_2} \times 108 - 107\right] \times 3$$

Solved Examples

1. Calculate the volume of 1 mole gas exerting pressure of 1 atm at a temperature of 273 K.

Sol. $V = \frac{nRT}{P} = 0.0821 \times 273 = 22.4$ L

2. Calculate the volume of 1 mole of gas exerting pressure of 1 atm at a temperature of 300 K.

Sol. $PV = nRT$

$$\therefore \quad V = \frac{nRT}{P} = 1 \times 0.0821 \times 300 = 24.3 \text{ L}$$

3. 44.8 L of oxygen contains how many moles of O_2?

Sol. Since T and P are not given, so number of mole cannot be calculated.

4. 22.4 L of aq. {H_2O] at STP contains how many moles?

Sol. 1 mL = 1 g

$$1 \text{ litre} = 1000 \text{ g} = \frac{1000}{18} \text{ moles}$$

Calculation of number of atoms and molecules in a given mass of substance.

5. How many atoms and molecules of sulphur are present in 64 g of S_8?

Sol. 1 mole of $S_8 = N_A$ molecules of $S_8 = 8 \times 32$ g

$$\therefore \text{ number of molecules} = \frac{64}{8 \times 32} = \frac{N_A}{4}$$

$$\therefore \text{ number of atom of sulphur} = 8 \times \frac{N_A}{4} = 2\,N_A$$

6. Calculate the number of molecules in

(i) 34.2 g of cone sugar ($C_{12}H_{22}O_{11}$)

(ii) 1 L of water assuming density 1 g

(iii) 1 drop of water having mass 0.05 g

Sol. (i) $\frac{34.2}{342} \times N_A = \frac{N_A}{10}$

(ii) 1 mL = 1 g

$$\therefore 1000 \text{ mL} = \frac{1000 \text{ g}}{18} N_A$$

(iii) $\frac{0.05}{18} \times N_A = \frac{N_A}{360}$

7. Elemental analysis of an organic compound containing C, H, N and O and weighing 7.3 g was found to contain 3.6 g of carbon, 0.7 g of H and 1.4 g of nitrogen. Calculate Empirical formula.

Sol.

H	0.7	$\frac{0.7}{1} = 0.7$	7
C	3.6	$\frac{3.6}{12} = 0.3$	3
N	1.4	$\frac{1.4}{14} = 0.1$	1
O	1.6	$\frac{1.6}{1.6} = 0.1$	1

∴ Empirical formula = C_3H_7NO

OR

$$C\frac{\text{weight}}{\text{Atomic weight}}H\frac{\text{weight}}{\text{Atomic weight}}$$

$$N\frac{\text{weight}}{\text{Atomic weight}}O\frac{\text{weight}}{\text{Atomic weight}}$$

$$C_{\frac{3.6}{12}}H_{\frac{0.7}{1}}N_{\frac{1.4}{14}}O_{\frac{1.6}{1.6}} = C_3H_7NO$$

8. Calculate the Empirical formula of the following minerals that have the following composition: $ZnSO_4$ = 56.14 H_2O = 43.86.

Sol.

$ZnSO_4$	56.14	$\frac{56.14}{161.4} = 0.35$	$\frac{0.35}{0.35} = 1$
H_2O	43.86	$\frac{43.86}{18} = 2.44$	$\frac{2.44}{0.35} = 7$

$ZnSO_4.7H_2O$

9. Calculate Empirical formula of hydrocarbon if 1.4 g of this compound is on complete combustion. Gives 4.4 g of CO_2 and 1.8 g of H_2O.

Sol. $C_xH_y + O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O$

∵ 1 mole of CO_2 contains 1 mole of C

∴ 44 g of CO_2 contains 12 gram of C

∴ 4.4 g of CO_2 contain 1.2 g of C

1 mole H_2O contains 2 mole of H.

18 gram H_2O contains 2 mole = 2 g

∴ 1.8 gram H_2O contains 2 mole = 0.2 g

C	1.2	$\frac{1.2}{1.2}$	0.1	1
H	0.2	$\frac{0.2}{1}$	0.2	2

CH_2 = EF

10. Calculate the weight of $KClO_3$ required and the weight of oxygen in product. If 1.49 g of KCl is obtained on heating, calculate the volume of oxygen at STP.

Sol. $2KClO_3 \rightarrow 2\ KCl + 3O_2$

Number of moles of KCl = $\frac{1.49}{74.5}$

2 moles of KCl produced from 2 moles of $KClO_3$.

∴ mass of $KClO_3$ = $n \times$ molecular weight

$$= \frac{1.49}{74.5} \times 122.5$$

and 2 moles of $KClO_3$ is required for 3 moles of O_2.

∴ number of moles of O_2 obtained

$$= \frac{3}{2}[n] = \frac{3}{2} \times \left[\frac{1.49}{74.5}\right]$$

∴ mass of $O_2 = \frac{3}{2}\left[\frac{1.49}{74.5}\right] \times 32$

∴ volume of oxygen at STP

$$= \frac{3}{2} \times \frac{1.49}{74.5} \times 22.4\ \text{L} = 0.672\ \text{L}$$

11. When 4 g of $CaCO_3$ and sand mixture is treated with excess of HCl, 0.88 g of CO_2 is produced. Calculate % weight of $CaCO_3$.

Sol. $CaCO_3 + 2HCl \rightarrow CO_2 + H_2O + CaCl_2$

Sand + HCl → No reaction

Number of moles of $CO_2 = \frac{0.88}{44} = 0.02$ mole

∴ number of moles of $CaCO_3$ = 0.02 moles

∴ % mass of $CaCO_3 = \frac{0.02 \times 100}{\text{Weight of mixture}} \times 100$

$$= \frac{0.02 \times 100}{4} \times 100 = 50\%$$

12. A sample of 5 g of natural gas consisting of methane and ethylene was burnt in excess of O_2 yielding 14.5 g of CO_2. Calculate the weight % of ethylene.

Sol. $CH_4 = x$ g

$C_2H_4 = 5 - x$ g

Number of Moles of $CH_4 = x/16$

Number of Moles of $C_2H_4 = 5 - x/28$

$CH_4 + O_2 \rightarrow CO_2 + 2\ H_2O$

$C_2H_4 + O_2 \rightarrow 2\ CO_2 + 2\ H_2O$

Number of Moles of $CO_2 = \frac{14.5}{44}$

[from methane and ethylene]

$$\frac{14.5}{44} = \left[\frac{5-x}{28} \times 2\right] + \left[\frac{x}{16} \times 1\right]$$

∴ % weight of ethylene = $\frac{5-x}{5} \times 100$

13. In a rocket motor filled with butane, how many kg of liquid oxygen should be provided for each kg of butane for its complete combustion?

Sol. $C_4H_{10} + \frac{13}{2} O_2 \rightarrow 4CO_2 + 5\ H_2O$

$[1 \times 10^3\ \text{g}]$

∴ number of moles of $C_4H_{10} = \frac{1000}{58}$

∴ number of moles of $O_2 = \left[\frac{1000}{58}\right] \times \frac{13}{2}$

∴ Mass of $O_2 = \left[\frac{1000}{58}\right] \times \frac{13}{2} \times 32$ gram = 3.586 Kg

14. In a sample of NaCl and KCl weight of mixture is 20.75 g. This was dissolved in water and heated with excess of $AgNO_3$. If weight of white precipitate of $AgNO_3$ is 43.05 g, calculate the weight of each component.

Sol. Weight of NaCl = x g

∴ weight of KCl = $20.75 - x$ g

$$NaCl \xrightarrow[H_2O]{AgNO_3} AgCl$$

$$\frac{x}{58.5} = \qquad (a \text{ mole})$$

$$KCl \xrightarrow[H_2O]{AgNO_3} AgCl$$

$$\frac{20.75 - x}{143.5} = \qquad (b \text{ mole})$$

$$a + b = \frac{43.05}{143.5} = \frac{x}{58.5} + \frac{20.75 - x}{74.5}$$

If chemical reaction are not balanced [Principle of Atomic conservation] [POAC]

According to this theory, if atoms are conserved, then moles of atoms shall also be conserved [POAC].

This concept is used when chemical reaction is not balanced and atleast one of the atoms is such that it is present only in one given compound and required compound.

$$KClO_3 \rightarrow KCl + O_2$$

Applied POAC on K atom

$$\frac{\text{Weight of } KClO_3}{\text{Molar Mass of } KClO_3} = \frac{\text{Weight of KCl}}{\text{Molar Mass of KCl}}$$

Applied POAC on oxygen atom

$$3 \times \text{moles of } KClO_3 = 2 \times \text{moles of } O_2$$

$$3 \times \frac{\text{Weight of } KClO_3}{\text{MM of } KClO_3} = 2 \times \frac{\text{Weight of } O_2}{\text{MM of } O_2}$$

15. $CaCO_3 \longrightarrow CaO + CO_2$

1000 g weight of CO_2 = ?

POAC on C atom

$1 \times$ mole of $CaCO_3$ = 1 mole of CO_2

$$\frac{\text{Weight of } CaCO_3}{\text{MM of } CaCO_3} = \frac{\text{Weight of } CO_2}{\text{MM of } CO_2}$$

$$\frac{1000}{100} = \frac{\text{weight of } CO_2}{44}$$

Weight of CO_2 = 440 g

16. Calculate the mass of compound $[K_2Zn_3[Fe(CN)_6]_2$ when 2.76 g of K_2CO_3 undergoes series of reaction such that all carbons convert into this complex. Given Molar Mass of complex compound (C.C) = 698.2 and MM of K_2CO_3 = 138.

Sol. $K_2CO_3 \rightarrow K_2Zn_3[Fe(CN)_6]_2$

Applied POAC on carbon

1 mole of K_2CO_3 = $12 \times$ moles of complex

$$\frac{\text{Weight of } K_2CO_3}{\text{MM of } K_2CO_3} = 12\left[\frac{\text{Weight of C.C}}{\text{MM of C.C}}\right]$$

$$\frac{2.76}{138} = 12\left[\frac{\text{Weight}}{698.2}\right] \quad \therefore \text{ Weight} = 1.163 \text{ gram}$$

17. For preparation of H_2SO_4 from iron pyrite $[FeS_2]$ involves following set of reaction:

$$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$$
$$SO_2 + O_2 \longrightarrow SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Calculate the weight of H_2SO_4 which can be obtained when 240 kg of FeS_2 is used.

Sol. Applied POAC of S

2 moles of FeS_2 = $1 \times$ moles of H_2SO_4

$$2\left[\frac{\text{Weight of } FeS_2}{\text{MM of } FeS_2}\right] = 1 \times \left[\frac{\text{Weight of } H_2SO_4}{\text{MM of } H_2SO_4}\right]$$

$$2\left[\frac{240 \times 10^3}{\text{MM of } FeS_2}\right] = 1 \times \left[\frac{\text{weight}}{98}\right]$$

Weight of H_2SO_4 = 392 kg

18. If 20 % $\frac{v}{V}$ is given then convert into % $\frac{w}{W}$ and % $\frac{w}{V}$.

If d is the density of solution.

Sol. 100 mL of solution contains 20 mL of NaOH and 80 mL of H_2O.

$$\% \frac{w}{W} = \frac{\text{Mass of solution} - \text{Mass of solvent}}{\text{Mass of solution}} \times 100$$

$$= \left[\frac{100d - 80 \times 1}{100d}\right] \times 100 = \left[\frac{100d - 80}{d}\right]\%$$

$$\frac{w}{V}\% = \left[\frac{100d - 80 \times 1}{100(\text{Volume of solution})}\right] \times 100 = [100d - 80]\%$$

19. Given 20 % $\frac{w}{V}$ of aq. NaOH. Then find its molarity.

Sol. 100 mL solution contains 20 g NaOH.

∴ 1000 mL solution contains 200 g NaOH

∴ number of moles = $\frac{200}{40}$ = 5 moles

and 1000 mL = 1 L

∴ molarity = $\frac{5}{1}$ = 5 M.

20. Convert 40% $\frac{w}{W}$ NaOH solution into molarity. If density of solution is d g/mL.

Sol. 100 g solution contains 40 g NaOH.

40 g of NaOH = 1 mole

$$\text{Volume of solution} = \frac{100}{d \times 1000} = \frac{1}{10d} \text{L}$$

$$\left[\text{Since } V = \frac{\text{Mass}}{\text{density}}\right]$$

∵ $\frac{1}{10d}$ L solution contains 1 mole of NaOH

$\therefore$ 1 L solution contains 1 mole of NaOH

$$= \frac{1}{\frac{1}{10d}} = 10\text{ dM}$$

$\therefore$ Molarity = 10 dM

21. Calculate molality of 20% by mass NaOH solution.

Sol. 20 % by mass means 20 g NaOH present in 80 g of solvent.

$$\therefore \quad \text{Molality } m = \frac{20/40}{80/1000} = \frac{20}{40} \times \frac{1000}{80}$$

22. A solution of I_2 in benzene has a mole fraction of $I_2 = 0.2$. If density of solute is 1.2 g/mL, calculate (i) Molality (ii) Molarity

Sol. I_2 in benzene means I_2 solute and benzene solvent

$$\text{and} \quad X_{I_2} = \frac{n_{I_2}}{\Sigma n}$$

$$n_{I_2} = X_{I_2} \times \Sigma n$$

$$\therefore \quad n_{C_6H_6} = x_{C_6H_6} \times \Sigma n$$

$$X_{I_2} = 0.2 \qquad \therefore\ X_{C_6H_6} = 1 - 0.2 = 0.8$$

$$m = \frac{x_{I_2} \times \Sigma n}{x_{C_6H_6} \times \Sigma n \times 78} \times 1000$$

$$M = \left[\frac{x_{I_2} \times \Sigma n}{\dfrac{[(x_{I_2} \times \Sigma n) \times 254] + (x_{C_6H_6} \cdot \Sigma n) \times 78}{1.2\text{ gram/ml}}}\right] \times 1000$$

23. Calculate molality of all ions present in 1 molar $Al_2(SO_4)_3$ solution. Given that density of solution = 2.34 g/mL.

Sol. $$m_{Al_2(SO_4)_3} = \frac{1}{1000 \times 2.342 - 1 \times 342} \times 1000$$

$$m_{Al^{+3}} = \frac{2}{2000} \times 1000 = 1\text{ m}$$

$$m_{SO_4^{--}} = \frac{3}{2000} \times 100 = \frac{3}{2}\text{ m}$$

Case II: Degree of Dissociation

$$= \frac{\text{Moles dissociated}\,(x)}{\text{Total number of moles before dissociation}}$$

$$\alpha = \frac{x}{a}$$

$$\therefore \quad x = a\alpha$$

$$\begin{array}{lllll}
\text{For } A & \longrightarrow & 3\,B & + & C \\
a & & 0 & & 0 \\
a - x & & 3x & & x \\
(a - a\alpha) & & (3a\alpha) & & (a\alpha)
\end{array}$$

24. Find the molarity of each ion in 0.1 M $BaCl_2$ considering degree of dissociation = 80 %

$$\begin{array}{lllll}
BeCl_2 & \longrightarrow & Be^{+2} & + & 2Cl^- \\
0.1 & & 0 & & 0 \\
0.1 - x & & x & & 2x
\end{array}$$

$\therefore$ molarity after ionisation

$$0.1 - \frac{0.1 \times 80}{100} \qquad a\alpha \qquad 2a\alpha$$

$$= \frac{0.1 \times 80}{100} \qquad \frac{2 \times 0.1 \times 80}{100}$$

$$M_{Be^{+2}} = 0.08\text{ M}$$

$$\text{and} \quad M_{Cl^-} = 0.16\text{ M}$$

$$\text{pH} = -\log[H^+]$$

$$[H^+] \to [1] \qquad 10^{-7} \qquad 10^{-14}$$

$$\text{PH} \quad O \xleftarrow{\text{Acidic}} \overset{\text{Neutral}}{7} \xrightarrow{\text{Basic}} 14$$

25. Calculate the degree of dissociation of pure water at 298 K if it is known that pH = 7.

Sol.
$$\begin{array}{lllll}
H_2O & \longrightarrow & H^+ & + & OH^- \\
55.55\text{ M} & & 0 & & 0 \\
[55.55 - 55.55\alpha] & & 55.55\alpha & & 55.55\alpha
\end{array}$$

but $[H^+] = 55.55\alpha = 1 \times 10^{-7}$

$$\therefore \quad \alpha = \frac{1 \times 10^{-7}}{55.55} = \frac{1}{55.55 \times 10^7} = 1.8 \times 10^{-9}$$

Hence, out of 55.55×10^7 molecule of water, only one molecule dissociate.

Note: $$\alpha = \frac{\text{concentration of any ion}}{\begin{array}{c}\text{concentration of that ion (theoritically)} \\ \text{(complete ionisation)}\end{array}}$$

26. If Molarity of Na_3PO_4 is 1 molar and concentration of Na ion is 0.2 M. Calculate % dissociation of Na_3PO_4.

Sol.
$$\begin{array}{lllll}
Na_3PO_4 & \longrightarrow & 3Na^+ & + & PO_4^{---} \\
1 & & 0 & & 0 \\
1 - x & & 3x & & x
\end{array}$$

If complete ionisation actually

1 mole gives 3 mole Na^+ and 1 mole PO_4^{---}

Given that $3x = 0.2$

$$\therefore \quad \alpha = \frac{0.2}{3} \times 100 = \frac{20}{3} = 6.6\ \%$$

27. **(i)** 200 mL of 1 M HCl solution is mixed with 800 mL of 2 M HCl solution. Calculate the molarity of final solution.

Sol. $$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Total volume}\,(V_1 + V_2)}$$

$$= \left[\frac{\dfrac{1 \times 200}{1000} + \dfrac{2 \times 800}{1000}}{800 + 200}\right] \times 1000$$

$$= 1.8\text{ M}$$

(ii) If density of solution is 1.2 g/mL, calculate molality.

Sol. $$m = \frac{1000\text{ M}}{1000d - \text{Molar Mass of solute}}$$

$$= \frac{1.8 \times 1000}{1000 \times 1.2 - 1.8 \times 36.5}\text{ m}$$

(iii) If sample of H_2SO_4 in 1.8 g/mL is 98% wt. What is the volume of acid that has to be taken to form 1 L of 0.2 M H_2SO_4 solution?

Sol. $\boxed{\begin{array}{l}98\text{ \% wt.}\\ 1.8\text{ g/mL}\end{array}} \xrightarrow{\text{diluted}} \boxed{\begin{array}{l}\text{1L of 0.2 M}\\ H_2SO_4\text{ solvent}\end{array}}$

Number of mole of solute before dilution = Number of mole of solute after dilution

$$V \times M = 1 \times 0.2 = \left[\frac{98/98}{\frac{100}{1.8}}\right] \times 1000$$

28. 10 mL of $H_2O[d = 1\text{ g/mL}]$ and 4 mL of CH_3OH $[d = 0.8\text{ g/mL})$ is mixed to form a solution. If the density of final solution is 1.1 g/mL, calculate the molarity of final solution.

Sol. $W_{H_2O} = 10 \times 1 = 10\text{ g}$

$W_{CH_3OH} = 4 \times 0.8 = 3.2\text{ g}$

Total weight of solution = 10 + 3.2 = 13.2 g

$\therefore$ volume of solution $= \dfrac{13.2}{1.1} = 12$ mL

$\therefore$ molarity of solution $= \left[\dfrac{3.2/32}{12}\right] \times 100$

> ***Note:***
> 1. If during mixing of solution, mass of final solution and density of final solution is given then volume of solution should be calculated by
> $$V = \frac{\text{Total mass}}{\text{Density of solution}}$$
> 2. If any one data of the following is not given: (a) mass of any mixing substance (b) density of resultant solution, then it has to be assumed that there is no volume contraction or expansion taking place and $V = V_1 + V_2 + \ldots\ldots$

29. 100 mL of 0.1 M of $Al_2(SO_4)_3$ is mixed with 100 mL of 0.1 M $AlCl_3$. Calculate molarity of Al^{+3} ion if final solution has density of 1.2 g/mL.

Sol. $n_{Al_2(SO_4)_3} = \dfrac{100 \times 0.1}{1000} = 0.01$ mole

$n_{AlCl_3} = \dfrac{100 \times 0.1}{1000} = 0.01$ mole

$\therefore$ n of Al^{+3}

0.02 mole + 0.01 mole = 0.03 mole

From $Al_2(SO_4)_3$ and $AlCl_3$

$\therefore$ molarity of Al^{+3}

$$= \frac{n_{Al^{+3}}}{\text{Total volume}}$$

$$= \left[\frac{0.03}{200}\right] \times 1000$$

$$= 1.5 \times 10^{-1}\text{ M}$$

30. Calculate $[H^+]$ concentration if 0.2 M of H_2SO_4 solution having volume 100 mL is mixed with 0.1 M of 300 mL of NaOH.

Sol. $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2\,H_2O$

before reaction

No. of moles of NaOH = 0.1 × 0.300

No. of moles of $H_2SO_4 = 0.2 \times 0.100$

No. of moles of H_2SO_4 after reaction

$$= 0.02 - \frac{0.003}{2} = .005$$

$\therefore$ $[H^+] = 2 \times 0.005$ Mole = 0.01 mole

$\therefore$ molarity $= \left[\dfrac{0.01}{400}\right] \times 1000 = 0.025$ M

31. 200 mL of 0.1 M NaCl is mixed with 100 mL of 0.2 M $AgNO_3$ solution. Calculate molarity of all the ions in final solution.

Sol.
$$\begin{array}{lllll}
NaCl & + \; AgNO_3 & \rightarrow & AgCl\downarrow & + \; NaNO_3\\
0.2 \times 0.1 & \;\; 0.1 \times 0.2 & & \text{ppt} & \\
0.02 & \;\; 0.02 & \therefore \text{ if no ion is formed} & & \\
0 & \;\; 0 & & 0.02 & \;\; 0.02
\end{array}$$

$\therefore$ $M_{Na^+} = \dfrac{0.02}{300} \times 1000$ and

$M_{NO_3^-} = \dfrac{0.02}{300} \times 1000$

32. 10 L mixture of C_2H_6 and C_3H_8 at STP on complete combustion gives 22 L of CO_2 at STP. Find the molar concentration of the mixture in molar ratio.

Sol. $C_2H_6 + \dfrac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

Since $V \propto$ Number of moles of gas

and $V_{CO_2} = 22\text{ L} = [V_{CO_2}]_{C_2H_6} + [V_{CO_2}]_{C_3H_8}$

$= 2V + 3(10 - V) = 22$

$\therefore$ $-V = -8$

$V = 8$ L

$\therefore$ $\dfrac{V_{C_2H_6}}{V_{C_3H_8}} = \dfrac{n_{C_2H_6}}{n_{C_3H_8}} = \dfrac{8}{2} = 4 : 1$

33. If volume of CO_2 is 24 L at 1 atm and 300 K in Q32, then calculate the molar composition of initial mixture.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$\therefore$ $V_2 = \dfrac{P_1V_1T_2}{P_2T_1} = \dfrac{1 \times 24 \times 273}{1 \times 300}$

$V_2 = 2V + 3[10 - V]$

> ***Note:***
> If in a question [volume or pressure] is given in different conditions then it is better to convert at STP condition by using $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

34. A mixture of C_2H_6 and C_3H_8 at 200 mm of Hg on complete combustion gives CO_2 at 450 mm Hg. Calculate molar ratio of initial mixture.

Sol. Since $P \propto$ Number of moles of gas

$$450 \text{ mm} = (P_{CO_2})_{C_2H_6} + (P_{CO_2})_{C_3H_8}$$

$$C_2H_6 + \frac{7}{2}O_2 \rightarrow \underset{(2x)}{2CO_2} + 3H_2O$$

$$C_3H_8 + 5O_2 \rightarrow \underset{3[200-x]}{3CO_2} + 4\,H_2O$$

$$\therefore \quad 450 = 2x + 3[200 - x]$$

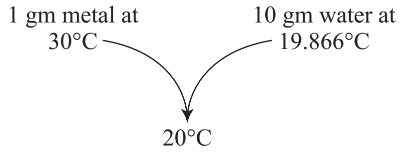
$$X = 150 = P_{C_2H_6}$$

$$\therefore \quad P_{C_3H_8} = 200 - 150 = 50$$

$$\therefore \quad \frac{n_{C_2H_6}}{n_{C_3H_8}} = \frac{3}{1}$$

35. 1 g of metal at 30º was immersed in 10 g of water at 19.886 ºC. If the final temperature is 20ºC then predict that metal could be iron (Specific heat of H_2O = 1 cal/g).

Sol.



Heat lost by metal = Heat gained by water

$$m_1C_1\Delta t_1 = m_2C_2\,\Delta t_2$$

$$1 \times C_1 \times [30 - 20] = 10 \times 1[20 - 19.886]$$

$$\therefore \quad C_1 = 0.114$$

$$\therefore \quad \text{atomic mass} = \frac{6.4}{0.114} = 56.2$$

36. A sample of Organic Compound weight 10 g in Victor mayer process was found to displace 2.463 mL at 1 atm and 300 K. Calculate Molar Mass of volatile substance.

Sol. $$n = \frac{\text{Weight}}{\text{Molar Mass}} = \frac{10}{\text{Molar Mass}} = \frac{P_{\text{atm}} \times V_{\text{Liter}}}{0.0821 \times T_{\text{Kelvin}}}$$

10 g → 2.463 mL [At P = 1 atm and T = 300 K]

$$\frac{10}{\text{Molar mass}} = \frac{1 \times 2.463 \times 10^{-3}}{0.0821 \times 300}$$

$$\therefore \quad \text{molar mass} = 10^5 \text{ g}$$

37. The vapour of W g sample of Organic Compound occupy V mL at STP in Victor mayer process. Calculate Molar mass of compound?

Sol. From V mL = W gram at STP

$$\therefore \quad 22400 \text{ mL} = \frac{W}{V} \times 22400 = \text{Molar mass}$$

38. 0.41 g of silver salt is obtained after reaction between dibasic acid and silver nitrate solution, which on heating gives 0.216 g of residue. Calculate MM of acid.

Sol. $w_1 = 0.41$ g, $w_2 = 0.216$ g

Acid ⇒ dibasic then

$$\text{MM} = \left\{\frac{w_1}{w_2} \times 108 - 107\right\} \times 2$$

$$= \left\{\frac{0.410}{0.216} \times 108 - 107\right\} \times 2 = 196$$

39. Estimation of Molar Mass of silver salt, acid graph of the residue obtained and the weight of silver salt was plotted as shown in following graph. If the acid is known to be monobasic, calculate Molar Mass of salt and Molar Mass of acid.

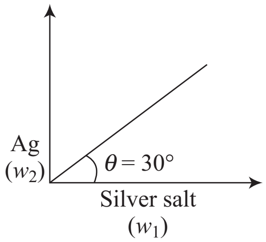


Fig. 1.4

Sol. We know $$\frac{w_1}{\text{Molar Mass of AgX}} = \frac{w_2}{\text{Molar Mass of Ag}}$$

$$\text{Slope} = \tan 30° = \frac{w_1}{w_2} = \frac{1}{\sqrt{3}}$$

$$\therefore \quad \frac{w_2}{w_1} = \frac{1}{\sqrt{3}} = \frac{\text{Molar Mass of Ag}}{\text{Molar Mass of AgX}}$$

$$\frac{1}{\sqrt{3}} = \frac{108}{\text{Molar Mass of AgX}}$$

Molar Mass of AgX = $108\sqrt{3}$

$$\therefore \quad \text{Molar Mass of HX} = [108\sqrt{3} - 107]$$

Exercise

LEVEL I

1. Select the correct statement(s) for $(NH_4)_3PO_4$.

(a) Ratio of number of oxygen atom to number of hydrogen atom is 1 : 3.

(b) Ratio of number of cation to number of anion is 3 : 1.

(c) Ratio of number of nitrogen atom to number of oxygen atom is 3 : 4.

(d) Total number of atoms in one mole of $(NH_4)_3PO_4$ is 20.

(a) ab (b) abc (c) bc (d) All

2. What volume (in mL) of liquid H_2O_2 has same number of atoms as there are number of atoms in 22.4 mL H_2O gas at 2 atm and 546 K?

[Given: Density of liquid H_2O_2 = 5.1×10^{-3} g/mL; Density of liquid H_2O = 1 g / mL]

(a) 2 (b) 5 (c) 3.5 (d) 4.2

3. A sample of $Mg_3(PO_4)_2$ contains 72 g Mg in the sample. Calculate the number of g molecule of oxygen in the sample.

(a) 2 (b) 3 (c) 3.5 (d) 4

4. What mass (in gram) of Na_2SO_4 would contain the same number of total ions as present in 930 g of $Ca_3(PO_4)_2$?

(a) 710 (b) 800 (c) 200 (d) 500

5. A sample of Cl contains 80% Cl^{35} and 20% Cl^{37} isotopes. The average number of neutrons per atom is

(a) 18.4 (b) 19.4 (c) 35.4 (d) 20.4

6. A sample of $K_2SO_4 . Al_2(SO_4)_3 . 24 H_2O$ contains 6.4 kg oxygen. Calculate mass of sulphur (in gram) in same sample.

(a) 1280 (b) 1000 (c) 128 (d) 12.8

7. A 448 L vessel contains $O_2(g)$ and CO_2 (g) in 2 : 3 ratio at 1 atm and 0°C. Calculate the number of moles of CO_2 (g) present in the vessel.

(a) 12 (b) 1.1 (c) 1.2 (d) 120

8. Find the value of **'*x*'**, if hydrated salt $A_2SO_4 . xH_2O$ undergoes 45% loss in mass on heating and becomes anhydrous (where atomic weight of 'A' is 7).

(a) 8 (b) 9 (c) 10 (d) 5

9. Calculate the volume of Cl_2 gas (in mL) liberated at 1 atm and 273 K when 1.74 g MnO_2 reacts with 2.19 g HCl according to the following reaction with % yield 40:

$MnO_2 + HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

(a) 336 mL (b) 112 mL (c) 134.4 mL (d) 44.8 mL

10. Calculate the mass % of $CaCO_3$ in the 103 g mixture containing $CaCO_3$ and Na_2CO_3, which produces 24 L of CO_2 at 1 atm and 300 K with excess of HCl.

[Given : R = 0.08 atm. lit / mol/ K]

(a) 50% (b) 48.5% (c) 53% (d) 40%

11. Calculate the mass of HCl (in g) produced if 2 g H_2 is mixed with 71 g Cl_2.

$H_2 + Cl_2 \longrightarrow 2HCl$

(a) 35.5 (b) 72 (c) 36.5 (d) 73

12. Select the correct statement(s):

(a) Number of oxygen atoms are same in 1 g O_2 and 1 g O_3.

(b) 1 g molecule of any substance contains equal number of atoms.

(c) Reactant having minimum number of moles, acts as limiting reagent.

(d) During a chemical reaction total number of moles may increase or constant.

13. Calculate the volume (in mL) of NO_2 at 1 atm and 273 K obtained by treating 12.7 g of Cu with excess of concentrated nitric acid from the following reaction:

$Cu(s) + HNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + H_2O\,(l) + NO_2$

(a) 8960 (b) 896 (c) 89.3 (d) 6900

14. *X* is molecular substance containing 21 atoms of carbon per molecule. The weight % of C in *X* is 50.4%. What is the molecular weight of *X* in amu?

(a) 500 (b) 200 (c) 300 (d) 400

15. Calculate pressure (in atm) exerted by gas at 27°C, which is produced by the complete decomposition of 162.5 g of $FeCl_3$ in 0.0821 L container according to the following reaction: (Assume volume occupied by the solid substances is negligible.)

$FeCl_3(s) \longrightarrow FeCl_2\,(s) + Cl_2\,(g)$

(a) 250 (b) 150 (c) 15 (d) 300

16. A term '*P*' is defined as

$P = 294 \times$ (Ratio of masses of $Al_2\,(SO_4)_3$ and H_2SO_4 in g each containing 96 g of sulphur).

Calculate *P*.

(a) 342 (b) 294 (c) 684 (d) 171

17. Calculate molality(m) of pure water if its density is 0.936 g/mL.

(a) 50 (b) 55.56 (c) 57.56 (d) 56.56

18. The volume (in mL) of 0.5 M NaOH required for the complete reaction with 150 mL of 1.5M H_3PO_3 solution is

(a) 1350 (b) 900 (c) 1250 (d) 1150

19. For the reaction,

$AlCl_3 + NaOH \longrightarrow Al(OH)_3 + NaCl$

if initially, 1 mole of each reactant is taken, then the number of moles of $AlCl_3$ remaining after the completion of reaction is

(a) 1 (b) $\frac{1}{3}$

(c) $\frac{2}{3}$ (d) None of these

20. A mixture of $CaCO_3$ and CaO on heating gives off 22.4 L of CO_2 gas at 273 K and 1 atm. If the same mass of mixture when treated with HCl required 219 g of HCl for complete reaction, then the mole % of $CaCO_3$ in the mixture is

(a) 50% (b) 33.33%

(c) 25% (d) None of these

21. The relative density of a mixture of CO_2 (g) and H_2O (g) w.r.t. gaseous hydrogen atoms is 30. The molecular % of the CO_2 is

(a) $\frac{600}{13}$ (b) $\frac{2400}{13}$%

(c) $\frac{1200}{13}$ (d) None of these

22. Molar mass of electron is nearly ($N_A = 6 \times 10^{23}$)

(a) 9.1×10^{-31} kg mol^{-1} (b) 9.1×10^{-31} g mol^{-1}

(c) 54.6×10^{-8} g mol^{-1} (d) 54.6×10^{-8} kg mol^{-1}

23. Calculate the number of moles of compound $(KHC_2O_4)_{0.95} \cdot H_2C_2O_4$ in its pure sample if sample contains 4 moles of oxygen atoms.

(a) 0.5 (b) 0.5×0.95

(c) $\frac{4}{(4 + 0.95 \times 4)}$ (d) $\frac{4}{0.95}$

24. What is the relationship between mole fraction of of a solute (X_A) and its molality (m). If molar mass of solvent is 100. (g/mol).

(a) $\dfrac{(X_A)}{10(1-X_A)}$ (b) $\dfrac{(X_A)}{100\,(1-X_A)}$

(c) $\dfrac{10(1-X_A)}{(X_A)}$ (d) $\dfrac{10(X_A)}{(1-X_A)}$

25. 100 mL of 0.1 M ammonium phosphite solution is mixed with 200 mL of 0.2 M sodium pyrophosphate solution. Assuming complete dissociation of each salt and no reaction occurs between the ions produced, calculate the concentration of total positive ions in millimoles per litre.

(a) 600 (b) 200 (c) 500 (d) 60

26. A mixture of C_2H_4, CO and N_2 gases having total pressure 250 mm of Hg in which 250 mm Hg of O_2 is added at 27°C and then sparked. After the system is brought to the original temperature, the total pressure becomes 370 mm of Hg. If the partial pressure of CO_2 is 200 mm of Hg, then calculate the sum of initial pressure of CO and O_2 in mm of Hg before the sparking

Given : At 27°C aqueous tension is 20 mm of Hg.

(a) 100 (b) 200 (c) 300 (d) 350

27. Human lungs can absorb 8 g O_2 per hour by respiration. If all oxygen atoms are converted to carbohydrates ($C_6H_{12}O_6$), how long will it take to produce 180 g $C_6H_{12}O_6$?

(a) 8 hr (b) 12 hr (c) 10 hr (d) 6 hr

28. If in a sample of oleum, mole fraction of SO_3 is 0.5, label the oleum sample.

(a) 109 % (b) 110.11 %

(c) 104.5 % (d) 114.22

29. Manganese oxide (MnO_2) is heated in a stream of hydrogen to give water and new oxide Mn_xO_y. If 17.4 g of MnO_2 produces 12.6 g of Mn_xO_y then $y : x$ will be

(a) 1 (b) $\dfrac{1}{2}$ (c) $\dfrac{3}{2}$ (d) $\dfrac{5}{2}$

30. A pure sample of an element 'E' is cut by knife into perfect cubes. If 7.5×10^{22} atoms are present in one such cube and 'a' is edge length of cube in cm, then what will be the value of a^6 **(in cm^6)**?

[Given : Atomic mass of $E = 32$, $N_A = 6 \times 10^{23}$, Density of element = 4/3 g/cm^3]

(a) 9 (b) 4 (c) 16 (d) 25

31. Which of the following option(s) is incorrect?

[Take H_2O to be solvent in every case and solute is completely soluble]

(a) If mass fraction of $CaBr_2$ and H_2O are same then molality of $CaBr_2$ is 5 m.

(b) If equal moles of NaCl and H_2O are taken then molality of NaCl is 55.55 m.

(c) If in place of NaCl we use NaBr as solute in option (2) then molality of NaCl changes.

(d) If mole fraction of NaCl is same as that of H_2O then molality of NaCl will be 55.55 m.

32. One of the major uses of H_2O_2 is for artificial respiration. It is stored in cylinder of 3 L capacity completely filled with H_2O_2 solution of '44.8 V'. In a hospital, patient under artificial respiration takes 200 mL O_2 per min at 1 atm at 273 K for 2.8 hours from cylinder.

[Assume volume of solution and rate of decomposition remain constant.]

Then which of the following statements is incorrect?

(a) Initial moles of H_2O_2 in a cylinder are 12.

(b) Volume of oxygen used for respiration is 33.6 L.

(c) Volume strength of H_2O_2 left in solution is 11.2 V.

(d) Volume strength of H_2O_2 left in solution is 33.6 V.

33. Two gases N_2 and H_2 are allowed to react completely to form mixture of $N_2H_2(l)$ and N_2H_4 (g) leaving no reactants. Formation of N_2H_2 (l) does not create any energy change whereas formation of 1 mL N_2H_4 (g) absorbs 2 J energy. Ratio of volume contraction to energy change **(in mL / Joule)** when 30 mL N_2 and 40 mL H_2 react under similar conditions of temperature and pressure.

(a) 3mL /J (b) 5mL /J

(c) 6mL /J (d) None of these

34. 150 mL mixture of CO and CO_2 is passed through a tube containing excess of red hot charcoal. The volume becomes 200 mL due to reaction.

$$CO_2\,(g) + C(s) \longrightarrow 2CO\,(g)$$

Select the correct statement(s).

(a) Mole percent of CO_2 in the original mixture is 50.

(b) Mole fraction of CO in the original mixture is 0.56.

(c) Original mixture contains 50 mL of CO_2.

(d) Original mixture contain 50 mL of CO.

35. A mixture of formic acid and oxalic acid is heated in the presence of H_2SO_4.

$$HCOOH \longrightarrow H_2O + CO$$
$$H_2C_2O_4 \longrightarrow H_2O + CO_2 + CO$$

The produced gaseous mixture is collected and cooled. On its treatment with KOH solution, the volume of gaseous mixture decreases by one-tenth. Calculate the molar ratio of the two acid in original mixture. [If the simplest ratio is a : b then find a + b.]

(a) 6 (b) 9 (c) 2 (d) 5

36. In a tyre of a 'ferrari' car, a tube having a volume of 12.3 L is filled with air at a pressure of 4 atm at 300 K. Due to travelling, the temperature of the tube and air inside it is raised to 360 K. The porosity (number of pores per unit area) of the tube material is 5×10^5 pores/cm^2 and each pore can transfer air from inside to outside of tube at the rate of 6.023×10^8 molecules per minute. Due to above factors, pressure reduces to 3.6 atm in 20 min. Calculate the total surface area (m^2) of the tube, assuming volume of tube to be constant. (R = 0.082 lit-atm/mole-K)

(a) 5000 (b) 500 (c) 4000 (d) 400

37. Calculate the number of milligrams of SO_2 in a sample of air, if in the following reaction 9 mL of 0.008 M $KMnO_4$ solution is required for titration.

$SO_2 + MnO_4^- \longrightarrow SO_4^{-2} + Mn^{+2}$

(a) 11.52 mg (b) 0.18 mg
(c) 0.072 mg (d) None of these

38. Two acids H_2SO_4 and H_3PO_4 are neutralised separately by the same amount of base, producing sulphate and dihydrogen phosphates respectively. The ratio of mass of H_2SO_4 and H_3PO_4 reacted with base respectively is

(a) 1 : 1 (b) 2 : 1
(c) 1 : 2 (d) Data insufficient

39. Calculate mass % of oxygen in water

(a) 88.88% (b) 73.68 %
(c) 20.61% (d) 25.63 %

40. 100 g '118% oleum' sample is mixed with 9 g of H_2O. The final solution has

(a) mass % of H_2SO_4 is 2.7.
(b) Mass % of combined SO_3 is 16.3.
(c) New labelling as 108.25% oleum.
(d) Mass % of free SO_3 is 80.

41. The two solutions of NaOH having molarity $\frac{M}{10}$ and $\frac{M}{30}$ are mixed to prepare 1 L of NaOH solution in such a way that 300 mL of final solution is completely neutralised by 10 mL of 0.5 M H_3PO_4 solution. Calculate the volume (in mL) of $\frac{M}{10}$ NaOH solution used.

[Assuming 100% dissociation]

(a) 250 mL (b) 350 mL
(c) 50 mL (d) 500 mL

42. 1 mole of ammonium phosphite will contain

(a) 2 moles of nitrogen atoms.
(b) 8 moles of hydrogen atoms.
(c) 12 moles of hydrogen atoms.
(d) 6 moles of hydrogen atoms.

43. In a container 6 L N_2 and 30 L H_2 are taken which react according to the following reactions and N_2H_2 reacts with H_2 to give N_2H_4.

$$N_2(g) + H_2(g) \longrightarrow N_2H_2(g)$$
$$N_2H_2(g) + H_2(g) \longrightarrow N_2H_4(l)$$

Find percentage of volume contracted.

(a) 50 (b) 40 (c) 30 (d) 60

44. Find the total number of carbon atom present in one molecule, if 0.078 g hydrocarbon having simplest formula unit CH, occupy 22.4 mL of volume at 1 atm and 0°C.

(a) 5 (b) 4 (c) 2 (d) 6

45. Find the % mass of Ca in 10 g of pure $CaCO_3$.

(a) 40 (b) 30 (c) 60 (d) 50

46. Find volume occupied by 1 molecule of $CH_3CH_2OCH_3$ having density of 0.8 g/cm^3.

[Given : $N_A = 6 \times 10^{23}$]

(a) 1.25×10^{-22} cm^3 (b) 2.25×10^{-22} cm^3
(c) 3.25×10^{-22} cm^3 (d) 1.00×10^{-22} cm^3

47. Calculate the number of Na^+ ion present in 142 amu of Na_2SO_4 in aqueous solution.

(a) 5 (b) 2 (c) 1 (d) 4

48. 1 mole of diatomic gas A_2 contains 32 and 36 moles of electrons and neutrons respectively. Find the mass number of element A.

(a) 32 (b) 68 (c) 40 (d) 34

49. Find the number of moles of Na_3PO_4 which contain as many ions as present in 6840 g of $Al_2(SO_4)_3$.

(a) 20 (b) 25 (c) 30 (d) 60

50. An equimolar mixture of $^{19}_{9}F$, $^{39}_{19}K$ and $_{32}X^{A}$ have average number of neutron of 25. Find average mass number of mixture.

(a) 22.5 (b) 21.5 (c) 45 (d) None

51. Find the correct option for 36 g $C_6H_{12}O_6$.

(a) 4.8 N_A molecules of $C_6H_{12}O_6$
(b) 19.2 N_A electrons
(c) 0.8 moles
(d) 0.6 g molecules of oxygen

52. To obtain maximum mass of NO_2 from a given mass of a mixture of NH_3 and O_2, the ratio of mass of NH_3 to O_2 should be

$$2NH_3 + \frac{7}{2}O_2 \longrightarrow 2NO_2 + 3H_2O$$

(a) $\frac{17}{40}$ (b) $\frac{4}{7}$
(c) $\frac{17}{56}$ (d) None of these

53. Find the mass (in g) of P_4O_{10} produced if 31 g of phosphorus (P_4) is mixed with 32 g of O_2.

(a) 26.8 (b) 56.8 (c) 568 (d) 5.68

54. If 200 mL of 0.1 M Na_2SO_4 is mixed with 100 mL of 0.2 M Na_3PO_4 solution, what is the molarity of Na^+ in the final solution, if final solution has a density of 1.2 g/mL.

(a) 0.196 M (b) 0.33 M
(c) 1.5 M (d) 0 .66 M

55. Mark the option containing temperature-independent concentration terms.

(I) ppm
(II) %w/w
(III) Volume strength of H_2O_2
(IV) % labelling (V) %w/v

(a) All except V (b) I, II, IV
(c) I, II only (d) Only II

56. Total number of electrons present in $_8{}^{18}O^{-2}$ is 1.2×10^{22} then the number of moles of oxide ion present is

(a) 2×10^{-3} mole (b) 10^{-3} mole
(c) 10 mole (d) 0.02 mole

57. Ratio of number of protons to neutrons in 3.011×10^{22} molecules of D_3O^+ is

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

58. 80 g of SO_x gas occupies 14 L at 2 atm and 273 K. The value of x is

(Use R = 0.0821L-atm/K-mole)

(a) 3 (b) 2 (c) 1 (d) None

59. Haemoglobin contains 0.25% iron by mass. The molecular mass of haemoglobin is 89600 then the number of iron atoms per molecule of haemoglobin (Atomic mass of Fe = 56) is

(a) 8 (b) 4 (c) 12 (d) 160

60. 12 g of mg was burnt in a closed vessel containing 32 g oxygen. Which of the following statements is not correct?

(a) 2 g of mg will be left unburnt.
(b) 0.75 gram-molecule of O_2 will be left unreacted.
(c) 20 g of MgO will be formed.
(d) The mixture at the end will weight 44 g.

61. Calculate maximum mass of $CaCl_2$ produced when 2.4×10^{24} atoms of calcium is taken with 96 L of Cl_2 gas at 380 mm pressure and at 27ºC.
[R : 0.08 atm L/mole-K and $N_A = 6 \times 10^{23}$]

(a) 111 g (b) 444 g
(c) 61 g (d) 222 g

62. A mixture containing 3 moles each of C_4H_8 and C_6H_6 undergoes complete combustion with O_2 to form CO_2 and H_2O. Calculate the total mass of CO_2 produced.

(a) 1320 g (b) 610 g
(c) 528 g (d) 792 g

63. An impure sample of $KClO_3$ of 50% purity on decomposition produces 67.2 L of oxygen at 0ºC and 1 atm. The other product of decomposition is KCl. The initial mass of impure original sample (in gram) taken is

(a) 245 (b) 122.5
(c) 490 (d) None of these

64. A cylinder of compressed gas contains nitrogen and oxygen gas in the mole ratio 3 : 1. If the cylinder is known to contain 2.40 g of oxygen, what is the total mass of gas mixture?

(a) 8.7 g (b) 7.2 g (c) 6.8 g (d) 6.3 g

65. If in urea $[CO(NH_2)_2]$ there are 20 g – atoms of nitrogen present then the mass of urea will be

(a) 600 g (b) 60 g
(c) 6 g (d) 120 g

66. The weight of 2.8 liter of gas at NTP is 3.50 g. Its vapour density is

(a) 14 (b) 28 (c) 32 (d) 20

67. If nickel oxide has the formula $Ni_{0.98}\,O_{1.00}$, then what fraction of nickel exist as Ni^{+3}?

(a) 96% (b) 4% (c) 98% (d) 2%

68. Find the number of iodine atoms present in 40 mL of its 0.1 M solution.

(a) 48.1×10^{20} (b) 4.81×10^{20}
(c) 6.02×10^{23} (d) None of these

69. Assuming complete ionisation, the pH of 0.1 M HCl is 1. The molarity of H_2SO_4 with same pH is

(a) 0.1 (b) 0.2 (c) 0.05 (d) 2

70. The mole fraction of solute in one molal aqueous solution is

(a) 0.009 (b) 0.018 (c) 0.027 (d) 0

71. If one million atoms of silver weight is 1.79×10^{-16} g, the gram atomic mass of silver is

(a) 107 g (b) 107.2 g
(c) 107.8 g (d) 108.2 g

72. How many g-atoms are present in 1.4 g of Nitrogen?

(a) 1 (b) 0.1 (c) 0.01 (d) 0.5

73. On heating a given mass of blue vitrol 95.7 g, anhydrous copper sulphate is obtained. The number of water molecules lost are

(a) 3 (b) 5
(c) 18.06×10^{23} (d) 30.10×10^{23}

74. The amount of zinc needed to produce 112 mL of H_2 at STP on reaction with dil H_2SO_4 will be

(a) 0.65 g (b) 0.325 g
(c) 6.5 g (d) 3.25 g

75. Calculate the number of electrons present in 18 mL of H_2O at 25ºC.

(a) 6.023×10^{23}
(b) 6.023×10^{24}
(c) $\frac{180}{22400} \times 6.023 \times 10^{23}$
(d) $\frac{180}{22.4} \times 6.023 \times 10^{23}$

76. Experimentally it is found that a metal oxide has formula $M_{0.98}O_1$. Metal M is present as M^{+2} and M^{+3} in its oxide. Fraction of metal which exist as M^{+3} would be

(a) 7.01% (b) 4.08%
(c) 6.05% (d) 5.08%

77. The ratio of masses of O_2 and N_2 in a particular gaseous mixture is 1 : 4. The ratio of number of their molecules is

(a) 1 : 8 (b) 3 : 16 (c) 1 : 4 (d) 7 : 32

78. A solution of H_2O_2 is labelled as 11.2 V. If the density of solution is 1.034 g/mL then identity the correct option.

(a) Molarity of solution = 2M
(b) Molality of solution = $\frac{1}{1.034}$
(c) $\% \frac{w}{w} = \frac{3400}{1034}$
(d) $\% \frac{w}{v} = \frac{34}{1000}$

79. A gaseous mixture of CO and CO_2 having total volume 150 mL is passed through a tube containing excess of red hot charcoal to cause the following reaction:

$$CO_{2(g)} + C_{(s)} \longrightarrow 2CO_{(g)}$$

The volume increases to 250 mL. Identify the correct statement.

(a) Original mixture contains 50% by moles CO.
(b) Original mixture contains 33.33% by moles CO.
(c) Original mixture contains 33.33% by moles CO_2.
(d) Mole fraction of CO_2 in the original mixture is 0.4.

80. Hydrogen gas is prepared in the laboratory by reacting dilute HCl granulated zinc. Following reaction takes place:

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

Calculate the volume of H_2 evolved at STP when 130.6 g of zinc reacts with HCl.

[Atomic mass of Zn = 65.3]

(a) 22.4 L (b) 44.8 L
(c) 11.35 L (d) 68.1 L

81. For a mixture of KCl and KNO_3 which of the following is possible percentage of K by mass?

(a) 10% (b) 45% (c) 70% (d) 90%

82. In 200 mL of aqueous HCl solution, excess of MnO_2 is added. If the liberated gas occupies 164.2 mL at 127ºC and 38 cm-Hg, then the molarity of HCl solution is (R = 0.0821 L atm/K mol)

$$MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$$

(a) 0.1 M (b) 0.2 M
(c) 0.4 M (d) 0.05 M

LEVEL II

1. Select the correct option for increasing order of number of atoms.

(I) 2 g of hydrogen (II) 16 g of sulphur
(III) 4 g of oxygen (IV) 31 g of phosphorus
(a) II > III > IV > I (b) IV > II > III > I
(c) I > IV > II > III (d) I = IV > II > III

2. Two elements *C* and *D* combine to form two compounds; C_xD_y and C_yD_x. 0.5 mole of C_yD_x weigh 40 g and 1 molecule of C_xD_y weigh 1.66×10^{-25} kg. The atomic weight of *C* and *D* are 20 and 40 respectively. What are '*x*' and '*y*'?

(a) 3, 2 (b) 1, 3 (c) 1, 2 (d) 2, 2

3. To form one molecule of Mg_3N_2, the total number of electron transferred from metal to non–metal is

(a) 6 N_A (b) 3 N_A (c) 3 (d) 6

4. A gaseous mixture contains SO_3 (g) and CH_4(g) in 5 : 1 ratio by mass. Calculate Q
where Q = 200 × ratio of total number of atoms present in SO_3(g) to total number of atoms present in CH_4(g).

(a) 160 (b) 16 (c) 320 (d) 32

5. Select the correct statement(s) for the following reaction:

$2A(s) + B(g) \rightarrow 3C(g) + 4D(l)$

(a) 2 moles of A always produce 3 moles of *C* and 4 moles of *D*
(b) 22.4 *l* of *B* (*g*) produces 3 moles of C at 1 atm and 273 K in excess of *A*.
(c) B will always remain in excess because volume of gas is very high than solid.
(d) Moles of *D* produced is always less than *C* because volume of liquid is less than gas.

6. An ore of iron contains FeS and some non-volatile impurity. On roasting this ore converts all FeS into Fe_2O_3 and 8% loss in weight was observed. Calculate mass percentage of FeS in ore?

$FeS + O_2 \rightarrow Fe_2O_3 + SO_2$

(a) 20 (b) 60 (c) 88 (d) 44

7. For the reaction,

$7A + 13B + 15C \rightarrow 17P$

if 15 moles of *A*, 26 moles of *B* and 30.5 moles of *C* are taken initially then limiting reactant is

(a) A (b) B
(c) C (d) None of these

8. The number of moles of KOH required for complete neutralisation of H_2SO_4 produced from dissolution of 500 g of 118% oleum in water is nearly

(a) 12 (b) 10 (c) 13 (d) 15

9. $Zn + O_2 \xrightarrow{90\%} ZnO$ ... (i)

$ZnO + H_2O \rightarrow Zn(OH)_2$ ... (ii)

If on taking 130 g of Zn with 100 g of O_2 and 50 g of H_2O afterwards 178.2 g $Zn(OH)_2$ is obtained, calculate the % yield of second reaction.

[Take Zn = 65]

(a) 100 (b) 75 (c) 10 (d) 80

10. A mixture of C_2H_4, CO and N_2 gases having total pressure 250 mm of Hg in which 250 mm Hg of O_2 is added at 27°C and then sparked. After the system was brought to the original temperature, the total pressure becomes 370 mm of Hg. If the partial pressure of CO_2 is 200 mm of Hg, then calculate the initial partial pressure of C_2H_4 (in mm of Hg)

[Given : At 27°C aqueous tension is 20 mm of Hg.]

(a) 40 (b) 50 (c) 60 (d) 75

11. A mixture of C_2H_4, CO and N_2 gases having total pressure 250 mm of Hg in which 250 mm Hg of O_2 is added at 27°C and then sparked. After the system was brought to the original temperature the total pressure becomes 370 mm of Hg. If the partial pressure of CO_2 is 200 mm of Hg, then calculate total O_2 consumed in mm of Hg.

[Given: At 27°C aqueous tension is 20 mm of Hg.]

(a) 150 (b) 170 (c) 200 (d) 220

12. To a 100 g an oleum sample labelled as '118% oleum', 9 g of water is added. Select the correct option(s).

(a) It contains only H_2SO_4 , SO_3 and SO_2.
(b) It contains H_2SO_4, SO_3 and H_2O.
(c) New solution will have labelling 109 %.
(d) % w/w of SO_3 is nearly 36.7 %.

13. Acid sample is prepared using HCl, H_2SO_4, H_2SO_3 and H_3PO_4 separately or as a mixture of any two or more. Calculate the minimum volume of 4% w/v NaOH added (in mL) to 294 g sample, in order to ensure complete neutralisation in every possible case.

(a) 9000 (b) 6000 (c) 4000 (d) 900

14. 30 mL gaseous mixture of methane and ethylene in volume ratio *X* : *Y* requires 350 mL air, containing 20% of O_2 by volume for complete combustion. If ratio of methane and ethylene is changed to $Y : X$, what will be the volume of air (in mL) required for complete reaction under similar condition of temperature and pressure?

(a) 400 (b) 200 (c) 300 (d) 800

15. The Haber's process for preparing ammonia involves direct conversion of hydrogen and nitrogen gases into NH_3 at high temperature and pressure using a catalyst

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

If air [consider it to contain 80% N_2, 20% O_2 by volume] is used as source for nitrogen, O_2 present in the air will oxidise NH_3 to NO as per the following reaction:

$4NH_3\ (g) + 5O_2\ (g) \rightarrow 4NO\ (g) + 6H_2O\ (g)$

Air and H_2 are taken in equal volumes in the beginning. Assume that both above reactions get completed and no other reaction is taking place. Select the correct statement(s).

(a) O_2 is completely exhausted.
(b) H_2 is not completely exhausted.
(c) N_2 is completely exhausted.
(d) NH_3 is completely exhausted.

16. Calcium phosphide Ca_3P_2 formed by reacting magnesium with excess calcium orthophosphate $Ca_3(PO_4)_2$, was hydrolysed by excess water. The evolved phosphine PH_3 was burnt in air to yield phosphrous pentoxide (P_2O_5). How many grams of magnesium metaphosphate would be obtained if 192 gram Mg were used? (Atomic weight of Mg = 24, $P = 31$)

$Ca_3(PO_4)_2 + Mg \rightarrow Ca_3P_2 + MgO$
$Ca_3P_2 + H_2O \rightarrow Ca(OH)_2 + PH_3$
$PH_3 + O_2 \rightarrow P_2O_5 + H_2O$
$MgO + P_2O_5 \rightarrow Mg(PO_3)_2$

(a) 11.52 g (b) 182 g
(c) 18.2 g (d) 24

17. A solution contains substances A and B in H_2O (solvent). The mole fraction of 'A' is 0.05 and molarity of 'B' is 7 M. The solution has a density of 1.14 g/mL. Calculate molarity of 'A'.
[Molecular weight of A = 10 g/mol; molecular weight of B = 30 g/mol]

(a) 2 M (b) 3 M
(c) 0.5 M (d) None of these

18. If 200 mL of 0.1 M Na_2SO_4 is mixed with 100 mL of 0.2 M Na_3PO_4 solution. Find molarity of Na^+ in the final solution, if final solution has density 1.2 g/mL.

(a) 0.196 M (b) 0.33 M
(c) 0.5 M (d) None of these

19. A solution of H_2O_2, labelled as '32V', was left open. Due to this, some H_2O_2 decomposed and the volume strength of the solution decreased. To determine the volume strength of the remaining H_2O_2 solution, 10 mL of this solution was taken and it was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.2 M $KMnO_4$ solution under acidic conditions. Calculate the volume strength of the diluted H_2O_2 solution.

(a) 28 V (b) 14 V (c) 32 V (d) 16.8 V

20. The number of oxygen atoms present in 24.5 g of H_3PO_4 is equal to

(a) Number of electrons present in 1.6 g methane (CH_4).
(b) Number of molecule of CO_2 present in 11.2 L at 1 atm and 546 K.
(c) Number of moles of proton present in N_A gram-atom of Hydrogen.
(d) Number of total atoms present in 4/3 mol of CO_2.

(a) a, c and d (b) a and c
(c) Only c (d) a and b

21. 25 mL of a solution containing HCl and H_2SO_4 required 10 mL of 1M NaOH solution for complete neutralisation. 20 mL of the same acid mixture on being treated with excess of $AgNO_3$ gives 0.1435 g of AgCl. If molarity of HCl is 'x' and that of H_2SO_4 is 'y'
$(x + y)$ will be

(a) 0.225 (b) 0 .125 (c) 1.25 (d) 0.05

22. Consider the given reaction.
$H_4P_2O_7 + 2NaOH \rightarrow Na_2H_2P_2O_7 + 2H_2O$
If 534 g of $H_4P_2O_7$ is reacted with 30×10^{23} molecules of NaOH then total number of molecules produced in the product is

(a) $2.5 \times N_A$ (b) $5 \times N_A$
(c) $7.5 \times N_A$ (d) $75 \times N_A$

23. The phosphorus pentaoxide used to produce phosphoric acid for cola soft drinks is prepared by burning phosphorus in oxygen. What is the % yield if 10 g of P_4O_{10} is isolated from the reaction $P_4 + 5O_2 \rightarrow P_4O_{10}$. Initially 0.2 mole of each P_4 and O_2 each are taken.

(a) 88.13 % (b) 98.1 %
(c) 68.1 % (d) 95. 1%

24. Automotive air bags are inflated when a sample of sodium azide (NaN_3) is rapidly decomposed [$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$]. What mass of sodium azide is required to produce 368 L of $N_2(g)$ with density 1.12 g/L?

(a) 0.638 kg (b) 1.2 kg
(c) 1.5 kg (d) 5 kg

25. A mixture of AgCl and AgBr undergoes a loss in weight by 8.9% when exposed to excess chlorination. The % by mass of AgCl in the original mixture is

(a) 37.6% (b) 17.8%
(c) 62.4% (d) 82.2%

26. Which of the following options does not represent concentration of semi-molal aqueous solution of NaOH having $d_{\text{solution}} = 1.02$ g/mL?

(a) Molarity $= \frac{1}{2}$M (b) $X_{NaOH} = \frac{9}{1009}$
(c) % w/w = 10% (d) % w/v = 2%

27. **Statement 1:** During the reaction: $N_2(g) + 2H_2(g) \rightarrow N_2H_4(l)$ volume contraction takes place.

Statement 2: Volume contraction always takes place when one of the product is in liquid state.

(a) Statements 1 and 2 are true. Statement 2 is the correct explanation for statement 1.
(b) Statements 1 and 2 are true. Statement 2 is NOT the correct explanation for statement 1.
(c) Statement 1 is true, statement 2 is false.
(d) Statement 1 is false, statement 2 is true.

28. **Statement 1:** For a very dilute solution, molality and molarity are always approximately equal

Statement 2: Mass of solution is always approximately equal to mass of solvent for a very dilute solution.

(a) Statements 1 and 2 are true. Statement 2 is the correct explanation for statement 1.
(b) Statements 1 and 2 are true. Statement 2 is NOT the correct explanation for statement 1.
(c) Statement 1 is false, statement 2 is true.
(d) Statement 1 is true, statement 2 is false.

29. **Statement 1:** As temperature increases, molality of solution decreases.

Statement 2: Molality of a solution is dependent on the mass of solute and solvent.

(a) Statements 1 and 2 are true. Statement 2 is the correct explanation for statement 1.
(b) Statements 1 and 2 are true. Statement 2 is NOT the correct explanation for statement 1.
(c) Statement 1 is true, statement 2 is false.
(d) Statement 1 is false, statement 2 is true.

30. SO_3 can be produced by the following two reactions:

$S_8 + O_2(g) \rightarrow SO_2(g)$
$SO_2(g) + O_2(g) \rightarrow SO_3(g)$

How many moles of S_8 are required to produce 20 mole of SO_3?

(a) $\frac{5}{2}$ mole (b) $\frac{5}{4}$ mole
(c) 10 mole (d) 5 mole

31. When $CH_4(g)$ is burnt in oxygen, it forms carbon dioxide and water. If 16 g of methane is mixed with 6.022×10^{24} molecules of oxygen at 1 atm, 300 K maximum volume of water that can be produced can be [Given : R = 0.0821 L-atm/mole K, $d_{H_2O(l)} = 1$ g/mL]

(a) 49.26 L (b) 44.8 L (c) 90 mL (d) 36 mL

32. Percentage loss in mass heating mixture of Na_2CO_3 and $CaCO_3$ containing equal masses of Na_2CO_3 and $CaCO_3$ is

(a) 44% (b) 25% (c) 22% (d) 50%

33. To an Eudiometry tube 10 mL of P, 30 mL of Q, 20 mL of R and 15 mL of S are added and subjected to sparking to cause the following reactions:

$2P_{(g)} + 3Q_{(g)} \rightarrow 2A_{(g)} + B_{(l)}$
$R_{(g)} + 2S_{(g)} \rightarrow 3A_{(g)} + 2C_{(g)}$

The volume change is given by

(a) 0 mL (b) 30 mL (c) 5 mL (d) 10 mL

34. 112.0 mL of gaseous NO_2 at 1 atm and 273 K was liquefied, the density of the liquid being 1.15 g/mL. Calculate the volume of and the number of molecules in the liquid NO_2.

(a) 0.10 mL and 3.01×10^{22}
(b) 0.20 mL and 3.01×10^{21}
(c) 0.20 mL and 6.02×10^{23}
(d) 0.40 mL and 6.02×10^{21}

35. Adipic acid HOOC–$(CH_2)_4$ COOH is used in making nylon. Calculate the weight of hydrogen atom present in 58.4 g of adipic acid.

(a) 4 g (b) 8 g (c) 40 g (d) 0.4 g

36. A gaseous mixture contains SO_3 (g) and C_2H_6 (g) in a 16 : 15 ratio by mass. The ratio of total number of atoms present in C_2H_6(g) and SO_3 (g) is

(a) 2 : 5 (b) 1 : 5 (c) 5 : 1 (d) 5 : 2

37. What amount of heat (in kJ) is released during formation of 31.2 g AsH_3 by the following reaction?
[Given: Atomic weight As = 75, H = 1
$2As\ (s) + 3H_2\ (g) \rightarrow 2\ AsH_3;\ \Delta H = -770$ kJ]

(a) 250 (b) 350 (c) 154 (d) 35

38. 5 mole of N_2 gas is added in a vessel at 1 atm and 300 K. Find the change in volume (in litre) of gas when 2 mole of He gas is added in it at same temperature and new pressure of 1.05 atm.
[Given: $R = 0.08$ atm L]

(a) 240 L (b) 40 L
(c) 100 L (d) 54 L

39. 1 atom of X, 2 atoms of Y and 3 atoms of Z combine together to give a molecule XY_2Z_3. Now we take 10 g of X and 2×10^{23} atoms of Y and 0.06 moles of Z in a container, to give 5.6 g of XY_2Z_3. What is the molar mass of Z.
[Given: $M_X = 60$ g/mol $M_Y = 80$ g/mol]

(a) 25 (b) 24 (c) 32 (d) 20

40. Hydrogen sulphide reacts with chloric acid in an aqueous solution liberating chlorine by the following reaction:

$H_2S + HClO_3 \rightarrow Cl_2 + H_2SO_4 + H_2O$

In an experiment, 40 mL of solution of chloric acid was allowed to react with sufficient amount of H_2S.

Cl_2 formed were reduced by 20 mL H_2O_2 by the following reaction:

$H_2O_2 + Cl_2 \rightarrow HCl + O_2\uparrow$

In the above reaction, 896 mL of O_2 was evolved at 1 atm and 273 K.

Which of the following option is incorrect for aforementioned experiment?

(a) Normality of H_2O_2 solution used is 4 N.
(b) Molarity of original $HClO_3$ solution used is 2 M.
(c) Equivalents of H_2S reacted with $HClO_3$ is 0.05.
(d) Moles of Cl_2 produced is 0.04.

LEVEL III

Paragraph for Q. Nos. 1 to 3

24 g pure sample of magnesium is burned in air to form magnesium oxide and magnesium nitride. When products are treated with excess of H_2O, 3.4 g of gaseous NH_3 is generated according to given reactions.

$$Mg + O_2 \rightarrow MgO$$
$$Mg + N_2 \rightarrow Mg_3N_2$$
$$Mg_3N_2 + 6H_2O \rightarrow 3Mg\,(OH)_2 + 2NH_3$$

1. Calculate the amount of magnesium oxide (in g) in products.

(a) 28 (b) 20 (c) 16.8 (d) 32

2. Calculate the amount of $Mg(OH)_2$ (in g) produced in the above reaction.

(a) 11.6 (b) 17.4 (c) 23.2 (d) 15.8

3. Calculate the mass % of Mg converted into Mg_3N_2.

(a) 20 (b) 30 (c) 35 (d) 40

Paragraph for Q. Nos. 4 to 5

12 mL gaseous mixture of an alkane and an alkene (containing same number of carbon atoms) require exactly 285 mL of air (containing 20% v/v O_2 and rest N_2) for complete combustion at 200 K. After combustion when gaseous mixture is passed through KOH solution it shows volume contraction of 36 mL.

4. Formula of alkane is

(a) C_5H_{12} (b) C_3H_8
(c) C_2H_6 (d) C_4H_{10}

5. Mole fraction of CO_2 in final gaseous sample is

(a) $\frac{6}{51}$ (b) $\frac{6}{44}$ (c) $\frac{6}{45}$ (d) $\frac{6}{13}$

Paragraph for Q. Nos. 6 to 7

1292.5 g of aquesous solution of '5 m' NaCl is kept in a large bucket. The bucket is placed under a tap from which '2 m' aqueous solution of NaCl is flowing. Rate of flow of solution from tap is 0.5 g/sec.

6. The total amount of solution (in g) finally present in bucket when solution present in bucket have concentration of NaCl 4 m is

(a) 558.5 (b) 1851
(c) 1351 (d) 1938.75

7. The time (in seconds) after which the bucket will have '4m' concentration of NaCl.

(a) 117 (b) 2000 (c) 1117 (d) 1292.5

Paragraph for Q. Nos. 8 to 10

Analysis of dissolved oxygen in river water is very essential to ensure that aquatic life is safe. As per European standards, dissolved oxygen should never be less than 6.4 mg/L and preferably should be greater than 9.6 mg/lit. A water body having value less than 6.4 mg/L is considered 'heavily polluted' and a water body having value greater than 9.6 mg/L is considered optimum fit for aquatic life. One method to measure dissolved oxygen is through Winkler titration. The method involves three stages:

Stage 1: The water sample is treated with excess of Mn^{2+} (aq) solution along with a base to cause the following reaction:

$$Mn^{2+}(aq) + 2OH^-(aq) \rightarrow Mn(OH)_2(s) \quad \text{...(i)}$$

The precipitate then reacts with dissolved oxygen as shown below.

$$2Mn(OH)_2(s) + \frac{1}{2}O_2(aq) + H_2O(l) \rightarrow 2Mn(OH)_3(s) \quad \text{...(ii)}$$

Stage 2: The solution is added with excess of acidified solution of KI to cause the following reaction:

$$2Mn(OH)_3(s) + 2KI + 3H_2SO_4$$
$$\rightarrow 2MnSO_4 + K_2SO_4 + I_2(aq) + 6H_2O \quad \text{...(iii)}$$

Stage 3: The I_2 produced is calculated by the following reaction by calculating the amount of $Na_2S_2O_3$ consumed.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \quad \text{...(iv)}$$

Using the above information answer the following questions:

8. If 1 L of water sample is taken then calculate the maximum volume of 0.01 M $Na_2S_2O_3$ solution required if the sample is considered 'heavily polluted'.

(a) 80 mL (b) 80 L (c) 120 mL (d) 120 L

9. If 1 L of water sample is taken then calculate maximum volume of 0.1 M $Na_2S_2O_3$ solution required if the sample is considered 'optimum fit' for aquatic life.

(a) 8 mL (b) 80 mL (c) 12 mL (d) 120 mL

10. Which of the following statements is correct w.r.t. above method?

(a) Greater the amount of dissolved oxygen, lesser will be moles of $Na_2S_2O_3$ required.
(b) Excess solution in Stage 1 ensure all dissolved oxygen reacts.
(c) Moles of $Mn(OH)_2(s)$ reacted and moles of $Mn(OH)_3$ formed will be different.
(d) 1 mole of dissolved oxygen will require 2 moles of $Na_2S_2O_3$ for estimation.

(One or more than one correct type)

11. Which of the following solutions will be definitely basic?

(a) 400 mL of 0.1 M NaOH is mixed with 100 mL of 0.4 M CH_3COOH.
(b) Equal volumes of same % w/v of NaOH and H_2SO_4 solutions are mixed.
(c) Different volumes of 0.2 M NaOH and 0.1 M HCl solutions are mixed.
(d) Equal masses of same % w/w NaOH and HCl solutions are mixed.

12. In the formation reaction of NH_3 from N_2 and H_2, 140 g of N_2 and 40 g H_2 were mixed. Select the option(s) which is are not correct.

(a) Maximum mass of NH_3 which can be formed is 180 g.
(b) If % yield of reaction is 80%, then H_2 consumed will be 32 g.

(c) Some N_2 (g) will be left after the reaction.
(d) If NH_3 formed is 85 g then % yield will be 50%.

13. 500 g of 109% labelled oleum is taken. Which of the following statement(s) is/are correct regarding this oleum sample?
(a) The maximum mass of H_2SO_4 which may be obtained from the sample is 509 g.
(b) When 100 g water is added in it, the sample finally contains 545 g H_2SO_4 and 55 g water.
(c) When 100 L water is added in it, the approximate molarity of H_2SO_4 solution obtained will be 0.056M.
(d) When 20 g water is added to it, the sample finally contains 520 g pure H_2SO_4.

14. When taken in an Eudiometer tube operating at room temperature and pressure and subjected to complete reaction, in which of the following options the contraction in volume is greater than or equal to 30% of original volume.
(a) CO(g) and O_2(g) taken in a molar ratio of 2 : 1.
(b) 10 mL of CH_4(g) and 30 mL of O_2(g).
(c) N_2(g) and H_2(g) taken in a molar ratio of 3 : 1.
(d) N_2 and H_2 taken in a molar ratio of 1 : 3

15. Which of the following is/are correct statement(s)?
(a) For the production of equimolar mixture of CO and CO_2 gases, 12 g carbon must be burnt with 24 g oxygen (assuming 100% yield of reactions).
(b) Molarity of any aqueous solution will be equal to its molality if the volume of solution (in mL) and the mass of solvent (in gram) are numerically same.
(c) Gases behave ideally in the conditions of their very low molar volumes and force of attraction between them.
(d) all of the above.

16. A gaseous organic compound $C_xH_{2y}O_y$ (M = 150) was burnt with four times the amount of O_2 gas as required for complete combustion. The resulting gases when cooled to 1 atm pressure and 300 K were found to occupy (4.926) L along with 0.9 g of water. Identify the correct option(s).
(a) If 10 mL of organic compounds is taken then oxygen taken should be 200 mL.
(b) Fraction of O by number in the compound is $\frac{2}{3}$.
(c) The compound should be $C_4H_6O_3$.
(d) Percent of H by mass in the compound will be $\frac{100}{15}$%.

17. The sample(s) containing same number of 'Na' atom as there are 'Na' atoms in 5.3 g of Na_2CO_3, is/are
(a) 4 g of NaOH
(b) 5.85 g of NaCl
(c) 0.25 mole of Na_2SO_4
(d) 5.6 g of Na_3PO_4

18. For the following reactions:
I. $(NH_4)_2SO_4 + 2NaOH \xrightarrow{40\ \%} Na_2SO_4 + 2H_2O + 2NH_3$
II. $NH_3 + HCl \xrightarrow{80\%} NH_4Cl$
If 4 g of NaOH is taken then
(a) produced moles of NH_4Cl (in IInd reaction) are 1.6 times of produced moles of Na_2SO_4 (in reaction I).
(b) reacting moles of HCl (in reaction II) is 20 % lesser than original $(NH_4)_2SO_4$ moles.
(c) reacting moles of HCl (in reaction II) is lesser than reacting moles NaOH (in reaction I).
(d) produced mass of NH_4Cl is 2.71 g.

19. Choose incorrect options.
(a) $2\ 25 \times 10^{-22}$g of $Ca(OH)_2$ containing 32 amu of O.
(b) If one atom of an element weighs 1.8×10^{-22} g, then its atomic mass is 108.36.
(c) 10 g of $CaCO_3$ contains 0.3 g atom of oxygen.
(d) Number of atoms in 2 moles of S_8 is greater than 5.5 moles of SO_2.

20. Which of the following is/are correct?
(a) The density of a gas depends upon pressure and temperature.
(b) The relative density of a gas depends upon pressure and temperature.
(c) The vapour density of a gas depends upon pressure and temperature.
(d) The relative density of SO_3 with respect to oxygen is 2.5 at 1 atm and 273 K.

21. A mixture of H_2 and O_2 having total volume 55 mL is sparked in an eudiometry tube and contraction of 45 mL is observed after cooling. What can be the composition of reacting mixture?
(a) 30 mL H_2 and 25 mL O_2
(b) 10 mL H_2 and 45 mL O_2
(c) 40 mL H_2 and 15 mL O_2
(d) 35 mL H_2 and 20 mL O_2

22. Which of the following is/are incorrect statement(s)?
(a) Vapour density of gaseous mixture decreases during the progress of
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ reaction.
(b) 22.4 L of H_2O at 1 atm and 273 K contains 6.02×10^{23} molecules of H_2O.
(c) 10 g of 104.5 % labelling oleum sample contains 2 g of free SO_3.
(d) Volume of solution is always equal to the sum of volume of solute and solvent.

23. Choose the correct statement(s).
(a) The mole is the amount of substance containing the same number of chemical units as there are atoms in exactly 12 g of ^{12}C.
(b) Avoggadro's number is the number of units in a mole.
(c) The weight of one gram-atom of an element means its atomic weight in g.
(d) One g-atom of each element contains the same number of atoms.

24. Select the incorrect statement(s).

(a) Mass of 6.022×10^{25} molecule of SO_3 is 8 kg.

(b) Number of oxygen atoms in 4.8 g of O_3 are 18.06×10^{23}.

(c) Mass of 22.7 mL of C_2H_6 at 1 bar pressure and 273 K is 30 g.

(d) Volume of 51 mg of NH_3 at 1 bar pressure and 273 K is 68.1 *l*.

25. Choose the incorrect option(s).

(a) 2.25×10^{-22} g of $Ca(OH)_2$ containing 32 amu of O.

(b) One atom of an element weighs 1.8×10^{-22} g, then its atomic mass is 108.36.

(c) 10 g of $CaCO_3$ contains 1 g atom of C.

(d) Number of atoms in 2 moles of S_8 is greater than 5.5 moles of SO_2.

26. Identify the incorrect statement(s).

(a) Molarity of very dilute solution with CCl_4 as solvent is greater than its molality if density of CCl_4 is 1.6 g/cm^3.

(b) An oleum with labelling $\frac{196}{178} \times 100$ will have mass % combined SO_3 equal to $\frac{160}{178} \times 100\%$.

(c) The value of universal gas constant is (0.0821×0.76) in mm of Hg – m^3/mole Kelvin.

(d) For an all gaseous reaction if volume changes during reaction at constant temperature and pressure then vapour density may remain constant.

(Column matching)

27. A_2 reacts with B_2 in either of the following ways depending upon supply of B_2:

$$A_2 + B_2 \rightarrow 2AB$$

$$A_2 + 3B_2 \rightarrow 2AB_3$$

Also, the products formed may also react with appropriate reactant remaining to form other product. Using this information, match composition of the final mixture for initial amount of reactants.

	Column I (Initial reactants)		**Column II (Final Products)**
(A)	4 moles of A_2 are mixed with 8 moles of B_2	(P)	None of the reactant is left
(B)	2 moles of A_2 are mixed with 5 moles of B_2	(Q)	Product contains both AB and AB_3
(C)	2 moles of A_2 are mixed with 1 moles of B_2	(R)	One of the reactant is left
(D)		(S)	Equal moles of AB and AB_3 are formed

28. Match the expressions/statements in **Column I** with expressions/Statements in **Column II.**

	Column I		**Column II**
(A)	1 mole of O_2	(P)	occupies 22.4 L at 1 atm and 0°C
(B)	1 mole of SO_2	(Q)	weighs 32 g
(C)	4 g of He	(R)	collection of N_A smallest existing independent species
(D)	1 g of H_2	(S)	occupies 12.3 L at 1 atm and 300 k

29. Match the expressions/statements **Column–I** with expressions/Statements in **Column–II.**

	Column I Atomic masses Isotope-I, Isotope-II, Avg		**Column II % composition of heavier isotope**
(A)	$(z - 1), (z + 2), z$	(P)	33.33 % by moles
(B)	$(z + 1), (z + 3), (z + 2)$	(Q)	50 % by moles
(C)	$z, 3z, 2z$	(R)	% by mass dependent on z
(D)	$(z - 1), (z + 1), z$	(S)	75 % by mass

30. Match the expressions/statements in **Column I** with expressions/Statements in **Column II.**

	Column I		**Column II**
(A)	1.0 g-ion of Na^+	(P)	6.02×10^{24} electron
(B)	23.0 g of Na	(Q)	7.224×10^{24} neutron
(C)	1.0 g-ion of Mg^{+2}	(R)	$6.02 \times 10^{23} \times 2 \times 1.6 \times 10^{-19}$ columb charge
(D)	24 g of Mg	(S)	7.224×10^{24} proton

31. Match the expressions/statements in **Column I** with expressions/Statements in **Column II.**

	Column I		**Column II**
(A)	0.5 mol of $CO_2(g)$	(P)	Occupy 11.2 L at 1 atm and 273 K
(B)	2 g of helium (g)	(Q)	mass = 24 g
(C)	0.5 g molecule of $O_3(g)$	(R)	total number of atoms = $1.5 \times 6.02 \times 10^{23}$
(D)	4.515×10^{23} molecules O_2	(S)	mass = 22 g of oxygen (g)
		(T)	3.01×10^{23} molecules

32. Match the expressions/statements in **Column I** with expressions/Statements in **Column II.**

	Column I		**Column II (No. of moles)**
(A)	Oxygen atoms in 0.5 mol $Ca_3(PO_4)_2$	(P)	8
(B)	Carbon atoms in 89.6 L CH_3 at 1 atm and 273 K.	(Q)	4

(C)	Sulphur atoms in 192 g of SO_2	(R)	5
(D)	'Cl' in 15×10^{23} molecules Cl_2O [Take $N_A = 6 \times 10^{23}$]	(S)	3
		(T)	6

33. Match the expressions/statements in **Column I** with expressions/Statements in **Column II.**

	Column I (No. of moles)		**Column II**
(A)	1 mole of O_2	(P)	Occupies 22.4 L at 1 atm and 0°C
(B)	1 mole of SO_2	(Q)	Weighs 32 g
(C)	4 g of He	(R)	Collection of N_A units of given substance
(D)	1 g of H_2	(S)	Occupies 12.3 L at 1 atm and 300 K
		(T)	Contains 2 g-atom of oxygen

(Integer type)

34. $KClO_4$ can be prepared by Cl_2 and KOH by a series of reactions as given below:

$Cl_2 + 2KOH \rightarrow KCl + KClO + H_2O$

$3KClO \rightarrow 2KCl + KClO_3$

$4KClO_3 \rightarrow 3KClO_4 + KCl$

If 10 moles of Cl_2 are mixed with 22 moles of KOH, calculate total moles of all the substance at the end of reaction. (Assuming 100% yield of all the reactions.)

35. Four identical bottles numbered from 1 to 4 are arbitrarily filled with four substances : $C_6H_{12}O_6$ (Glucose), CH_3COOH (Acetic acid), $CH_3–COCH_3$ (Acetone) and HCHO (Formaldehyde) (No specific order). Based on following information given, identify the substances filled.

Information-I : Percentage of C is same in compounds filled in bottles 1, 3, 4 but different in 2.

Information-II : Vapour density of compound filled in bottle 4 = 3 × vapour density of compound filled in bottle 1.

After identifying the substances filled in different bottles, arrange them in decreasing order of their molecular masses.

[For example, If molecular mass order is 4 > 3 > 2 > 1 then answer is 4321]

[Assuming normal behaviour of all the substances.]

36. 1000 g of a mixture of Na_2CO_3, Na_2SO_4 and NaOH for complete neutralisation requires 511 g of HCl. The same mixture when reacted with excess of $BaCl_2$ solution, produced 466 g of white precipitate of $BaSO_4$. Calculate mass % of NaOH in mixture.

37. 10.48 g of chloroplatinate salt of diacidic organic base was subjected to heating to obtain 3.9 g of white shining residue. Molar mass of the organic base is given by

(a) 1048 (b) 228 (c) 114 (d) 72

38. Different acid samples are prepared by using H_2SO_4, HCl, HNO_3, H_3PO_2 and $HClO_4$ separately or as a mixture. Calculate minimum volume of 20% w/v NaOH solution required (in mL) to completely neutralise any sample which can be prepared if mass of the sample cannot exceed 292 g.

[Round-off answer to nearest integer if required]

39. Calculate a four-digit number "abcd" from the following information.

ab = Volume of water (in L) required to obtain 3 L of 17% w/v $AgNO_3$ solution from a stock solution of $AgNO_3$ having molarity 3 M.

cd = Mole percentage of ethane in a mixture of ethane and argon having mass fraction of Argon equal to $\frac{4}{7}$.

[if your answers are 6 and 25 fill 0625]

40. 10 mL of a gaseous organic compound $C_xH_yO_zN_p$ (molar mass = 61) is taken in an eudiometry tube and mixed with sufficient oxygen gas such that volume becomes 42.5 mL. On sparking, some contraction was observed. On passing the residual gas through alcoholic KOH, a contraction of 20 mL was observed. The volume of the residual gas is 5 mL. All volumes are measured at room temperature and pressure. Calculate the value of the four digit number '*xyzp*'.

41. 10 mL of a mixture of CO (*g*) and CH_4(*g*) was mixed with 22 mL of O_2 gas and subjected to sparking. The contraction observed when the residual gases are passed through alc. KOH is given by *x* mL. Find *x*?

[All volumes are measured at same temperature and pressure]

42.

Compositions	**Solution codes**
(a) 100 g SO_3 and 200 g H_2SO_4	8
(b) 80 g SO_3 and 80 g H_2SO_4	6
(c) 5 moles SO_3 and 5 moles H_2SO_4	4
(d) 6 moles SO_3 and 5 moles H_2SO_4	2

Calculate a four-digit number 'abcd' which is obtained by writing solution codes of above compositions in the increasing order of % labelling of above oleum.

43. Three substances A, B and C can react to form C and D as shown below.

$2A + 3B + C \rightarrow 4D + 2E$

If molar masses of A, B, C and D are 40, 30, 20 and 15 respectively and 570 g of mixture of A, B, and C is reacted then calculate maximum mass of E which can be obtained (in gram).

44. If 246 g of a triatomic ideal gas having only one type of atoms is found to occupy 44.8 L at 2 atm and 546 K then what will be the atomic weight of the element?

45. 100 mL of 0.2M H_2SO_4 solution is mixed with 400 mL of 0.05M $Ba_3(PO_4)_2$. The concentration of $[Ba^{+2}]$ ion in resulting solution is xM. Find the value of $100 \times x$?

46. Acrylonitrile, C_3H_3N, is the starting material for the production of a kind of synthetic fibre (acrylies). It can be made from propylene, C_3H_6, by reaction with nitric oxide, NO as
$C_3H_6(g) + NO(g) \rightarrow C_3H_3N(g) + H_2O(g) + N_2(g)$ (Unbalanced)
How many kilograms acrylonitrile are obtained from 420 kg of propylene and excess NO?

47. 10 mL gaseous C_4H_x requires exactly 55 mL O_2 for complete combustion. What is the value of 'x'.

48. In 1200 g solution, 12 g urea (NH_2CONH_2) is present. If density of the solution is 1.2 g/mL, then the molarity of the solution is xM. Find 10x?

49. In the following reactions if initially 100 moles of A were taken then calculate sum of moles of D and C after the reaction.

$$A \xrightarrow{40\%} 3B + D$$

$$2B \xrightarrow{50\%} 4C$$

50. Calculate the sum of molality and molarity of a pure liquid (molar mass M = 50) having density $d = 2$ g/mL.

51. What would be the maximum volume (in mL) of 3 M HCl solution that can be prepared by using 2 M, 1 L HCl and 5 M, 2 L HCl kept in separate vessels.

52. 20 mL of a mixture of C_2H_6 and C_3H_8 gases in X : Y mole ratio, is burnt completely by which 52 mL CO_2 gas is evolved. If 20 mL of a mixture of CH_4 and C_4H_{10} gases in Y : X mole ratio is burnt completely, then what is the volume (in mL) of CO_2 gas evolved?

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

JEE Main

1. How many moles magnesium phosphate, $Mg_3(PO_4)_2$, will contain 0.25 mole of oxygen atoms? **[AIEEE 2006]**
(a) 2.5×10^{-2} (b) 0.02
(c) 3.125×10^{-2} (d) 1.25×10^{-2}

2. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is **[AIEEE 2006]**
(a) 0.44 mol kg^{-1} (b) 1.14 mol kg^{-1}
(c) 3.28 mol kg^{-1} (d) 2.28 mol kg^{-1}

3. In the reaction : $2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^{-}(aq) + 3H_2(g)$ **[AIEEE 2007]**
(a) 6 L HCl(aq) is consumed for every 3 L H_2(g) produced.
(b) 33.6 L H_2(g) produced regardless of temperature and pressure for every mole Al that reacts.
(c) 67.2 L H_2(g) at STP is produced for every mole Al that reacts.
(d) 11.2 L H_2(g) at STP is produced for every mole HCl(aq) consumed.

4. The density (in g mL^{-1}) of a 3.6 M sulphuric acid solution that is 29 % H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be **[AIEEE 2007]**
(a) 1.64 (b) 1.88 (c) 1.22 (d) 1.45

5. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl because HCl **[AIEEE 2008]**
(a) gets oxidised by oxalic acid to chlorine.
(b) furnishes H^+ ions in addition to those from oxalic acid.
(c) reduces permanganate to Mn^{2+}.
(d) oxidises oxalic acid to carbon dioxide and water.

6. The mass of potassium dichromate crystals required to oxidise 750 cm^3 of 0.6 M. Mohr's salt solution is (molar mass = 392) **[AIEEE 2011]**
(a) 0.49 g (b) 0.45 g
(c) 22.05 g (d) 2.2 g

7. The molality of a urea solution in which 0.0100 g of urea, $[(NH_2)_2CO]$ is added to 0.3000 dm^3 of water at STP is **[AIEEE 2011]**
(a) 5.55×10^{-4} m (b) 33.3 m
(c) 3.33×10^{-2} m (d) 0.555 m

8. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity if this solution is **[AIEEE 2012]**
(a) 0.50 M (b) 1.78 M
(c) 1.02 M (d) 2.05 M

9. The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be **[JEE Main 2013]**
(a) 0.875 M (b) 1.00 M
(c) 1.75 M (d) 0.0975 M

10. A gaseous hydrocarbon gives 0.72 g of water and 3.08 g of CO_2 upon combustion. The empirical formula of hydrocarbon is **[JEE Main 2013]**
(a) C_2H_4 (b) C_3H_4
(c) C_6H_5 (d) C_7H_8

11. The ratio of masses of oxygen and nitrogen in a particular gaseous mixture is 1 : 4. The ratio of number of their molecule is **[JEE Main 2014]**
(a) 1 : 4 (b) 1 : 8 (c) 7 : 32 (d) 3 : 16

JEE Advanced

Single Correct Answer Type

12. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is **[IIT JEE 2007]**
(a) 3 (b) 4 (c) 5 (d) 6

13. Given that the abundance of isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe is 5%, 90% and 5% respectively. The atomic mass of Fe is **[IIT JEE 2009]**

(a) 55.85 (b) 55.95
(c) 55.75 (d) 55.05

14. Dissolving 120 g of urea [Mw = 60] in 1000 g of water gave a solution of density 1.15 g mL^{-1}. The molarity of solution is **[IIT JEE 2011]**
(a) 1.78 M (b) 2.00 M
(c) 2.05 M (d) 2.22 M

Integer Answer Type

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

16. Silver (atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3}. The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. Find the value of x. **[IIT JEE 2010]**

17. Find the value of n in the molecular formula $Be_nAl_2Si_6O_{18}$. **[IIT JEE 2010]**

18. Among the following, what is the number of elements showing only one non-zero oxidation state ? O, Cl, F, N, P, Sn, Tl, Na, Ti **[IIT JEE 2010]**

19. 29.2 % (w/w) HCl stock solution has a density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. Find the volume of (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl. **[IIT JEE 2012]**

20. If the value of Avogadro number is 6.023×10^{23} mol^{-1} and the value of Boltzmann constant is 1.380×10^{28} J K^{-1}, then find the number of significant digits in the calculated value of the universal gas constant. **[JEE Advanced 2014]**

21. The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (molecular weight = 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin? **[2015 JEE Main]**
(a) $\frac{1}{103}$ (b) $\frac{1}{206}$
(c) $\frac{2}{309}$ (d) $\frac{1}{412}$

22. 3g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is **[2015 JEE Main]**
(a) 18 mg (b) 36 mg
(c) 42 mg (d) 54 mg

Answer Key

LEVEL I

1. (b)	2. (b)	3. (d)	4. (a)	5. (a)	6. (a)	7. (a)	8. (d)	9. (c)	10. (b)
11. (d)	12. (a)	13. (a)	14. (a)	15. (b)	16. (a)	17. (b)	18. (b)	19. (c)	20. (b)
21. (a)	22. (d)	23. (c)	24. (d)	25. (a)	26. (d)	27. (b)	28. (b)	29. (b)	30. (a)
31. (c)	32. (c)	33. (a)	34. (c)	35. (b)	36. (a)	37. (a)	38. (c)	39. (a)	40. (c)
41. (a)	42. (a)	43. (a)	44. (d)	45. (a)	46. (a)	47. (b)	48. (d)	49. (b)	50. (c)
51. (b)	52. (c)	53. (b)	54. (b)	55. (b)	56. (a)	57. (b)	58. (b)	59. (b)	60. (a)
61. (d)	62. (a)	63. (c)	64. (a)	65. (a)	66. (a)	67. (b)	68. (a)	69. (c)	70. (b)
71. (c)	72. (b)	73. (c)	74. (b)	75. (b)	76. (b)	77. (d)	78. (c)	79. (b)	80. (b)
81. (b)	82. (d)								

LEVEL II

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

LEVEL III

1. (a)	2. (b)	3. (b)	4. (b)	5. (b)	6. (b)	7. (c)	8. (a)	9. (c)	10. (b)
11. (a, b)	12. (a, b, c)		13. (b, c)	14. (a, b, d)		15. (a, b)	16. (a, d)	17. (a, b, d)	

18. (a, b) 19. (a, d) 20. (a, d) 21. (a, c) 22. (a, b, d) 23. (a, b, c, d) 24. (b, c, d)
25. (a, c, d) 26. (b, d) 27. (A) → P, Q, S; (B) → P, Q; (C) → R
28. (A) → P, Q, R; (B) → P, R; (C) → P, R; (D) → S 29. (A) → P, R; (B) → Q, R; (C) → Q, S; (D) → Q, R
30. (A) → P, Q; (B) → Q; (C) → P, Q, R, S; (D) → Q, S 31. (A) → P, R, S, T; (B) → P; (C) → P, Q, T; (D) → Q, R
32. (A) → Q; (B) → Q; (C) → S; (D) → R 33. (A) → P, Q, R, T; (B) → P, R, T; (C) → P, R; (D) → S
34. (32) 35. (4123) 36. (8) 37. (114) 38. (1600) 39. (0251) 40. (2711) 41. (10) 42. (8426) 43. (390)
44. (41) 45. (8) 46. (530) 47. (6) 48. (2) 49. (160) 50. (60) 51. (1500) 52. (44)

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (c) 2. (d) 3. (d) 4. (c) 5. (c) 6. (c) 7. (a) 8. (d) 9. (a) 10. (d)
11. (c) 12. (d) 13. (b) 14. (c) 15. (3) 16. (7) 17. (2) 18. (2) 19. (8) 20. (4)
21. (d) 22. (d)

Hints and Solutions

LEVEL 1

1. (a) (1) Oxygen atom : Hydrogen atom
4 : 12 [1 : 3]
(2) $3NH_4^+$: $1\,PO_4^{3-}$ [3 : 1]
(3) N atom : Oxygen atom [3 : 4]
(4) $(NH_4)_3PO_4$ | 3N + 12 H + P + 4 O
1 mole
1 mole of $(NH_4)_3PO_4$ having 20-Mole of atoms and or $(20 \times N_A)$ atoms.

2. (b) $PV = nRT$

$= 1 \times 10^{-3}$ number of moles

$\therefore$ No of moles of of atom $= 3 \times 10^{-3}$

Let volume of H_2O_2 is V mL

Mass of $H_2O_2 = V \times d = V \times 5.1 \times 10^{-3}$

$$\text{Moles of } H_2O_2 = \frac{V \times 5.1 \times 10^{-3}}{34}$$

$$\text{Number of moles of atoms} = \frac{V \times 5.1 \times 10^{-3}}{34} \times 4$$

$$= 3 \times 10^{-3}$$

V of H_2O_2 = 5 mL

3. (d) 72 g Mg is present in

1 mole $Mg_3(PO_4)_2$

$\therefore$ 8 moles of O atoms

4 moles of O_2 molecules

4 gm molecules of O_2 are present

4. (a) 930 gm of $Ca_3(PO_4)_2$ = 3 mole of $Ca_3(PO_4)_2$

= 15 moles of ions

5 moles of Na_2SO_4 = 15 mole of ions

weight of $Na_2SO_4 = 5 \times 142$

= 710 g

5. (a) Average atomic weight $= \Sigma X_i M_i$

$= 35 \times 0.8 + 37 \times 0.2$

$= 35.4$

Average number of neutrons

$$= \frac{18 \times 80 + 20 \times 20}{100} = 18.4$$

6. (a) $K_2SO_4 . Al_2(SO_4)_3 \cdot 24\, H_2O$

6.4 kg oxygen

[moles of substance × 40] = number of mole of oxygen

$40 \times x \times 16 = 6400$ g= wt of oxygen

$x = 10$ moles

number of moles of $S = 4 \times 10$ moles = 40 moles

weight of sulphur $= 40 \times 32 = 1280$ g

7. (a) 448 l O_2 and $CO_2(g)$ 2 : 3

$$\text{Volume of } CO_2 = \frac{3}{5} \times 448 = 268.8\ l$$

$$\text{Number of moles of } CO_2 = \frac{268.8\text{L}}{22.4\text{L}} = 12 \text{ mole}$$

8. (d) $A_2SO_4 \cdot xH_2O$

$A_2SO_4 \cdot xH_2O \longrightarrow A_2SO_4 + xH_2O$

$$\%\text{ of } H_2O = \frac{x \times 18}{110 + x \times 18} \times 100 = 45$$

$1800\,x = 4950 + 810\,x$

$1800\,x - 810\,x = 4950$

$990\,x = 4950$

$x = 5$

9. (c) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

$$n_{MnO_2} = \frac{1.74}{87} = 0.02$$

$$n_{HCl} = \frac{2.19}{36.5} = 0.06$$

No of moles /stoichiometric cofficient least for HCl

$\therefore$ HCl is limiting reagent

4 mole of HCl gives 1 mole of Cl_2

1 mole of HCl gives 1/4 mole of Cl_2

0.06 mole of HCl gives $1/4 \times 0.06$ mole of $Cl_2 = 0.015$ Mole

$$\% \text{ yield} = \frac{\text{Actual product formed}}{\text{theoritical product formed}} \times 100$$

$$40 = \frac{x}{0.015} \times 100$$

$$x = 40 \times \frac{0.015}{100} = 0.006 \text{ moles } Cl_2$$

Volume of Cl_2 at 1 atm, 273 K = 0.006 × 22.4 (lit.) = 134.4 ml

10. **(b)** $(CaCO_3 + Na_2CO_3)$ mixture = 103 g

Let moles of $CaCO_3 = x$

moles of $Na_2CO_3 = y$

$$\overset{x}{CaCO_3} + \overset{y}{Na_2CO_3} + HCl \longrightarrow \overset{1}{CO_2} \text{ and other products.}$$

CO_2 produced have C atoms from Na_2CO_3 and $CaCO_3$

moles of CO_2 produce = $PV = nRT$

$$1 \times 24.63 = n \times 0.0821 \times 300$$

$$n = 1$$

Apply POAC on C atom

$$1 \times x + y \times 1 = 1$$

$$x + y = 1$$

$$100\,x + 106\,y = 103 = \text{wt of mixture}$$

$$6x = 3;\ x = 0.5;\ y = 0.5$$

weight of $CaCO_3$ = 50 g

weight of Na_2CO_3 = 53 g

$$\% \, CaCO_3 = \frac{50}{103} \times 100 = 48.54\ \%$$

11. **(d)** $\underset{2\text{ g}}{H_2} + \underset{71\text{ g}}{Cl_2} \longrightarrow 2HCl$

1 mole of H_2 react with 1 mole Cl_2 gives 2 mole HCl

∴ No of moles of HCl produced

= 2 moles = 2 × 36.5 g = 73 g

12. **(a)** Conceptual

13. **(a)** $Cu + 4\,HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

1 mole Cu Provide 2 moles NO_2

$$\frac{12.7}{63.5} \text{ Mole Cu provide} = 2 \times \frac{12.7}{63.5} \text{ Mole } NO_2$$

$$n_{NO_2} = 0.4$$

∴ Volume = 0.4 × 22.4 × 1000 mL = 8960 mL

14. **(a)** Mass of carbon in 1 molecule of $X = 21 \times 12 = 252$ amu if % weight of carbon is 50.4 % in molecule then

$$\text{Molecular mass of } X = \frac{252 \times 100}{50.4} = 500 \text{ amu}$$

15. **(b)** $FeCl_3(s) \longrightarrow FeCl_2(s) + \frac{1}{2} Cl_2(g)$

1 mol $FeCl_3(s)$ given 0.5 mol $Cl_2(g)$

$$P = \frac{0.5 \times 0.0821 \times 300}{0.0821} = 150 \text{ atm}$$

16. **(a)** $P = 294\left[\dfrac{54 + 96 \times 3}{98 \times 3}\right] = 294\left[\dfrac{342}{294}\right] = 342$

17. **(b)** $m = \dfrac{\left(\dfrac{936}{18}\right)}{\left(\dfrac{936}{1000}\right)} \Rightarrow \dfrac{(52 \times 1000)}{936} \Rightarrow 55.56$

18. **(b)** $H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_3 + 2H_2O$

Number of moles of H_3PO_4 = ½ No of moles of NaOH

$$\frac{150 \times 1.5}{1000} = \frac{1}{2} \times \frac{V}{1000} \times \frac{0.5}{1}$$

$$V = 900 \text{ mL}$$

19. **(c)** $\underset{1}{AlCl_3} + \underset{1}{3NaOH} \longrightarrow Al(OH)_3 + 3NaCl$

1 mole $AlCl_3$ Require 3 mole NaOH for Completion of Reaction

∴ No of moles of $AlCl_3$ react with 1 mole

$$NaOH = \frac{1}{3} \text{ Mole}$$

∴ Moles of $AlCl_3$ left $= 1 - \dfrac{1}{3} = \dfrac{2}{3}$ Mole

20. **(b)** $\underbrace{a \text{ mole } CaCO_3 + b \text{ mole } CaO}_{}$

$$CaCO_3 \longrightarrow CaO + CO_2$$

a mole $CaCO_3$ give 22.4 litre or 1 mole CO_2

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

1×100 gram $CaCO_3$ React with $2 \times 36.5 = 73$ gram HCl

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

∴ Wt of HCl react with CaO

= 219 – 73 = 146 gram

$$n_{HCl} = \frac{146}{36.5} = 2b = 4 \text{ mole}$$

∴ $b = 2$ mole

= 2 × 56 = 112 gram

Mole % of $CaCO_3$

$$\frac{1}{3} \times 100 = 33.33\%$$

21. **(a)** $RD = \dfrac{d_{\text{gas}}}{d_{\text{ref.gas}}} = \dfrac{M_{\text{gas}}}{M_{\text{ref. gas}}} \left[\because d = \dfrac{PM}{RT}\right]$

$$RD = \frac{M_{\text{gas}}}{1} \Rightarrow M_{\text{gas}} = 30$$

$$M_{\text{avg}} = \frac{W_T}{n_T}$$

$CO_2 : H_2O$

Mole a b

$$30 = \frac{a \times 44 + b \times 18}{a + b} \Rightarrow 30a + 30b = 44a + 10b$$

$$14a = 12b \Rightarrow \frac{a}{b} = \frac{6}{7}$$

$$\text{Mole \% of } CO_2 = \frac{a}{a+b} \times 100 = \frac{6}{13} \times 100 = \frac{600}{13}$$

22. **(d)** Mass of 1 electron = 9.1×10^{-31} kg

Molar mass of Electron mean mass of N_Ae^-

$= 9.1 \times 10^{-31} \times 6.022 \times 10^{23} = 54.8 \times 10^{-8}$ kg/ mole

23. **(c)** $(KHC_2O_4)_{0.95} \cdot HC_2O_4$

[4 + 0.95 × 4] mole oxygen atom present in 1 mole compound

$\therefore$ 1 mole oxygen atom present in $\dfrac{1}{[4+0.95\times 4]}$ Mole compound

$\therefore$ 4 mole oxygen atom present in $\dfrac{1}{[4+0.95\times 4]}$ Mole compound

24. **(d)** $M = \dfrac{\text{No of moles of solute } (W_A)}{\text{Wt of solvent (gm)}} \times 1000$ (i)

$$x_A = \frac{n_A}{\Sigma n}$$

$$n_A = x_A \Sigma n$$

$$\frac{W_A}{M_A} = X_A \Sigma n$$

$\therefore$ $W_A = X_A \Sigma_n M_A$ = wt of solute

$\therefore$ $W_B = X_B \Sigma_n M_B$ = wt of solute

From equation (1)

$$m = \frac{x_A \Sigma n M_A}{x_B \Sigma n M_B} \times 1000$$

$$= \frac{x_A}{x_B} \times \frac{1000}{M_B}$$

$$= \frac{x_A}{(1-x_A)} \times \frac{1000}{100} = \frac{10 X_A}{1 - X_A}$$

25. **(a)** 100 mL of 0.1 M $(NH_4)_2HPO_3$

10 mm of $(NH_4)_2HPO_4$

NH_4^+ HPO_4^{2-}

20 mm 10 mm × 0.2 M = 40 mm

$Na_4P_2O_7 \longrightarrow$ 200 mL + 0.2 M = 40 mm

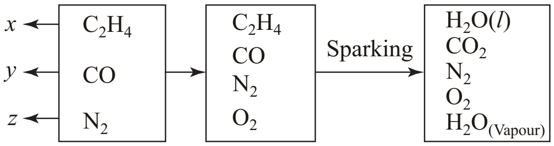
Na^+ $P_2O_7^{4-}$

4 × 40 mm 40 mm

Total millimoles of positive ions = 180

Conc. (mm/litre) = $\dfrac{180}{0.3\,L} = \dfrac{1800}{3} = 600$

26. **(d)**



$x + y + z = 250$ ...(i)

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O\ (l)$

$(2x + y) + z + [(250 - (3x + y/2)] + 20 = 370$

$CO + O_2 \longrightarrow CO_2(g)$

$2x + y = 200$ ...(ii)

$-x + y/2 + z = 100$ ...(iii)

From (i), (ii) and (iii)

$x = 50, y = 100$ and $z = 100$

$\therefore$ $P_{CO} + P_{O_2} = 100 + 250 = 350$ mmHg

27. **(b)** $3O_2 \longrightarrow C_6H_{12}O_6$

For 1 mole Glucose requires 3 mole O_2

$\dfrac{8}{32}$ mole (O_2) in 1 hour is taken

1 mole (O_2) in taken in $\dfrac{1}{8/32}$ hour $= \dfrac{32}{8}$ hour

$\therefore$ 3 mole (O_2) in taken in $\dfrac{32 \times 3}{8} = 12$ hours.

28. **(b)** If total moles = 1

moles of SO_3 = mole of H_2SO_4 = 0.5

mass of $SO_3 + H_2SO_4 = 40 + 49 = 89$ g

$SO_3 + H_2O \longrightarrow H_2SO_4$

0.5 0.5

mass of H_2O require = 0.5 × 18 = 9 g

89 g require 9 g H_2O

100 g require = 10.11 g

% Labelling = (100 + 10.11) = 110.11%

29. **(b)** $MnO_2 + H_2 \longrightarrow Mn_xO_y + H_2O$

17.4 g 12.6 g

$\dfrac{17.4}{87}$ $\dfrac{12.6}{55x + 16y}$

Applying POAC on Mn atom

$$\frac{1}{5} = \frac{12.6x}{55x + 16y}$$

$63x = 55x + 16y$

$8x = 16y$

$$\left[\frac{y}{x} = \frac{1}{2}\right]$$

30. **(a)** Moles of element in cube $= \dfrac{7.5 \times 10^{22}}{6 \times 10^{23}} = \dfrac{1}{8}$

Mass of element in cube $= \dfrac{1}{8} \times 32$ g = 4 g

Volume of cube $= \dfrac{4}{4/3} = 3\ cm^3 = \dfrac{\text{Mass}}{\text{density}}$

$a^3 = 3\ cm^3$ $\therefore$ $a^6 = 9\ cm^6$

31. **(c)** (1) $m = \dfrac{\text{mass of } CaBr_2}{\text{M.W.} \times \text{mass of } H_2O} \times 1000$

$$m = \frac{1000}{200} = 5m$$

(2) $m = \dfrac{0.5}{0.5 \times 18} \times 1000 = 55.5$

(3) $m = \dfrac{0.5}{0.5 \times 18} \times 1000 = 55.5$

(4) As mole fraction of NaCl and H_2O are same which means both have same moles hence m will be 55.5.

32. **(c)** $M = 44.8/11.2 = 4$

(1) moles of H_2O_2 in 3L = $3 \times 4 = 12$

(2) volume of H_2O_2 (used) = $(60 \times 0.2 \times 2.8) = 33.6$ L

$$\text{Mole of } O_2 \text{ used} = \frac{33.6}{22.4} = 1.5$$

Mole of H_2O_2 used = $2 \times 1.5 = 3.0$

(3) $2H_2O_2 \longrightarrow H_2O + O_2$

moles (H_2O_2) = $2 \times 1.5 = 3$ moles

moles of H_2O_2 left = $12 - 3 = 9$

M (H_2O_2) = 9 mole/3L = 3M

(4) V.S. = $3 \times 11.2 = 33.6$ V

33. **(a)** $N_2 + H_2 \longrightarrow N_2H_2(l) + N_2H_4(g)$

POAC on N $\quad$ a mole $\quad$ b mole

$30 \times 2 = 2a + 2b \Rightarrow a + b = 30$

POAC on H $\quad$ $40 \times 2 = 2a + 4b \Rightarrow a + 2b = 40$

$b = 10,\ a = 20$

V.C. = $(30 + 40) - 10 = 60$ mL

Energy change = $10 \times 2 = 20$

60/20 = 3

34. **(c)** When mixture is pass through hot graphite CO_2 will be converted into CO as C is present in excess

$CO_2(g) + C(s) \longrightarrow 2CO\ (g)$

x mL $\qquad$ $2x$ mL

Initial mixture 150 mL

Volume of $CO_2 = x$ mL

Volume of CO = $150 - x$

Which is already present in mixture

Total volume after reaction = $150 - x + 2x = 200$

$x = 50$ mL $\quad$ Volume of CO_2 in original mixture = 50

Volume of CO in original mixture = 100

$$\text{Mole fraction of CO in original mixture} = \frac{100}{150} = 0.66$$

35. **(b)** $HCOOH \longrightarrow H_2O + CO$

a mole gives $\quad a \quad a$

$H_2C_2O_4 \longrightarrow H_2O + CO_2 + CO$

b mole gives $\quad b \quad b \quad b$

Since H_2O exist in liquid state.

$$\frac{\text{volume of } CO_2}{\text{total volume } (CO + CO_2)} = \frac{b}{a+b+b} = \frac{1}{10}$$

$$10b = a + 2b$$

$$8b = a$$

mole ratio 8 : 1 $\qquad$ $8 + 1 = 9$

36. **(a)** $\text{Initial moles of air} = \dfrac{4 \times 12.3}{0.082 \times 300} = 2$

$$\text{mole of air after 20 minutes} = \frac{3.6 \times 12.3}{0.082 \times 300} = 1.5$$

mole of air leaked in 20 min. 0.5

molecule escape = $0.5\ N_A$

Let surface area A cm^2

Total molecule escape in 20 min.

$0.5 \times 10^5 \times A \times 6.023 \times 10^8 \times 20 = 0.5\ N_A$

$A = 5 \times 10^7$ cm^2

$A = 5000$ m^2

37. **(a)** $\underset{n_f=2}{\overset{+4}{SO_2}} + \underset{n_f=5}{\overset{+7}{MnO_4^-}} \longrightarrow \overset{+6}{SO_4^{-2}} + Mn^{+2}$

Let x mole of SO_2

(equivalent of SO_2 = equivalent of $KMnO_4$)

$$x \times 2 = \frac{9 \times 0.008 \times 5}{1000}$$

$$x = \frac{9 \times 0.008 \times 5}{1000 \times 2}$$

weight of SO_2, $= x \times 64$

$$= \left(\frac{9 \times 0.008 \times 5 \times 1000 \times 64}{1000 \times 2}\right)\text{mg} = 11.52 \text{ mg}$$

38. **(c)** 98 gram $\quad$ 80 gram

$H_2SO_4 + \quad 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

$H_3PO_4 + \quad NaOH \longrightarrow NaH_2PO_4 + H_2O$

98 gram $\quad$ 40 gram

40 gram NaOH reacts with 49 gram H_2SO_4 and 98 gram H_3PO_4 to form sulphate and dihydrogen phosphate.wt. ratio

H_2SO_4 : H_3PO_4

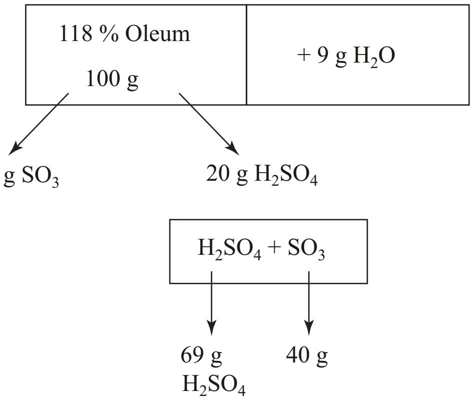
49 $\quad$ 98

1 : 2 Ans.

39. **(a)** Mol % of oxygen Present in

$$H_2O = \frac{16}{18} \times 100 = 88.88\%$$

40. **(c)**



(1) % H_2SO_4 by wt. = 63.30 %

(2) Mass % of combined $SO_3 \Rightarrow = 51.67\%$

(3) with 109 g New oleum water can react = 9 g

$\therefore$ with 100 g New oleum water can react = new labelling = $100 + 8.25 \Rightarrow 108.25$ %

(4) $\text{Mass \% of free } SO_3 = \dfrac{40}{109} \times 100 \Rightarrow 36.69\%$

41. **(a)** $3NaOH + H_3PO_4 \longrightarrow Na_3PO_4 + 3H_2O$

Total m moles of $H_3PO_4 = (10 \times 0.5) = 5$

$\therefore$ Require NaOH = 15 m moles

$$\text{for Molarity of NaOH required} = \frac{15}{300} \Rightarrow \frac{1}{20}$$

$$\frac{V_1\left(\frac{1}{10}\right)+V_2\left(\frac{1}{30}\right)}{V_1+V_2}=\frac{1}{20}$$

$$\frac{2}{3}V_2+2V_1=V_1+V_2$$

$$V_1=\frac{1}{3}V_2$$

$$V_1=\frac{V_2}{3}$$

$V_2 = 3V_1$

$V_1 + V_2 = 1000$ mL

$4V_1 = 1000$ mL $\Rightarrow V_1 = 250$ mL

42. **(a)** $(NH_4)_2HPO_3$

43. **(a)**

$$\begin{array}{lll} N_2(g) \quad + & H_2(g) & \longrightarrow \quad N_2H_2(g) \\ 6 & 30 & 0 \\ \text{LR} & & \\ 0 & 24 & 6 \\ N_2H_2(g) \ + & H_2(g) & \longrightarrow \quad N_2H_4(l) \\ 6 & 24 & 0 \\ \text{LR} & & \\ 0 & 18 & 6 \end{array}$$

Volume contraction = (30 + 6) – 18 = 18 L

% of volume contracted = $\frac{18}{36}\times 100 = 50\%$

44. **(d)** wt = 0.078 gram

$PV = nRT$

$$1\times\frac{22.4}{1000}=n\times 0.0821\times 273$$

$$=\frac{0.078}{M\text{ mass}}\times 0.0821\times 273$$

M Mass of hydrocarbon = 78

EF mass = 13

molecular formula = C_6H_6

45. **(a)** 10 gm $CaCO_3$ contains 4 g Ca

$$\%\text{ mass}=\frac{4}{10}\times 100=40\%$$

46. **(a)** Volume of 1 mole of $CH_3CH_2OCH_3$ $\frac{M\text{ mass}}{\text{density}}$

$$=\frac{60}{0.8}=75\text{ cm}^3$$

Volume occupied by 1 molecule = $\frac{75}{6\times 10^{23}}$

$= 1.25 \times 10^{-22}$ cm^3

47. **(b)** $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$

1 molecule gives 2 ions of Na^+

48. **(d)** One mole A_2 contain 32 mole electron and 36 mole neutrons.

So, Number of electron in one molecule = 32

Number of electron in one atom = $\frac{32}{2} = 16$

Number of neutron in one molecule = 36

Number of neutron in one atom = $\frac{36}{2} = 18$

Mass number = number of proton + number of neutron

= 16 + 18 = 34

49. **(b)** Mol. wt. of $Al_2(SO_4)_3 = 342$

No. of moles of $Al_2(SO_4)_3 = \frac{6840}{342} = 20$ moles

no. of moles of ions in it = 20 × 5 = 100 mole

$\because$ 4 moles of ions are present in 1 mole Na_3PO_4

$\therefore$ 100 moles of ions are present in $\frac{100}{4}$ mole Na_3PO_4

50. **(c)** ${}_9F^{19}$ ${}_{19}K^{39}$ ${}_{32}X^A$

1 : 1 : 1 Mole ratio

10 : 20 : (A – 32) Number of neutron

Average number of neutron

$$=\frac{10\times 1+20\times 1+(A-32)}{3}=25$$

$A - 2 = 75 \quad \therefore \quad A = 77$

$$\therefore \quad \text{av. mass}=\frac{1\times 19+1\times 39+1\times 77}{3}$$

Average Mass = 45

51. **(b)** Molecular weight of $C_6H_{12}O_6 = 180$

Number of mole of $C_6H_{12}O_6 = \frac{36}{180} = 0.2$ mole

Number of electron in one molecule of $C_6H_{12}O_6$

$= 6 \times 6 + 12 \times 1 + 6 \times 8 = 96$

Number of electron in 0.2 mole $C_6H_{12}O_6 = 0.2 \times 96 \times N_A = 19.2\ N_A$

52. **(c)** $2NH_3 + \frac{7}{2}O_2 \longrightarrow 2NO_2 + 3H_2O$

$w_1 \qquad w_2$

$$\frac{\frac{w_1}{17}}{2}=\frac{\frac{w_2}{32}}{\frac{7}{2}};\ \frac{w_1}{w_2}=\frac{2}{32\times 7}\times 2\times 17;=\frac{17}{56} \qquad \text{Ans.}$$

53. **(b)** $P_4 \quad + \quad 5O_2 \longrightarrow P_4O_{10}$

$\frac{31}{4\times 31}$mole $\qquad \frac{32}{32}$mole

$\because$ O_2 is limiting reagent

So, Number of mole of P_4O_{10} formed = $\frac{1}{5}$ mole

wt. of P_4O_{10} formed = $\frac{1}{5} \times 284 = 56.8$ gm

54. **(b)** Moles of $Na_2SO_4 = 200 \times 0.1 \times 10^{-3}$

Moles of $Na^+ = (200 \times 0.1 \times 10^{-3}) \times 2 = (2 \times 10^{-2}) \times 2$

Moles of $Na_3PO_4 = 100 \times 0.2 \times 10^{-3}$

Moles of $Na^+ = (100 \times 0.2 \times 10^{-3}) \times 3 = 2 \times 10^{-2} \times 3$

Total moles of $Na^+ = 5 \times 2 \times 10^{-2} = 10^{-1}$

$$M_{\text{Na}^+} = \frac{10^{-1}}{300} \times 1000 = \frac{1}{3} = 0.33 \text{ M} \qquad \text{Ans}$$

55. **(b)** $\text{PPM} = \dfrac{\text{Parts of solute}}{\text{Part of solution}} \times 10^6 = \dfrac{\text{wt of solute}}{\text{wt of solution}} \times 10^6$

$$\frac{w}{w}\% = \frac{\text{wt of solute}}{\text{wt of solution}} \times 100$$

% Labeling of OLEUM = 100 + wt of water added for obtaining maximum wt of H_2SO_4 in 100 gram Oleum. Since $V \propto T$ So above concentration term independent of temperature or volume.

56. **(a)** No of e^- in one O^{--} ion = 8 + 2 = 10e

10e^- present in one O^{--} ion

∴ 1 e^- present in one $\frac{1}{10}O^{--}$ ion

∴ 1.2×10^{22} present in one $\frac{1}{10} \times 1.2 \times 10^{22}$

$= 1.2 \times 10^{21}$ oxideion

$$= \frac{1.2 \times 10^{21}}{6 \times 10^{23}} \text{mole}$$

$= 2 \times 10^{-3}$ Mole

57. **(b)** No of proton in one $D_3O^+ = 3 + 8 = 11$

No of neutron in one $D_3O^+ = 3 + 8 = 11$

∴ ratio of $\frac{n}{p} = \frac{11}{11} = 1:1$ any amount

Since Deuterium have 1P, ln and 1 e^-

Oxygen atom have 8P, 8n and 8e^-

58. **(b)** $n = \dfrac{PV}{RT} = \dfrac{wt}{Mwt}$

$$\frac{2 \times 14}{0.0821 \times 273} = \frac{80}{Mwt}$$

$$\frac{28}{22.4} = \frac{80}{Mwt}$$

$$Mwt = \frac{80 \times 22.4}{28} = 64$$

$64 = 32 + x\,[16]$

∴ $x = 2$

59. **(b)** $\dfrac{\text{wt of iron}}{M \text{ Mass}} \times 100 = 0.25$

$$= \frac{x \times 56}{89600} = \frac{0.25}{100}$$

$$x = \frac{89600 \times 0.25}{56 \times 100} = 4$$

60. **(a)** $Mg + \frac{1}{2}O_2 \longrightarrow MgO$

Here Mg L.R. ∴ 12 g = $\frac{1}{2}$ mole Mg gives

$\frac{1}{2}$ mole MgO

∴ wt of MgO = $\frac{1}{2} \times 40 = 20$ g

12 + 32 = 44 g (Mass conservation)

61. **(d)** $n_{C_a} = \dfrac{2.4 \times 10^{24}}{6 \times 10^{23}} = 4$ Mole

$$n_{Cl_2} = \frac{Pv}{RT} = \frac{\frac{380}{760} \times 96}{0.0800 \times 300} = \frac{0.5 \times 96}{24.00} = \frac{48}{24} = 2 \text{ Mole}$$

$Ca + Cl_2 \longrightarrow CaCl_2$

4 2 0

2 0 2 Mole = 2 × 111 = 222 g

62. **(a)** $C_4H_8 + 6O_2 \longrightarrow 4\,CO_2 + 4H_2O$

3 mole C_4H_8 give $\longrightarrow 3 \times 4\,CO_2$ = 12 Mole CO_2

$C_6H_6 + O_2 \longrightarrow 6\,CO_2 + 3H_2O$

3 Mole C_6H_6 gives $\longrightarrow 6 \times 3\,CO_2$ = 18 Mole CO_2

12 + 18 = 30 Mole CO_2 = 30 × 44 = 1320 gram.

63. **(c)** $2KClO_3 \xrightarrow{50\%} 2KCl + 3O_2$

$$n_{O_2} = \frac{67.2}{22.4} = 3 \text{ Mole}$$

3 Mole O_2 produced from 50% impure $KClO_3$

∴ Moles of pure $KClO_3$ in impure Sample

$= 2 \times \frac{2}{3} \times 3 = 4$ Mole

$= 4 \times [39 + 35.5 + 48\,] = 490$ gram.

64. **(a)** No of moles of $N_2 = 3a$

No of moles of $O_2 = a$

$$a = \frac{2.4}{32}$$

∴ No of moles of $N_2 = 3 \times \frac{2.4}{32}$

Wt of $N_2 = 3 \times \frac{2.4}{32} \times 28 = 6.3$ gram

∴ Total Mass = 6.3 + 2.4 = 8.7 gram

65. **(a)** Urea $NH_2\,CONH_2$ have 2 atom of Nitrogen in one Molecule or 2 gram atom in 1 Mole

∴ 20 gram atom in 10 Mole urea = 10 × 60 = 600 gram

66. **(a)** $\dfrac{2.8}{22.4} = \dfrac{3.5}{M \text{ Mass}}$

$$M \text{ Mass} = \frac{22.4 \times 3.5}{2.8}$$

∴ $VD = \dfrac{M \text{ Mass}}{2} = 14$

67. **(b)** $Ni_{0.98}\,O_{100} \Rightarrow Ni_{98}\,O_{100}$

$x\,[+3] + (98 - x) \times 2 + 100\,(-2) = 0$

$3x + 196 - 2x = 200$

$x = 4$

$$\frac{4}{98} \times 100 \simeq 4\%$$

68. **(a)** No of moles $I_2 = \frac{40}{1000} \times 0.1$

$\therefore$ No of atom $= \left[\frac{40}{1000} \times 0.1 \times 6.022 \times 10^{23}\right] \times 2$

$= 48.17 \times 10^{20}$

69. **(c)** $[H^+] = 0.1$ M

$H_2SO_4 \longrightarrow 2H^+ + SO_4^-$

$[H^+] = 0.1$ M

$\therefore M_{H_2SO_4} = \frac{0.1\text{ M}}{2} = 0.05$ M

70. **(b)** 1 Molal aq solution means
1 Mole in 1000 gram = 55.5 mole water

$\therefore$ Mole fraction $= \frac{1}{1+55.5} = \frac{1}{56.5} = 0.0179 = 0.018$

71. **(c)** 1 Million = 10^6
Wt of 10^6 atom $= 1.79 \times 10^{-16}$ g

$\therefore$ Wt of 1 atom $= \frac{1.79 \times 10^{-16}}{10^6}$

$\therefore$ wt of N_A atom $= \frac{1.79 \times 10^{-16}}{10^6} \times 6.022 \times 10^{23}$

$= 17.9 \times 6.022 = 107.79$

72. **(b)** gram atom or Mole

$\frac{1.4}{14} = 0.1$ gram atom

73. **(c)** $CuSO_4 \cdot 5H_2O \longrightarrow CuSO_4 + 5H_2O$
wt of $CuSO_4 = 95.7$
No of Moles of $CuSO_4$ = No of moles of blue vitriol

$= \frac{95.7}{63.5 + 96} = \frac{95.7}{159.5}$

$\therefore$ No of water Molecule

$= \frac{95.7}{159.5} \times 6.022 \times 10^{23} \times 5 = 18.06 \times 10^{23}$

74. **(b)** $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

No of moles of $H_2 = \frac{112}{22400} = \frac{1}{200}$ moles

no of moles of H_2 = No of moles of Zn

$= \frac{1}{200}$ Moles

$= \frac{1}{200} \times 65 = 0.325$ g

75. **(b)** No of moles $= \frac{18\text{ mL} \times 1\text{ g/mL}}{18} = 1$ mole

No of e^- in one molecule of $H_2O = 2 + 8 = 10$
$\therefore$ Total No of e^- in 1 Mole $= 10 \times 6.022 \times 10^{23}$
$= 6.022 \times 10^{24}$

76. **(b)** $n \times 2 + (0.98 - n) \times 3 = 1 \times (-2)$
$n = 0.94$

$\therefore$ number of $M^{+3} = 0.04$

Percentage of $M^{+3} = \frac{0.04}{0.98} \times 100 = 4.08\%$

77. **(d)** $\frac{n_{O_2}}{n_{N_2}} = \frac{\frac{1}{32}}{\frac{4}{28}} = \frac{7}{32}$

78. **(c)** $M = \frac{V}{11.2} = \frac{11.2}{11.2} = 1$ M

$M = \frac{w}{v}\% \frac{10}{M_A}$

$1 = \frac{w}{v}\% \times \frac{10}{34}$

$\frac{w}{v}\% = 3.4\%$

$M = \frac{w}{w}\% \frac{10d}{M_A}$

$1 = \frac{w}{w}\% \times \frac{10 \times 1.034}{34}$

$\therefore \quad \frac{w}{w}\% = \frac{34}{10.34} = \frac{3400}{1034}$

79. **(b)** CO(a mL) + CO_2 (150-a mL) = 150 mL initially
$CO_2 + C(s) \rightarrow 2CO$
(150 – a)mL CO_2 gives 2 [150 – a] mL CO
Total volume after reaction
$a + 2[150 - a] = 250$
$300 - a = 250$

$$\left.\begin{array}{l} a = 50\text{ mL} = V_{CO} \\ V_{CO_2} = 100\text{ ml} \end{array}\right] \text{inoriginal mixture}$$

$\frac{50}{150} \times 100 = 33.33\%$

80. **(b)** $Zn + 2HCl \rightarrow ZnCl_2 + H_2$

$\frac{130.6}{65.3}$ = No of moles of Zn = No of mole of H_2

$\therefore \quad V_{H_2} = \frac{130.6}{65.3} \times 22.4 = 44.8$ L

81. **(b)** % wt of K in KCl $= \frac{39}{74.5} \times 100 = 52.34\%$

% wt of K in $KNO_3 = \frac{39}{101} \times 100 = 39\%$

$\therefore$ % of K vary between 39% to 52.34% in mixture of KCl and KNO_3

82. **(d)** $MnO_2 + 4HCl \longrightarrow MnCl_2\text{ (g)} + Cl_2 + 2H_2O$
164.2 mL

$$n_{Cl_2} = \frac{PV}{RT} = \frac{\frac{38}{76} \times \frac{164.2}{1000}}{0.0821 \times 400} = \frac{1}{400}\text{ mole}$$

$\therefore \quad n_{HCl} = \frac{1}{100}\text{ mole} = M \times 0.2$

$$\text{Molarity} = \frac{1}{20} = 0.05\text{ M}$$

LEVEL II

1. **(c)** (I) 2 g of hydrogen

   number of moles $= \frac{2}{1} = 2 \times N_A$ number of atoms

   (II) 16 g of sulphur
   number of moles

   $= \frac{16}{32} = \frac{1}{2} \times N_A$ number of atoms

   (III) 4 g of oxygen

   number of moles $= \frac{4}{16} = \frac{1}{4} \times N_A$ number of atom

   (IV) 31 g of phosphorus

   number of moles $= \frac{31}{31} = 1 \times N_A$ number of atoms

   I > IV > II > III

2. **(c)** Weight of 1 molecule of $C_xD_y = 1.66 \times 10^{-25}$ kg
   weight of 1 mole $C_xD_y = 100$ g
   $x \times 20 + y \times 40 = 100$
   weight of 1 mole $C_yD_x = 80$ g
   $20y + 40x = 80$
   or
   $40y + 80x = 160$
   $40y + 20x = 100$
   $60x = 60$
   ∴ $x = 1$ and $y = 2$

3. **(d)** In one molecule of $Mg_3N_2 \cdot 3Mg^{+2}$ are present
   ∴ total number of electron transferred = 3 × 2 = 6

4. **(a)** Weight ratio = 5 : 1

   ∴ Molar ratio $= \frac{5}{80} : \frac{1}{16}$

   ∴ ratio of atoms
   $N_A \times 4 : 5 \times N_A$ number of atoms

   $$Q = \frac{200 \times \frac{5}{80} \times N_A \times 4}{\frac{1}{16} \times N_A \times 5}$$

   $Q = 200 \times \frac{4}{5}$ $\quad 1(SO_3) : 1(CH_4)$ mole ratio

   $Q = 160$

5. **(b)** $2A(s) + B(g) \longrightarrow 3C(g) + 4D(l)$

   $\frac{22.4\text{ L}}{22.4\text{ L}}$ = 1 mole B gives 3 moles of C in excess of A

   here B is L. R.

6. **(b)** Let the mass of sample is 100
   Let the mass of FeS is x
   ∴ Mass of impurities will be $100 - x$
   After reaction,
   Loss = 8 gm
   Remaining mass of sample = 92 g
   Since loss is due to FeS converting into Fe_2O_3
   ∴ Mass of impurities still remain same $= 100 - x$
   ∴ Mass of Fe_2O_3 formed $= x - 8$

   $$2FeS + \frac{7}{2}O_2 \longrightarrow Fe_2O_3 + 2SO_2$$

   Apply POAC on Fe atom

   $$\frac{x}{88} = \frac{x-8}{160} \times 2$$

   ∴ $x = 88$ gram or 88%

7. **(b)**

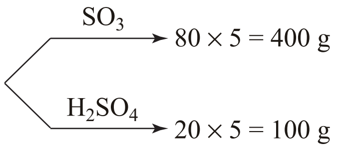
   $$\begin{array}{ccccccc} 7\,A & + & 13\,B & + & 15\,C & \longrightarrow & 17\,P \\ \frac{15}{7} & & \frac{26}{13} & & \frac{30.5}{15} & & \\ 2.1428 & & 2 & & 2.033 & & \end{array}$$

   LR = B

   If $\frac{\text{No of moles}}{\text{Stoichimetric coefficient}}$ Least

   behave as L.R.

8. **(a)** 118%



   100 OLEUM given = 118 g H_2SO_4

   500 OLEUM given = 590 g $= \frac{590}{98}$

   Mole H_2SO_4 = 6 moles
   $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + H_2O$
   ∴ No. of moles of KOH required 6 × 2 = 12 mole for complete neutralisation.

9. **(a)** $2\,Zn + O_2 \xrightarrow{90\%} 2ZnO$

   No. of moles of Zn $= \frac{130}{65} = 2$ moles

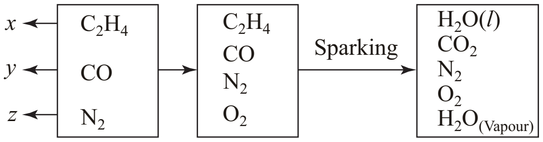
   No. of moles of $O_2 = \frac{100}{32} = 2$ moles

   ∴ Zn (LR)

   No. of moles of ZnO $= \frac{90}{100} \times n_{Zn} = 2$ moles

   $2ZnO + H_2O \rightarrow 2Zn(OH)_2$
   Since 1.8 mole ZnO Produced 1.8 mole $Zn(OH)_2$
   ∴ % yield of reaction 100%

10. **(b)**



$x + y + z = 250$ ... (i)

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O\ (l)$

$(2x + y) + z + [(250 - (3x + y/2)] + 20 = 370$

$CO + O_2 \longrightarrow CO_2(g)$

$-x + y/2 + z = 100$ ...(iii)

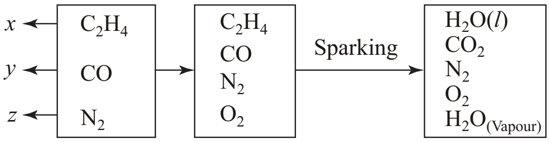
$2x + y = 200$ ...(ii)

From (i), (ii) and (iii)

$x = 50,\ y = 100$ and $z = 100$

Partial Pressure of C_2H_4 = 50 mmHg

11. **(c)**



$x + y + z = 250$ ...(i)

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O\ (l)$

$(2x + y) + z + [(250 - (3x + y/2)] + 20 = 370$

$CO + O_2 \longrightarrow CO_2(g)$

$-x + y/2 + z = 100$ ...(iii)

$2x + y = 200$ ...(ii)

From (i), (ii) and (iii)

$x = 50,\ y = 100$ and $z = 100$

∴ Total Oxygen consume = 200 mmHg

12. **(d)** 118% oleum means in 100 gram oleum by adding 18 gram water it gives 118 gram H_2SO_4 n_{H_2O} added = n_{SO_3} Present in 100 gram Oleum by adding 9 gram or $\frac{1}{2}$ mole water $\frac{1}{2}$ mole SO_3 change into H_2SO_4 and $\frac{1}{2}$ mole SO_3 = 40 gram SO_3 present in 109 gram Oleum

$$\therefore \%\ \text{wt of } SO_3 = \frac{40}{109} \times 100 = 36.7\%$$

13. **(a)**

HCl	H_2SO_4	H_2SO_3	H_3PO_4
36.5	98	82	98

4% w/v ⇒ 1 Molar NaOH

$H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + 3H_2O$

3 9 moles

Moles of NaOH required = 9 = $M_1V_1 \Rightarrow V_1$ = 9 litres

V_1 = 9000 mL

14. **(a)** $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

x mL

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

y mL

Volume of hydrocarbon $(x + y)$

$$\text{Volume of } O_2 = \frac{20}{100} \times 350 = 2x + 3y$$

$x + y = 30$ ...(1)

$2x + 3y = 70$ ...(2)

$2x + 2y = 60$

$y = 10$

Thus volume of C_2H_4 = 10 mL

volume of CH_4 = 20 mL

If ratio changed $y : x$ then

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

y

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

x

Total $O_2 = 10 \times 2 + 20 \times 3 = 80$ mL

$$\text{Volume of } O_2 = \frac{20}{100} \times \text{volume of air} = 80 \text{ mL}$$

Volume of air = 400 mL.

15. **(a)** Let 100 mL of air and 100 mL of H_2 is taken 100 mL air contain 80 mL N_2 and 20 mL O_2

$N_2\ (g) + 3H_2\ (g) \longrightarrow 2NH_3\ (g)$

80 100 $\frac{2}{3} \times 100 = 66.67$

L.R.

$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$

66.67 20 L.R.

H_2 and O_2 Limiting regent

∴ Completely exhausted.

16. **(b)** $Ca_3(PO_4)_2 + 8Mg \longrightarrow Ca_3P_2 + 8MgO$

Excess 8 mole 1 mole 8 mole

$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

1 mole Excess 3 mole 2 mole

$2PH_3 + 4O_2 \longrightarrow P_2O_5 + 3H_2O$

2 mole Excess 1 mole 3 mole

$MgO + P_2O_5 \longrightarrow Mg(PO_3)_2$

8 mole 1 mole 1 mole

LR wt = 182 gram.

17. **(b)** In 1 Liter or 1000 mL

$w_{sol.} = V \times d = 1140$ gram

$w_B = 7 \times 30 = 210$ gram

$w_A + w_{solvent} = 930$

$10n_A + w_{solvent} = 930$

$$x_A = 0.05 = \frac{n_A}{n_A + 7 + \frac{W_{H_2O}}{18}}$$

18. **(b)** Moles of $Na_2SO_4 = 200 \times 0.1 \times 10^{-3}$

Moles of $Na^+ = (200 \times 0.1 \times 10^{-3}) \times 2 = (2 \times 10^{-2}) \times 2$

Moles of $Na_3PO_4 = 100 \times 0.2 \times 10^{-3}$

Moles of $Na^+ = (100 \times 0.2 \times 10^{-3}) \times 3 = 2 \times 10^{-2} \times 3$

Total moles of $Na^+ = 5 \times 2 \times 10^{-2} = 10^{-1}$

$$M_{Na^+} = \frac{10^{-1}}{300} \times 1000 = \frac{1}{3} = 0.33 \text{ M} \qquad \text{Ans}$$

19. **(b)** Milli equivalent of H_2O_2 = Milli equivalent of $KMnO_4$

$2 \times M \times 10 = 25 \times 0.2 \times 5$

$M = 1.25$

Volume strength of H_2O_2 = 11.2 × molarity

⇒ $11.2 \times 1.25 = 14$ V

20. **(b)** Number of mole atoms of

$$O = \frac{24.5}{98} \times 4 = 1 \text{ mol atom} = N_A \text{ atoms}$$

$$\text{number of electrons} = \frac{1.6}{16} \times 10 \times N_A \text{ electrons}$$

$$= N_A \text{ electrons}$$

Number of molecules

$$= \frac{PV}{RT}\times N_A = \frac{1\times 11.2\times N_A}{0.0821\times 546} = \frac{N_A}{4}$$

N_A moles of H = N_A moles of P^+

Total number of atoms = $\frac{4}{3}\times 3\times N_A = 4\,N_A$ atoms

21. **(a)** Let molarity of HCl is x and H_2SO_4 is y
m mole m mole

$$\underbrace{x\times 25 + 2y\times 25}_{m\text{ mole of }[H^+]} = 10\times 1$$

Applying POAC on Cl Atom

$$\frac{20\times x}{1000} = \frac{0.1435}{143.5} = 10^{-3}$$

$$x = \frac{1}{20} = 0.05\text{ M}$$

$$y = \frac{8.75}{50} = 0.175\text{ M}$$

22. **(c)** $H_4P_2O_7 + 2\,NaOH \longrightarrow Na_2\,H_2\,P_2\,O_7 + 2H_2O$

$$\begin{array}{ll} \frac{534}{178} & \frac{30\times 10^{23}}{6\times 10^{23}} \\ \text{3 Mole} & \text{5 Mole} \\ & \text{(L.R.)} \end{array}$$

No of moles of $Na_2H_2P_2O_7 = \frac{5}{2}$ moles = 2.5

no. of moles of H_2O = 5 Mole
Total No. of Moles of product = 5 + 2.5 = 7.5
Total No. of molecules of product = 7.5 N_A

23. **(a)** $P_4 + 5\,O_2 \rightarrow P_4O_{10}$
0.2 0.2
L.R.

expected No of moles $P_4O_{10} = \frac{0.2}{5} = 0.04$ mole

expected wt of $P_4O_{10} = 0.04\times 284 = 11.36$

$$\%\text{ yield} = \frac{\text{actual wt}}{\text{expected wt}}\times 100$$

$$= \frac{10}{11.36}\times 100 = 88.13\%$$

24. **(a)** $2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$
wt of N_2 = Vxd = 368 × 1.12

No. of moles of $N_2 = \frac{368\times 1.12}{28}$

$\therefore$ No. of moles of $NaN_3 = \frac{2}{3}\times\left(\frac{368\times 1.12}{28}\right)$

$\therefore$ wt of $NaN_3 = \frac{2}{3}\times\left[\frac{368\times 1.12}{28}\right]\times(23+42)$ gram

= 0.638 Kg

25. **(c)** During excess chlorination All Ag Br change into AgCl.

26. **(c)** Semimolal = $\frac{1}{2}$m means $\frac{1}{2}$mole NaOH in 1000 gram water

$\therefore$ wt of solution = $\frac{1}{2}\times 40 + 1000 = 1020$ gram

$$\therefore \quad \frac{w}{w}\% = \frac{20}{1020}\times 100 = 1.96\%$$

27. **(c)** Volume contraction occur if No of moles of gaseous product less than No of moles of gaseous reactant

28. **(c)** $m = \frac{1000M}{1000d - MM_A}$
w = wt of solute +wt of solvent
for very dilute solution wt of solute + wt of solvent
= wt of solvent.

29. **(d)** No of moles of solute in 1 Kg of solvent independent of volume or temp.

30. **(a)** $S_8 \longrightarrow SO_3$
Apply POAC on S atom

$$8\times n_{S_8} = 1\times 20$$

$$\therefore \quad n_{S_8} = \frac{20}{8} = \frac{5}{2}\text{moles}$$

31. **(d)**

$$\begin{array}{lllllll} CH_4 & + & 2O_2 & \rightarrow & CO_2 & + & 2H_2O \\ \text{1 mole} & & \text{10 mole} & & 0 & & 0 \\ \text{LR} & & & & & & \end{array}$$

$\therefore \quad n_{H_2O}$ Produced = 2 × 1 = 2 moles

2 × 18 g = 36 g = 36 mL.
(at 27°C water exist in liquid state)

32. **(c)** $Na_2\,CO_{3\text{w gram}} \rightarrow$ Melt (Do not decompose)
$CaCO_3 \rightarrow CaO + CO_2$

w gram $CaCO_3$ or $\frac{w}{100}$ mole $CaCO_3$ gives $\frac{w}{100}$ moles CO_2

$$n_{CO_2} = \frac{w}{100}$$

wt of $CO_2 = \frac{w}{100}\times 44 = 0.44$ w

$$\therefore\ \%\text{ loss in wt} = \frac{\text{wt of }CO_2}{\text{wt of reactant taken}}\times 100$$

$$= \frac{0.44w}{w+w}\times 100 = 22\%$$

33. **(a)** Conceptual

34. **(b)** No of moles of $NO_2 = \frac{112}{22400} = \frac{1}{200}$mole

$\therefore$ wt of $NO_2 = \frac{1}{200}\times 46$ g = 0.23

$$\therefore\ \text{Volume} = \frac{\text{wt}}{\text{density}} = \frac{0.23}{1.15} = 0.2\text{ mL}$$

No of molecules = n. N_A

$$= \frac{1}{200} \times 6.022 \times 10^{23}$$

$$= 3.01 \times 10^{21} \text{ molecules}$$

35. **(a)** Mol. wt. of adipic acid = 146

No. of mole of adipic acid = $\frac{58.4 \text{ g}}{146 \text{ g}} = 0.4$ mole

∵ One molecule of adipic acid contains 10 H-atoms.

∴ No. of mole of H-atom in given adipic acid

= 0.4 × 10 mole = 4 mole.

wt. of H-atom = 4 g = 4000 mg

36. (c)

$$\begin{array}{lcl} SO_3 & : & C_2H_6 \\ \frac{16}{80} & : & \frac{15}{30} \\ \frac{1}{5} & & \frac{1}{2} \\ \text{Mole } 2 & : & 5 \\ \text{Atom } 8 & : & 40 \end{array}$$

∴ ratio of No atoms in C_2H_6 and SO_3

40 : 8 ⇒ 5 : 1

37. **(c)** Given: $2As(s) + 3H_2(g) \longrightarrow 2AsH_3$; $\Delta H = -770$ kJ

∴ Heat of formation of AsH_3

$$= \frac{-770}{2} = -385 \text{ kJ/mole.}$$

no. of mole of AsH_3 given = $\frac{31.2}{78} = 0.4$ mole

then heat released = 385 × 0.4 = 154 kJ.

38. **(b)** Initial volume = $\frac{n_1RT}{P_1} = \frac{5 \times R \times 300}{1} = 1500\,R$ L

Final volume = $\frac{(n_1+n_2)RT}{P_2} = \frac{(5+2)R \times 300}{1.05}$

= 2000 R L

Change in volume = 2000 R – 1500 R

= 500 R

= 500 × 0.08

= 40 L

39. **(d)**

$$\begin{array}{ccccccc} X & + & 2y & + & 3z & \rightarrow & xy_2z_3 \\ \frac{10}{60} & & \frac{2\times10^{23}}{6\times10^{23}} & & 0.6 & & \\ \frac{1}{6} & & \frac{1}{3} & & \frac{6}{100}\text{mole} & & \end{array}$$

Here Z(L R) because Number of moles/Stoichiometry coefficient minimum

∴ Moles of $XY_2\,Z_3 = \frac{1}{3}$ Moles of z

$$= \frac{1}{3} \times \frac{6}{100} = \frac{1}{50}\text{mole}$$

$$\frac{1}{50} = \frac{5.6}{M \text{ mass}}$$

$$\frac{1}{50} = \frac{5.6}{60+160+3z}$$

$220 + 3Z = 280$

$3Z = 60$

$Z = 20$

40. **(c)** $N_{H_2O_2} = \frac{V}{5.6}$

V = volume of O_2 evolved at STP from 1 L H_2O_2 solution

Moles of Cl_2 = moles of O_2 = $\frac{896}{22400} = 0.04$

equivalent of H_2S = equivalent of $HClO_3$

= equivalent of $Cl_2 = n_f \cdot$ N

= 10 × 0.04 = 0.4

$$H_2S + 8HClO_3 \longrightarrow 4Cl_2 + H_2SO_4 + H_2O$$

No of moles of $HClO_3 = \frac{1}{2}$ moles of Cl_2

$$= \frac{1}{2} \times 0.04 = 0.02 \text{ moles}$$

$$M = \frac{0.02}{40\times10^{-3}} = \frac{20}{40} = \frac{1}{2}\text{M} = 0.5 \text{ M}$$

LEVEL III

1. **(a)** $2\,Mg + O_2 \longrightarrow 2MgO$

$3\,Mg + N_2 \longrightarrow Mg_3N_2$

$Mg_3N_2 + 6H_2O \longrightarrow 3Mg\,(OH)_2 + 2NH_3$

3.4 g

Wt of $NH_3 = 3.4$ g

$$n_{NH_3} = [n_{Mg}]\left[\frac{1}{3}\right]\left[\frac{2}{1}\right]$$

$$n_{NH_3} = \frac{2}{3} \times n_{Mg}$$

$$\frac{w_{Mg}}{24} \times \frac{2}{3} = \frac{3.4}{17}$$

w_{Mg} = 7.2 gm which converted into 3.4 g NH_3

wt. of Mg left = 24 – 7.2 = 16.8 g

2 mole Mg gives = 2 mole MgO

$$\frac{16.8}{24}\text{mole Mg give}\frac{16.8}{24}\text{mole MgO}$$

$$\therefore \quad \text{wt of MgO} = \frac{16.8}{24} \times 40 \times 28 \text{ g}$$

2. **(b)** Factor level method in

$3\,Mg + N_2 \longrightarrow Mg_3N_2$

$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

$$n_{Mg(OH)_2} = [n_{Mg}]\left[\frac{1}{3}\right]\left[\frac{3}{1}\right]$$

$$\frac{7.2}{24} = \frac{w_{Mg(OH)_2}}{58}$$

$$w_{Mg(OH)_2} = 17.4 \text{ g}$$

3. **(b)** % Mg = $\frac{7.2}{24} \times 100 = 30\ \%$

4. **(b)** $\underset{x\text{mL}}{C_nH_{2n+2}} + \frac{3n+1}{2}O_2 \longrightarrow nCO_2 + (n+1)\,H_2O$

nx mL CO_2 gas

$$\underset{12-x}{C_nH_{2n}} + \frac{3n}{2}\ O_2 \longrightarrow nCO_2 + nH_2O$$

n(12 – x) mL CO_2 gas

$$\left(\frac{3n+1}{2}\right)x + \frac{3n}{2}(12-x) = \frac{285}{100}\times 20$$

Total volume of $CO_2 = nx + (12 - x)n = 36$

$\Rightarrow \quad nx + 12x - nx = 36$

$12n = 36 \ \therefore\ n = 3$

$3nx + x + 36n - 3nx = 114$

$36n + x = 114$ ...(1)

$12n = 36$

$n = 3$ ...(2)

$x = 6$ mL

∴ Alkane is C_3H_8

5. **(b)** $C_3H_8(g) + 5\ O_2\ (g) \longrightarrow 3\ CO_2\ (g) + 4H_2O\ (l)$

6 mL 30 mL 18 mL 24 mL

$$C_3H_6\ (g) + \frac{9}{2}O_2\ (g) \longrightarrow 3\ CO_2\ (g) + 3H_2O\ (l)$$

6 mL 27 mL 18 mL 18 mL

mole fraction of CO_2

$$= \frac{V_{CO_2}}{V_{N_2} + V_{CO_2}} = \frac{36}{228+36} \Rightarrow \frac{36}{264} = \frac{6}{44}$$

6. **(b)** 1292.5 gram solution of bucket contains 5 mole NaCl in 1 kg water

Let x moles of NaCl and y kg of water is added to bucket from tap

$$\frac{x}{y} = 2, \qquad \frac{5+x}{1+y} = 4$$

$\Rightarrow \quad x = 1$ mol.

$$y = \frac{1}{2}\text{kg}$$

amount of solution finally present

$= 1292.5 + x \times 58.5 + y \times 1000$

$= 1292.5 + 58.5 + 500$

$= 1851$

7. **(c)** Total wt of NaCl and water added to bucket from tap = 58.5 + 500 = 558.5 gram

Time taken $\frac{558.5}{0.5}$ = 1117 sec.

8, 9, 10.

$$2\ Mn\ (OH)_2 + \frac{1}{2}O_2 + H_2\ O(l) \rightarrow 2\ Mn\ (OH)_3$$

$$n_{Mn(OH)_3} = \frac{2}{1/2}no_2$$

$2\ Mn\ (OH)_3 + 2\ KI + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + I_{2\ (aq)} + 6H_2O$

$$n_{I_2} = \frac{1}{2}n_{Mn(OH)_3}$$

$$I_2 + 2Na_2\ S_2O_3 \rightarrow 2\ NaI + Na_2\ S_4\ O_6$$

$$n_{Na_2S_2O_3} = \frac{2}{1}n_{I_2}$$

$$n_{Na_2S_2O_3} = \frac{2}{1}\times\frac{1}{2}\times\frac{4}{1}\times no_2$$

$$n_{Na_2S_2O_3} = 4 \times no_2$$

In heavily polluted water = 6.4 mg / Liter O_2 is present

$$n_{Na_2S_2O_3} = 4 \times no_2$$

$$0.01 \times V\ L = 4 \times \frac{6.4}{1000\times 32}$$

$V = 0.08$ L **= 80 mL**

For optimum fit water = 9.6 mg/Liter O_2 is present

$$0.1 \times V/L = 4\times\frac{9.6}{1000\times 32}$$

$V = 0.012$ L = **12 mL**

In order to react with O_2 in Stage I solution of Mn^{+2} should be excess

11. **(a, b)**

(i)

$$\begin{array}{ccccccc} NaOH & + & CH_3COOH & \rightarrow & CH_3COONa & + & H_2O \\ 0.4\times 0.1 & & 0.100\times 0.4 & & & & \\ 0.04\text{ mole} & & 0.04\text{ mole} & & 0 & & 0 \\ 0 & & 0 & & 0.04\text{ mole} & & 0.04\text{ mole} \end{array}$$

Salt of weak acid and strong base formed ∴ basic

(ii) $M = \frac{W}{V}\%\frac{10}{M_A} = \frac{x\times 10}{40}$ for NaOH

$M = \frac{x\times 10}{98}$ for H_2SO_4

$(n_fMV)_{NaOH} > (n_fMV)_{H_2SO_4}$ ∴ basic

(iii) If volume of NaOH < $\frac{\text{Volume of HCl}}{2}$ then basic

(iv) 40 gram NaOH means 1 mole NaOH and 40 gram HCl means $\frac{40}{36.5} > 1$

∴ Solution acidic in nature

12. **(a, b, c)**

$$\begin{array}{cccc} N_2\ + & 3H_2 & \rightarrow & 2NH_3 \\ \frac{140}{28} & \frac{40}{2} & & 0 \end{array}$$

5 mole 20 mole 0

0 5 mole 10 mole

$10 \times 17 = 170$ gram

⇒ $\% \text{ Yield} = 80 = \dfrac{\text{Actual wt}}{\text{expeted wt}} \times 100$

$$\frac{80}{100} = \frac{w}{30}$$

∴ $w = 24$ gram.

⇒ N_2 (L. R) completely consumed in reaction

⇒ $\dfrac{50}{100} = \dfrac{w}{170}$

∴ $w = 85$ gram.

13. **(b, c)** 109% OLEUM by adding 9 gram water in 100 gram OLEUM it gives 109 gram H_2SO_4. SO in 500 gram OLEUM of water required = $\dfrac{500}{100} \times 9 = 45$

∴ Total wt = 545 gram

∴ by adding 100 gram water 545 gram H_2SO_4 and 55 gram water present in solution

$$M = \frac{nH_2SO_4}{V\text{ L}} = \frac{545}{98 \times 100}\text{L} = 0.056\text{ M}$$

14. **(a, b, d)**

(i) $2\,CO + O_2 \rightarrow 2\,CO_2$

$2a$ a 0

0 0 $2a$

$V_i = 3a$ $V_f = 2a$

$\Delta v = 3a - 2a = a$

$$\frac{a}{3a} \times 100 = 33.3\%$$

(ii) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

10 30

0 10 10

$V_i = 40$ mL

$V_f = 20$ mL

∴ $\dfrac{\Delta v}{v} \times 100 = \dfrac{20}{40} \times 100 = 50\%$

15. **(a, b)** $C + O_2 \rightarrow CO + CO_2$

POAC on C atom

$$1 \times \frac{12}{12} = 1 \times n_{CO} + 1 \times n_{CO_2} = a + b \qquad \text{(i)}$$

POAC on oxygen atom

$$2 \times \frac{24}{32} = 1 \times a + 2b$$

$$\frac{3}{2} = a + 2b \qquad \text{(ii)}$$

(ii) – (i)

$b = \dfrac{1}{2}$ mole and $a = \dfrac{1}{2}$ mole.

⇒ If mass = Volume means density = 1 m/mL

∴ $M = m$

16. **(a, d)** Conceptual

17. **(a,b,d)** $\dfrac{5.3}{106} \times 2N_A = \dfrac{4}{40} \times N_A$

$$= \frac{5.85}{58.5}N_A = \frac{5.6}{164} \times 3N_A \neq 2 \times 0.25N_A$$

18. **(a, b)** $nNa_2SO_4 = \dfrac{1}{2} \times \dfrac{40}{100} \times \dfrac{4}{40} = \dfrac{2}{100} = 2 \times 10^{-2}$

$$nNH_3 = \frac{1}{2} \times \frac{40}{100} \times \frac{4}{40} \times 2 = \frac{40}{100} \times \frac{4}{40}$$

$$nNH_4Cl = \frac{40}{100} \times \frac{4}{40} \times \frac{80}{100} = 32 \times 10^{-3}$$

$$\frac{32 \times 10^{-3}}{2 \times 10^{-2}} = 1.6 \text{ times}$$

⇒ $n_{NaOH} > n_{HCl}$ always in above reaction

If % yield 100%

Then $n_{NaOH} = n_{HCl}$

⇒ mass of $NH_4Cl = 32 \times 10^{-3} \times 53.5 = 1.712$ g.

19. **(a, d)** $\dfrac{225 \times 10^{-22}}{74} = 3 \times 10^{-22}$ mole

$= 3 \times 10^{-22} \times 6 \times 10^{23}$

$= 180$ molecule

$= 2 \times 180$ Oxygen atom

$= 2 \times 180 \times 16$ amu

⇒ $1.8 \times 10^{-22} \times 6.022 \times 10^{23} = 108.396$

⇒ $\dfrac{10}{100} = 0.1$ mole $CaCO_3$

0.1 mole $CaCO_3$ contains 0.3 gram atom of oxygen

⇒ $2 \times 8 \times N_A < 5.5 \times 3 \times N_A = 16\, N_A < 16.5\, N_A$

20. **(a, d)** $P = \dfrac{nRT}{V}$

$$P = \frac{w}{V} \times \frac{RT}{M_{\text{mass}}}$$

$$P = \frac{dRT}{M_{\text{mass}}}$$

$$\frac{P \times M_{\text{mass}}}{RT} = d$$

→ relative density independent of P and T

→ V.D = $\dfrac{M_{\text{mass}}}{2}$ which is independent of P or T

→ $\dfrac{M_{\text{mass}} \text{ of } SO_3}{M_{\text{mass}} \text{ of } O_2} = \dfrac{80}{32} = 2.5$

21. **(a, c)**

$H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O(l)$

⇒ 30 25 —

0 10 —

Volume contraction = 55 – 10 = 45

$H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O(l)$

⇒ 10 45 0

0 5 —

∴ volume contraction = 55 – 5 = 50 mL

$H_2 + \frac{1}{2}\ O_2 \to H_2O(l)$

⇒ 40 15 0

10 0 —

∴ Volume contraction 55 – 10 = 45

$H_2 + \frac{1}{2}\ O_2 \to H_2O(l)$

⇒ 35 20 0

0 2.5 —

55 –2.5 = 52.5 mL

volume contraction 55 – 2.5 = 52.5 mL

22. (a, b, d) Since $\Delta ng = 0$ ∴ V. Density constant.

$$\Rightarrow 22.4\ \text{L} = \frac{22400\ \text{ml} \times 1\ \text{gm/ml}}{18} \times 6.02 \times 10^{23}\ \text{molecules}$$

$$\Rightarrow \quad \text{in 100 gram OLEUM } \frac{4.5}{18} = \frac{1}{4}\text{mole } SO_3 \text{ Perfect}$$

$$\therefore \quad \text{in 10 gram OLEUM} = \frac{1}{10} \times \frac{1}{4} = \frac{1}{40}\text{mole}$$

$$= \frac{1}{40} \times 80 = 2 \text{ gram } SO_3$$

$$\Rightarrow \quad V_{\text{Solution}} = \frac{V_1 d_1 + V_2 d_2}{\text{(d) solution}}$$

∴ Volume contraction and volume expansion possible.

23. (a, b, c, d)

⇒ Both have N_A particle

⇒ N_A particle means 1 mole

⇒ 1 gram atom = Atomic wt in gram = 1 mole

⇒ 1 gm atom have N_A atom

24. (b, c, d) $\dfrac{6.022 \times 10^{25}}{6.022 \times 10^{23}} \times 80\ \text{gm} = 8\ \text{kg}$

$$\Rightarrow \quad \frac{4.8}{48} = 0.1\ \text{mole}$$

$= 0.1\ N_A$ molecule

$= 0.3\ N_A$ Oxygen atom

$= 0.3 \times 6.02 \times 10^{23} = 1.806 \times 10^{23}$

$$\Rightarrow \quad \frac{22.7}{22400} \times 30\ \text{gram}$$

$$\Rightarrow \quad \frac{51 \times 10^{-3}}{17} = \frac{V}{22.4} = 67.2 \times 10^{-3}\text{L}$$

25. (a, c, d) $\dfrac{2.25 \times 10^{-22}}{74} = 3 \times 10^{-24}\text{mole}$

$= 3 \times 10^{-22} \times 6 \times 10^{23}$

$= 1.80$ molecule

$= 2 \times 1.80$ Oxygen atom

$= 2 \times 1.80 \times 16$ amu

⇒ $1.8 \times 10^{-22} \times 6.022 \times 10^{23} = 108.396$

⇒ $\dfrac{10}{100} = 0.1$ mole $CaCO_3$ contains 0.1 gram atom C

⇒ $2 \times 8 \times N_A < 5.5 \times 3 \times N_A = 16\ N_A < 16.5\ N_A$

26. (b, d)

(A) $\text{Molarity} = \dfrac{\text{Mole}}{\text{Liter}}$

In case of very dilute solution

Volume of solution = Volume of solvent

molality = mole/kg

1 kg of solvent = 1000 gram

as density of solvent CCl_4 = 1.6 g/mL

$$\therefore \text{ Volume of solvent} = \frac{1000}{1.6}\text{ml}$$

∴ molarity > molality

(B) $\dfrac{196}{178} \times 100\%$ OLEUM

178 gm oleum means 80 g SO_3 and 98 gm H_2SO_4

$$\text{\% of combine } SO_3 = \frac{\frac{80}{98} \times 100}{178}$$

(C) 0.0821 L atm K^{-1} mol^{-1}

$0.0821 \times 10^{-3} m^3 \times 760$ mm Hg K^{-1} mol^{-1}

$0.0821 \times 10^{-3} \times 760$ Hg m^3 mol^{-1} K^{-1}

0.0821×0.76 Hg m^3 mol^{-1} K^{-1}

(D) Volume change as $\Delta ng \neq O$

So vapour density will change

A, C are correct

and B D are incorrect

27. (A - p, q, s); (B - p, q); (C - r)

(A) $A_2 \to B_2 \to 2AB$

4 8 0

0 4 8

$2AB + 2B_2 \to 2AB_3$

8 4 0

4 0 4

(B) $A_2 + B_2 \to 2AB$

2 5 0

0 3 4

$2AB + 2B_2 \to 2AB_3$

4 3 0

1 0 3

(C) $A_2 + B_2 \to 2AB$

2 1 0

1 0 2

28. (A - p, q, r); (B - p, r); (C - p, r); (D - s)

(A) 1 Mole O_2 = 22. 4 Liter at STP

= 1 × 32 gram

= $1 \times N_A$ O_2 Molecules

(B) 1 Mole SO_2 = 22.4 Liter at STP

= 1 × 64 gram

= $1 \times N_A$ SO_2 Molecules

(C) 4 gram He = 1 mole

= 22.4 Liter at STP

= N_A atom

(D) 1 gram $H_2 = \frac{1}{2}$ Mole

$= \frac{1}{2} \times 22.4 = 11.2$ Liter at STP or 12.3 L at 1 atm and 300 K

$= \frac{1}{2} \times N_A$ (H_2 Molecule.)

29. (A - p, r); (B - q, r); (C - p, s); (D - q, r)

Isotope-I = M_1

Isotope-II = M_2

$$\% \text{ by mole} = \frac{M_{avg} - M_1}{M_2 - M_1} \times 100$$

$$\% \text{ by mass} = \% \text{ by mole} \times \frac{M_2}{M_{avg}}$$

(A) $\frac{(Z) - (Z-1)}{(Z+2) - (Z-1)} \times 100 = \frac{1}{3} \times 100 = 33.33\%$

$\% \text{ by mass} = 33.33 \times \frac{(Z+2)}{Z}$

(B) $\frac{(Z+2) - (Z+1)}{(Z+3) - (Z+1)} \times 100 = \frac{1}{2} \times 100 = 50\%$

$50 \times \frac{(Z+3)}{(Z+2)} = \frac{50Z + 150}{Z+2}$

(C) $\frac{2Z - Z}{3Z - Z} \times 100$

$= \frac{Z}{2Z} \times 100 = 50$

$= 50 \times \frac{3Z}{2Z} = 75\%$

(D) $\frac{(Z) - (Z-1)}{(Z+1) - (Z-1)} \times 100$

$= \frac{1}{2} \times 100 = 50$

$= \frac{50 \times (Z+1)}{Z}$

$= \frac{50Z + 50}{Z}$

30. (A - p, q); (B - q); (C - p, q, r, s); (D - q, s)

(A) 1 g ion Na^+ = 1 Mole Na^+
= $10 \times N_A$ electron
= $11 \times N_A$ Proton
= $1.6 \times 10^{-19} \times 6.022 \times 10^{23}$ coulomb Charge
= $12 \times N_A$ neutron

(B) 23 g Na = 1 Mole Na Atom
= $11 \times N_A$ electron
= $11 \times N_A$ Proton
= $12 \times N_A$ Neutron

(C) 1 g ion Mg^{+2} = 1 Mole Mg^{+2} ion
= $10 \times N_A$ electron
= $12 \times N_A$ Proton
= $12 \times N_A$ Neutron
= $2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{23}$ Coulomb charge

(D) 24 g Mg = 1 Mole Mg
= 12 N_A electron
= 12 N_A Proton
= 12 N_A neutron

31. (A - p, r, s, t); (B - p); (C - p, q, t); (D - q, r)

0.5 mole $CO_2 = 0.5 \times 22.4 = 11.2$ L
$= 0.5 \times 44 = 22$ g
$= 0.5 \times 3N_A = 1.5 \times 6.022 \times 10^{23}$ atom
$= 0.5 \times N_A = 3.01 \times 10^{23}$ Molecule

(B) 2 gram He = $\frac{1}{2}$ Mole = 11.2 Liter at STP

(C) 0.5 gm molecule O_3 = 0.5 mole O_3
= 11.2 L at STP
= 0.5 N_A Molecule
= $0.5\ N_A \times 3 = 1.5 \times 6.02 \times 10^{23}$ atom
$= 0.5 \times 48$ g
= 24 g

(D) $\frac{4.515}{6.02} \times \frac{10^{23}}{10^{23}} = 0.75$ mole
$= 0.75 \times 32 = 24$ gram
$= 0.75 \times N_A \times 2$ atom

32. (A - q); (B - q); (C - s); (D - r)

(A) No of oxygen atom = $0.5 \times 8\ N_A = 4\ N_A$

(B) No of carbon atom in CH_3 radical = $\frac{89.6}{22.4} = 4\ N_A$

(C) No of S atom in 192 gm of $SO_2 = \frac{192}{64} = 3\ N_A$

(D) No of Cl atom in 15×10^{23} Molecule = $\frac{15 \times 10^{23}}{6 \times 10^{23}} \times 2 = 5\ N_A$

33. (A - p, q, r, t); (B - p, r, t); (C - p, r); (D - s)

(A) 1 mole of O_2 :- Occupies 22.4 lit at 1 atm and 0°C weighs 32 gm.
Contains 2 mole of (O), oxygen atom Collection of N_A units of given substance.

(B) 1 mole of SO_2 :- Weight 64 gm, occupies 22.4 lit at 1 atm and 0°C,
Collection of N_A units of given substance.

(C) 4 g of He :- Occupies 22.4 lit at 1 atm and 0°C.
Collection of N_A units of given substance.

(D) 1 g of H_2 :- Occupies 12.3 lit at 1 atm and 300 K.

34. $[Cl_2 + 2\ KOH \rightarrow KCl + KClO + H_2O] \times 12$
$[3KClO \rightarrow 2KCl + KClO_3] \times 4$
$4\ KClO_3 \rightarrow 3\ KClO_4 + KCl]$

$$\begin{array}{llllll} 12\,Cl_2 + & 24\,KOH & \rightarrow 3\,KClO_4 + & 21\,KCl + & 12\,H_2O \\ 10 & 22 & & & \\ 0 & 2 \text{ gives} & \frac{3}{12}\times 10 & \frac{21}{12}\times 10 & 10 \end{array}$$

After reaction KOH $= 2$

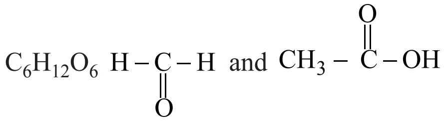
$KClO_4 = 2.5$

$KCl = 17.5$

$H_2O = 10$

Total $=$ 32.0 mole substance after reaction

35. % of C same (40%) for C : H : O ⇒ 1 : 2 : 1



$C_6H_{12}O_6$ $H-\underset{\overset{\|}{O}}{C}-H$ and $CH_3-\overset{\overset{O}{\|}}{C}-OH$

V. D of $C_6H_{12}O_6 = 6 \times$ V. D. of $CH_2O = 3 \times$ V. D. of CH_3CO_2H

∴ in bottle 4 is $C_6H_{12}O_6$ (M mass = 180)

and in bottle 1 is CH_3CO_2H (M mass = 60)

in bottle (2) $CH_3\,COCH_3$ (M mass = 58)

M mass $C_6H_{12}O_6 > CH_3COOH > CH_3\,CO\,CH_3 > HCHO$

or V. D. (4) (1) (2) (3)

Since V.D $= \dfrac{M_{\text{mass}}}{2}$

36. If No of moles of $Na_2CO_3 = a$ mole

No of moles of $Na_2SO_4 = b$ mole

No of moles of NaOH $= c$ mole

$a \times 106 + b \times 142 + c \times 40 = 1000$ gram.

No of moles of HCl required for neutralisation of mixture $2a + c = \dfrac{511}{36.5} = 14$

No of moles of $BaCl_2$ = No of moles of $BaSO_4$

= No of moles of Na_2SO_4 (b)

$$= \frac{466}{137+96} = \frac{466}{233} = 2 \text{ moles}$$

$106a + 40c = 1000 - 284 = 716$

$80a + 40c = 14 \times 40 = 560$

$$a = \frac{156}{26} = 6$$

$c = 14 - 12 = 2$

so wt of NaOH $= 2 \times 40 = 80$ gm

% of NaOH $= \dfrac{80}{1000} \times 100 = 8\%$

37. $B \xrightarrow{nH_2PtCl_6} \underset{\substack{w_1 \text{ gram} \\ (10.48\,\text{gm})}}{B_2[H_2PtCl_6]_n} \xrightarrow{\Delta} \underset{\substack{w_2 \text{ gram} \\ (10.48)}}{n\text{Pt}}$

POAC on Pt atom

$$M \text{ mass of } \left[\frac{w_1}{w_2} \times 195 - 410\right] \times \frac{n}{2}$$

$$= \left[\left(\frac{10.48}{3.9}\right) \times 195 - 410\right] \times \frac{2}{2} = 114$$

38. Molar mass of $H_2SO_4 = 98$ ⇒ require 80 gram NaOH for neutralization

Molar mass of HCl = 36.5 = require 40 gram Na OH for neutralisation

Molar mass of $HNO_3 = 63$ = require 40 gram Na OH for neutralisation

Molar mass of $H_3\,PO_2 = 3 + 31 + 32 = 66$ = require 40 gram Na OH for neutralisation

Molar mass of $HClO_4$ = 1 35.5 + 64 = 100.5 = require 40 gram NaOH neutralisation

∴ minimum volume of NaOH neutralise by $HClO_4$

No of moles of $HClO_4 = \dfrac{292}{100.5}$ = No of moles of NaOH = M.V

$$= \left(\frac{w}{v}\% \frac{10}{M_A}\right) V$$

$$\frac{292}{100.5} = 20 \times \frac{10}{40} \times V$$

$$\therefore \quad V = \frac{292}{502.5} = 581 \text{ml}$$

Maximum value of NaOH required if only HCl present in solution

$$\frac{292}{36.5} = 20 \times \frac{10}{40} \times V$$

$$V = \frac{292}{36.5 \times 5} = 1.6 \text{ L} = 1600 \text{ ml}$$

∴ To neatralise mixture or any separate solution V_{NaOH} used From 581 mL to 1600 mL

∴ Ans. 1600 mL

39. 17% $\dfrac{w}{v}$ means 17 gram $AgNO_3$ in 100 mL

in 100 mL solution weight of $AgNO_3 = 17$ gram

∴ In 1 mL solution weight of $AgNO_3$ $\dfrac{17}{100}$

∴ in 3000 mL solution weight of $AgNO_3$

$$= \frac{17}{100} \times 3000 = 510 \text{ gram}$$

No of moles of $AgNO_3 = \dfrac{510}{170} = 3$ moles

$$\therefore \quad M_2 = \frac{3}{3} = 1\,\text{M}$$

$M_1V_1 = M_2V_2$

$3 \times V_1 = 1 \times 3$

$V_1 = 1$ Liter

∴ $V_{\text{H2O}} = 3 - 1 = 2$ Liter ∴ $ab = 02$

Mass of Ar $= 4a$

Mass of etnane $= 7a$

Mole percentage of ethane $\dfrac{\dfrac{7a}{30}}{\dfrac{7a}{30}+\dfrac{4a}{18}} \times 100$

$$= \frac{0.233}{0.233 + 0.222} \times 100 = 51\%$$

$Cd = 51$

$\therefore$ $abcd = 0251$

40. $C_xH_YO_ZN_P \xrightarrow[\text{combution}]{+O_2} x co_2 + \frac{y}{2}H_2O + \frac{P}{2}N_2$

$12x + y + 16z + 14P = 61$

Compound (10 mL) on combustion gives 20 mL CO_2 means

$\therefore$ $10x = 20$

$x = 2$

Volume of residual gas $N_2 = 5$ mL

$\therefore$ $\frac{P}{2} \times 10 = 5$

$P = 1$

Y and Z can not be – Ve or fraction

$\therefore$ $y = 7$ and $z = 1$

$\therefore$ $12 \times 2 + 7 + 16 + 14 = 61$ M mass

$\therefore$ correct and 2711

41. $CO \xrightarrow{+O_2} CO_2$

$CH_4 \xrightarrow{+O_2} CO_2 + H_2O(l)$

volume of $(CO + CH_4) = 10$ mL **Since 1 mol CO gives 1 mol CO_2 and 1 mol CH_4 gives 1 mol CO_2**

$\therefore$ Volume of CO_2 released = 10 mL

$\therefore$ Volume contraction = 10 mL

(since all CO_2 absorbed by KOH)

42. If No of moles of SO_3 or (mass of SO_3) Per 100 gram Oleum or (Per 100 gram H_2SO_4) high than % Labelling of Oleum high

(1) In 200 gram H_2SO_4 wt of SO_3 = 100 gram

$\therefore$ in 100 gram H_2SO_4 wt of SO_3 = 50 gram

(2) In 80 gram H_2SO_4 wt of SO_3 = 80 gram

$\therefore$ In 100 gram H_2SO_4 wt of SO_3 = 100 gram

(3) In $5 \times 98 = 490$ gram H_2SO_4 wt of $SO_3 = 5 \times 80 = 400$ gram

$\therefore$ In 100 gram H_2SO_4 wt of $SO_3 = \frac{400}{490} \times 100$

$= 81.6$

(4) In $5 \times 98 = 490$ gram H_2SO_4 wt of $SO_3 = 6 \times 80$

$= 480$

In 100 gram H_2SO_4 wt of $SO_3 = \frac{480}{490} \times 100$

$= 98$ gram

$100 > 98 > 81.6 > 50$

Solution code $6 > 2 > 4 > 8$ $\therefore$ correct Ans 8426

43. $2A \quad + \quad 3B \quad + \quad C \rightarrow \quad 4D + 2E$

$2a$ moles $\quad 3a$ moles $\quad a$ moles

for obtaining maximum mass of E there should be no reactant after reaction

$\therefore$ $2a \times 40 + 3a \times 30 + a \times 20 = 570$

$80a + 90a + 20a = 570$

$190a = 570$

$a = 3$

$\therefore$ $n_A = 6$ mole

$n_B = 9$ mole

$n_C = 3$ mole

gives 4×3 mole of D and 2×3 moles of E

$\therefore$ Mass of $D = 12 \times 15 = 180$ g

Mass of $A + B + C$ = mass of (D) + (E) (mass conservation)

$570 = 180$ + mass of E

mass of E = 390 g

44. $n = \frac{PV}{RT}$

$$= \frac{2 \times 44.8}{0.821 \times 546} = \frac{2 \times 22.4 \times 2}{0.0821 \times 273 \times 2} = 2 \text{ moles}$$

wt of 2 mole of triatomic gas = 246

$\therefore$ Molar mass = $\frac{246}{2} = 123$

$\therefore$ Atomic mass = $\frac{123}{3} = 41$

45. $3H_2SO_4 \quad + \quad Ba_3(PO_4)_2 \rightarrow 3BaSO_4\downarrow + 2H_3PO_4$

$0.2 \times 0.1 \qquad 0.4 \times 0.05$

0.02 mole $\qquad$ 0.02 mole

Here H_2SO_4 L. R

$\therefore$ remaing moles of $Ba_3(PO_4)_2 = 0.02 - \frac{0.02}{3}$

$= \frac{0.04}{3}$ Mole

$\therefore$ No of moles of Ba^{+2} ion $= 3 \times \frac{0.04}{3} = 0.04$ Mole

Volume of solution = 0.1 + 0.4 = 0.5 L

$\therefore$ $M = \frac{0.04}{0.5} = 0.08M = x$

$\therefore$ $100x = 0.08 \times 100 = 8$

46. $C_3H_6 + NO \rightarrow C_3H_3N + H_2O + N_2$

POAC on C atom

$$3 \times \frac{420 \times 10^3}{42} = 3 \times \frac{\text{wt}}{53}$$

$\therefore$ **wt of C_3H_3N = 530 Kg**

47. $C_4Hx + \left(4 + \frac{x}{4}\right)O_2 \rightarrow 4CO_2 + \frac{x}{2}H_2O$

10 ml $\qquad \left(4 + \frac{x}{4}\right) \times 10$

$$\left(4+\frac{x}{4}\right)\times 10 = 55$$

$$4+\frac{x}{4} = 5.5$$

$$\frac{x}{4} = 1.5$$

$x = 6$

48. Wt of solution = 1200 g
wt of solute = 12 g
density solution = 1.2 g/ mL

$\therefore$ Volume of solution = $\frac{1200}{1.2}$ = 1000 mL

$$M = \frac{\text{No of moles of solute}}{\text{volume of solution}} = \frac{12/60}{1\,\text{L}}$$

$$x = \frac{1}{5}$$

$$\therefore \quad 10x = \frac{1}{5}\times 10 = 2$$

49. $$\underset{100}{A} \xrightarrow{40\%} \underset{3\times100\times0.4}{3B} + \underset{1\times100\times0.4=40}{D}$$

$$2B \xrightarrow{50\%} 4C$$

$$120 \quad \frac{4}{2}\times 120\times 0.5$$

$$120 + 40 = 160$$

50. $$M = \frac{d\times 1000}{50} = \frac{2\times 1000}{50} = 40$$

40 Mole in 1 Liter or in 2 kg
$\therefore$ No of moles in 1 kg = 20 mole = m
40 + 20 = 60

51. $5\times x + 2\times 1 = 3\,(1+x)$
$5x - 3x = 1$

$$x = \frac{1}{2}\,\text{L}$$

$\therefore$ Total volume = 1000 mL + 500 mL = 1500 mL.

52. $C_2H_6 + O_2 \rightarrow 2\,CO_2 + 3H_2O$
x mL C_2H_6 gives $2x$ ml CO_2
$C_3H_8 + O_2 \rightarrow 3CO_2 + 4\,H_2O$
$(20-x)$ mL C_3H_8 gives $3(20-x)$ mL CO_2
$2x + 60 - 3x = 52$
$x = 8,\ y = 12$
$8 : 12 = 2 : 3$

$\mathbf{CH_4 \rightarrow CO_2 + H_2O}$
12 mL CH_4 gives 12 mL CO_2
$C_4H_{10} \rightarrow 4CO_2$
8 mL C_4H_{10} gives 4 × 8 mL CO_2
$\therefore$ V_{CO_2} Total = 12 + 32 = 44 mL

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. **(c)** 8 mol O atom present in 1 mol $Mg_3\,(PO_4)_2$.

$\therefore$ 25 mol of 'O' atoms are in $\frac{1}{8}\times 0.25 = 3.125\times 10^{-2}$ mole

2. **(d)** $\text{Molality} = \frac{\text{moles of the solute}}{\text{mass of the solvent in kg}}$
Weight of acetic acid = 2.05 × 60 = 123
Weight of solution = 1000 × 1.02 = 1020
$\therefore$ Weight of water = (1020 – 123) = 897 g

$$\therefore \quad \text{Molality} = \frac{2.05\times 1000}{897} = 2.28\ \text{m}$$

3. **(d)** $2Al(s) + 6HCl\,(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^{-}(aq) + 3H_2(g)$
$\because$ 6 moles of HCl produces = 3 moles of H_2
= 3 × 22.4 L of H_2 at STP

$\therefore$ 1 mole of HCl produces = $\frac{3\times 22.4}{6}$ L of H_2 at STP
= 11.2 L of H_2 at STP

4. **(c)** $$M = \frac{W_A}{M_A}\times\frac{100}{V}$$

$$M = \frac{W_A}{V}\times 100\times\frac{10}{M_A}$$

$$\frac{W}{V}\%\times\frac{10}{M_A} = \frac{w}{w}\%\frac{10d}{M_A}$$

$$3.6 = \frac{29\times 10\times d}{98}$$

$d = 1.21$ gm/mL

5. **(c)** Titration of oxalic acid by $KMnO_4$ in the presence of HCl gives unsatisfactory result because HCl is a better reducing agent than oxalic acid and HCl reduces preferably MnO_4^{-} to Mn^{2+}.

6. **(c)** Mohr's salt is $FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$
Only oxidizable part Fe^{2+} is
$[Fe^{2+} \rightarrow Fe^{3+} + e^{-}]\times 6$
$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O$
$6Fe^{2+} + Cr_2O_7^{2-} + 14H^{+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$
Millimoles of Fe^{2+} = 750 × 0.6 = 450

Moles of Fe^{2+} = $\frac{450}{1000}$ = 0.450 mol
6 mol of Fe^{2+} react with 1 mol $Cr_2O_7^{2-}$

$\therefore$ 0.450 mol Fe^{2+} = $\frac{0.450}{6}$ = 0.075 mol $Cr_2O_7^{2-}$
= 0.075 × 294 g = 22.05 g

7. **(a)** $\text{Molality} = \frac{\text{moles of the solute}}{\text{mass of the solvent in kg}}$

$W_B = WH_2 = V\cdot d = 0.3\,\text{L}\times 1 = 300\,\text{mL}\times 1 = 300$ gram

$$m = \frac{W_A}{M_A} \times \frac{1000}{W_B} = \frac{0.01}{60} \times \frac{1000}{60}$$
$$= 5.55 \times 10^{-4}\,\text{mol kg}^{-1}$$

8. **(d)** Total mass of solution = 1000 g water + 120 g urea = 1120 g
Density of solution = 1.15 g/mL

Thus, volume of solution = $\frac{\text{mass}}{\text{density}} = \frac{1120\,\text{g}}{1.15\,\text{g/mL}}$
= 973.91 mL = 0.974 L

Moles of solute = $\frac{120}{60}$ = 2 mol

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{volume (L) of solution}}$$
$$= \frac{2\text{ mol}}{0.974\text{ L}} = 2.05\text{ mol L}^{-1}$$

9. **(a)** The molarity of a resulting solution is given by

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$
$$= \frac{750 \times 0.5 + 250 \times 2}{750 + 250} = \frac{875}{1000} = 0.875\text{ M}$$

10. **(d)** 18 g H_2O contains 2 gH
∴ 0.72 g H_2O contains 0.08 g H.
44 g CO_2 contains 12 g C.
∴ 3.08 g CO_2 contains 0.84 g C.
$\therefore \text{C : H} = \frac{0.84}{12} : \frac{0.08}{1} = 0.07 : 0.08 = 7 : 8$
∴ Empirical formula = C_7H_8

11. **(c)** The number of moles is given by

$$\text{Number of moles} = \frac{\text{weight (W)}}{\text{molecular weight (M)}}$$

Thus, ratio of moles of O_2 and N_2 is given by

$$\frac{n_{O_2}}{n_{N_2}} = \left(\frac{\frac{W_{O_2}}{M_{O_2}}}{\frac{W_{N_2}}{M_{N_2}}}\right) = \left(\frac{W_{O_2}}{W_{N_2}}\right)\left(\frac{M_{N_2}}{M_{O_2}}\right)$$
$$= \left(\frac{1}{4}\right) \times \left(\frac{28}{32}\right) = \frac{7}{32}$$

Hence, ratio of n_{O_2} and n_{N_2} is 7 : 32

12. **(d)** The following reaction occurs:
$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$
From the above equation, we find that Mohr's salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) and dichromatic reacts in 6 : 1 molar ratio.

13. **(b)** The atomic mass of iron is
$$= \frac{(5 \times 54) + (90 \times 56) + (5 \times 57)}{100} = 55.95$$

14. **(c)** Total mass of solution = 1000 + 120 = 1120 g

Total volume of solution in (L) = $\frac{1120}{1.15} \times 10^3$

$$M = \frac{W}{M} \times \frac{1}{V(\text{in } L)} = \frac{120}{60} \times \frac{1.15 \times 10^3}{1120} = 2.05\text{ M}$$

15. **(c)** The least significant figure in titre values is 3.

Average titre value = $\frac{25.2 + 25.25 + 25}{3} = \frac{75.4}{3} = 25.1$

The number of significant in average titre value will also be 3.

16. **(7)** $d = \frac{\text{mass}}{V} \Rightarrow$ 10.5 g/cc means in 1 cc
⇒ 10.5 g of Ag is present

Number of atoms of Ag in 1 cc ⇒ $\frac{10.5}{108} \times N_A$

In 1 cm number of Ag atom = $\sqrt[3]{\frac{10.5 \times N_A}{108}}$

In 1 cm^2, number of atoms of Ag = $\left(\frac{10.5}{108}N_A\right)^{2/3}$

In 10^{-12} m^2 or 10^{-8} cm^2, number of atoms of Ag

$$= \left(\frac{10.5}{108}N_A\right)^{2/3} \times 10^{-8}$$
$$= \left(\frac{10.5 \times 6.022 \times 10^{23}}{108}\right)^{2/3} \times 10^{-8} = 1.5 \times 10^7$$

Hence $x = 7$.

17. **(2)** $Be_nAl_2Si_6O_{18}$
$(2n) + (3 \times 2) + (4 \times 6) + (-2 \times 18) = 0$
or $2n + 30 - 36 = 0$
or $2n = 6$
or $n = 3$

18. **(2)** Na shows only +1
F shows only –1

19. **(8)** Stock solution of HCl = 29.2 % (w/w)

$$M = \frac{W_A}{M_A} \times \frac{1000}{V}$$
$$M = \frac{W_A}{V} \times 100 \times \frac{10}{M_A}$$
$$\frac{W}{V}\% \times \frac{10}{M_A} = \frac{w}{w}\% \frac{10d}{M_A}$$

Molarity of stock solution of HCl = $M = \frac{w}{w}\% \frac{10d}{M_A}$

$$= \frac{29.2 \times 10 \times 1.25}{36.5} = 10$$

If volume of stock solution required = V mL then
$10 \times V = 0.4 \times 200$
$V = 8$ mL

20. **(4)** $\frac{R}{N}$ = Boltznann constant

$\Rightarrow$ R = Boltzann constant $\times N$

$6.023 \times 10^{23} \times 1.380 \times 10^{-23} = 8.312$

It has four significant figures.

21. **(d)** $2C_8H_7SO_3Na + Ca^{2+} \rightarrow (C_8H_7SO_3)_2Ca + 2Na^+$

$\because$ 2 moles of $C_8H_7SO_3Na$ combines with 1 mol Ca^{2+}

$\therefore$ 1 mole of $C_8H_7SO_3Na$ will combine with $\frac{1}{2}$ mol Ca^{2+}

$\therefore$ $\frac{1}{206}$ mole of $C_8H_7SO_3Na$ will combine with

$$\frac{1}{2} \times \frac{1}{206} \text{mol } Ca^{2+} = \frac{1}{412} Ca^{2+}$$

22. **(d)** Given, initial strength of acetic acid = 0.06 N

Final strength = 0.042 N; Volume given = 50 mL

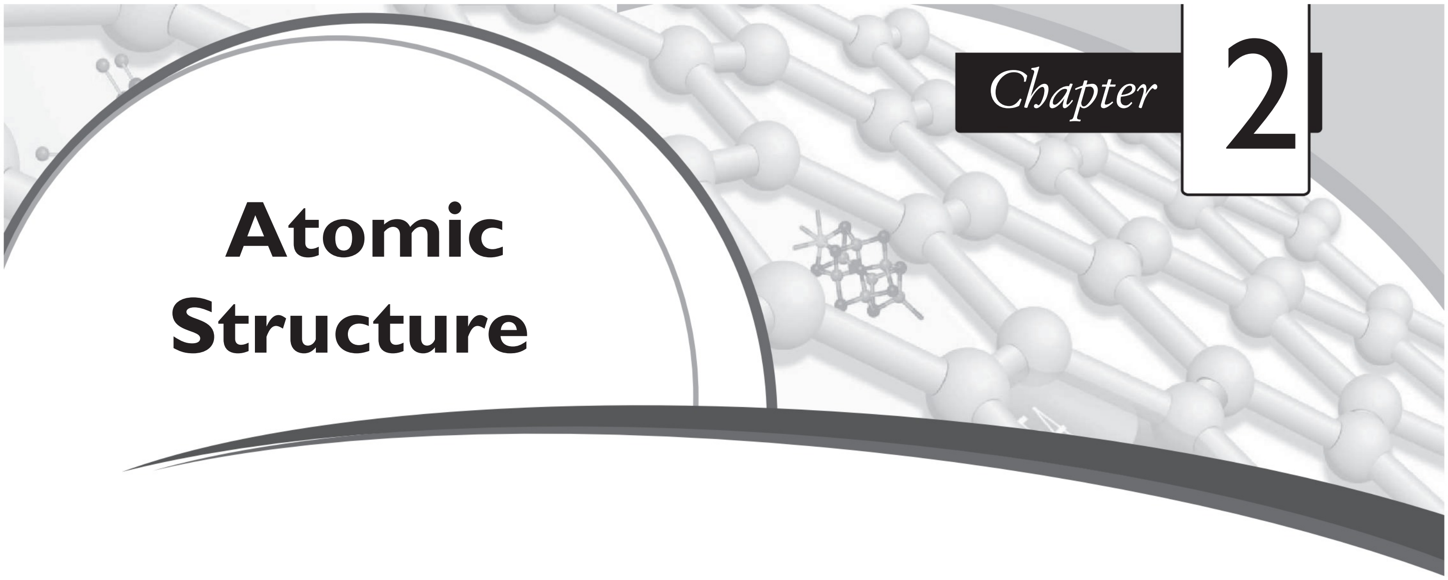
$\therefore$ Initial millimoles of $CH_3COOH = 0.06 \times 50 = 3$

Final millimoles of $CH_3COOH = 0.042 \times 50 = 2.1$

$\therefore$ Millimoles of CH_3COOH adsorbed = 3 – 2.1

= 0.9 mmol

= 0.9 × 60 mg = 54 mg



Chapter 2

Atomic Structure

Key Concepts

DALTON'S THEORY OF ATOM

Atom was considered as a hard, dense and smallest indivisible particle of matter. It cannot be destroyed or created.

Drawbacks

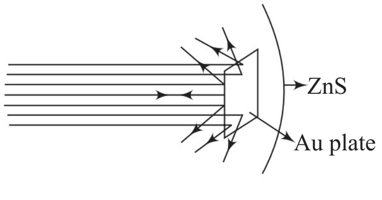
The discovery of various sub. atomic particle *e*, *p*, *n*, *x*-ray.

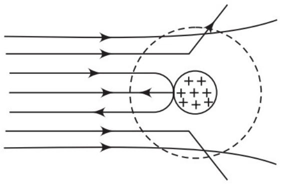
MODELS OF ATOM

Thomson's Model

Atom is electrically neutral. It contains positive as well as negative charges. According to Thomson, atom is a uniform sphere of positive charge with electron embedded in it. This was known as *plum pudding modle* at that time.

Rutherford's Scattering Experiments





Result

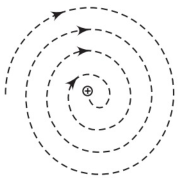
1. Most of the α-particle passed through the foil.
2. Some of them were deflected through small angles.
3. Very few (1 in 20,000) were deflected at large angles (180°).

Rutherford Model

1. The atom of an element consist of a small positively charged nucleus which is situated at the centre of the atom and carries almost the entire mass of the atom.
2. An electron rotates arround the nucleus. Since very few α-particles (1 out of 20,000) are returned back it means the size of the nucleus is very small and is very rigid.
3. The order of diameter of an atom is 10^{-10} m or 1 Å and of the nucleus is 10^{-15} m = 1 fm.
4. $r_n = (1.33 \times 10^{-15})\ A^{1/3}$ m. A = mass number r_n = radius of Nucleus of any element having mass number A.

Failure of Rutherford Model

1. According to electromagnetic theory, when a charged particle moves with acceleration, they emit energy in the form of electromagnetic radiation. According to Rutherford model electrons are revolving around nucleus and emit energy in the form of electromagnetic radiation. As a result of which electron loses energy continuously and should collapse on nucleus following a spherical path. Rutherford model failed to explain the stability of atom.



2. If electrons loose energy continuously the observed spectrum may be continuous but it will consist of well-defined line of definite frequency. Hence the loss of energy by the electron is not continuous in an atom.

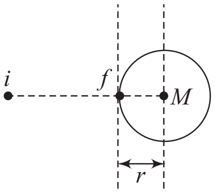
Calculation of distance between α particle and centre of nucleus:

Total energy at initial point

$$T_i = \text{K.E.} + \text{P.E.} = \frac{1}{2}mv^2 + 0 \qquad \text{...(i)}$$

Total energy at final point

$$T_f = 0 + \frac{K \cdot q_1 q_2}{r} \qquad \text{...(ii)}$$



By energy conservation law

$T_i = T_f$

q_2 = charge on Nucleus of an element

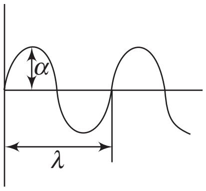
q_1 = charge and particle = $2 \times 1.6 \times 10^{-19}$ C

m = mass of ∝ particle = $4 \times 1.6 \times 10^{-27}$ Kg

$$\frac{1}{2} m v^2 = \frac{K \cdot q_1 q_2}{r}$$

$$r = \frac{2K \cdot q_1 q_2}{m v^2}$$

$$= \frac{2 \times 9 \times 10^9 \times (2 \times 1.6 \times 10^{-19})(Z \times 1.6 \times 10^{-19})}{4 \times 1.6 \times 10^{-27} \cdot v^2}$$



Wave: It is a disturbance in medium through which transfer of energy takes place from one place to other without the transfer of matter.

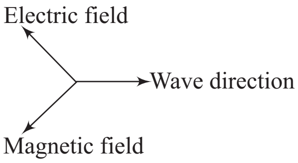
Parameters:

(i) **Wavelength:** Distance covered by the wave in completion of one cycle.

(ii) **Frequency (ν):** The number of cycles completed in 1 sec.

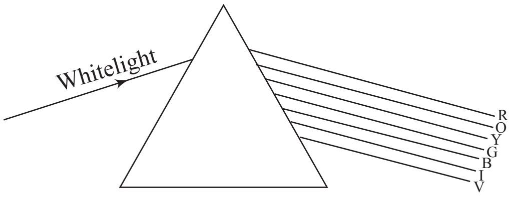
(iii) **Time period:** Time taken by the wave in one cycle completion where $T = \frac{1}{\nu}$

(iv) **Wave No.** $\bar{\nu} = \frac{1}{\lambda}$



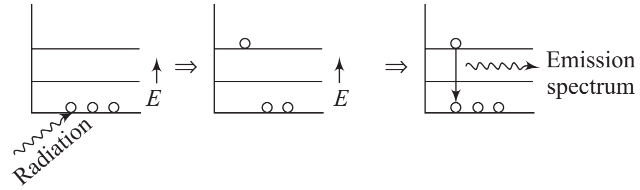
Electromagnetic waves do not require any medium to propagate from one place to another place. It has two components: (i) Electric field and (ii) Magnetic field. They are perpendicular to one another and to the direction of propagation. Light is an electromagnetic wave.

When white light is passed through prism it get dispersed into different colours. It is called *spectrum of white light*.



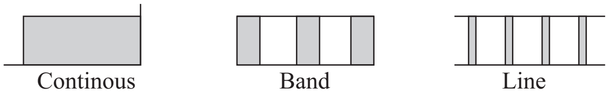
Types of Spectrum

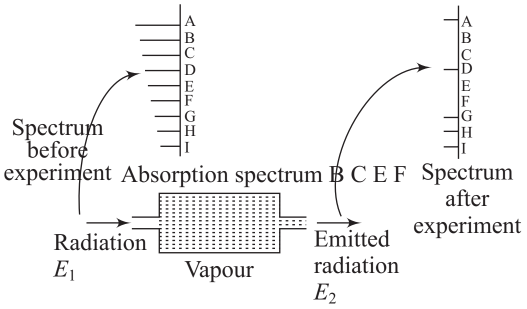
1. Emmision spectrum: When any substance absorbs energy or radiation, its atoms get excited to higher energy state. After some time when they return to their original state, they emit radiation and spectrum. This is called emission spectrum.



2. Absorption spectrum: When radiation is passed through a substance, certain wavelength absorbed and when this outcoming radiation is analysed at the photographic plate we observe dark line at plane of observed wave length. This is called *absorption spectrum*.

It may be continuous, band or line.

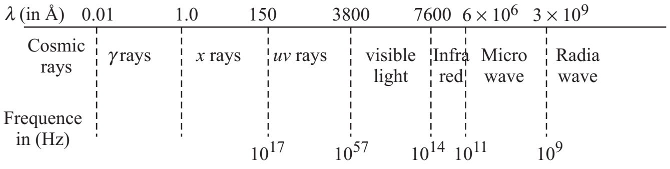




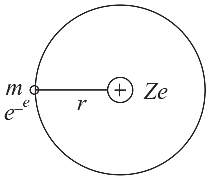
Quantum theory of radiation: According to Max Plank, radiation emitted from hot bodies, radiant energy (light or heat) is not emitted continuously but discontinuously in the form of small packets called Quanta. It means atoms or molecules emit or absorb the energy in the form of Quanta [$E = h\nu$]. They absorb or emit energy as $h\nu$, $2h\nu$ ... not in the form of 1/2 $h\nu$, $3/2h\nu$, etc., i.e., fraction of Quanta is not possible.

$E = h\nu$ [h = Plank constant = 6.63×10^{-34} J.S.]

and TE = n ($h\nu$) n is the number of Quanta of particular frequency.



Bohr's atomic model



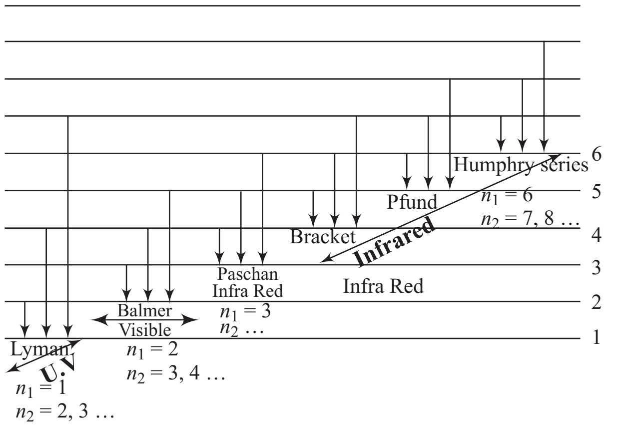
1. According to Bohr's atomic model, e^- rotate around the nucleus in a circular orbit. The required centripetal force is provided by electrostatic force of attraction between the electron and nucleus.

$$\frac{mv^2}{r} = \frac{Ke \times Ze}{r^2}$$

2. Electrons revolve in those orbit which have angular momentum equal to $\frac{nh}{2\pi}$ (where n is an integer 1, 2, 3,...)

$$mvr = \frac{nh}{2\pi}$$

3. Each allowed orbit have definite energy. These are called *stationary orbit*. Electrons when revolve in stationary orbit do not radiate energy. The energy of stationary orbit increases as we move farther from the nucleus.
4. Electrons emits energy only when it transitions from higher energy states to lower energy states.



First line α Line [minimum energy line]

$$\frac{1}{\lambda} = Rz^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] R = 1.097 \times 10^7$$

Second line β line.

Calculation of radius, energy and velocity of e^- in n^{th} Bohr atom

Electrostatic force of attraction provide required centripetal force

$$F = \frac{K(Ze)e}{r^2} = \frac{mv^2}{r} \qquad ...(i)$$

$$mvr = \frac{nh}{2\pi} \qquad ...(ii)$$

$$\therefore \quad m^2v^2r^2 = \frac{n^2h^2}{4\pi^2}$$

$$\therefore \quad r = \left[\frac{n^2h^2}{4\pi^2 m \times KZe^2}\right]$$

$$r = \frac{h^2}{4\pi^2 mKe^2} \times \frac{n^2}{Z} \text{ and } v^2 = \frac{n^2h^2}{4\pi^2 m^2 r^2}$$

$$= \frac{[6.63 \times 10^{-34}]^2}{4 \times (3.14)^2 \times 9.1 \times 10^{-31} \times 9 \times 10^9 \times (1.6 \times 10^{-19})^2}$$

$$\times \frac{n^2}{z} \text{ m/sec.}$$

$$\boxed{r = 0.529 \frac{n^2}{Z} \text{Å}}$$

$$mvr = mv \times \left(0.529 \frac{n^2}{z} \text{A}°\right) = \frac{nh}{2\pi}$$

$$\varpi = 2.18 \times 10^6 \; \frac{Z}{n} \text{ m/sec.}$$

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

$$\text{P.E.} = -\frac{KZe^2}{r} \text{ and K.E.} = \frac{1}{2}mv^2$$

We know $\frac{mv^2}{r} = \frac{KZe^2}{r^2}$

$$\therefore \qquad \text{K.E.} = \frac{1}{2}mv^2 = \frac{1}{2}\left[\frac{KZe^2}{r}\right]$$

$$\therefore \qquad \text{T.E. = K.E. + P.E.} = \frac{1}{2}\left[\frac{KZe^2}{r}\right] + \left[-\frac{KZe^2}{r}\right]$$

$$\boxed{\text{T.E.} = -\frac{1}{2}\frac{KZe^2}{r}}$$

$$= -\frac{1}{2} \frac{9 \times 10^9 \times (1.6 \times 10^{-19})^2 Z}{0.529 \times 10^{-10} \frac{n^2}{Z}}$$

$$\boxed{\text{T.E.} = -13.6\left(\frac{z^2}{n^2}\right)\text{ev/atom}}$$

$$\boxed{\text{T.E.} = -313.6\left(\frac{z^2}{n^2}\right)\text{Kcal/mole}}$$

1 eV = 1.6×10^{-19} joule

Result Species having only one electron system around nucleus in any orbit

(i) Total Energy = –Kinetic Energy of electron
(ii) Potential Energy = 2 Total Energy
(iii) Ionisation Energy = Kinetic energy = –Total Energy

Drawbacks of Bohr's Model

1. It explains the spectrum of species having only one electron H atom, He^+ ion and Li^{++} ion. It does not explain the spectral of atoms having more than one electron.

2. When a resolving power spectroscope is used it was observed that the spectral line in H spectrum is not a single line but a collection of several lines which are very close to one another. Bohr's theory does not explain the fine spectrum of H atom.
3. It does not explain the splitting of spectral lines into a group of finite lines under the influence of magnetic field [Zeman effect] and electric field [Stark effect]. Jusitification of quantisation angular momentum.
4. Spectrum of isotope of H was expected to be same by Bohr's theory but it is different by experiment.

Ionisation energy: Minimum amount of energy which is required to eject the electron from the atom from its ground state.

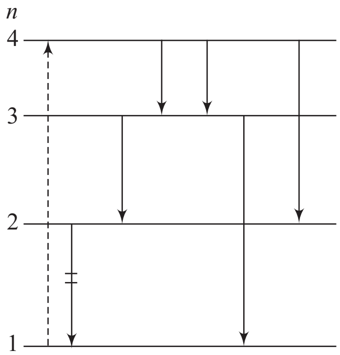
$$E_\infty = 0$$

$$\therefore \quad \text{IE} = E_\infty - E_n = 0 - [E_n]$$

$$\boxed{IE = -E_n}$$

Total number of spectral line that can be obtained when electron in n^{th} energy state gets transitioned.

$$= \frac{(\Delta n)(\Delta n + 1)}{2}$$



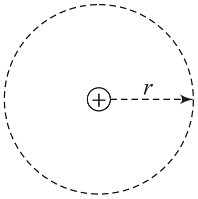
$$\Delta E = E_{n_2} - E_{n_1} = \frac{hc}{\lambda} = 13.6\frac{z^2}{n_2^2} - \left[-\frac{13.6z^2}{n_1^2}\right] = \frac{hc}{\lambda}$$

$$= 13.6\,evZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = \frac{hc}{\lambda} \Rightarrow \frac{1}{\lambda} = \frac{13.6}{hc}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]ev$$

$$\frac{1}{\lambda} = R_h Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad R_H = 1.097 \times 10^7\ \text{m}^{-1}$$

R_h = Rydberg constant

Frequency of revolution:



Distance travelled in 1 revolution = $2\pi r$ meter.

Distance travelled in $2\pi r$ meter ⟶ 1 revolution

$$\therefore \quad \text{Distance travelled in 1 metre} \longrightarrow \frac{1}{2\pi r}\ \text{revolution}$$

$$\therefore \quad \text{Distance travelled in V meter} \longrightarrow \frac{V}{2\pi r} = \text{Frequency}$$

$$\therefore \quad \text{Time taken} = \left[\frac{2\pi r}{V}\right]\ \text{second}$$

De Broglie Equation

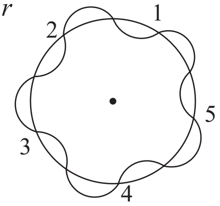
According to this theory, small particles like electrons, protons, neutron, α particle, etc., behave as particle nature as well as wave nature. The wavelength of particle is given by

$$\boxed{\lambda = \frac{h}{mv} = \frac{h}{P(\text{momentum})}}$$

Proof of Bohr's Theory by De broglie Relationship

When electrons rotate around nucleus in any orbit, the number of completed wave is equal to the number of orbit.

It means No. of waves = No. of oribtal



From $\boxed{n\lambda = 2\pi r}$ or $n\left[\frac{h}{mv}\right] = 2\pi r$

$n = 1$ $\quad 1\lambda = 2\pi r$

$n = 2$ $\quad 2\lambda = 2\pi r$ $\quad \boxed{mvr = \frac{nh}{2\pi}}$ proved.

$n = 5$ $\quad 5\lambda = 2\pi r$

Some relations:

1. Between Momentum (P**)** and Kinetic Energy (K.E.)
2. Between K.E. and **Wave length** (λ)

$$\boxed{\lambda = \frac{h}{P} = \frac{h}{\sqrt{2KE.m}} = \frac{h}{\sqrt{2q \times V \times m}}}$$

for Electron

$$\lambda = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 1.6 \times 10^{-19} \times 9.1 \times 10^{-31} \times V}} = \sqrt{\frac{150}{V}}\ \text{Å}$$

Since

$$\text{K.E.} = \frac{1}{2}mv^2 \Rightarrow 2\text{K.E.} = mv^2$$

$$\Rightarrow \quad 2\text{K.E.} \cdot m = (mv)^2 = (P)$$

$$\therefore \quad \boxed{P = \sqrt{2\text{KE} \cdot m}}$$

3. Relation between K.E. and mass of particle for same value of de broglie wavelength.

We know $\lambda = \frac{h}{\sqrt{2(\text{KE}).m}}$ $\quad \therefore \quad \lambda^2 = \frac{h^2}{2\text{KE}.m}$

∴ for same λ (Wave length)

$$\therefore \quad \boxed{\text{KE} \propto \frac{1}{m}}$$

mass of e^- < Proton < Neutron < α particle

∴ for same de-Brogile Wave length order of kinetic energy

e^- > Proton > Neutron > α particle

Heisenberg Uncertainity Principle

It is impossible to measure both the position and velocity (or momentum) of a microscopic particle simultaneously with absolute accuracy.

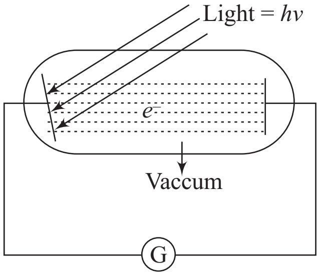
According to this theory, product of uncertainity in position and uncertainity in momentum is always greater than or equal $\frac{h}{4\pi}$.

$$(\Delta p)\,(\Delta x) \geq \frac{h}{4\pi}$$

$$\Delta x \times m \cdot \Delta V = \frac{h}{4\pi}$$

$$\boxed{\Delta x \times \Delta V = \frac{h}{4\pi m}}$$

Photoelectric effect: Hertz (1887) discovered that when a beam of light of suitable wavelength falls on a clean metal plate (such as cesium) in vacuum, electrons are emitted from the surface of the metal plate. This phenomenon involving the emission of electrons from the surface of a metal by the action of light is known as *photoelectric effect*. The electrons so emitted are called *photoelectrons*.



Photon energy = K.E. of e^- + threshold energy.

K.E. of e^- = photon energy – threshold energy.

$$\boxed{\frac{1}{2}mv^2 = h\nu - h\nu_0 = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right] = h\nu - \phi}$$

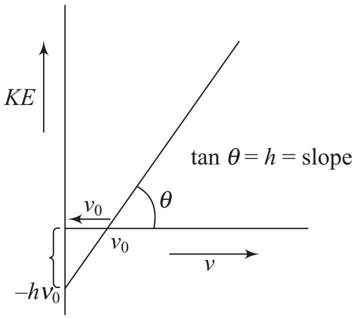
ν_0 = Threshold frequency or critical frequency.

λ_0 = Threshold wavelength or critical wavelength.

Experimental Result

1. If $\nu < \nu_0 \Rightarrow$ Photoelectric effect does not occur. What ever intensity is high.
2. If $\nu > \nu_0 \Rightarrow$ Photoelectric effect. If intensity Increases number of ejected electron Increases and K.E. remain same.
3. If ν Increases then K.E. of ejected e Increases since K.E. = $h\nu - h\nu_0$

   We know K.E. = $h\nu - h\nu_0 \equiv y = mx - C$.



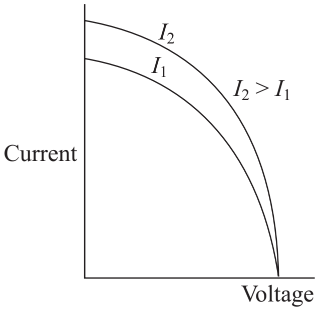
> ***Note:***
> 1. Current depends on intensity. $i \propto I$ (intensity)
> 2. K.E. depends upon frequency and K.E. $\propto$ frequency.

Stopping potential: It is the minimum required potential to stop moving electrons.

$$\text{K.E.} = \frac{1}{2}mv^2 = h\nu - W$$

$$= \text{Applied voltage} \times \text{charge } [q \times V]$$

V = stopping potential



Stopping potential is same.

QUANTUM NUMBER

The set of four integers required to define an electron completely in an atom are called *quantum number*.

1. **Principle quantum number:** It was proposed by Bohr.

   It is called orbit, shell or energy level.

   It is denoted by n. value of n is positive integer. It is denoted by KLMNOP.........

   It shows the average distance from the nucleus $r = 0.529\,\frac{n^2}{z}$ Å.

   It show the average energy of electron

   $$E = -13.6\,\frac{z^2}{n^2}\text{ eV.}$$

   Maximum number of electron in any orbit is given by $2n^2$

   It has maximum number of subshell = n

   Maximum number of orbital = n^2.
2. **Azimuthal quantum number:**

   It was proposed by Sommer Field.

   It is donated by l.

   It shows the shape of orbital.

   Value of l for any value of n 0, 1, 2, 3 ...(n – 1)

   $l = 0 \Rightarrow s$ subshell

   $l = 1 \Rightarrow p$ subshell

   $l = 2 \Rightarrow d$ subshell

   $l = 3 \Rightarrow f$ subshell

   It has maximum no. of electron In any subshell = 2(2l + 1)

Maximum no. of orbital In any subshell = $(2l + 1)$

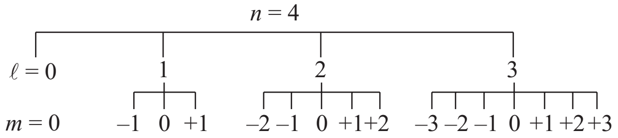
	l	**Naming**
1	0	s
2	0, 1	sp
3	0, 1, 2	spd
4	0, 1, 2, 3	spdf

l	**subshell**	**shape**
0	s	spherical
1	p	dumble
2	d	double dumble
3	f	complex

The value of Azimuthal angular momentum

$$= \frac{h}{2\pi}\sqrt{l(l+1)} = \text{orbital angular moment}$$

3. **Magnetic quantum number:**
   It shows the orientation of electron around nucleus.
   It is represented by '*m*'.
   The value of *m* for any value of *l* is $[-l...0...+l]$
   Total number of orbital in any subshell = $(2l + 1)$

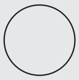
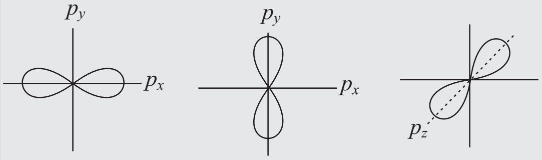
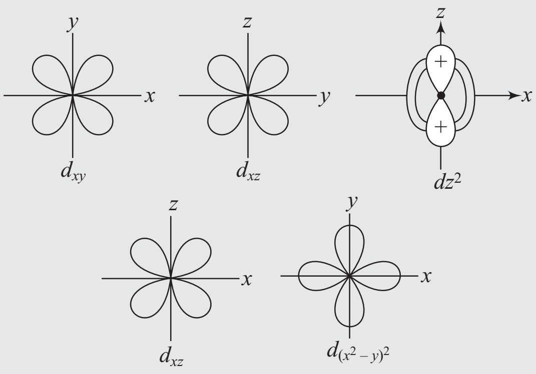


Spin quantum number:
It shows the rotation of electron on its self axis.

It has value $+\frac{1}{2}$ and $-\frac{1}{2}$ where $+ve$ sign shows a clockwise and $-ve$ sign shows anticlockwise rotation.

$$\text{Spin angular moment} = \frac{h}{2\pi}\sqrt{s(s+1)}$$

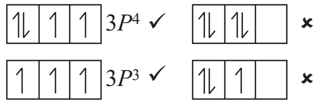
SHAPE OF ORBITAL

s-orbital	
p-orbital	
d-orbital	

ELECTRONIC RULE

Pauli rule: According to this rule, 2 electron in an atom cannot have same set for all four quantum numbers. In other words, we can say an orbital cannot have more than two electron.

Hund's rule of maximum multiplicity: Electrons are distributed among the orbital of the subshell in such a way as to give the maximum number of unpaired electron with a parallel spin. Pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital belonging to that subshell has got one electron each.



Auf bau principle: The electrons are added progresively to various subshell in the order of increasing energies starting with the subshell of the lowest energy.

Or

the order of ascending energy of subshell can be calculated from $(n + l)$.

Lower the value of $(n + l)$ for an subshell having lower energy. If two subshell have same the value of $(n + l)$ then the subshell which has low value of '*n*' will have low energy.

Orbital	***n***	***l***	***n + l***
1*s*	1	0	1
2*s*	2	0	2
2*p*	2	1	3
3*s*	3	0	3
3*p*	3	1	4
3*d*	3	2	5
4*s*	4	0	4
4*p*	4	1	5
4*d*	4	2	6
4*f*	4	3	7
5*s*	5	0	5
5*p*	5	1	6

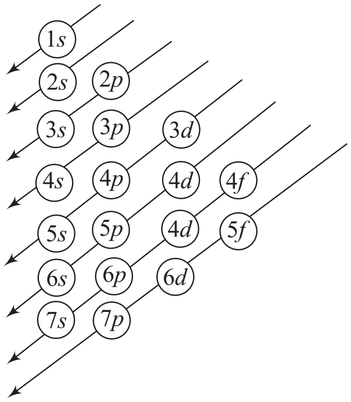
Multiplicity: $2|S| + 1$

S = total spin.

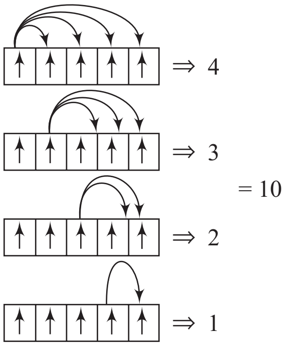
for ns^2np^3

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

$$\text{Multiplicity} = 2\left|\frac{3}{2}\right| + 1 = 4$$



Exchange energy = It is the number of possible transition of electron in the same subshell.



Node and nodal plane: It is the space where probability of finding electron is zero. The plane where probability of finding electron is zero is called nodal plane.

Schrödinger Wave Equation

This model is based on particle and wave nature of electrons known as *wave mechanical model of an atom*.

$$\frac{\partial^2 x}{\partial x^2} + \frac{\partial^2 y}{\partial y^2} + \frac{\partial^2 z}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

h = Plank constant, E = Potential electron
V = Potential energy, m = Mass of electron
ψ = Wave function

Significance of ψ: The wave function may be regarded as the amplitude of vibration expressed in terms of coordinate x, y, z. The wave function may have positive or negative values depending on the values of coordinate.

Significance of ψ^2: For electromagnetic radiation, the square of amplitude is proportional to the intensity of light. ψ^2 at any point is proportional to the probability of finding of electron.

Orbital: Region or space where probability of finding electron is maximum (90 – 95%).

Probability curve: It was found that wave function ψ can be expressed as a product of two functions.

$$\psi[r \cdot \theta\phi] = \underset{\substack{\text{radial}\\\text{function}}}{\underset{\downarrow}{R(r)}} \cdot \underset{\substack{\text{angular}\\\text{function}}}{\underset{\downarrow}{f(\theta\phi)}}$$

wave function of different Hydrogen orbital

$$\text{for } 1s = R(r) = \frac{2}{a^{3/2}}\, e^{-\sigma}$$

$$\text{for } 2s = R(r) = \frac{1}{2\sqrt{2}\, a_0^{3/2}}\, (2 - \sigma)\, e^{-\sigma/2}$$

$$\text{for } 2p = R(r) = \frac{1}{2\sqrt{6}\, a_0^{3/2}}\, \sigma e^{-\sigma/2}$$

e^{-x} = Hyperbola curve

$$\text{when } a_0 = \frac{h^2}{4\pi^2 mke^2} = 0.529\ \text{Å}$$

$$\sigma = \frac{r}{a_0}$$

R = wave function
r = distance from nucleus
R^2 = intensity of wave function
Angular node = l
Radial node = $n - l - 1$
Total node in a shell

$$(n - l - 1) + l = n - 1$$

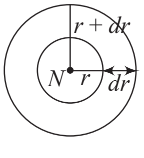
Radial Probability Density

The square of the radial wave function for an orbital gives the radial probability density of finding an electron at a point at distance 'r' per unit volume.

Radial Probability Distributed Function ($4\pi r^2 R^2$)

The radial probability density at a radial distance 'r' is R^2. Therefore, radial probability of finding the electron in a volume dv will be $R^2 dv$.

Radial probability is the probability of finding electron in a radial shell between spheres of radius 'r' and '$r + dr$' where dr is small radial distance volume (dv) of spherical shape of thickness 'dr'.



$$dv = \frac{4}{3}\pi(r+dr)^3 - \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi[(r+dr)^3 - r^3]$$

$$= \pi[(r^3 + dr^3 + \underset{\substack{\downarrow \\ \text{neglect}}}{3r^2dr} + \underset{\substack{\downarrow \\ \text{neglect}}}{3rdr^2} - r^3]$$

$$dv = \frac{4}{3}\pi[3r^2dr], \qquad dv = 4\pi r^2 dr$$

Total probability distribution = $R^2 \cdot dv = R^2(4\pi r^2 dr)$

$= (4\pi r^2)\ dr$ = radical distribution function

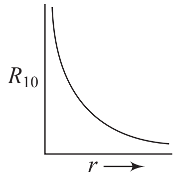
$Z_{\text{effective}} = Z - \sigma$

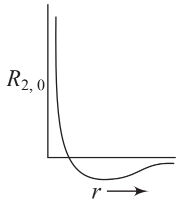
σ can be calculated by Slater Rule

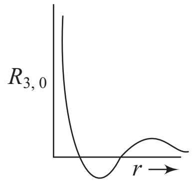
(i) σ for $1s$ or $1s^2 = 0.30$

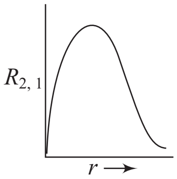
(ii) σ for ns and $ns\ np$ electron = [Valance electron – 1] × 0.35 + [$(n-1)$ Shells electron] × 0.85 + [Rest electron from $(n-1)$ shell and nucleus] × 1

(iii) σ for d/f electron = [given d/f electron – 1] × 0.35 + [Rest electron from given d/f and nucleus] × 1

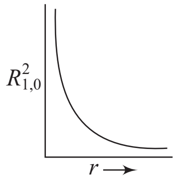


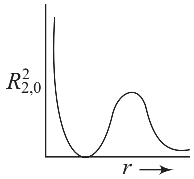


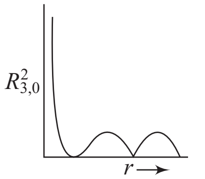


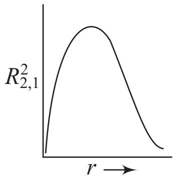


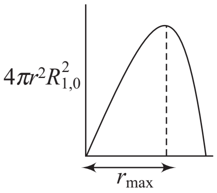
for (1s) (2s) (3s) (2p)



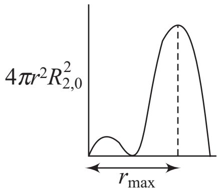




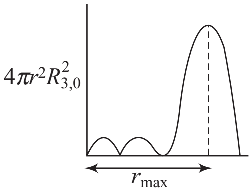




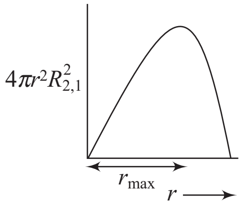
(1s)



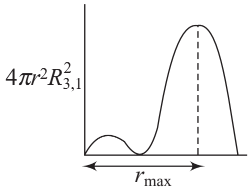
(2s)



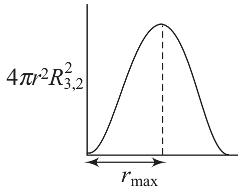
(3s)



(2p)

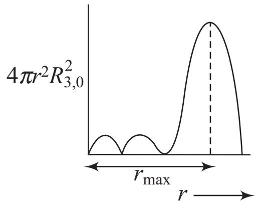


(3p)

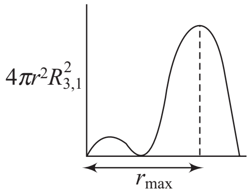


(3d)

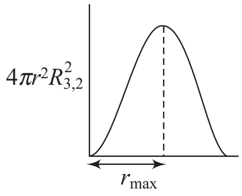
Comparision between 3s, 3p and 3d.



(3s)



(3p)



(3d)

Solved Examples

1. Find the ratio of frequencies of violet light ($\lambda = 4.10 \times 10^{-5}$ cm) to that of red light ($\lambda = 6.56 \times 10^{-5}$ cm). Also determine the ratio of energies carried by them.

Sol. We know $E = \dfrac{hc}{\lambda} = h\nu$

$$C = \nu\lambda \text{ and } E = \frac{hc}{\lambda} = h\nu$$

$$\frac{\nu_v}{\nu_R} = \frac{\lambda_R}{\lambda_v} = 1:1.6 \quad \frac{E_V}{E_R} = \frac{\nu_V}{\nu_R} = \frac{\lambda_R}{\lambda_V} = 1:1.6 = 0.625:1$$

2. A 100 W power source emits green light at a wavelength $\lambda = 5000$ A. How many photons per minute are emitted by the source?

T.E. = $P \times t = 100 \times 60$

Energy emitted by source (T.E.) = power × time

= Number of photon × Energy of one photon

$$\text{Energy of one photon} = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{5 \times 10^{3} \times 10^{-10}}$$

∴ Number of photons emitted

$$= \frac{\text{T.E.}}{\text{Energy of one photon}} = \frac{100 \times 60 \times 5 \times 10^{3} \times 10^{-10}}{6.63 \times 10^{-34} \times 3 \times 10^{8}}$$

$$= 1.5 \times 10^{22}$$

3. Find the ionisation energy of H, He^+, Li^{++}.

Sol. $E_H = -13.6\left[\dfrac{Z^2}{n^2}\right]$ ev/atom

$$E_1 = -13.6\left[\frac{1}{1}\right] = -13.6 \text{ eV}$$

$$E_\infty = 0$$

∴ $\Delta E = E_\infty - E_1 = 13.6$ eV for hydrogen atom

$$= 0 - \left[-\frac{13.6[2]^2}{1}\right] = 13.6 \times 4 \text{ eV for He}^+$$

$$= 0 - \left[\frac{13.6[3]^2}{1}\right] = 13.6 \times 9 \text{ eV for Li}^{++}$$

4. Find the wavelength of the radiation which is required for the very first transition of H atom?

Sol. $E_2 - E_1 = \dfrac{hc}{\lambda}$ very first transition means $n(2)$ to $n(1)$

$$-13.6 \times \frac{1}{2^2} - \left[-\frac{13.6 \times 1}{1^2}\right] = \frac{hc}{\lambda} = 10.2 \text{ eV} = \frac{hc}{\lambda}$$

$$\therefore \quad \lambda = \frac{10.2 \times 1.6 \times 10^{-19}}{6.63 \times 10^{-34} \times 3 \times 10^{8}} \text{ metre}$$

5. A radiation of wavelength 50 nm incident on H atom in ground state. Find the kinetic energy of ejected electron.

Sol. $\Delta E(\text{joul}) = \dfrac{hc}{\lambda} = \dfrac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{\lambda(\text{meter})}$

$$\Delta E(\text{ev}) = \frac{1242}{\lambda(\text{nm})} = \Delta E(\text{ev})$$

$$\text{T.E.} = \frac{1242}{50(\text{nm})} \text{ eV} = 24.84 \text{ eV and I.E.} = 13.6 \text{ eV}$$

K.E. = T.E. – I.E. = 24.84 – 13.6 = 11.24 eV

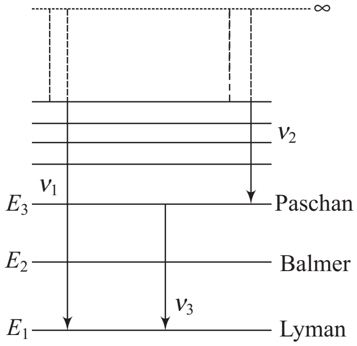
6. Find the longest wavelength of the radiation which is required to pickout the electron from the first excited state of Paschan series?

Sol. First excited state of Paschan series means $n = 4$

$$\therefore \quad E_4 = -13.6\left[\frac{1}{4^2}\right] = -0.85 = \frac{hc}{\lambda}$$

$$E_\infty = 0 \quad \therefore \Delta E = 0.85 = \frac{hc}{\lambda} \quad \therefore \lambda = \frac{1242}{0.85} \text{nm}$$

7. The frequency of series limit of Lyman series is ν_1 and series, limit of Paschan series is ν_2, and frequency of emission of electronic energy from 3 to 1 is ν_3. Find the relation between ν_1, ν_2 and ν_3.



Sol. $E_\infty - E_1 = h\nu_1$ $\qquad E_\infty - E_3 = \text{h}\nu_2$

$E_3 - E_1 = h\nu_3$

From the figure

$$h\nu_3 = h\nu_1 - h\nu_2$$

$$\nu_3 = \nu_1 - \nu_2$$

8. Find the magnitude of the current flowing in fourth Bohr orbit in hydrogen atom in one revolution.

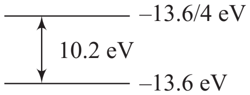
Sol. $i = \dfrac{q}{T} = \dfrac{e}{\dfrac{2\pi r}{V}} = \dfrac{eV}{2\pi r}$

We know $V = 2.18 \times 10^6\left[\dfrac{1}{n}\right]$ and $r = 0.529 \times 10^{-10}\dfrac{[n^2]}{Z}$, $n = 4$

$$\therefore \quad i = \frac{[1.6 \times 10^{-19}] \times \left[2.18 \times 10^6 \times \frac{1}{4}\right]}{0.529 \times 10^{-10}\left[\frac{1}{4^2}\right]} \text{amp.}$$

9. A particle having K.E. 5 eV collides with the atom at ground state. Predict the collision: Elastic or non-elastic?

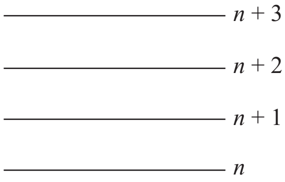
Sol. We know minimum energy required would be 10.2 eV for the transition since it is only 5 eV. So collission will be perfectly elastic.



10. A hydrogen-like species is observed to emit six radiation originating from all possible transition between a group of level. These levels have energy between –0.85 eV to –0.544 eV eV including both level. Find (a) Quantum numbers and (b) Atomic number.

Sol. $E_n = -13.6\dfrac{z^2}{n^2} = -0.85$ eV

6 radiation means $\Delta n = 3$



$$E_{(n+3)} = -13.6\frac{z^2}{(n+3)^2}$$

$$= -0.54$$

$$\frac{E_n}{E_{(n+3)}} = \frac{(n+3)^2}{(n)^2}$$

$$\therefore \quad \frac{n+3}{n} = \sqrt{\frac{85}{54}} = 1.25, \qquad n = 12$$

$$\therefore \quad E_n = -13.6\frac{Z^2}{n^2} = -0.85 \quad Z \text{ can be calculated}$$

11. Calculate the wavelength of photo electron which is ejected from ground state of hydrogen atom by absorbing 14 eV photon?

Sol. K.E. = T.E. – I.E.

here ΔE = K.E. = 14 – 13.6 = 0.4 eV

e^- eject from atom if given Total Energy (T.E.) > Ionisation Energy (I.E.)

$$\therefore \quad \lambda = \frac{6.625\times10^{-34}}{\sqrt{2[0.4\times1.6\times10^{-19}).9.1\times10^{-31}}}$$

12. Arrange in increasing order K.E. of electron, protons neutron and α particle.

Sol. When All have the same *de broglie* wavelength.

∴ for same λ (Wave length)

$$\therefore \quad \boxed{\text{KE} \propto \frac{1}{m}}$$

K.E. $\propto \dfrac{1}{m}$ for same wavelength

Since order of mass $m_e < m_p < m_n < m_\alpha$

∴ Order of Kinetic Energy $\alpha < n < P < e$

13. Show that *de broglie* wavelength of electron acceleration through V volt is nearly given by $\lambda = \left(\dfrac{150}{V}\right)^{\frac{1}{2}}$ A.

Sol. We know for $\lambda = \dfrac{h}{p}$

$$\therefore \quad \lambda = \frac{h}{\sqrt{2(\text{KE})m}} = \frac{h}{\sqrt{2(q.V)m}}$$

For charge Particle

KE = Charge × Voltage

For electron

$$\lambda = \frac{6.625\times10^{-34}}{\sqrt{2\times V\times1.6\times10^{-19}\times9.1\times10^{-31}}}$$

$$= \frac{12.27\times10^{-10}}{\sqrt{V}} \text{ meter}$$

$$= \frac{12.27}{\sqrt{V}}\text{Å} \approx \sqrt{\frac{150}{V}}\text{Å}$$

14. Calculate *de broglie* wavelength of an electron accelerated through a potential difference of

(a) 75 volt (b) 300 volt

Sol. (a) $\lambda = \sqrt{\dfrac{150}{V}}$ Å = 1.414 Å

(b) $\lambda = \sqrt{\dfrac{150}{300}}$ Å = 0.7 Å

15. Calculate the uncertainity of position of electron if it is equal to uncertainity of distance travelled by electron in 1 sec.

Sol. $\Delta x = \Delta V$ (Heisen berg)

$$\therefore \quad (\Delta x)\cdot(\Delta x) = \frac{h}{4\pi m}$$

$$\therefore \quad \Delta x = \sqrt{\frac{h}{4\pi m}}$$

16. If the velocity of electron in third orbit of He$^+$ ion is 'x', calculate the velocity of electron in second orbit of Li^{+2} ion.

Sol. We know $v = 2.18\times10^6\dfrac{Z}{n}$ m/sec

For He$^+$ $Z = 2$ and $n = 3$

$$2.18\times10^6\times\frac{2}{3} = x \qquad \ldots\text{(i)}$$

For He$^+$ $z = 2$ and $n = 3$

$$2.18\times10^6\times\frac{3}{2} = V \qquad \ldots\text{(ii)}$$

Equation (ii)/(i)

$$\therefore \quad \frac{V}{x} = \frac{3}{2}\times\frac{3}{2} = \frac{9}{4}$$

$$v = \frac{9}{4}x$$

17. Calculate K.E. and P.E. of electron in third orbit of H atom.

Sol. We know T.E. = –K.E. and P.E. = 2 × Total Energy

and $\text{T.E.} = -13.6\dfrac{z^2}{n^2} = \dfrac{-13.6\times1}{3^2} = \dfrac{-13.6}{9} = -1.51$ eV

∴ K.E. = 1.51 eV and P.E. = 2 × 1.51 = –3.02 eV

18. Suppose the potential energy between electron and proton at a particular distance r is given by $\dfrac{-Ke^2}{3r^3}$. Use Bohr's theory to obtain energy of such a hypothetical atom.

Sol. $d(U) = F \times dr$

$$F = \frac{dU}{dr} = \frac{d\left[\dfrac{-Ke^2}{3r^3}\right]}{dr} = \frac{-Ke^2}{3}\left[\frac{dr^{-3}}{dr}\right] = \frac{Ke^2}{3} \times 3r^{-4}$$

$F = \mathrm{Ke}^2 r^{-4}$ = electrostatic force of attraction

and we know $F = \dfrac{mv^2}{r}$ (from Bohr's theory)

$$\frac{Ke^2}{r^4} = \frac{mv^2}{r} \qquad \text{...(i)}$$

$$\therefore \quad \text{K.E.} = \frac{1}{2}mv^2$$

$$\boxed{\text{KE} = \frac{1}{2}\frac{Ke^2}{r^3}}$$

We know $mvr = \dfrac{nh}{2\pi} \quad \Rightarrow \quad m^2v^2r^2 = \dfrac{n^2h^2}{4\pi^2}$

$$\Rightarrow \quad m(mv^2)r^2 = \frac{n^2h^2}{4\pi^2}$$

From (1)

$$m\left[\frac{Ke^2}{r^3}\right]r^2 = \frac{n^2h^2}{4\pi^2} \therefore \frac{4\pi^2Ke^2m}{n^2h^2}$$

$$\text{T.E.} = \text{K.E.} + \text{P.E.} = \frac{1}{2}\frac{Ke^2}{r^3} + \left[\frac{Ke^2}{3r^3}\right] \boxed{\text{T.E.} = \frac{Ke^2}{6r^3}}$$

$$= \frac{Ke^2}{6\left[\dfrac{4\pi^2mKe^2}{n^2h^2}\right]^3}$$

$$\text{T.E.} = \boxed{\frac{n^6h^6}{384\pi^6K^2e^4m^3}}$$

19. Suppose P.E. between electron and proton at a separation 'r' is given by $u = K \ln r$. K is a constant. For such a hypothetical atom, calculate the radius of n^{th} Bohr orbit and energy.

Sol. $u = K \ln r$

$$F = \frac{du}{dr} = \frac{d[K \ln r]}{dr}$$

$$F = \frac{d[\ln r]}{dr} = \frac{K}{r} = F$$

(Electrostatic force of attraction) Provide centripetal force

$$\frac{mv^2}{r} = \frac{K}{r} \quad \therefore \quad v = \sqrt{\frac{K}{m}}$$

$$K = mv^2$$

We know

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi mr}$$

$$\sqrt{\frac{K}{m}} = \frac{nh}{2\pi mr}$$

$$r = \frac{nh}{2\pi m}\sqrt{\frac{m}{K}}$$

$$\boxed{r = \frac{nh}{2\pi\sqrt{Km}}}$$

T.E. = K.E. + P.E.

$$= \frac{1}{2}mv^2 + K \ln r$$

$$= \frac{1}{2}K + K \ln r$$

$$= K\left[\frac{1}{2} + \ln r\right]$$

$$\boxed{\text{T.E.} = K\left[\frac{1}{2} + \ln\frac{nh}{2\pi\sqrt{Km}}\right]}$$

20. If the ratio of K.E. of ejected photoelectron is $\dfrac{1}{K}$ when photo frequency v_1 and v_2 given. The calculate threshold frequency of metal?

We know K.E. $= h(v - v_0)$

Kinetic Energy $(\text{K.E.}_{1}) = h(v_1 - v_0) \quad v_2 - v_0 = K[v_1 - v_0]$

Kinetic Energy $(\text{K.E.}_{2}) = h(v_2 - v_0) \quad v_2 - v_0 = Kv_1 - Kv_0$

$$\frac{\text{K.E.}_1}{\text{K.E.}_2} = \frac{1}{K} = \frac{v_1 - v_0}{v_2 - v_0} \qquad v_0(K - 1) = Kv_1 - v_2$$

$$\therefore \quad \boxed{v_0 = \frac{[kv_1 - v_2]}{(k - 1)}}$$

Exercise

LEVEL I

1. The energy of hydrogen atom in its ground state is –13.6 eV. The energy of the level corresponding to $n = 5$
(a) –0.54 eV (b) –5.40 eV
(c) –0.85 eV (d) –2.72 eV

2. The spectrum of He^+ is expected to be similar to that of -
(a) Li^+ (b) He (c) H (d) Na

3. What possibly can be the ratio of the *de Broglie* wavelength for two electrons having the same initial energy and accelerated through 50 volts and 200 volts?
(a) 3 : 10 (b) 10 : 3 (c) 1 : 2 (d) 2 : 1

4. The uncertainty in the momentum of an electron is 1.0×10^{-5} kg m s^{-1}. The uncertainty of its position will be ($h = 6.626 \times 10^{-34}$ kg m^2 s^{-1})
(a) 1.05×10^{-28} m (b) 1.05×10^{-26} m
(c) 5.27×10^{-30} m (d) 5.25×10^{-28} m

5. The orbital with zero angular momentum is
(a) *s* (b) *p* (c) *d* (d) *f*

6. The electronic configuration of the Mn^{4+} ion is
(a) $3d^4 4s^0$ (b) $3d^2 4s^1$ (c) $3d^1 4s^2$ (d) $3d^3 4s^0$

7. Which of the following ions has the maximum number of unpaired *d*-electrons?
(a) Zn^{2+} (b) Fe^{2+} (c) Ni^{3+} (d) Cu^+

8. The total spin resulting from a d^7 configuration is
(a) 1 (b) 2 (c) 5/2 (d) 3/2

9. $\begin{bmatrix} \text{Given: } K & L & M & N \\ 2 & 8 & 11 & 2 \end{bmatrix}$
The number of electrons present in $l = 2$ is
(a) 3 (b) 6 (c) 5 (d) 4

10. The value *l* and m for the last electron in the Cl^- ion are
(a) 1 and 2 (b) 2 and +1
(c) 3 and –1 (d) 1 and –1

11. The maximum energy is present in any electron at
(a) Nucleus
(b) Ground state
(c) First excited state
(d) Infinite distance from the nucleus

12. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon?
(a) 3*s* (b) 2*p* (c) 2*s* (d) 1*s*

13. The third line in Balmer series corresponds to an electronic transition between which Bohr's orbits in hydrogen?
(a) 5 → 3 (b) 5 → 2 (c) 4 → 3 (d) 4 → 2

14. Correct set of four quantum numbers for valence electron of rubidium ($Z = 37$) is
(a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$
(c) $5, 1, 1, +\frac{1}{2}$ (d) $6, 0, 0, +\frac{1}{2}$

15. The orbital diagram in which the Aufbau's principle is violated is
(a) $\begin{array}{cccc} 2s & 2p_x & 2p_y & 2p_z \\ \uparrow\downarrow & \uparrow\downarrow & \uparrow & \end{array}$ (b) $\begin{array}{cccc} 2s & 2p_x & 2p_x & 2p_x \\ \uparrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \end{array}$
(c) $\begin{array}{cccc} 2s & 2p_x & 2p_x & 2p_x \\ \uparrow\downarrow & \uparrow & \uparrow & \uparrow \end{array}$ (d) $\begin{array}{cccc} 2s & 2p_x & 2p_x & 2p_z \\ \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow \end{array}$

16. The total number of neutrons in dipositive zinc ions with mass number 70 is
(a) 34 (b) 40 (c) 36 (d) 38

17. Which of the following sets of quantum numbers represents an impossible arrangement

	n	*l*	*m*	*s*
(a)	3	2	–2	$\frac{1}{2}$
(b)	4	0	0	$\frac{1}{2}$
(c)	3	2	–3	$\frac{1}{2}$
(d)	5	3	0	$\frac{1}{2}$

18. The explanation for the presence of three unpaired electrons in the nitrogen atom can be given by
(a) Pauli's exclusions principle
(b) Hund's rule
(c) Aufbau's principle
(d) Uncertainty principle

19. The electronic configuration of an element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$. This represents its
(a) Excited state
(b) Ground state or cationic form
(c) Cationic form only
(d) None of these

20. Which of the following has the maximum number of unpaired electron (atomic number of Fe 26)?
(a) Fe (b) Fe (II) (c) Fe (III) (d) Fe (IV)

21. Which quantum number is not related with Schrodinger equation?
(a) Principal (b) Azimuthal
(c) Magnetic (d) Spin

22. If λ_0 is the threshold wavelength for photoelectric emission, λ wavelength of light falling on the surface of metal, and *m* mass of electron, then *de Broglie* wavelength of emitted electron is

(a) $\left[\frac{h(\lambda\lambda_0)}{2mc(\lambda_0-\lambda)}\right]^{\frac{1}{2}}$ (b) $\left[\frac{h(\lambda_0-\lambda)}{2mc\lambda\lambda_0}\right]^{\frac{1}{2}}$

(c) $\left[\frac{h(\lambda-\lambda_0)}{2mc\lambda\lambda_0}\right]^{\frac{1}{2}}$ (d) $\left[\frac{h\lambda\lambda_0}{2mc}\right]^{\frac{1}{2}}$

23. It is known that atoms contain protons, neutrons and electrons. If the mass of neutron is assumed to half of its original value whereas that of proton is assumed to be twice of its original value then the atomic mass of ${}^{14}_{6}C$ will be

(a) Same (b) 25 % more
(c) 14.28 % more (d) 28.5 % less

24. The shortest wavelength of He^+ in Balmer series is x. Then longest wavelength in the Paschene series of Li^{+2} is

(a) $\frac{36x}{5}$ (b) $\frac{16x}{7}$ (c) $\frac{9x}{5}$ (d) $\frac{5x}{9}$

25. An electron in a hydrogen atom in its ground state absorbs energy equal to ionisation energy of Li^{+2}. The wavelength of the emitted electron is

(a) 3.32×10^{-10} m (b) 1.17 Å
(c) 2.32×10^{-9} nm (d) 3.33 pm

26. In compound $FeCl_2$, the orbital angular momentum of last electron in its cation and magnetic moment (in Bohr Magneton) of this compound are

(a) $(\sqrt{6})\hbar, \sqrt{35}$ (b) $(\sqrt{6})\hbar, \sqrt{24}$
(c) 0 (d) None of these

27. An electron, a proton and an alpha particle have kinetic energy of 16 E, 4E and E respectively. What is the qualitative order of their *de Broglie* wavelengths?

(a) $\lambda_e > \lambda_p = \lambda_\alpha$ (b) $\lambda_p = \lambda_\alpha > \lambda_e$
(c) $\lambda_p > \lambda_e > \lambda_\alpha$ (d) $\lambda_\alpha < \lambda_e >> \lambda_p$

28. Given ΔH for the process $Li\ (g) \longrightarrow Li^{+3}\ (g) + 3e^-$ is 19800 kJ/mole and IE_1 for Li is 520 then IE_2 and IE_1 of Li^+ are respectively (approx value)

(a) 11775, 7505 (b) 19280, 520
(c) 11775, 19280 (d) Data insufficient

29. The ratio of difference in wavelengths of first and second lines of Lyman series in H-like atom to difference in wavelength for second and third lines of same series is

(a) 2.5 : 1 (b) 3.5 : 1 (c) 4.5 : 1 (d) 5.5 : 1

30. Which of the following statements is INCORRECT?

(a) $\frac{e}{m}$ ratio for canal rays is maximum for hydrogen ion.

(b) $\frac{e}{m}$ ratio for cathode rays is independent of the gas taken.

(c) The nature of canal rays is dependent on the electrode material.

(d) The $\frac{e}{m}$ ratio for electron is expressed as $\frac{E^2}{2B^2V}$, when the cathode rays go undeflected under the influence of electric field (E), magnetic field (B) and V is potential difference applied across electrodes.

31. The quantum numbers of four electrons (e1 to e4) are given below.

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

The correct order of decreasing energy of these electrons is

(a) $e4 > e3 > e2 > e1$ (b) $e2 > e3 > e4 > e1$
(c) $e3 > e2 > e4 > e1$ (d) none

32. If radius of second stationary orbit (in Bohr's atom) is R. Then radius of third orbit will be

(a) $R/3$ (b) $9R$ (c) $R/9$ (d) 2.25 R

33. The wavelength associated with a gold weighing 200 g and moving at a speed of 5 m/h is of the order

(a) 10^{-10} m (b) 10^{-20} m
(c) 10^{-30} m (d) 10^{-40} m

34. If the nitrogen atom had electronic configuration $1s^7$, it would have energy lower than that of normal ground state configuration $1s^2\ 2s^2\ 2p^3$, because the electrons would be closer to the nucleus. Yet 1 s^7 is not observed because it violates

(a) Heisenberg uncertainty principle
(b) Hunds rule
(c) Pauli's exclusion principle
(d) Bohr postulate of stationary orbits

35. The total number of electrons in 'Cu' atom having magnetic quantum number (m = 0) will be

(a) 13 (b) 8 (c) 10 (d) 12

36. Find the number of electrons with the value of azimuthal quantum number 'l' = 1 for Cd^{2+}.

(a) 18 (b) 20 (c) 22 (d) 24

37. Two bulbs A and B are emitting monochromatic light of wavelength such that A can just ionise H atoms and B can just ionise He^+ ions. If the power of A and B are 30 W and 40 W respectively, calculate the ratio of number of photons emitted per second by bulb A to bulb B.

(a) 4 (b) 5 (c) 3 (d) 7

38. In a sample of hydrogen atoms, electrons jump from 10th excited state to ground state. If x is the number of different ultraviolet radiations, y is the number of different visible radiations and z is the number of different infrared radiations. The value of $z - (x + y)$ is
[Assume all the Balmer lines lie within visible region.]

(a) 17 (b) 18 (c) 19 (d) 36

39. A $4\pi r^2\ \psi^2\ (r)$ *vs* r plotted for a H-orbital curve contains '3' maxima. If orbital contains 2 angular node then orbital is

(a) 5d (b) 4d (c) 5p (d) 4p

40. In a hydrogen atom, in transition of electron, a photon of energy 2.55 eV is emitted. Then the change in wavelength of the electron is
(a) 3.32 Å (b) 6.64 Å
(c) 9.97 Å (d) None of these

41. The ratio of the wavelength of a proton and α-particle will be 1 : 2 if their
(a) velocity of proton to velocity of α particle is in the ratio 1 : 8.
(b) velocity of proton to velocity of α particle is in the ratio 8 : 1.
(c) kinetic energy of proton to kinetic energy of α particle is in the ratio 64 : 1.
(d) kinetic energy of proton to kinetic energy of α particle is in the ratio 6 : 1.

42. Choose the correct statement.
(I) d_{yz} orbital lies in the xz plane.
(II) p_z orbital lies along x-axis.
(III) Lobes of Px orbital are at 90° with z-axis
(IV) Lobes of d_{xy} orbital are at 90° with z-axis.
(a) III, IV (b) II, III
(c) I, II (d) All of these

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

	n	l	m	s
(I)	4	0	0	$+\frac{1}{2}$
(II)	3	2	0	$-\frac{1}{2}$
(III)	3	1	1	$+\frac{1}{2}$
(IV)	3	0	0	$-\frac{1}{2}$

(a) I > IV (b) II > I
(c) II > III (d) I = III
(a) a, b, c (b) b, c
(c) b, c, d (d) All of these

44. Find the product of multiplication of number of electrons corresponding to $(n + l) = 3$ and $l = 2$ in Cu (29).
(a) 80 (b) 90 (c) 70 (d) 60

45. Which of the following may represent the possible quantum numbers for the last electron of Ga?
(I) $3, 1, +1, +\frac{1}{2}$ (II) $4, 0, +1, +\frac{1}{2}$
(III) $4, 1, 0, -\frac{1}{2}$ (IV) $4, 1, +1, +\frac{1}{2}$
(a) III, IV (b) II, III
(c) III, IV (d) All of these

46. For which of the following species, Bohr's theory is not applicable?
(a) Be^{+3} (b) Li^{+2} (c) He^{+2} (d) H

47. Which of the following postulates does not belong to Bohr's model of the atom?
(a) Angular momentum is an integral multiple of $\frac{h}{2\pi}$.
(b) The electron stationed in the orbit is stable.
(c) The path of an electron is circular.
(d) The change in the energy levels of electron is continuous.

48. In which orbit of the hydrogen atom is the speed of the electron maximum?
(a) $n = 2$ (b) $n = 1$ (c) $n = 3$ (d) $n = 4$

49. For an electron, the product vn (velocity × principal quantum number) will be independent of the
(a) principal quantum number
(b) velocity of the electron
(c) energy of the electron
(d) frequency of its revolution

50. Assume that the potential energy of a hydrogen atom in its ground state is zero. Then its energy in the first excited state will be
(a) 13.6 eV (b) 27.2 eV
(c) 23.8 eV (d) 10.2 eV

51. In an atom, two electrons move around the nucleus in circular orbits of radii R and $4R$. The ratio of the time taken by them to complete one revolution is
(a) 1 : 4 (b) 4 : 1 (c) 1 : 8 (d) 8 : 7

52. The wavelength of a spectral line for an electronic transition is inversely related to
(a) the number of electrons undergoing the transition.
(b) the nuclear charge of the atom.
(c) the difference in the energy of the energy levels involved in the transition.
(d) the velocity of electron undergoing the transition.

53. When the electron of a hydrogen atom jumps from $n = 4$ to $n = 1$ state, the number of spectral lines emitted is
(a) 15 (b) 6 (c) 3 (d) 4

54. When the frequency of light incident on a metallic plate is doubled, the K.E. of the emitted photoelectron will be
(a) doubled
(b) halved
(c) increased but more than doubled of the previous K.E.
(d) Quantum number remains unchanged.

55. The electrons, identified by quantum numbers n and l, (i) $n = 4, l = 1$, (ii) $n = 4, l = 0$, (iii) $n = 3, l = 2$, and (iv) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to highest, as
(a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
(c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii)

56. The correct set of four quantum number for the outermost electrons of rubidium ($z = 37$) is
(a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$

(c) $5, 1, 1, +\frac{1}{2}$ (d) $6, 0, 0, +\frac{1}{2}$

57. The number of electrons in sulphur atom having $n + l = 3$ is

(a) 2 (b) 4 (c) 6 (d) 8

58. The orbital angular momentum of an electron in 2*s*-orbital is

(a) $h/4p$ (b) zero

(c) $h/2p$ (d) $\sqrt{2}h/2\pi$

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

(a) $x = y = z$ (b) $x < y < z$

(c) $x < z < y$ (d) $z\ y < x$

60. The radial distribution curve of the orbital with double dumbbell shape in the fourth principle shell consists of '*n*' nodes, *n* is

(a) 2 (b) 0 (c) 1 (d) 3

61. The increasing order (lowest first) for the values of e/m (charge/mass) for electron (*e*), proton (*p*), neutron (*n*) and alpha particle (α) is

(a) e, p, n, α (b) n, p, e, α

(c) n, p, α, e (d) n, α, p, e

62. The ratio of charge and mass would be greater for

(a) Proton (b) Electron

(c) Neutron (d) Alpha

63. Calcium (Ca) has atomic number 20 and mass number 40. Which of the following statements is not correct about Ca atom?

(a) The number of protons is same as the number of neutrons.

(b) The number of electrons is same as the number of neutrons.

(c) The number of protons is half of the number of neutrons.

(d) The number of nucleons is double the number of neutrons.

64. The triad of nuclei that is isotonic is

(a) ${}^{14}_{6}C, {}^{15}_{7}N, {}^{17}_{9}F$ (b) ${}^{12}_{6}C, {}^{14}_{7}N, {}^{19}_{9}F$

(c) ${}^{14}_{6}C, {}^{14}_{7}N, {}^{17}_{9}F$ (d) ${}^{14}_{6}C, {}^{14}_{7}N, {}^{19}_{9}F$

65. Rutherford's experiment on scattering of particles showed for the first time that the atom has

(a) electrons (b) protons

(c) nucleus (d) neutrons

66. The value of Bohr radius of hydrogen atom is

(a) 0.529×10^{-8} cm (b) 0.529×10^{-10} cm

(c) 0.529×10^{-12}cm (d) 0.529×10^{-6} cm

67. Ratio of radii of second and first Bohr orbits of H-atom is

(a) 2 (b) 4 (c) 3 (d) 5

68. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom

(a) He^+ ($n = 2$) (b) Li^{+2} ($n = 2$)

(c) Li^{2+} ($n = 3$) (d) Be^{3+} ($n = 2$)

69. Of the following transitions in hydrogen atom, the one which gives an absorption line of maximum wavelength is

(a) $n = 1$ to $n = 2$ (b) $n = 3$ to $n = 8$

(c) $n = 2$ to $n = 1$ (d) $n = 8$ to $n = 3$

70. Electromagnetic radiation with maximum wavelength is

(a) ultraviolet (b) radiowave

(c) X-ray (d) infrared

71. The wave number of the first line in the Balmer series of hydrogen atom is 15200 cm^{-1}. What is the wave number of the first line in the Balmer series of Be^{3+}?

(a) 2.432×10^5 cm^{-1} (b) 15200 cm^{-1}

(c) 415200 cm^{-1} (d) 215200 cm^{-1}

72. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of which order

(a) 10^{-10} m (b) 10^{-20} m

(c) 10^{-30} m (d) 10^{-40} m

73. If the following matter waves travel with equal velocity, the longest wavelength is that of

(a) electron (b) proton

(c) neutron (d) alpha particle

74. If the velocity of hydrogen molecule is 5×10^4 cm sec^{-1}, then its *de Broglie* wavelength is

(a) 2 Å (b) 4 Å (c) 8 Å (d) 100 Å

75. Correct set of four quantum numbers for the valence (outermost) electron of Ca

(a) 4, 0, 0, + 1/2 (b) 5, 1, 0, + 1/2

(c) 4, 1, 1, + 1/2 (d) 6, 0, 0, + 1/2

76. The quantum numbers of most energetic electron in Ar atom when it is in first excited state is

(a) 2, 1, 0, 1/2 (b) 4, 1, 1, ½

(c) 4, 0, 0, 1/2 (d) 4, 1, 0, 1/2

77. The outermost electronic configuration of the most electronegative element is

(a) ns^2np^3 (b) ns^2np^4 (c) ns^2np^5 (d) ns^2np^6

78. Which of the following orbitals is associated with the angular nodes?

(a) *s*-orbials (b) *p*-orbitals

(c) *d*-orbitals (d) *f*-orbitals

79. The energy of the second Bohr orbit in the hydrogen atom is –3.41 eV. The energy of the second Bohr orbit of He^+ ion would be

(a) –0.85 eV (b) –13.64 eV

(c) –1.70 eV (d) –6.82 eV

80. The ratio of energy of the electron in ground state of hydrogen to the electron in first excited state of Be^{+3} is

(a) 4 : 1 (b) 1 : 4 (c) 1 : 8 (d) 8 : 1

81. The ratio of the difference in energy of electron between the first and second Bohr's orbit to that between second and third Bohr's orbit is

(a) $\frac{1}{3}$ (b) $\frac{27}{5}$ (c) $\frac{9}{4}$ (d) $\frac{4}{9}$

82. The first emission line in the atomic spectrum of hydrogen in the Balmer series appears at

(a) $\frac{9R_H}{400}\text{cm}^{-1}$ (b) $\frac{7R_H}{144}\text{cm}^{-1}$
(c) $\frac{3R_H}{4}\text{cm}^{-1}$ (d) $\frac{5R_H}{36}\text{cm}^{-1}$

83. What element has a H-like spectrum and whose lines have wavelengths four times shorter than those of atomic hydrogen?
(a) He (b) He^+ (c) H (d) Li^{+2}

84. The second line of Lyman series of H coincides with the sixth line of Paschen series of an ionic species X. Find X assuming R to be same for both H and X?
(a) He^+ (b) Li^{+2} (c) Li^+ (d) H

85. The work function for a metal is 4 eV. To emit a photo electron of zero velocity from the surface of the metal, the wavelength of incident light will be
(a) 2700 Å (b) 1700 Å
(c) 5900 Å (d) 3100 Å

86. If λ_1 and λ_2 denote the *de Broglie* wavelength of two particles with same masses but charges in the ratio of 1 : 2 after they are accelerated from rest through the same potential difference, then
(a) $\lambda_1 = \lambda_2$ (b) $\lambda_1 < \lambda_2$
(c) $\lambda_1 > \lambda_2$ (d) None of these

87. The velocity of electron of H-atom in its ground state is 2.2×10^6 m/s. The *de Broglie* wavelength of this electron will be
(a) 0.33 nm (b) 23.3 nm
(c) 45.6 nm (d) 100 nm

88. The wavelength associated with a golf ball weighing 0.200 g and moving at a speed of 5 m/h is of the order
(a) 10^{-10} m (b) 10^{-27} m
(c) 10^{-30} m (d) 10^{-40} m

89. An electron in a H-like atom is in an excited state. It has a total energy of –3.4 eV. Calculate the *de Broglie's* wavelength?
(a) 66.5 Å (b) 6.66 Å
(c) 60.6 Å (d) 6.06 Å

90. Non-directional orbital is
(a) 3*s* (b) 4*f* (c) 4*d* (d) 4*p*

91. The ionisation energy of a hydrogen atom in terms of Rydberg constant (R_H) is given by the expression
(a) R_Hhc (b) R_Hc
(c) $2R_Hhc$ (d) R_HhcN_A

92. The ratio of the energies of photons of 2000 Å to that of 4000 Å is
(a) 2 (b) 4 (c) $\frac{1}{2}$ (d) $\frac{1}{4}$

93. For a '*d*' electron, the orbital angular momentum is
(a) $\sqrt{6}\hbar$ (b) $\sqrt{2}\hbar$ (c) $\hbar$ (d) $2\hbar$

94. The energy of an electron in the first Bohr orbit of H-atom is –13.6 eV. The possible energy value of the excited state in the Bohr orbit of H-atom is
(a) –4.2 eV (b) –3.4 eV
(c) –6.8 eV (d) +6.8 eV

95. If uncertainty in position of an electron was zero, the uncertainty in its momentum will be
(a) zero (b) $\frac{h}{2\pi}$ (c) $\frac{h}{4\pi}$ (d) Infinity

96. Which of the following represents the correct set of the four quantum numbers of 4*d*-electrons?
(a) $4, 3, 2, +\frac{1}{2}$ (b) 4, 2, 1, 0
(c) $4, 3, -2, \frac{1}{2}$ (d) $4, 2, 1, -\frac{1}{2}$

97. The first emission line in the atomic spectrum of hydrogen in the Balmer Series appears at
(a) $\frac{9R_H}{400}\text{cm}^{-1}$ (b) $\frac{7R_H}{144}\text{cm}^{-1}$
(c) $\frac{3R_H}{4}\text{cm}^{-1}$ (d) $\frac{5R_H}{36}\text{cm}^{-1}$

98. The fourth line of the Balmer series corresponds to electron transition between which energy levels
(a) 6 and 2 (b) 5 and 2
(c) 4 and 1 (d) 5 and 1

99. The ionisation potential of hydrogen atom is 13.6 eV. The ionisation potential of Be^{3+} ion is
(a) 217.6 eV (b) 109.8 eV
(c) 54.4 eV (d) 136.0 eV

100. If 10^{-17} J of light energy is needed by the interior of human eye to see an object, the photons of green light ($\lambda = 550$ nm) needed to see the object are
(a) 27 (b) 28 (c) 29 (d) 30

101. The energy of a photon having wavelength 700 nm is
(a) 1.77 eV (b) 2.47 eV
(c) 700 eV (d) 3.57 eV

102. A 1-kW radio transmitter operates at a frequency of 880 Hz. How many photons per second does it emit?
(a) 1.71×10^{21} (b) 1.71×10^{30}
(c) 6.02×10^{23} (d) 2.85×10^{26}

103. The ratio of the *e*/*m* values of a proton and an *a*-particle is
(a) 2 : 1 (b) 1 : 1 (c) 1 : 2 (d) 1 : 4

104. Which particle among the following will have the smallest *de Broglie* wavelength, assuming that they have the same velocity?
(a) A positron (b) A photon
(c) An *a*-particle (d) A neutron

105. The energy needed to excite a hydrogen atom from its ground state to its third excited state is
(a) 12.1 eV (b) 10.2 eV
(c) 0.85 eV (d) 12.75 eV

106. The wavelength of the third line of the Balmer series for a hydrogen atom is
(a) $\frac{21}{100R_\infty}$ (b) $\frac{100}{21R_\infty}$
(c) $\frac{21R_\infty}{100}$ (d) $\frac{100R_\infty}{21}$

107. When the value of the azimuthal quantum number is 3, the maximum and the minimum values of the spin multiplicities are

(a) 4, 3 (b) 8, 1 (c) 1, 3 (d) 8, 2

108. The energy of an electron in the first Bohr orbit of H-atom is –13.6 eV. The possible energy value of the 3rd excited state for electron in Bohr orbit of hydrogen is

(a) –3.4 eV (b) – 0.85 eV
(c) – 6.8 eV (d) + 6.8 eV

109. For the hydrogen atom, the energy of the electron is defined by the factor $E_n = -13.58/n^2$ eV. Here n is positive integer. The minimum quantity of energy which it can absorb in its primitive stage is

(a) 1.00 eV (b) 3.39 eV
(c) 6.79 eV (d) 10.19 eV

110. The radius of Bohr's first orbit in hydrogen atom is 0.053 nm. The radius of second orbit in He^+ can be

(a) 0.0265 nm (b) 0.0530 nm
(c) 0.106 nm (d) 0.2120 nm

111. The ratio of the radii of the first three Bohr orbits is

(a) 1 : 0.5 : 0.33 (b) 1 : 2 : 3
(c) 1 : 4 : 9 (d) 1 : 8 : 27

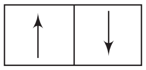
112. An electron has wavelength 1 Å. The potential by which the electron is accelerated will be

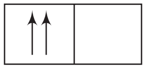
(a) 0.0926 V (b) 0.0502 V
(c) 0.0826 V (d) 150 V

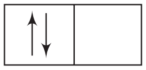
113. Atomic number of chromium is 24, then Cr^{3+} will be

(a) diamagnetic (b) paramagnetic
(c) ferromagnetic (d) None of these

114. Which of the following arrangement of two electrons in two degenerated orbitals is not possible at all?

(a) 

(b) 

(c) 

(d) All

115. A compound of vanadium possesses a magnetic moment of 1.73 BM. The oxidation state of vanadium in this compounds is

(a) 1 (b) 2
(c) 4 (d) Cannot be predicted

116. Uncertainty in position and momentum are equal. Uncertainty in velocity is

(a) $\sqrt{h/\pi}$ (b) $\sqrt{h/2\pi}$
(c) $1/2m\sqrt{h/\pi}$ (d) None of these

117. The second line of Lyman series of H coincides with the sixth line of Paschen series of an ionic species X. Find X assuming Rydberg constant to be same for both H and X?

(a) Li^{+2}-ion (b) Li^{+}-ion
(c) He^{+}-ion (d) None of these

118. Two particles A and B are in motion. If the wavelengths associated with particle A is 5×10^{-8} m, calculate the wavelength of particle B if momentum of B is half of A.

(a) 10^{-8} m (b) 10^{-7} m (c) 10^{-5} m (d) 10^{-3}m

119. The energy for an electron is an orbit of hydrogen atom is given by, $E_n = -\dfrac{13.6}{n^2} Z^2 \text{ eV}$. Calculate the energy of the orbit having a radius $9r_1$ where r_1 is the radius of the first orbit?

(a) –1.51 eV (b) 10.2 eV
(c) 13.6 eV (d) 1.36 eV

120. An electron in a Bohr orbit of hydrogen atom with the quantum number n_2 has an angular momentum 4.2176 $\times 10^{-34}$ kg m^2 s^{-1}. If electron drops from this level to the next lower level, find the wavelength of this line.

(a) 18.75×10^{-7} m (b) 1.87×10^{-7} m
(c) 187.5×10^{-7} m (d) 0.187×10^{-7} m

121. The maximum wavelength of light that can excite an electron from first to third orbit of hydrogen atom is

(a) 487 nm (b) 170 nm
(c) 103 nm (d) 17 nm

122. The work function for a metal is 4 eV. To emit a photo electron of zero velocity from the surface of the metal, the wavelength of incident light should be (nearly)

(a) 2700 Å (b) 1700 Å
(c) 5900 Å (d) 3100 Å

123. The total energy of the electron in the hydrogen atom in the ground state is –13.6 eV. The K.E. of this electron is

(a) 13.6 eV (b) Zero
(c) –13.6 eV (d) 6.8 eV

124. Which of the following sets of quantum numbers represents the highest energy of an atom?

(a) $n = 4, l = 0, m = 0, s = +\dfrac{1}{2}$

(b) $n = 3, l = 0, m = 0, s = +\dfrac{1}{2}$

(c) $n = 3, l = 1, m = 1, s = +\dfrac{1}{2}$

(d) $n = 3, l = 2, m = 1, s = +\dfrac{1}{2}$

125. Which option gives the values of the quantum numbers for the 21st electron of scandium ($Z = 21$)?

(a) $3, 1, 1, +\dfrac{1}{2}$ (b) $3, 2, 2, +\dfrac{1}{2}$

(c) $3, 2, -3, -\dfrac{1}{2}$ (d) $3, 1, 2, -\dfrac{1}{2}$

126. The number of unpaired electrons in Mn^{4+} ($Z = 25$) is

(a) four (b) two (c) five (d) three

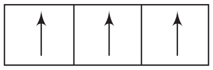
127. The value of the magnetic moment of a particular ion is 2.83 Bohr magneton. The ion is

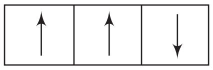
(a) Fe^{2+} (b) Ni^{2+} (c) Mn^{2+} (d) Co^{3+}

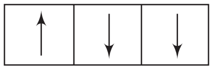
128. The number of spherical nodes in 3p orbitals is

(a) one (b) three (c) two (d) zero

129. Which of the following electronic configurations have zero spin multiplicity?

(a) 

(b) 

(c) 

(d) none of these

130. The fraction of volume occupied by the nucleus with respect to the total volume of an atom is

(a) 10^{-15} (b) 10^{-5} (c) 10^{-30} (d) 10^{-10}

131. Which of the following is iso-electronic with neon-

(a) O^{2-} (b) F^+ (c) Mg (d) Na

132. The MRI (magnetic resonance imaging) body scanners used in hospitals operate with 400 MHz radio frequency energy. The wavelength corresponding to this radio frequency is

(a) 0.75 m (b) 0.75 cm (c) 1.5 m (d) 2 cm

133. Radius of Nucleus of atom having Atomic mass = 64 will be

(a) 5 fm (b) 9 fm

(c) 10 fm (d) 85 fm

134. What is likely to be principal quantum number for a circular orbit of diameter 20 nm of the hydrogen atom if we assume Bohr orbit be the same as that represented by the principal quantum number?

(a) 10 (b) 14 (c) 12 (d) 16

135. Choose the correct relationship.

(a) E_1 of H = 1/2 E_2 of He^+ = 1/3 E_3 of Li^{2+} = 1/4 E_4 of Be^{3+}

(b) $E_1(H) = E_2(He^+) = E_3(Li^{2+}) = E_4(Be^{3+})$

(c) $E_1(H) = 2E_2(He^+) = 3E_3(Li^{2+}) = 4E_4(Be^{3+})$

(d) No relation

136. If the value of $E = -78.4$ kcal/mole, the order of the orbit in hydrogen atom is

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

137. If velocity of an electron in first orbit of H atom is V, what will be the velocity of 3rd orbit of Li^{+2}?

(a) V (b) $V/3$ (c) 3 V (d) 9 V

138. In a certain electronic transition in the hydrogen atoms from an initial state (A) to a final state (B), the difference in the orbit radius $|r_1 - r_2|$ is 624 times the first Bohr radius. Identify the transition.

(a) $5 \rightarrow 1$ (b) $25 \rightarrow 1$ (c) $8 \rightarrow 3$ (d) $7 \rightarrow 5$

139. Match the following:

(a)	Energy of ground state of He^+	(i)	–6.04 eV
(b)	Potential energy of I orbit of H-atom	(ii)	–27.2 eV
(c)	Kinetic energy of II excited state of He^+	(iii)	8.7×10^{-18} J
(d)	Ionisation potential of He^+	(iv)	–54.4 eV

(a) A – (i), B – (ii), C – (iii), D – (iv)

(b) A – (iv), B – (iii), C – (ii), D – (i)

(c) A – (iv), B – (ii), C – (i), D – (iii)

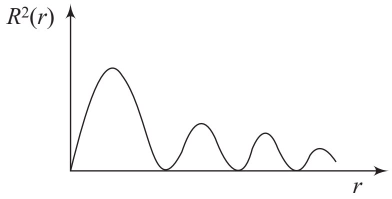
(d) A – (ii), B – (iii), C – (i), D – (iv)

140. From the following observations, predict the type of orbital.

Observation 1: $x\,y$ plane acts as nodal plane.

Observation 2: The angular function of the orbital intersect the three axis at origin only.

Observation 3: $R^2(r)$v/s r curve obtained for the orbital is



(a) $5p_z$ (b) $6d_{xy}$ (c) $6d_{x^2-y^2}$ (d) $6\,d_{yz}$

141. Consider the following nuclear reactions involving X and Y:

$$X \longrightarrow Y + {}^4_2\text{He}$$

$$Y \longrightarrow {}_8\text{O}^{18} + {}_1\text{H}^1$$

If both neutrons as well as protons in both sides are conserved in nuclear reaction then identify period number of X and moles of neutrons in 4.6 g of X.

(a) 3, 2.4 N_A (b) 3, 2.4

(c) 2, 4.6 (d) 3, 0.2 N_A

142. Electromagnetic radiations having $\lambda = 310$ Å are subjected to a metal sheet having work function = 12.8 eV. What will be the velocity of photoelectrons with maximum kinetic energy.

(a) 0, no emission will occur

(b) 2.18×10^6 m/s

(c) $2.18\sqrt{2} \times 10^6$ m/s

(d) 8.72×10^6 m/s

143. If in Bohr's model, for unielectronic atom, time period of revolution is represented as $T_{n,\,z}$ where n represents shell number and z represents atomic number then the value of $T_{1,\,2} : T_{2,\,1}$ will be

(a) 8 : 1 (b) 1 : 8

(c) 1 : 1 (d) None of these

144. Which of the following orbital is non-directional?

(a) s (b) p

(c) d (d) All of these

145. Uncertainty in position is twice the uncertainty in momentum Uncertainty in velocity is

(a) $\sqrt{\frac{h}{\pi}}$ (b) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$

(c) $\frac{1}{2m}\sqrt{\hbar}$ (d) $\frac{h}{4\pi}$

146. For which orbital angular probability distribution is maximum at an angle of 45° to the axial direction?

(a) $d_{x^2-y^2}$ (b) d_{z^2}

(c) d_{xy} (d) P_x

147. Which orbit will be the first to have 'g' subshell?

(a) 3rd (b) 4th (c) 5th (d) 6th

148. Frequency of revolution of e^- in shell

(a) $\dfrac{2\pi r}{V}$ (b) $\dfrac{\frac{4}{3}\pi r^3}{V}$

(c) $\dfrac{V}{2\pi r}$ (d) $\dfrac{qV}{2\pi r}$

149. The decreasing order of energy of the $3d$, $4s$, $3p$, $3s$ orbitals is

(a) $3d > 3s > 4s > 3p$ (b) $3s > 4s > 3p > 3d$

(c) $3d > 4s > 3p > 3s$ (d) $4s > 3d > 3s > 3p$

150. If n and l are respectively the principle and azimuthal quantum numbers, then the expression for calculating the total number of electrons in any orbit is

(a) $\displaystyle\sum_{l=1}^{l=n} 2(2l+1)$ (b) $\displaystyle\sum_{l=1}^{l=n-1} 2(2l+1)$

(c) $\displaystyle\sum_{l=0}^{l=n+1} 2(2l+1)$ (d) $\displaystyle\sum_{l=0}^{l=n-1} 2(2l+1)$

LEVEL II

1. Select the correct statement for Ne.

(a) It is not isoelectronic with H_2O.

(b) Last electron enters in *s*-orbital.

(c) The value of '*m*' must be zero for last electron.

(d) The value of '*l*' must be '1' for last electron.

2. Give the correct order of initials True (T) or False (F) for the following statements:

(I) Number of electrons having '$l = 0$' is 10 in *Pd*.

(II) The value of Z_{eff} for $3d$ electron of Cr and $3d$ electron of Mn is same as the number of electron in '*d*' subshell of Cr and Mn are same.

(III) Multiplicity of Fe is equal to Ni^{+2}.

(IV) Value of $\left(\dfrac{l}{n}\right)$ for last electron of element having atomic number 57 is 0.4.

(a) T T T T (b) F T T T

(c) T F T F (d) F F F T

3. 'A^{+2}' is isoelectronic with 'CO_2' and has (Z+2) neutron (Z is atomic number of A), then select the correct option(s).

(I) Mass number of A^{+2} is 50.

(II) Last electron enters in '*s*' orbital in element '*A*'.

(III) Number of unpaired electron in '*A*' is 4.

(IV) During formation of A^{+2}, electron(s) are removed from '*s*' as well as '*d*' subshell.

(a) I, IV (b) II, III (c) III, IV (d) All

4. Calculate '*Q*' for last electron of Ga where $Q = n + l +$ maximum possible value of '*m*'.

(a) 6 (b) 8 (c) 7 (d) 5

5. Which of the following is / are true?

(I) Multiplicity in Fe^{3+} is greater than that in Co^{3+}.

(II) Ti^{3+}, Cr^{+}, Sc^{2+} ions are diamagnetic.

(III) Value of $(n + l + m)$ for last electron of Mg is 3.

(IV) The value of Z_{eff} for $3s$ electron of Cl is 10.9.

(a) I, IV (b) I, III

(c) III, IV (d) All of these

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

(I) It is isotonic with Mg^{24}.

(II) The ratio of n to l for last electron in atom of above element is 2.

(III) Atom of the above element is isoelectronic with H_2O.

(IV) Atom of the above element is paramagnetic.

(a) I, IV (b) II, III (c) III, IV (d) All

7. If the Aufbau principle is not followed and subshells of a shell are progressively filled according to their energy, which of the following elements is paramagnetic?

(a) Mg (b) Ca (c) Ni (d) Zn

8. Find the total number of species having magnetic moment value of 2.84 B.M. from following species:

Fe^{+2}, Cr, Cr^{3+}, Ti^{2+}, Mn^{2+}, V^{3+}

(a) 2 (b) 3 (c) 4 (d) 5

9. Select the correct statement(s).

(I) Maximum number of electrons having $s = +\dfrac{1}{2}$ in sulphur is 9.

(II) If electron has zero magnetic quantum number then it must be present in *s*-orbital.

(III) All isoelectronic ions have same value of Z_{eff}.

(IV) Number of subshell present in a n^{th} shell is equal to '*n*'.

(a) I, IV (b) II, III

(c) III, IV (d) All of these

10. Total number of electrons having $l = 2$ in Fe^{+2} according to Aufbau principle ($n + l$ rule) is

(a) 5 (b) 4 (c) 3 (d) 6

11. Similar to quantum number n, l, m a set of new quantum numbers was introduced with similar logic but different values defined as

$x = 1, 2, 3...$ all (+*ve*) integral values

$y = (x - 1)(x - 2)(x - 3)...$ No (–*ve*) value

$z = +(y + 1/2)$ to $-(y + 1/2)$ in integral steps

For each value of (z), there will be two electrons, if $(x + y)$ rule is followed similar to $(n + l)$ rule then number of electron in third shell for Zn (Atomic number = 30) is

(a) 12 (b) 13 (c) 14 (d) 15

12. Select the incorrect statement(s) (According to Bohr model).

(a) Total energy = $\dfrac{-2\pi^2K^2Z^2e^4m}{n^2h^2}$

(b) Radius of orbit = $\dfrac{n^2h^2}{4\pi^2KZe^2m}$

(c) Velocity of electron in an orbit = $\dfrac{2\pi KZe^2}{nh}$

(d) Frequency of revolution of an electron in an orbit $= \dfrac{n^3h^3}{4\pi K^2Z^2e^4m}$

13. The electrons in a sample of gaseous Li^{2+} ions which are initially present in a particular excited state makes a transition to a lower level. The emitted photons are absorbed by a sample of H-atoms which are present in their ground state. This sample of H-atoms on de-excitation gives maximum 6 different types of spectral lines. Find the quantum number of initial excited state of Li^{2+} ions.

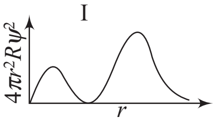
(a) 11 (b) 12 (c) 13 (d) 14

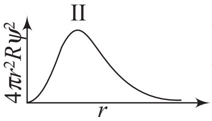
14. The radial wave function for 1s electron in H-atom is $R = \dfrac{2}{a_0^{3/2}}e^{-r/a_0}$ where a_0 = radius of first orbit of H-atom. The ratio of probability of 1*s* electron in hydrogen atom at distance a_0 from nucleus to that at distance $\dfrac{a_0}{2}$ from nucleus is

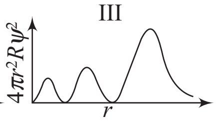
(a) equal (b) $\dfrac{1}{e}$ times

(c) $\dfrac{4}{e}$ times (d) $\dfrac{e}{4}$ times

15. Which of the following has correct the matching of curve and orbital?







(I) I (2*p*) II (1*s*) III (4*p*)
(II) I (3*p*) II (3*d*) III (3*s*)
(III) I (4*d*) II (2*p*) III (5*d*)
(IV) I (2*s*) II (4*f*) III (3*d*)

(a) II, III (b) I, III (c) III, IV (d) All

16. If the position of an electron can be determined within ±0.0001 Å precision when momentum of electron is $\dfrac{h}{2\pi a_0}$, where a_0 is 0.529 Å, find the ratio of minimum uncertainty in momentum to given momentum. [$h = 6.626 \times 10^{-34}$]

(a) 2423 (b) 2645 (c) 2768 (d) 2357

17. An unknown particle having double charge as proton moves with wavelength λ. It is accelerated from the rest through a potential difference of $\dfrac{V}{8}$ volts, while proton itself moves with same wavelength λ when accelerated from rest through a potential difference 'V' volts. The particle is

(a) He^+ (b) Li^{2+} ion (c) He^{2+} (d) Be^{2+}

18. When photons of wavelength $\lambda = 253.7$ nm is subjected on Cu plate (work function = 4.65 eV) then photoelectrons are emitted. The magnitude of potential required to stop photocurrent completely is 0.24 V. The kinetic energy of ejected electron is

(I) 0.24 eV (II) 0.20 eV
(III) 0.10 eV (IV) 2.4 eV

(a) I, II, III (b) II, III, IV
(c) I, III, IV (d) All of these

19. The distance of spherical nodes from nucleus for the given orbital are

$$\Psi_{\text{radial}} = \frac{1}{9\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}[(\sigma^2 - 4\sigma + 3)] \quad \exp(-\sigma/2)$$

where a_0 and Z are the constants and $\sigma = \dfrac{2Zr}{a_0}$.

(a) Zero, infinity (b) $\dfrac{a_0}{Z}, \dfrac{1}{2}\dfrac{a_0}{Z}$

(c) $\dfrac{3}{2}\dfrac{a_0}{Z}, \dfrac{1}{2}\dfrac{a_0}{Z}$ (d) $\dfrac{a_0}{Z}, \dfrac{3}{2}\dfrac{a_0}{Z}$

20. The difference in angular momentum associated with the electron in two successive orbits of hydrogen atoms is

(a) $\dfrac{h}{\pi}$ (b) $\dfrac{h}{2\pi}$ (c) $\dfrac{h}{2}$ (d) $\dfrac{(n-1)h}{2\pi}$

21. The shortest λ for the Lyman series of hydrogen atom is … (Given: $R_H = 109678$ cm^{-1})

(a) 911.7 Å (b) 700 Å
(c) 600 Å (d) 811 Å

22. The velocity of an electron in the first Bohr orbit of a hydrogen atom is 2.19×10^6 ms^{-1}. Its velocity in the second orbit would be

(a) 1.10×10^6 ms^{-1} (b) 4.38×10^6 ms^{-1}
(c) 5.5×10^5 ms^{-1} (d) 8.76×10^6 ms^{-1}

23. The atomic spectrum of Li^{+2} – ion arises due to the transition of an electron from n_2 to n_1. If $n_1 + n_2 = 4$ and $(n_2 - n_1) = 2$, find the wavelength of the third line of this series in Li^{+2}-ion.

(a) 1.08 nm (b) 10.8 nm
(c) 108 nm (d) 1080 nm

24. If the wavelength is equal to the distance travelled by the electron in one second, then

(a) $\lambda = \dfrac{h}{p}$ (b) $\lambda = \dfrac{h}{p}$

(c) $\lambda = \sqrt{\dfrac{h}{p}}$ (d) $\lambda = \sqrt{\dfrac{h}{m}}$

25. According to the Schrodinger model, nature of electron in an atom is

(a) Particles only
(b) Wave only
(c) Both simultaneously
(d) Sometimes waves and sometimes particle

26. Which of the following describes orbital?

(a) ψ (b) ψ^2
(c) $|\psi^2|\psi$ (d) All of these

27. In order to have the same wavelength for the electron (mass m_e) and the neutron (mass m_n), their velocities should be in the ratio (electron velocity/neutron velocity)

(a) m_n/m_e (b) $m_n \times m_e$ (c) m_e/m_n (d) one

28. Which of the following is true about ψ

(a) ψ represents the probability of finding an electron around the nucleus.

(b) ψ represent the amplitude of the electron wave.

(c) Both A and B

(d) None of these

29. Consider an electron in the n^{th} orbit of a hydrogen atom in the Bohr model. The circumference of the orbit can be expressed in terms of the *de Broglie* wavelength λ of the electron as

(a) $(0.529)\, n\lambda$ (b) $\sqrt{n}\lambda$

(c) $(13.6)\, \lambda$ (d) $n\lambda$

30. A particle X moving with a certain velocity has a de Broglie wavelength of 1A°. If particle Y has a mass of 25% that of X and velocity 75% that of X, de Broglie's wavelength of Y will be

(a) 3 A° (b) 5.33 A° (c) 6.88 A° (d) 48 A°

31. What are the values of the orbital angular momentum of an electron in the orbitals 1*s*, 3*s*, 3*d* and 2*p*?

(a) 0, 0, $\sqrt{6}\hbar, \sqrt{2}\hbar$ (b) 1, 1, $\sqrt{4}\hbar, \sqrt{2}\hbar$

(c) 0, 1, $\sqrt{6}\hbar, \sqrt{3}\hbar$ (d) 0, 0, $\sqrt{20}\hbar, \sqrt{6}$

32. If m = magnetic quantum number and l = azimuthal quantum number, then

(a) $m = l + 2$ (b) $m = 2l^2 + 1$

(c) $l = \dfrac{m-1}{2}$ (d) $l = 2m + 1$

33. The number of unpaired electrons in Mn^{4+} ($Z = 25$) is

(a) Four (b) Two (c) Five (d) Three

34. After *np* orbitals are filled, the next orbital filled will be

(a) $(n + 1)\, s$ (b) $(n + 2)\, p$

(c) $(n + 1)\, d$ (d) $(n + 2)\, s$

35. The value of the magnetic moment of a particular ion is 2.83 Bohr magneton. The ion is

(a) Fe^{2+} (b) Ti (c) Mn^{2+} (d) Co^{3+}

36. In Bohr's model of the hydrogen atom, the ratio between the period of revolution of an electron in the orbit of $n = 1$ to the period of the revolution of the electron in the orbit $n = 2$ is

(a) 1 : 2 (b) 2 : 1 (c) 1 : 4 (d) 1 : 8

37. Let υ_1 be the frequency of the series limit of the Lyman series, υ_2 be the frequency of the first line of the Lyman series, and υ_3 be the frequency of the series limit of the Balmer series.

(a) $\upsilon_1 - \upsilon_2 = \upsilon_3$ (b) $\upsilon_2 - \upsilon_1 = \upsilon_3$

(c) $\upsilon_3 = 1/2\, (\upsilon_1 - \upsilon_3)$ (d) $\upsilon_1 + \upsilon_2 = \upsilon_3$

38. The energies of energy levels A, B and C for a given atom are in the sequence $E_A < E_B < E_C$. If the radiations of wavelengths λ_1, λ_2 and λ_3 are emitted due to the atomic transitions C to B, B to A and C to A respectively then which of the following relations is correct?

(a) $\lambda_1 + \lambda_2 + \lambda_3 = 0$ (b) $\lambda_3 = \lambda_1 + \lambda_{22}$

(c) $\lambda_3 = \lambda_1 + \lambda_2$ (d) $\lambda_3 = \dfrac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$

39. The wavelengths of photons emitted by electron transition between two similar levels in H and He^+ are λ_1 and λ_2 respectively. Then

(a) $\lambda_2 = \lambda_1$ (b) $\lambda_2 = 2\lambda_1$

(c) $\lambda_2 = \lambda_1/2$ (d) $\lambda_2 = \lambda_1/4$

40. If first ionisation potential of an atom is 16 V, then the first excitation potential will be

(a) 10.2 V (b) 12 V (c) 14 V (d) 16 V

41. In which transition minimum energy is emitted?

(a) $\infty \to 1$ (b) $2 \to 1$

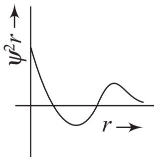
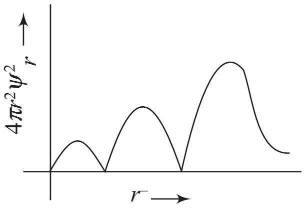
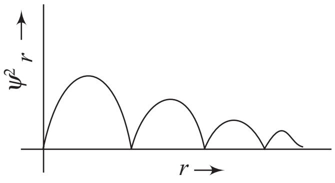
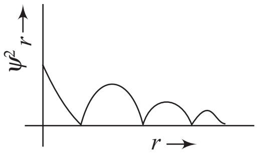
(c) $3 \to 2$ (d) $n \to (n - 1)\ (n \geq 4)$

42. Number of visible lines when an electron returns from fifth orbit to ground state in H spectrum is

(a) 5 (b) 4 (c) 3 (d) 10

LEVEL III

1.

	Column-I		**Column-II**
(A)		(p)	s-orbital
(B)		(q)	p-orbital
(C)		(r)	d-orbital
(D)		(s)	f-orbital
		(t)	Radial probability distribution function.

(a) (I) P (II) P, Q, R, S, T (III) Q, R, S (IV) P
(b) (I) Q (II) Q, R, S, T (III) P, Q, R, S (IV) P
(c) (I) P, R (II) P, Q, R, S (III) Q, R (IV) S
(d) (I) P, Q, R (II) Q, S, T (III) P, Q, S (IV) R

2. Matrix matching

Column-I		**Column-II**	
(A)	Lyman series	(p)	Visible region
(B)	Balmer series	(q)	Infrared region
(C)	Paschen series	(r)	Utraviolet region
(D)	Brackett series	(s)	$n_2 = 4$ to $n_2 = 3$
		(t)	$n_2 = 5$ to $n_2 = 1$

3. Matrix matching

Column-I		**Column-II**	
(A)	2*p* orbital	(p)	Number of spherical nodes = 0
(B)	3*d* orbital	(q)	Number of nodal plane = 0
(C)	2*s* orbital	(r)	Orbital angular momentum number = 0
(D)	4*f* orbital	(s)	Azimuthal quantum number = 0

4. Matrix matching

Column-I		**Column-II**	
(A)	Radius of n^{th} orbit	(p)	Inversely proportional to z
(B)	Energy of n^{th} orbit	(q)	Integral multiple of $\frac{h}{2\pi}$
(C)	Velocity of electron in the n^{th} orbit	(r)	Proportional to n^2
(D)	Angular momentum of electron	(s)	Inversely proportional to n
		(t)	Proportional to Z^2

5. Matrix matching

Column-I		**Column-II**	
(A)	H	(p)	Radius of 4^{th} orbit 0.53×4 Å
(B)	He^+	(q)	Energy of second orbit = –13.6 eV
(C)	Be^{3+}	(r)	Radius of second orbit = $0.53 \times >$ 4 Å
(D)	Li^{2+}	(s)	Velocity of electron in the third orbit
		(t)	Energy of fourth orbit = –13.6 eV

6.

Column-I		**Column-II**	
(A)	Aufbau principle	(p)	Line spectrum in visible region
(B)	*de Broglie*	(q)	Orientation of an electron in an orbital
(C)	Angular momentum	(r)	Photon
(D)	Hund's rule	(s)	$\lambda = h/mv$
(E)	Balmer series	(t)	Electronic configuration
(F)	Planck's law	(u)	mvr

7.

Column-I		**Column-II**	
(A)	Cathode rays	(p)	Helium nuclei
(B)	dumb bell	(q)	Uncertainty principle
(C)	Alpha particles	(r)	Electromagnetic radiation
(D)	Moseley	(s)	*p*-orbital
(E)	Heisenberg	(t)	Atomic number
(F)	X-ray	(u)	Electrons

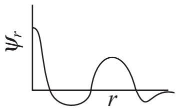
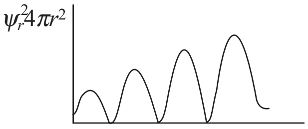
8. Frequency = f, Time period = T, Energy of n^{th} orbit = E_n, radius of n^{th} orbit = r_n, Atomic number = Z, Orbit number = n:

Column-I		**Column-II**	
(A)	f	(p)	n^3
(B)	T	(q)	Z^2
(C)	E_n	(r)	$\frac{1}{n^2}$
(D)	$\frac{1}{r_n}$	(s)	Z

9.

Column-I		**Column-II**	
(A)	Lyman series	(p)	Maximum number of spectral line observed = 6
(B)	Balmer series	(q)	Maximum number of spectral line observed = 2
(C)	In a sample 5 → 2	(r)	Second line has wave number $\frac{8R}{9}$
(D)	In a single isolated H-atom for 3 → 1 transition	(s)	Second line has wave number $\frac{3R}{4}$
		(t)	Total number of spectral line is 10

10. Column I and Column II contain data on Schrodinger Wave-Mechanical model, where symbols have their usual meanings. Match the columns.

Column-I		**Column-II**	
(A)		(p)	4*s*
(B)		(q)	5*px*
(C)	$Y(q, f) = K$ (independent of *q* and *f*)	(r)	3*s*
(D)	atleast one angular node is present	(s)	6*dxy*

Passage 1

In an atom, when an electron jumps from higher energy level to lower energy level, it emits energy in the form of electromagnetic radiations. When these electromagnetic radiations are passed through a prism and received on a photographic film, some lines are observed and those lines are called spectral lines.

For hydrogen-like species when jump takes from any excited state to ground state ($n = 1$), line produced in that case is called a Lyman series line.

If transition occurs from third or above levels to second level, then corresponding lines produced are called Balmer lines.

Similarly for next level, it is called Paschen series line.

11. In a gaseous sample 3 atoms of a Hydrogen-like species are present and all atoms are in fourth excited state then calculate the maximum number of different spectral lines that can be produced.

(a) 10 (b) 7 (c) 12 (d) 8

12. If there are 3 atoms of a Hydrogen like specie in second, third and fourth excited state respectively, then how many maximum total different Balmer and Paschen lines can be produced?

(a) 2 (b) 3 (c) 4 (d) 5

Passage 2

Alpha particles capture free moving electrons having wavelength 0.25 nm and form excited H-like species. In this excited state, electron has circumference 6 times the wavelength of electron. Bohr's quantisation rule is applicable.

13. The energy of photon emitted in this process will be

(a) 20.49 eV (b) 22.49 eV
(c) 25.51 eV (d) 27.51 eV

14. What is the number of maximum possible spectral lines obtained in Balmer series, when electron makes transition to ground state?

(a) 15 (b) 4 (c) 6 (d) 10

15. When electrons make transition to ground state, the largest wavelength (in nm) in the emitted radiations is [Given : "*E*" represents energy level in eV]

(a) $\dfrac{1240}{|E_6 - E_5|}$ (b) $\dfrac{1240}{|E_2 - E_1|}$

(c) $\dfrac{1240}{|E_6 - E_1|}$ (d) $\dfrac{1240}{|E_5 - E_4|}$

Passage 3

The magnetic quantum number is denoted by letter *m*, and for a given value of *l*, it can have all the values ranging from $-l$ to $+l$ including zero of *l*, *m* has $2l + 1$ values. For example, if $l = 2$, *m* can values, i.e., $m = -2, -1, 0, +1, +2$. This implies that there are five different orientations of the *d*-subshell. In other words, *d*-subshell has five *d*-orbitals.

16. How many electrons can fit into the orbitals that comprise the third quantum shell $n = 3$?

(a) 2 (b) 8 (c) 18 (d) 32

17. The maximum number of electron that can be accommodated in *f*-shell is

(a) 2 (b) 8 (c) 18 (d) 14

18. Which of the following is correct for 2*p*-orbitals?

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

Passage 4

A German physicist gave a principle about the uncertainties in simultaneous measurement of position and momentum of small particles. According to that physicist, it is impossible to measure simultaneously the position and momentum of small particle simultaneously with absolute accuracy or certainty. If an attempt is made to measure any one of these two quantities with higher accuracy, the other becomes less accurate. The product of the uncertainty in position (Δx) and uncertainty momentum (Δp) is always constant and is equal to or greater than $\dfrac{h}{4\pi}$, where *h* is Plank's constant, i.e.,

$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi}$$

19. Uncertainty in position is twice the uncertainty in momentum. Uncertainty velocity is

(a) $\sqrt{\dfrac{h}{\pi}}$ (b) $\dfrac{1}{2m}\sqrt{\dfrac{h}{\pi}}$

(c) $\dfrac{1}{2m}\sqrt{h}$ (d) $\dfrac{1}{2\sqrt{2}m}\sqrt{\dfrac{h}{\pi}}$

20. The uncertainty in position of an electron ($m = 9.1 \times 10^{-28}$ gm) moving with a velocity 3×10^4 cm/s accurate up to 0.001% will be

(a) 3.84 cm (b) 1.92 cm
(c) 7.68 cm (d) 5.76 cm

21. If uncertainty in the position of an electron is zero, the uncertainty in its momentum would be

(a) zero (b) $< h/4\pi$
(c) $> h/4\pi$ (d) Infinite

Passage 5

It is tempting to think that all possible transitions are permissible, and that an atomic spectrum arises from the transition of an electron from any initial orbital to any other orbital. However, this is not so, because a photon has an intrinsic spin angular momentum of $\sqrt{2}\frac{h}{2\pi}$ corresponding to S = 1 although it has no charge and no rest mass. On the other hand, an electron has two types of angular momentum: orbital angular momentum, $L = \sqrt{l(l+1)}\frac{h}{2\pi}$ and spin angular momentum, $L_s \left(= \sqrt{s(s+1)}\frac{h}{2\pi} \right)$ arising from orbital motion and spin motion of electron, respecitvely. The change in angular momentum of the electron during any electronic transition must compensate for the angular momentum carried away by the photon. To satisfy this condition, the difference between the azimuthal quantum numbers of the orbitals within which transition takes place must differ by one. Thus, an electron in a *d*-orbital (l = 2) cannot make a transition into an *s*-orbital (l = 0) because the photon cannot carry away enough angular momentum. An electron as is well known, possesses four quantum numbers n, l, m and s. Out of these four, l determines the magnitude of orbital angular momentum (mentioned above) while m determines its Z-component as $m\left(\frac{h}{2\pi}\right)$. The permissible values of only integers from $-l$ to $+l$. While those for l are also integers starting from 0 to (n – 1). The values of l denotes the subshell. For l = 0, 1, 2, 3, 4… the sub-shells are denoted by the symbols *s*, *p*, *d*, *f*, *g*…. respectively.

22. The maximum orbital angular momentum of an electron with n = 5 is

(a) $\sqrt{6}\frac{h}{2\pi}$ (b) $\sqrt{12}\frac{h}{2\pi}$

(c) $\sqrt{42}\frac{h}{2\pi}$ (d) $\sqrt{20}\frac{h}{2\pi}$

23. The orbital angular momentum of an electron in *p*-orbital makes an angle of 45° from Z-axis. Hence Z-component of orbital angular momentum of electron is

(a) $\frac{h}{\pi}$ (b) $\left(\frac{h}{2\pi}\right)$ (c) $-\frac{h}{\pi}$ (d) $-\left(\frac{h}{2\pi}\right)$

24. The spin-only magnetic moment of a free ion is $\sqrt{8}$ B.M. The spin angular momentum of electron will be

(a) $\sqrt{2}\frac{h}{2\pi}$ (b) $\sqrt{8}\frac{h}{2\pi}$ (c) $\sqrt{6}\frac{h}{2\pi}$ (d) $\sqrt{\frac{3}{4}}\frac{h}{2\pi}$

Passage 6

For a single electron atom or ion, the wave number of radiation emitted during the transition of electron from a higher energy state ($n = n_2$) to a lower energy state ($n = n_1$) is given by the expression:

$$\bar{v} = \frac{1}{\lambda} = R_H \cdot z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad \text{…(i)}$$

where $R_H = \frac{2\pi^2 m k^2 e^4}{h^3 c}$ = Rydberg constant for H-atom

where the terms have their usual meanings.

Considering the nuclear motion, the most accurate would have been to replace mass of electron (m) by the reduced mass (m) in the above expression, defined as

$$\mu = \frac{m' \cdot m}{m' + m}$$

where $m\phi$ = mass of nucleus.

For Lyman series: n_1 = 1 (fixed for all the lines) while n_2 = 2, 3, 4, … infinite for successive lines, i.e., first, second, third … infinite lines, respectively. For Balmer series: n_1 = 2 (fixed for all the lines) while n_2 = 3, 4, 5 … infinite for successive lines.

25. The ratio of the wave numbers for the highest energy transition of e^- in Lyman and Balmer series of H-atom is

(a) 4 : 1 (b) 6 : 1 (c) 9 : 1 (d) 3 : 1

26. If proton in H-nucleus be replaced by positron having the same mass as that of proton but same charge as that of proton, then considering the nuclear motion, the wave number of the lowest energy transition of He^+ ion in Lyman series will be equal to

(a) 2 R_H (b) 3 R_H (c) 4 R_H (d) R_H

Passage 7

The sum of spins of all electrons is the total spin(S) and $2S + 1$ and is called spin multiplicity of the electronic configuration. Hund's rule defines the ground state configuration of electrons in degenerate orbitals, i.e., orbitals within the same subshell which have the same values of n and l, states that in degenerate orbitals pairing of electrons does not occur unless and until all such orbitals are filled singly with their parallel spin. However, degeneracy of orbitals of a given subshell may be destroyed in an inhomogeneous magnetic field like Octahedral field, tetrahedral field, etc. For example, *d*-orbital is five-fold degenerate and degeneracy is destroyed in an applied magnetic field provided that it is in homogenous condition. This is called splitting of *d*-orbital. In an octahedral field (O_h), splitting of *d*-orbital takes place such that d_{xy}, and d_{xz} orbitals (triply degenerate) have lower energy than $d_{x^2-y^2}$ and (doubly degenerate) d_{z^2} which may again split into two levels: $d_{x^2-y^2}$ and the former having higher energy than the latter. The pairing of electron in lower energy may occur if the energy difference between the two level called splitting energy (D.E.) is greater than the pairing energy, E_p, i.e., the increase in energy resulting from interelectronic repulsion during pairing so as to yield an electronic configuration of the lowest possible energy state, i.e., the ground state. This condition is met only in the strong magnetic field. In tetrahedral field (T_d), the splitting is just the reverse of the O_h field. A spinning electron behaves as though it were a tiny bar magnet with poles lying on the axis of spin. The magnetic moment of any atom, ion or molecule due to spin called spin-only magnetic moment (m_s) is given by the formula:

$\mu_s = \sqrt{n(n+2)}$ B.M where n = number of unpaired electron(s).

27. The spin-only magnetic moment of Cr^{3+} (EC [Ar] $3d^3$) in strong O_h magnetic field is equal to

(a) $\sqrt{3}$ B.M (b) $\sqrt{8}$ B.M

(c) $\sqrt{15}$ B.M (d) Zero

28. The spin-multiplicity of Fe^{3+} (Ec[Ar]$3d^5$) in its ground state but placed in a strong O_h magnetic field is

(a) 6 (b) 2 (c) 3 (d) 4

29. **Statement 1:** The kinetic energy of an electron is greater than α-particle having same momentum.

Statement 2: Mass of α-particle is greater than the mass of electron.

(a) Statements 1 and 2 are true. Statement 2 is the correct explanation for statement 1.

(b) Statements 1 and 2 are true. Statement 2 is NOT the correct explanation for Statement 1.

(c) Statement 1 is true, Statement 2 is false.

(d) Statement 1 is false, Statement 2 is true.

30. **Statement 1:** For hydrogen orbital energy increases as $1s < 2s < 2p < 3s < 3p < 3d < 4s < 4p$ …

Statement 2: The orbital with lower ($n + l$) value has lesser energy and hence filled up first.

31. **Statement 1:** When two or more empty orbitals of equal energy are available. One electron must be placed in each until they are all half-filled.

Statement 2: The pairing of electron is an unfavourable phenomenon.

32. **Statement 1:** The Paschen series in the spectrum of hydrogen lies in the infra-red region.

Statement 2: The Paschen series is born of transition of electrons onto the second orbit from higher orbits.

33. **Statement 1:** The principal quantum number, n, can have whole number values 1, 2, 3, … etc.

Statement 2: The angular momentum quantum number can never be equal to n.

34. Question: Is the specie paramagnetic?

Statement 1: The atomic number of specie is 29.

Statement 2: The charge on the specie is +1.

(a) Statement (1) alone is sufficient but statement (2) is not sufficient.

(b) Statement (2) alone is sufficient but statement (1) is not sufficient.

(c) Both statements together are sufficient but neither statement alone is sufficient.

(d) Statements (1) and (2) together are not sufficient.

(Assersion and Reason)

These questions contains, Statement I (assertion) and Statement II (reason).

(a) Statement I is true, Statement II is true; Statement II is the correct explanation for Statement I.

(b) Statement I is true, Statement II is true; Statement II is NOT a correct explanation for statement-I

(c) Statement I is true, Statement II is false.

(d) Statement I is false, Statement II is true.

35. **Statement I:** Nodal plane of p_x atomic orbital in yz plane.

Statement II: In p_x, atomic orbital electron density is zero in the yz plane.

36. **Statement I:** No two electrons in an atom can have the same values of four quantum numbers.

Statement II: No two electrons in an atom can be simultaneously in the same shell, same subshell, same orbitals and have the same spin.

37. **Statement I:** p-orbital has dumb-bell shape.

Because

Statement II: Electrons present in p-orbital can have one of three values for 'm', i.e., 0, +1, –1

38. **Statement I:** The ground state configuration of Cr is $3d^5\ 4s^1$.

Statement II: A set of exactly half-filled orbitals containing parallel spin arrangement provide extra stability.

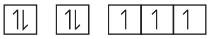
39. **Statement I:** Mass numbers of the elements may be fractional.

Statement II: Mass numbers are obtained by the sum of mass of electron and neutron.

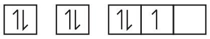
40. **Statement I:** Limiting line in the Balmer series has a wavelength of 36.4 mm.

Statement II: Limiting lines is obtained for a jump of electron from $n = \infty$ to $n = 2$ for Balmer series.

41. **Statement I:** The electronic configuration of nitrogen atom is represented as



not as



Statement II: The configuration of ground state of an atom is the one which has the greatest multiplicity.

42. **Statement I:** The configuration of B atom cannot be $1s^2\ 2s^3$.

Statement II: Hund's rule demands that the configuration should display maximum multiplicity.

43. **Statement I:** $2p$ orbitals do not have spherical nodes.

Statement II: The number of spherical nodes in p-orbitals is given by (n – 2).

44. **Statement I:** In Rutherford's gold foil experiment, very few α-particles are deflected back.

Statement II: Nucleus present inside the atom is heavy.

45. **Statement I:** Each electron in an atom either +½ or –½ spin quantum number

Statement II: Spin quantum numbers are obtained by Bohr's Theory.

46. **Statement I:** There are two spherical nodes in 3*s*-orbital.

Statement II: There is no angular node in 3*s*-orbital.

47. Choose the correct relation on the basis of Bohr's theory.

(a) Velocity of electron $\propto \frac{1}{n}$

(b) Frequency of revolution $\propto \frac{Z^2}{n^3}$

(c) Radius of orbit $\propto n^2Z$

(d) Force on electron $\propto \frac{Z^3}{n^4}$

48. A hydrogen - like atom has ground state binding energy 122.4 eV. Then

(a) its atomic number is 3.

(b) an electron of 90 eV can excite it to a higher state.

(c) an 80 eV electron cannot excite it to a higher state.

(d) an electron of 8.2 eV and a photon of 91.8 eV are emitted when a 100 eV electron interacts with it.

49. Energy equivalent of 10.00 cm^{-1} is –

(a) 2×10^{-22} J per photon

(b) 2.9×10^{-2} kcal mol^{-1} photon

(c) 1.2×10^{-1} kJ mol^{-1} photon

(d) 2×10^{-15} ergs per photon

50. Radiation of wavelength 200 Å falls on a platinum surface. If the work function of the metal is 5 eV, which of the following results are correct about experiment?

(a) The velocity of photoelectrons increases with increase in intensity of radiation.

(b) Photo-emission of electrons takes place.

(c) The threshold frequency of the metal is 1.21×10^{15} sec^{-1}.

(d) The velocity of the photo-electrons is 4.48×10^6 m/sec.

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

(a) Fe^{3+} and Mn^{2+} have equal paramagnetic character.

(b) Cu_2Cl_2 and $CuCl_2$ are coloured.

(c) MnO_4^- is purple in colour because of unpair *d* electrons.

(d) The magnetic moment of Fe^{2+} and Co^{3+} is equal to $2\sqrt{6}$ B.M.

52. What is the number of waves made by an elelctron moving in an orbit having maximum magnetic quantum number +3?

53. What is the number of spectral lines produced when an electron jumps from fifth orbit to second orbit in the hydrogen atom?

54. What is the orbital angular momentum of 2*s* electron?

55. The angular momentum of an electron is $\frac{h}{\pi}$. The Bohr's orbit in which the electron is revolving is.

56. What is the the number of radial nodes of 2*p* orbital?

57. An oil drop has -6.39×10^{-19} Coulomb charge. What is the number of electrons in the oil drop?

58. What is the number of waves made by a Bohr electron in Hydrogen atom in one complete revolution in the third orbit?

59. The number of nodal plane in d_{xy} orbital.

60. What is the number of nodes in the radial distribution curve of 2*s* orbital?

61. Magnetic moment of M^{x+} is $\sqrt{24}\,BM$. What is the number of unpaired electrons in M^{x+}?

62. The wave function of an orbital is represented as ψ_{420}. What is the azimuthal quantum number of that orbital?

63. The number of concentric spherical surfaces for 3*s* orbital at which the probability of finding electron is zero, are

64. What is the number of electrons with $l = 2$ in the ground state of Chromium atom?

65. What is the value of '*n*' of the highest excited state that an electron of hydrogen atom in the ground state can reach when 12.09 eV energy is given to the hydrogen atom?

66. A transition metal cation M^{+3} has magnetic moment $\sqrt{35}\,BM$. What is the number of unpaired electrons in *ns* orbital of M^{+3}?

(Note: Transition metal exhibit ferromagnetic property)

67. The circumference of the second, orbit of electron in hydrogen atom is 400 nm, the *de Broglie* wavelength of electron corresponding to the circumference of same orbit is 200 nm. What is the number of waves made by an electron?

68. What is the number of waves made by a Bohr electron in an orbit of maximum magnetic quantum 3?

69. How many elements does the last electron have the quantum numbers of $n = 4$ and $l = 1$?

70. What is the orbital angular momentum of an electron in 3*s* – orbital?

71. How many *d* – electrons in Cu^+(At.No = 29) can have the spin quantum $\left(-\frac{1}{2}\right)$?

72. What is the maximum number of electrons in an atom that can have the quantum numbers $n = 4$, $m_e = \pm 1$?

73. What is the number of radial nodes for 3*P* – orbital?

74. How long would it take a radio wave of frequency 6×10^3 sec^{-1} to travel from Mars to Earth, a distance of 8×10^7 km?

75. The energy levels of hypothetical one electron atom are shown below.

0 eV —— $n = \infty$
–0.50 eV —— $n = 5$
–1.45 eV —— $n = 4$
–3.08 eV —— $n = 3$
–5.3 eV —— $n = 2$
–15.6 eV —— $n = 1$

(a) Find the ionisation potential of atom?

(b) Find the short wavelength limit of the series terminating at $n = 2$?

(c) Find the wave number of photon emitted for the transition made by the electron from third orbit to first orbit?

(d) Find the minimum energy that an electron will have after interacting with this atom in the ground state, if the initial kinetic energy of the electron is (i) 6 eV and (ii) 11 eV?

76. Suppose 10^{-17} J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ($\lambda = 550$ nm) are needed to generate this minimum amount of energy?

77. Find the number of photons of radiation of frequency $5 \times 10^{13}\ s^{-1}$ that must be absorbed in order to melt one g ice when the latent heat of fusion of ice is 330 J/g.

78. The eyes of certain member of the reptile family pass a single visual signal to the brain when the visual receptors are struck by photons of wavelength 850 nm. If the total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

79. The wavelength of a certain line in the Paschen series is 1093.6 nm. What is the value of n_{high} for this line $[R_H = 1.0973 \times 10^{+7}\ \text{m}^{-1}]$?

80. Wavelength of the Balmer H_α line (first line) is 6565 Å. Calculate the wavelength of H_β (second line).

81. Calculate the Rydberg constant R if He^+ ions are known to have the wavelength difference between the first (of the longest wavelength) lines of Balmer and Lyman series equal to 133.7 nm.

82. Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum.

83. A photon having $\lambda = 854$ Å causes ionisation of a nitrogen atom. Give the I.E. per mole of nitrogen in KJ.

84. Calculate energy of electron which is moving in the orbit that has its radius, 16 times the radius of first Bohr orbit for H-atom.

85. The electron energy in hydrogen atom is given by $E_n = \dfrac{-21.7 \times 10^{-12}}{n^2}$ ergs. Calculate the energy required to remove an e^- completely from $n = 2$ orbit. What is the largest wavelength in cm of light that can be used to cause this transition?

86. Calculate the wavelength in angstrom of photon that is emitted when an e^- in Bohr orbit $n = 2$ returns to the orbit $n = 1$. The ionisation potential of the ground state of hydrogen atom is 2.17×10^{-11} erg/atom.

87. The velocity of e^- in a certain Bohr orbit of the hydrogen atom bears the ratio of 1 : 275 to the velocity of light. What is the quantum number "n" of the orbit.

88. A doubly ionised lithium atom is hydrogen like with atomic number $Z = 3$. Find the wavelength of the radiation required to excite the electron in Li^{2+} from the first to the third Bohr orbit.

89. Estimate the difference in energy between I and II Bohr orbit for a hydrogen atom. At what minimum atomic number a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen-like species does this atomic number correspond to?

90. 1.8 g atoms of hydrogen are excited to radiations. The study of spectra indicates that 27% of the atoms are in third energy level and 15% of atoms in second energy level and the rest in ground state. If I.P. of H is 21.7×10^{-12} erg. Calculate

(i) number of atoms present in third and second energy level.

(ii) total energy evolved when all the atoms return to ground state.

91. One mole He^+ ions are excited. Spectral analysis showed existence of 50% ions in 3rd orbit, 25% in 2nd and rest in ground state. Calculate total energy evolved when all the ions return to the ground state in terms of N_A and ΔE.

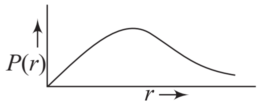
92. The energy of an excited H-atom is –3.4 eV. Calculate angular momentum of e^-.

93. The vapours of Hg absorb some electrons accelerated by a potential difference of 4.5 volt. As a result of it, light is emitted. If the full energy of single incident e^- is to be converted into light emitted by single Hg atom, find the wave number of the light.

94. The hydrogen atom in the ground state is excited by means of monochromatic radiation of wavelength $x\ A^0$. The resulting spectrum consists of 15 different lines. Calculate the value of x.

95. A plot of $P(r)$ of 1s electron of H-atom versus distance from the nucleus (r) is shown in the figure given below. Find the value of r corresponding to the maximum in terms of a_0 where the maximum occurs.
Given:

$$P(r) = 4\pi r^2 \psi^2 \qquad \psi_{1s}\ (\text{for H-atom}) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$



96. Absorption of energy by an atom of hydrogen in the ground state results in the ejection of electron with *de-Broglie* wavelength $\lambda = 4.7 \times 10^{-10}$ m. Given that the ionisation energy is 13.6 eV, calculate the energy of photon which caused the ejection of electron.

97. Photo-chemical dissociation of oxygen results in the production of two oxygen atoms, one in the ground state and one in the excited state.

$$O_2 \xrightarrow{hv} O + O^*$$

The maximum wavelength needed for this is 174 nm. If the excitation energy $O \rightarrow O^*$ is 3.15×10^{-19}J. How much energy in kJ/mole is needed for the dissociation of one mole of oxygen into normal atoms in ground state?

98. If the average lifetime of an excited state of H atom is of order 10^{-8} sec, estimate how many orbits an e^- makes when it is in the state $n = 2$ and before it suffers a transition to $n = 1$ state.

99. Calculate the frequency of e^- in the first Bohr orbit in a H-atom.

100. A single electron orbits around a stationary nucleus of charge +Ze where Z is a constant from the nucleus and e is the magnitude of the electric charge. The hydrogen like species required 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Find the value of Z give the hydrogen like species formed.

101. A stationary He^+ ion emitted a photon corresponding to a first line of the Lyman series. The photon liberated a photoelectron from a stationary H atom in ground state. What is the velocity of photoelectron ?

102. Calculate the threshold frequency of metal if the binding energy is 180.69 kJ mol^{-1} of electron.

103. Calculate the binding energy per mole when threshold wavelength of photon is 240 nm.

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. The increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (α) is **[IIT-JEE 1984]**

(a) e, p, n, α (b) n, p, e, α
(c) n, p, α, e (d) n, α, p, e

2. The triad of nuclei that is isotonic is **[IIT-JEE 1988]**

(a) ${}^{14}_{6}C, {}^{15}_{7}N, {}^{17}_{9}F$ (b) ${}^{12}_{6}C, {}^{14}_{7}N, {}^{19}_{9}F$
(c) ${}^{14}_{6}C, {}^{14}_{7}N, {}^{17}_{9}F$ (d) ${}^{14}_{6}C, {}^{14}_{7}N, {}^{19}_{9}F$

3. Rutherford's experiment on scattering of particles showed for the first time that the atom has **[IIT-JEE 1981]**

(a) electrons (b) protons
(c) nucleus (d) neutrons

4. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order **[IIT-JEE 2000]**

(a) 10^{-10}m (b) 10^{-20} m (c) 10^{-30}m (d) 10^{-40}m

5. Correct set of four quantum numbers for the valence (outermost) electron of rubidium ($Z = 37$) is **[IIT-JEE 1984]**

(a) 5, 0, 0, + ½ (b) 5, 1, 0, + ½
(c) 5, 1, 1, + ½ (d) 6, 0, 0, + ½

6. The outermost electronic configuration of the most electronegative element is **[IIT-JEE 1988]**

(a) ns^2np^3 (b) ns^2np^4 (c) ns^2np^5 (d) ns^2np^6

7. Naturally occurring boron consists of two isotopes whose atomic weights are 10.01 and 11.01. The atomic weight of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. **[IIT-JEE 1978]**

8. The energy of the electron in the second and the third Bohr's orbits of the hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from the third to the second orbit. **[IIT-JEE 1981]**

9. Calculate the wavelength in Angstroms of the photon that is emitted when an electron in the Bohr orbit, $n = 2$ returns to the orbit, $n = 1$ in the hydrogen atom. The ionisation potential of the ground state hydrogen atom is 2.17×10^{-11} erg per atom. **[IIT-JEE 1982]**

10. The electron energy in hydrogen atom is given by $E = (-21.7 \times 10^{-12})/n^2$ ergs. (a) Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition? **[IIT-JEE 1984]**

11. What is the maximum number of electrons that my be present in all the atomic orbitals with principle quantum number 3 and azimuthal quantum number 2? **[IIT-JEE 1985]**

12. According to Bohr's theory, the electronic energy of hydrogen atom in the n^{th} Bohr's orbit is given by

$$E_n = \frac{-21.76\times10^{-19}}{n^2}\,\text{J}$$. Calculate the longest wavelength of light that will be needed to remove an electron from the third Bohr orbit of the He^+ ion. **[IIT-JEE 1990]**

13. A ball of mass 100 g is moving with 100 ms^{-1}. Find its wavelength. **[IIT-JEE 2004]**

14. Find the velocity (ms^{-1}) of electron in first Bohr's orbit of radius a_0. Also find the de Broglie's wavelength (in m). Find the orbital angular momentum of $2p$ orbital of hydrogen atom in units of $h/2p$. **[IIT-JEE 2005]**

15. Estimate the difference in energy between first and second Bohr orbit for a hydrogen atom. At what minimum atomic number, a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with = 3.0 $\times 10^{-8}$ m? Which hydrogen atom-like species does this atomic number correspond to? **[IIT-JEE 1993]**

16. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum? **[IIT-JEE 1993]**

17. Find out the number of waves made by a Bohr electron in one complete revolution in its third orbit. **[IIT-JEE 1994]**

18. Iodine molecule dissociates into after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of I_2 = 240 kJ mol^{-1}.) **[IIT-JEE 1995]**

19. Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. **[IIT-JEE 1996]**

20. With what velocity should an *a*-particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} metre from the nucleus of a copper atom? **[IIT-JEE 1997]**

21. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å? **[IIT-JEE 1997]**

22. Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H-H bond is 436 kJ mol^{-1}. **[IIT-JEE 2000]**

23. Wavelength of high energy transition of H-atoms is 91.2 nm. Calculate the corresponding wavelength of He atoms. **[IIT-JEE 2003]**

24. The Schrodinger wave equation for hydrogen atom is **[IIT-JEE 2004]**

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r_0}{a_0}\right)e^{-r_0/a_0}$$

where a_0 is Bohr's radius. If the radial node in 2*s* be at r_0, find r_0 in terms of a_0.

25. Match the columns according the Boh's theory.

E_n = Total energy

K_n = Kinetic energy

V_n = Potential energy

r^n = Radius of n^{th} orbit **(2006, 6M)**

Column I		**Column II**	
(A)	$V_n/K_n = ?$	(p)	0
(B)	If radius of n^{th} orbit $\propto E_n^x,\ x = ?$	(q)	–1
(C)	Angular momentum in lowest orbital	(r)	–2
(D)	$\frac{1}{r^n} \propto z^y,\ y = ?$	(s)	1

26. Match the entries in column I with the related quantum number(s) in Column II. **(2008, 6M)**

Column I		**Column II**	
(A)	Orbital angular momentum of the electron in a hydrogen- like atomic orbital	(p)	Principal quantum number
(B)	A hydrogen – like one electron wave function obeying Pauli's principle	(q)	Azimuthal quantum number
(C)	Shape, size and orientation of hydrogen- like atomic orbitals	(r)	Magnetic quantum number
(D)	Probability density of electron at the nucleus in hydrogen – like atom	(s)	Electron spin quantum number

Comprehension-Based Questions

The hydrogen- like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light, the ion undergoes transition to a state S_2. The state S_2 has one radial node and its energy is equal to the ground state energy of the hydrogen atom.

27. The state S_1 is **(2010)**
(a) 1*s* (b) 2*s* (c) 2*p* (d) 3*s*

28. Energy of the state S_1 in units of the hydrogen atom ground state energy is **(2010)**
(a) 0.75 (b) 1.50 (c) 2.25 (d) 4.50

29. The orbital angular momentum quantum number of the state S_2 is **(2010)**
(a) 0 (b) 1 (c) 2 (d) 3

Integer-Type Questions

30. The maximum number of electrons that can have principal quantum number, $n = 3$ and spin quantum number, $m_s = -\frac{1}{2}$, is **(2011)**

31. Which of the following is the energy of a possible excited state of hydrogen? **[2015 Main]**
(a) +13.6 eV (b) –6.8 eV
(c) –3.4 eV (d) +6.8 eV

32. The correct set of four quantum numbers for the valence electrons of rubidium atm ($Z = 37$) is **[2013 Main]**
(a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$
(c) $5, 1, 1, +\frac{1}{2}$ (d) $5, 0, 1, +\frac{1}{2}$

33. Energy of an electron is given by $E = -2.78 \times 10^{-18}\ \text{J}\left(\frac{Z^2}{n^2}\right)$. Wavelength of light required to excite an electron in an hydrogen atom from level n = 1 to n = 2 will be **[2013 Main]**
($h = 6.62 \times 10^{-34}$ Js and $c = 3.0 \times 10^{8}\ \text{ms}^{-1}$)
(a) 1.214×10^{-7} m (b) 2.816×10^{-7} m
(c) 6.500×10^{-7} m (d) 8.500×10^{-7} m

34. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a_0 is Bohr radius] **[2012]**
(a) $\frac{h^2}{4\pi^2 m a_0^2}$ (b) $\frac{h^2}{16\pi^2 m a_0^2}$
(c) $\frac{h^2}{32\pi^2 m a_0^2}$ (d) $\frac{h^2}{64\pi^2 m a_0^2}$

35. In an atom, the total number of electrons having quantum numbers $n = 4$, $|m| = 1$ and $m_2 = -\frac{1}{2}$ is **[2014 Adv.]**

36. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of the de-Broglie wavelength of He gas at –73°C is '*M*' times that of the de-Broglie wavelength of Ne at 727°C M is **[2013 Adv.]**

Answer Key

LEVEL I

1. (a) 2. (c) 3. (d) 4. (c) 5. (a) 6. (d) 7. (b) 8. (d) 9. (a) 10. (d)
11. (d) 12. (d) 13. (b) 14. (a) 15. (b) 16. (b) 17. (c) 18. (b) 19. (b) 20. (c)
21. (d) 22. (a) 23. (c) 24. (b) 25. (b) 26. (b) 27. (a) 28. (a) 29. (b) 30. (c)
31. (c) 32. (d) 33. (c) 34. (c) 35. (a) 36. (a) 37. (c) 38. (a) 39. (a) 40. (b)
41. (b) 42. (a) 43. (a) 44. (a) 45. (c) 46. (c) 47. (d) 48. (b) 49. (a) 50. (c)
51. (c) 52. (c) 53. (b) 54. (c) 55. (a) 56. (a) 57. (d) 58. (b) 59. (c) 60. (c)
61. (d) 62. (b) 63. (c) 64. (a) 65. (c) 66. (a) 67. (b) 68. (d) 69. (b) 70. (b)
71. (a) 72. (c) 73. (a) 74. (b) 75. (a) 76. (c) 77. (c) 78. (a) 79. (b) 80. (b)
81. (b) 82. (d) 83. (b) 84. (b) 85. (d) 86. (c) 87. (a) 88. (b) 89. (b) 90. (a)
91. (a) 92. (a) 93. (a) 94. (b) 95. (d) 96. (d) 97. (d) 98. (a) 99. (a) 100. (b)
101. (a) 102. (b) 103. (a) 104. (c) 105. (d) 106. (b) 107. (d) 108. (b) 109. (d) 110. (c)
111. (c) 112. (d) 113. (b) 114. (b) 115. (c) 116. (c) 117. (a) 118. (b) 119. (a) 120. (a)
121. (c) 122. (d) 123. (a) 124. (d) 125. (b) 126. (d) 127. (b) 128. (a) 129. (d) 130. (a)
131. (a) 132. (a) 133. (a) 134. (b) 135. (b) 136. (c) 137. (a) 138. (b) 139. (c) 140. (d)
141. (b) 142. (c) 143. (d) 144. (a) 145. (c) 146. (c) 147. (c) 148. (c) 149. (c) 150. (d)

LEVEL II

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

LEVEL III

1. (A) → P; (B) → P, Q, R, S, T; (C) → Q, R, S; (D) → P
2. A → r, t; B → p; C → q, s; D → q
3. A → p; B → p; C → p, q, r, s; D → p
4. A → r, p; B → r, t; C → s; D → q
5. A → r; B → q; C → p, t; D → s
6. (A) → t; (B) → s ; (C) → u ; (D) → q ; (E) → p; (F) → r
7. (A) → u ; (B) → s ; (C) → p ; (D) → t ; (E) → q ; (F) → r
8. (A) → q ; (B) → p ; (C) → q, r ; (D) → r, s
9. (A) → r ; (B) → s; (C) → p; (D) → q
10. A → P, B→p, q, s, C→p, r, D → q, s
11. (b) 12. (b) 13. (c) 14. (b) 15. (a) 16. (c) 17. (d) 18. (d) 19. (d) 20. (b)
21. (d) 22. (d) 23. (b) 24. (a) 25. (a) 26. (b) 27. (c) 28. (b) 29. (a) 30. (d)
31. (c) 32. (c) 33. (b) 34. (c) 35. (a) 36. (a) 37. (b) 38. (a) 39. (e) 40. (a)
41. (a) 42. (b) 43. (a) 44. (b) 45. (e)
46. (b) 47. (a, b, d) 48. (a, c, d) 49. (a, b, c, d) 50. (b, c, d)
51. (a, d) 52. (4) 53. (6) 54. (0) 55. (2) 56. (0) 57. (4) 58. (3) 59. (2) 60. (1)
61. (4) 62. (2) 63. (2) 64. (5) 65. (3) 66. (0) 67. (2) 68. (4) 69. (6) 70. (0)
71. (5) 72. (12) 73. (1) 74. (2.66×10^2 sec.)

75. (a) [15.6] (b) [233.9 nm] (c) [1.808×10^7 m^{-1}] (d) [–9.6 eV and –4.6 eV] 76. [28] 77. [10^{22}]
78. [1.35×10^5] 79. [6] 80. [4863 Å] 81. [1.096×10^7m^{-1}] 82. [1.827×10^5J/m]
83. [1400 KJ/mole] 84. [–0.85 eV] 85. [5.425×10^{-12} ergs. 3.66×10^{-5}cm] 86. [1220 Å]
87. [2] 88. [108.8 eV] 89. [10.2 eV, He] 90. [0.486 N_A, 0.27 N_A, 56.65×10^{11} erg]
91. [0.5 NA $(E_2 - E_1)$ + 0.25 $N_A(E_2 - E_1)$] 92. $\frac{h}{\pi}$ 93. [0.0036 nm^{-1}] 94. 932 Å 95. $r = a_0$
96. [3.271×10^{-18} J] 97. [498.3 KJ/mole] 98. [8×10^6] 99. [2.3×10^{13}Hz] 100. [5]
101. [3.09×10^6 m/sec.] 102. [$v_0 = 6.626 \times 10^{-34}$] 103. 318.9 Kj/mole]

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (d) 2. (a) 3. (c) 4. (c) 5. (a) 6. (c) 7. [B – 11.01 80%, 20% and B 10.01]
8. [6603 Å] 9. [12220 Å] 10. [3.67×10^{-5} cm] 11. (10) 12. [2055 Å]
13. [6.62×10^{-25} Å] 14. [2.18×10^6 m sec^{-1}, 3.3 Å, $\sqrt{2}\frac{h}{\pi}$] 15. [He$^+$] 16. [$n \to 2$ to $n \to 1$] 17. [3]
18. [2.16×10^{-20}J] 19. 27419.25 cm^{-1}] 20. [6.3×10^6m sec^{-1}] 21. [63.3 volt] 22. [98.18 KJ]
23. [22.8 nm] 24. [$r_0 = 2a_0$] 25. A → r; B → q, C → p, D → s
26. A → q; B → p, q, r, s; C → p, q, r ; D → p, q, r 27. (b) 28. (c) 29. (b) 30. (9) 31. (c)
32. (a) 33. (a) 34. (c) 35. (6) 36. (5)

Hints and Solutions

LEVEL I

1. **(a)** $E_5 = -13.6 \times \frac{1}{(5)^2} = -0.54$ eV

2. **(c)** Li^{+2} and He^+ both have same number of electron so spectrum pattern will be similar.

3. **(d)** $\lambda = \frac{h}{\sqrt{2mqV}} \qquad \lambda \propto \frac{1}{\sqrt{V}}$

$$\frac{\lambda_1}{\lambda_2} = \sqrt{\frac{V_2}{V_1}} = \sqrt{\frac{200}{50}} = \frac{2}{1}$$

4. **(c)** $\Delta x \cdot \Delta p = \frac{h}{4\pi}$

put value $\Delta p = 1.0 \times 10^{-5}$ kg ms^{-1}

5. **(a)** Orbital angular momentum

$$= \sqrt{l(l+1)} \cdot \frac{h}{2\pi} \qquad \text{for } l = 0$$

6. **(d)** ${}_{25}Mn = 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^2$

$Mn^{+4} = 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^3, 4s^0$

7. **(b)** ${}_{30}Zn^{2+} = 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}$
(unpaired de$^-$ = 0)
${}_{26}Fe^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$(unpaired de$^-$ = 4)
${}_{28}Ni^{3+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$(unpaired de$^-$ = 3)
${}_{29}Cu^{+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$(unpaired de$^-$ = 1)

8. (d) d^7 =

↑↓	↑↓	↑	↑	↑

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

9. **(a)** $K = 2e^- = 1s^2$
$L = 8e^- = 2s^2\ 2p^4$
$M = 11e^- = 3s^2\ 3p^6\ 3d^3$
$N = 2e^- = 4s^2$
$l = 2$ for d ∴ $e^- = 3$

10. **(d)** $Cl^- = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
For last e^- $n = 3$, $l = 1$, $m = \pm 1$ or 0 or -1

11. **(d)** $E_n = -\frac{13.6z^2}{n^2}$eV

as move away from the nucleus, the energy increases, hence, energy is maximum at infinite distance from the nucleus.

12. **(d)** When an electron jump from higher level to lower level, it emits the photon and lower level to higher level. It absorbs photon. Hence, '1s' only absorbs photon because it is lowest energy level.

13. **(b)** $\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

In Balmer series, electron jumps from higher energy level to second energy level. Hence third line form when electrons jump from fifth energy level to 2 energy level. 5 → 2

14. (a) $_{37}Rb = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^1$

n	l	m	s
5	0	0	+ 1/2

15. (b) Aufbau's principle : electron fills in orbital increasing order of energy level.

16. (b) ${}^{70}_{30}\text{Zn}^{2+} = n = A - Z = 70 - 30 = 40$

17. (c) $n > l,\quad m = -l\ \text{ to } +l$

n	l	s
3	2	½

The value of (m) is wrong

$l = 2,\ m = -2, -1, 0, +1, +2$

18. (b) Hund's rule

19. (b) $\text{Cr} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$; $\text{Mn}^+ = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

i.e., it represents both ground state and cationic form.

20. (c) $\text{Fe}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5\ \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

21. (d) Schrödinger's equation gives only n, l and m quantum number. Spin quantum number is not related to Schrodinger equation.

22. (a) $$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + \frac{1}{2}mv^2$$

$$\text{K.E.} = hc\left(\frac{\lambda_0 - \lambda}{\lambda\lambda_0}\right) = \frac{1}{2}mv^2$$

$$\left(\frac{h^2}{2m\lambda_e^2}\right) = hc\left(\frac{\lambda_0 - \lambda}{\lambda\lambda_0}\right)\left(\therefore \lambda = \frac{h}{\sqrt{2mK\cdot E}}\right)$$

$$\lambda_e^2 = \frac{\lambda\lambda_0 h}{[\lambda_0 - \lambda]2mc}$$

$$\lambda_e = \left[\frac{h\lambda\lambda_0}{2mc[\lambda_0 - \lambda]}\right]^{\frac{1}{2}}$$

23. (c) m_n = mass of neutron; m_p = mass of proton

$$\frac{m_n}{2} \qquad 2m_p$$

atomic mass $\Rightarrow (m_n + m_p)$ $\quad [m_n \sim m_p]$

$\Rightarrow\quad (8 + 6) = 14\ m_p$

new atomic mass $\Rightarrow (4 + 12) = 16\ m_p$

$$\%\text{ increase} = \frac{16 - 14}{14} \times 100 = 14.28\ \%$$

24. (b) $$\frac{1}{\lambda} = R_H Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

for shortest wavelength $n_2 = \infty$, $n_1 = 2$

$$\frac{1}{\lambda} = R_H 2^2\left[\frac{1}{4} - \frac{1}{\infty}\right] \quad \lambda = \frac{4}{4R_H} = \frac{1}{R_H} = x$$

for longest wavelength of Parchan series $n_2 = 4$, $n_1 = 3$

$$\frac{1}{\lambda} = R_H \cancel{z}^2\left[\frac{1}{9} - \frac{1}{16}\right] \quad \frac{1}{\lambda} = R_H 3^2\left[\frac{7}{9\times16}\right]$$

$$\lambda = \frac{9\times16}{9\times7}\times\frac{1}{R_H} \Rightarrow \lambda = \frac{16}{7}x$$

25. (b) $(\text{IE})_{\text{Li}^{2+}} = (\text{IE})_\text{H} \times Z^2$

$= 21.8 \times 10^{-19} \times 9$ J/atom

$\therefore$ Kinetic energy of ejected electron

$= 8 \times 21.8 \times 10^{-19}$ J atom

$$\lambda = \frac{h}{\sqrt{2\text{KE}\cdot m}} = \frac{h}{\sqrt{2qV\cdot m}}$$

$$\lambda = \frac{6.62\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times2.18\times10^{-19}\times8}}$$

$\lambda = 1.17$ Å

26. (b) $\text{Fe}^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

Unpaired electron (n) = 4

Magnatic moment

$= \sqrt{n(n+2)}\ BM = \sqrt{4(6)} = \sqrt{24}\ BM$

Orbital angular momentum

$= \sqrt{l\times(l+1)}\,\hbar = \sqrt{2(3)}\,\hbar \Rightarrow \sqrt{6}\,\hbar$

27. (a) $$\lambda = \frac{h}{\sqrt{2KE\cdot m}} \qquad \lambda \propto \frac{1}{\sqrt{2qV\cdot m}}$$

$$\lambda_e \propto \frac{1}{\sqrt{M_e\times16E}};\ \lambda_{p^+} = \frac{1}{\sqrt{M_p\times4E}}$$

$$\lambda_\alpha \propto \frac{1}{\sqrt{4M_p\times4E}};\ \text{hence } \lambda_e > \lambda_{p+} = \lambda_\infty$$

28. (a) $\text{Li (g)} \longrightarrow \text{Li}^+ + e^-$; $\quad \Delta\text{H} = 520$

$\text{Li}^+ \text{(g)} \longrightarrow \text{Li}^{+2} + e$; $\quad \Delta\text{H} = a$ KJ/mol

$\text{Li}^{2+} \text{(g)} \longrightarrow \text{Li}^{2+} + e$; $\quad \Delta\text{H} = b$ KJ/mol

$b = (IE_2)_{\text{Li}^+}$ and $(\text{IE})_{\text{Li}^{2+}} = (\text{IE})_n \times z^2 = 1313 \times 9$

$b = (IE_2)_{\text{Li}^+} = 11817$ KJ/mol

$520 + a + 11817 = 19800$

$(IE_2)_{\text{Li}^+} = a = 7463$ KJ/mol

29. (b) $$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow R_H\left(\frac{n_2^2 - n_1^2}{n_1^2 n_2^2}\right)$$

$$\lambda = \frac{(n_2^2\,n_1^2)}{(n_2^2 - n_1^2)} \times \frac{1}{R_H}$$

First line of Lymen series $n_2 = 2$, $n_1 = 1$

Second line of Lymen series $n_2 = 3$, $n_1 = 1$

Third line of Lymen series $n_2 = 4$, $n_1 = 1$

30. (c) The anode ray/canal ray is independent to the electrode material.

31. **(c)** Energy order decide from $(n + l)$ rule; $(n + l)$ is minimum, energy is minimum. If $(n + l)$ value is equal, lower the value of 'n', lower the energy.

$$e3 > e2 > e4 > e1$$

32. **(d)** $r_1 = \frac{r_2}{n^2}\, r_1 = \frac{r}{4}$; $\quad r_3 = r_1 \times n_2$

$$r_3 = r/4 \times 9 \qquad r_3 = 2.25R$$

33. **(c)** $\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-34} \times 3600}{0.2 \times 5}$

$$\lambda = 2.38 \times 10^{-30} \text{ metre}$$

34. **(c)** According to Paulis, an orbital can accomdate maximum two electrons. Hence Paulis exclusion principle violates.

35. Cu(29) = $1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 4s^1 \quad 3d^{10}$

Form $(m = 0)$ = 2 + 2 + 2 + 2 + 2 + 1 + 2

= 13 electron

36. Cd^{+2} $[z = 48]$

Azimuthal $l = 1$ only for p-orbital

upto 48 → $2p^6\ 3p^6\ 4p^6 = 18e$

37. $A \longrightarrow 30$ W $\qquad E_A$ (photon) = 13.6 eV

$B \longrightarrow 40$ W $\qquad E_B$ (photon) $= 13.6 \times 2^2 = 4 \times 13.6$ eV

For $A(13.6 \times 1.6 \times 10^{-19}) \times n_A = 30$

For $B\ (4 \times 13.6 \times 1.6 \times 10^{-19}) \times n_B = 40$

$$\frac{n_A}{4n_B} = \frac{3}{4}$$

$$\Rightarrow \quad \frac{n_A}{n_B} = \frac{3}{1}$$

38. $n_2 = 11$ higher state

$n_1 = 1$ lowest state

U.V. = 11 – 1 = 10

Visible = 11 – 2 = 9

Remaining $= \frac{11 \times 10}{2} - 19 = 55 - 19$

(z) I.R. = 36

Hence, $z - (x + y) = 36 - (9 + 10) = 17$

39. Number of angular nodes $= l = 2$ (d-orbitals) and number of maxima $= n - l = 3 \Rightarrow n = 5$

40. $2\pi r_n = n\lambda$

$$4 \longrightarrow 2$$

$$\lambda_4 = \frac{2\pi r_4}{4} \qquad \lambda_2 = \frac{2\pi r_2}{2}$$

$$\lambda_4 - \lambda_2 = 2\pi\left[\frac{0.529(4)^2}{1 \times 4} - \frac{0.529(2)^2}{2}\right]\text{Å}$$

$$= 2\pi\,(0.529) \times 2$$

$$= 4\pi r_1 = 6.64 \text{ Å}$$

41. $\frac{\lambda_P}{\lambda_\alpha} = \left(\frac{1}{2}\right) = \frac{\dfrac{h}{m_p \cdot v_p}}{\dfrac{h}{m_\alpha v_\alpha}} = \frac{m_\alpha v_\alpha}{m_p \cdot v_p}$

$$\frac{m_P}{m_\alpha} = \frac{1}{4} \quad ; \quad \text{or } \frac{1}{2} = \frac{4}{1} \cdot \frac{v_\alpha}{v_p}$$

$$\frac{v_p}{v_\alpha} = \frac{8}{1} \quad ; \quad \text{or } \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mKE}}$$

Now,

$$\frac{\lambda_p}{\lambda_\alpha} = \frac{1}{2} = \frac{\dfrac{h}{\sqrt{2m_p \cdot KE_p}}}{\dfrac{h}{\sqrt{2m_\alpha \cdot KE_\alpha}}} \quad ; \quad \text{or} \left(\frac{1}{2}\right)^2 = \frac{2m_\alpha \cdot KE_\alpha}{2m_p \cdot KE_p} = \frac{1}{4}$$

$$\text{or,} \quad \frac{4}{1} \cdot \frac{\text{K.E.}_\alpha}{\text{K.E.}_p} = \frac{1}{4} \quad ; \quad \therefore \frac{\text{K.E.}_p}{\text{K.E.}_\alpha} = \frac{16}{1}$$

44. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

$(n + l) = 3$ means

$2p^6$ and $3S^2$

$l = 2$ means $3d^{10}$

$n + l = 3 \Rightarrow 8$ electron

$l = 2 \Rightarrow 10$ electron

$8 \times 10 = 80$

45. Ga last e^{-1} in $4P^1$

$\therefore \quad n = 4, l = 1$

$m = -1$ or O or $+1$

$S = +½$ or $-½$

or single e^- system.

46. Bohr's theory is applicable to H and H-like species.

47. Conceptual

48. $V_n = 2.18 \times 10^8 \times \frac{Z}{n}\text{cms}^{-1}$

for V_n to be maximum; for hydrogen atom

$Z = 1, n = 1 \therefore V = 2.18 \times 10^8$ cms^{-1}

49. We know that $v \propto \frac{1}{n}$ and n = principal quantum number. Therefore, vn will be independent of the principal quantum number.

50. –P.E. = 2K.E. = 2 × (+13.6) = 27.2 eV.

$\therefore \quad$ P.E. = –27.2 eV

P.E. with respect to ground state = 27.2 eV, which we assume to be zero.

$$\text{K.E.} = -\frac{13.6}{n^2}\text{eV}$$

For the first excited state, $n = 2$.

$$\therefore \quad \text{K.E.} = -\frac{13.6}{2^2}\text{eV} = -3.4 \text{ eV}$$

Total energy = (27.2 –3.4)eV = 23.8eV.

51. $T = \frac{2\pi r_n}{u_n} = \frac{2\pi r_1 \times n^2}{u_1/n}$ or $\qquad T \propto n^3$; $n = 2$ here

52. $\Delta E = E_2 - E_1$; $E_2 - E_1$ or $\lambda \propto \frac{1}{(E_2 - E_1)}$

53. N = number of lines emitted

$$= \frac{\text{diff.} \times (\text{diff.} + 1)}{2} = \frac{3(3+1)}{2} = \frac{12}{2} = 6$$

54. $h\nu_1 = h\nu_0 + \text{K.E.}_1$

$2h\nu_1 = h\nu_0 + \text{K.E.}_1$

$\text{K.E.} = h\nu_1 - h\nu_0$

The value of K.E. will increase but more than double of the previous K.E.

55. Aufbau's principle

56. For outermost electron of Rb, the configuration is $5s^1$.

57. The electronic configuration of sulphur atoms $1s^2s^22p^63s^23p^4$, the orbitals with $(n + l) = 3$ are $2p$ and $3s$, therefore 8 electrons in sulphur atom have $(n + l) = 3$.

58. Orbital angular momentum

$$= \sqrt{l(l+1)}\frac{h}{2\pi} = \sqrt{0(0+1)}\frac{h}{2\pi} = 0$$

59. Number of unpaired electrons in V, Cr and Mn is 3, 6 and 5.

60. Double dumb bell shaped in 4th principle quantum number means $4d$

$n - l - 1 = 4 - 2 - 1 = 1$

61. Charge/mass for $n = 0, \alpha = \frac{2}{4}, p = \frac{1}{1}, e = \frac{1}{1/1837}$

So, order is n, α, p, e.

62. Charge/mass for

$n = 0$, $\alpha = 2/4$, $p = 1/1$ and $e = \frac{1}{1/1837}$

63. Number of p, n and e are 20, 20 and 20.

64. Isotonic : same number of neutrons

65. Conceptual

66. $r = r_0\frac{n^2}{Z} = 0.529 \times 10^{-8}\,\text{cm}$

67. $\frac{\text{Radius of second Bohr orbit}}{\text{Radius of first Bohr orbit}} = \frac{0.529}{0.529} \times \frac{2^2}{1} = 4$

68. $r_{\text{Be}}^{3+} = \frac{0.529 \times (2)^2}{4} = 0.529$

69. Absorption line in the spectra arise when energy is absorbed, i.e., electron shifts from lower to higher orbit. Maximum wavelength means minimum energy so, the transition involving minimum energy is the right option.

70. Conceptual

71. $\bar{V}_H = R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$; $Z = 1$ for H-atom

$\bar{V}_{\text{Be}^{3+}} = R_H \times 16\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$; $Z = 4$ for Be^{3+}

Thus, $\bar{V}_{\text{Be}^{3+}} = 16\bar{V}_H = 16 \times 15200\,\text{cm}$

$= 2.432 \times 10^5\,\text{cm}^{-1}$.

72. $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{(0.2) \times 5/(60 \times 60)} = 2.37 \times 10^{-30}\,\text{m}$

73. $\lambda = \frac{h}{mv}$ λ will be large if m is small.

74. According to *de Broglie*

$$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-27}\,\text{erg sec}}{\frac{2}{6.023 \times 10^{23}} \times 5 \times 10^4\,\text{cm/sec}}$$

$$= 4 \times 10^{-8}\,\text{cm} = 4\text{Å}$$

75. $Z = 20$, so electronic configuration is

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$

$\therefore$ for outer most electron $4s$ electron $n = 4$, $l = 0$, $m = 0$, $s = +\frac{1}{2}$

76. The electronic configuration of Ar atom is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$. In its first excitation state, the electron from $3p$ will unpair and shift to $4s$ where its quantum numbers will be 4, 0, 0, ± ½.

77. Most electro-negative element is F.

$\therefore$ electronic configuration: ns^2np^5

78. Angular nodes are only associated with directional orbital.

79. $E_{2(\text{He}^+)} = \frac{E_1}{n^2} = -13.6 \times \frac{2^2}{n^2} = -13.6 \times \frac{4}{4} = -13.6\,\text{eV}$

80. $E_n = -13.6 \times \frac{Z^2}{n^2}$

$$\frac{E_{n(\text{H})}}{E_{n(\text{Be}^{+3})}} = \frac{1}{\frac{4^2}{4}} = \frac{1}{4} = 1:4$$

81. Ratio $= E_2 - E_1/E_3 - E_2 = \frac{3}{4}\Big/\frac{5}{36} = \frac{27}{5}$

82. $\frac{1}{\lambda} = R_HZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$ for Balmer series

$$\frac{1}{\lambda} = R_H \times 1^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{R_H5}{36}\text{cm}^{-1}$$

83. $\frac{1}{\lambda_H} = R_H \times 1^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$ ...(A)

$\frac{1}{\lambda_X} = R_H \times Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$ ...(B)

Dividing (A) by (B), we get

$\frac{\lambda_X}{\lambda_H} = \frac{1}{Z^2}$

$\frac{1}{4} = \frac{1}{Z^2}$

$Z = 2$ (He^+)

84. for hydrogen

$$Z_H^2 \times \left(\frac{1}{1} - \frac{1}{3^2}\right) = Z_X^2\left(\frac{1}{3^2} - \frac{1}{9^2}\right)$$

sixth line of Paschen series = 9

$$\frac{8}{9} = Z_X^2\left(\frac{1}{9} - \frac{1}{81}\right)$$

$$\frac{8}{9} = Z^2\,\frac{8}{81}$$

$Z^2 = 9$

$Z = 3$ (Li^{+2})

85. $h\nu = h\nu_0$ zero velocity K.E. = 0

$h\nu = h\nu_0$

$h\nu = 4$ eV

$$\frac{hc}{\lambda} = 4 \text{ eV}$$

$$\lambda = \frac{h \times c}{4 \text{ eV}} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{4 \times 1.6 \times 10^{-19}} = 3100 \text{ Å}$$

86. $\lambda = \frac{h}{\sqrt{2mKE}}$ K.E. = eV K.E. = eV = qV

same mass

$$\frac{\lambda_1}{\lambda_2} = \frac{\sqrt{\text{KE}_2}}{\sqrt{\text{KE}_1}} = \frac{\sqrt{2}}{1}$$

$\therefore \quad \lambda_1 = \sqrt{2}\,\lambda_2$

87. $\lambda = \frac{h}{mV} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.2 \times 10^{6}}$

$= 0.33 \times 10^{-9}$

$= 0.33$ nm

88. $\lambda = \frac{h}{mV} = \frac{6.626 \times 10^{-34}}{0.200 \times 10^{-3} \times 5/3600}$

$= 2.3853 \times 10^{-27}$ m

89. Total energy = $-\frac{e^2}{2r_n} = -3.4 \text{ eV} = \frac{E_1}{n^2}$

$$\therefore \quad n^2 = \frac{-13.6}{-3.4} = 4$$

$n = 2$

The velocity in second orbit

$$= \frac{U_1}{2} = \frac{2.18 \times 10^{8}}{2} \text{ (cm sec}^{-1}\text{)}$$

$$\lambda = \frac{h}{mu} = \frac{6.626 \times 10^{-27} \times 2}{9.1 \times 10^{-28} \times 2.18 \times 10^{8}}$$

$= 6.6 \times 10^{-10} = 6.6$ Å

90. Shape of *s*-orbital is spherical, so it is non–directional orbital.

91. $\frac{1}{\lambda} = R_H Z^2\left(\frac{1}{1^2} - \frac{1}{\infty}\right)$

$$E = \frac{hc}{\lambda} = \frac{R_H hcZ^2}{1}$$

92. $E = \frac{hc}{\lambda}$

$\Rightarrow \quad \lambda \propto \frac{1}{E}$

$$\therefore \quad \frac{\lambda_1}{\lambda_2} = \frac{E_2}{E_1} = \frac{4000 \text{ Å}}{2000 \text{ Å}}$$

$\therefore \quad \lambda_1 : \lambda_2 = 2 : 1$

93. For a '*d*' electron, $l = 2$

Orbital angular momentum

$$= \sqrt{l(l+1)}\,\frac{h}{2\pi} = \sqrt{6}\,\frac{h}{2\pi} \quad \text{or} \quad \sqrt{6}\hbar$$

94. $E = -13.6\, eV \times \frac{1^2}{2^2} = -3.4 \text{ eV}$

95. $\Delta P \cdot \Delta x \geq \frac{h}{4\pi}$

96. $n = 4$

$l = 2$

$m = -2, -1, 0, +1, +2$

$s = \pm\frac{1}{2}$

97. $\frac{1}{\lambda} = R_H (1)^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$

$$= R_H \cdot \left(\frac{5}{36}\right)\text{cm}^{-1} \text{ or } \bar{\nu} = \left(\frac{5R_H}{36}\right)\text{cm}^{-1}$$

98. For Balmer series $n_2 = 2$

Fourth line is 6 to 2

99. I.P. = $-E_1 = -13.6 \times \frac{2^2}{n^2} = -\frac{-13.6 \times 4^2}{1^2}$ (for I.P., *n* always = 1)

= 217.6 eV

100. Required energy = 10^{-17} J = $n \times \frac{hc}{\lambda}$

$$\Rightarrow \quad n \times \frac{6.625 \times 10^{-34} \times 3 \times 10^{8}}{550 \times 10^{-9}} \text{J} = 10^{-17}\text{J}$$

$\therefore \quad n = 28$

101. $E(\text{eV}) = \frac{hc}{\lambda} = \frac{1242}{\lambda(\text{nm})} = \frac{1242}{700 \text{ nm}} = 1.77 \text{ eV}$

102. $E = h\nu$

$= (6.62 \times 10^{-34}$ Js) $(880\ s^{-1})$

$= 5.831 \times 10^{-31}$ J.

Number of photons emitted = $\frac{1}{5.831} \times 10^{+31} = 1.71 \times 10^{30}$ per second.

103. For a proton ($^1_1$H), $\frac{e}{m} = \frac{1}{1}$

For an *a*-particle ($^4_2$He), $\frac{e}{m} = \frac{2}{4} = \frac{1}{2}$

$$\frac{(e/m)_p}{(e/m)_\alpha} = \frac{1/1}{1/2} = 2:1$$

104. The *de Broglie* equation is $\lambda = \frac{h}{p} = \frac{h}{mv}$

Here h and v are constant. So $\lambda \propto \frac{1}{m}$.

Since the a-particle has the highest mass among the given entities, it has the smallest *de Broglie* wavelengths.

105. $E_n = -\frac{13.6}{n^2} Z^2$, where $n = 1$ for ground state, 2 for first excited state, and so on. $Z = 1$ for hydrogen.

106. $\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ for H atom.

For the Balmer series,

$n_1 = 2$ and $n_2 = 5$ (for the third line).

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = \frac{21}{100} R_\infty$$

$$\lambda = \frac{100}{21 R_\infty}$$

107. $l = 3$ mean f subshell have 7 orbital.

Maximum multiplicity for the f orbitals (7 electrons)

$= 2s + 1 = 2 \times 7/2 + 1 = 8$

Minimum multiplicity for the f orbital (1 electron)

$= 2s + 1 = 2 \times 1/2 + 1 = 2$

108. $E_n = -13.6 \times \frac{Z^2}{n^2} \text{eV}$

For the 3rd excited Bohr's orbit of H atom

$\Rightarrow$ $Z = 1, n = 4$

$E_1 = -13.6$ eV

For 3rd excited state of hydrogen

$$E_2 = -13.6 \times \frac{1^2}{4^2} = -0.85 \text{ eV}$$

109. $E_n = \frac{-13.58}{n^2}$

at $n = 1$, $E_1 = -13.58$ eV

(In primitive stage) $n = 2$, $E_2 = -3.395$ eV

Energy absorbed $= -3.395 + 13.58 = 10.19$ eV

110. $r_n = r_1 \times \frac{n^2}{Z}$

$$r_2 = r_1 \times \frac{4^2}{2} = 0.106 \text{ nm}$$

111. $r_n = r_0 \times \frac{n^2}{Z}$, here $Z = 1$

$r_n \propto n^2$

So $r_1 : r_2 : r_3 \ldots = n_1^2 : n_2^2 : n_3^2 \ldots$

$= 1^2 : 2^2 : 3^2$

$= 1:4:9$

112. If electron is accelerated by V volt

$$\text{K.E.} = \text{eV} = \frac{1}{2} mv^2$$

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{h}{\sqrt{2eVm}}; \lambda = 1 \text{ Å}$$

On solving $\lambda = \sqrt{\frac{150}{V}}$ Å for electron

$$\lambda = 1 \text{ Å} = \sqrt{\frac{150}{V}} \quad \therefore \quad V = 150 \text{ Volt}$$

113. Number of unpaired electrons in $Cr^{3+} = 3$

114. Violates Hund's law

115. $1.73 = \sqrt{n(n+2)}$ $V = 3d^3 4S^2$

$n = 1$

Oxidation state = 4

116. $\Delta p \cdot \Delta x \geq \frac{h}{4\pi}$

Given $\Delta p = \Delta x$

$$(m\Delta v)^2 \geq \frac{h}{4\pi}$$

$$\Delta v \geq \frac{1}{2m} \sqrt{\frac{h}{\pi}}$$

117. For the second line of Lyman series of H,

$n_1 = 1, n_2 = 3$

$$\frac{1}{\lambda_H} = R \times 1^2 \left[\frac{1}{1^2} - \frac{1}{3^2} \right] = \frac{8R}{9}$$

$$\therefore \quad \lambda_H = \frac{9}{8R} \qquad \ldots\text{(i)}$$

For the sixth line of Paschen series,

$n_1 = 3, n_2 = \infty$

$$\frac{1}{\lambda_x} = RZ^2 \left[\frac{1}{3^2} - \frac{1}{\infty^2} \right] = RZ^2 \left[\frac{1}{9} - \frac{1}{0} \right] = \frac{RZ^2}{9}$$

$$\therefore \quad \lambda_x = \frac{9}{RZ^2} \qquad \ldots\text{(ii)}$$

But, $\lambda_H = \lambda_X$

i.e.; $\frac{9}{8R} = \frac{9}{RZ^2}$ $\quad \therefore Z^2 = 8$

$$Z = \sqrt{8} \simeq 3$$

i.e., Li^{+2} – ion.

118. According to the question

$$\lambda = \frac{h}{p}$$

$$\lambda_A = \frac{h}{p_A} \qquad \ldots\text{(i)}$$

$$\lambda_B = \frac{h}{p_B} \qquad \ldots\text{(ii)}$$

$$\frac{\lambda_A}{\lambda_B} = \frac{p_B}{p_A} \qquad \lambda_B = 10^{-7} \text{ m}$$

119. We know that

$r_n = r_1 \times n^2$

$9r_1 = r_1 \times n^2$

$\therefore\ n^2 = 9$

$\therefore\ n = 3$

$$\therefore\ E_3 = -\frac{13.6}{3^2} = -1.51\,\text{eV}$$

120. According to Bohr's atomic model

$mvr = nh/2\pi$

$$4.2176 \times 10^{-34} = n_2 \times \frac{6.62 \times 10^{-34}}{2 \times 3.14}$$

$\therefore\ n_2 = 4$

$$\frac{1}{\lambda} = R \times 1^2 \left[\frac{1}{3^2} - \frac{1}{4^2}\right]$$

$\therefore\ \lambda = 18.75 \times 10^{-7}$ m

121. $E_3 - E_1 = \Delta E = \frac{hc}{\lambda}$

$$\lambda = \frac{hc}{\Delta E} \text{ or } \lambda(\text{nm}) = \frac{1242}{\Delta E(\text{rev})} = \frac{1242}{12.4\text{ ev}}$$

$\lambda = 1030$ Å = 103 nm

122. $h\nu$ = work function + K.E.;
Given K.E. = 0;

Thus, $h\nu = 4$ eV or $4 = \frac{1242}{\lambda(\text{nm})}$

123. $\text{K.E.} = \frac{1}{2}mu^2 = \frac{Ze^2}{2r}$, $\text{T.E.} = -\frac{Ze^2}{2r}$ $\therefore$ (A)

124. The state corresponds to the 3*d* atomic orbitals.

125. The 21st electron corresponds to $3d^1$. For this orbital, $n = 3, l = 2, m = 2, s = +\frac{1}{2}$.

126. Mn^{4+} (21 electrons) = $[Ar]3d^3$ contains three unpaired electrons.

127. The spin-only formula is given by $m_{\text{spin only}} = \sqrt{n(n+2)}\ BM$

n = No of unpaired e^-

The value of m = 2.83 BM corresponds to the presence of two unpaired electrons. So the ion is Ni^{2+} ($3d^8$).

128. For the 3*p* orbital, $n = 3$, $l = 1$.
The number of spherical nodes = $n - l - 1 = 3 - 1 - 1 = 1$

129. Spin multiplicity = $(2S + 1)$.

130. (a) $\frac{r_A}{r_N} = 10^5$

$$\frac{V_A}{V_N} = \left(\frac{r_A}{r_N}\right)^3 = (10^5)^3 = 10^{-15}$$

131. (a) neon and O^{-2} have 10 electron

132. (a) $\lambda = \frac{C}{\nu} = \frac{3 \times 10^8}{400 \times 10^6} = 0.75$ m

133. (a) $R = R_0 A^{1/3} = 1.33 \times 10^{-13} \times (64)^{1/3}$ cm
$= 5.32 \times 10^{-13} \approx 5$ fm

$\because$ 1 fm = 10^{-15} m ≈ 5 fm

134. (b) $d = 20$ nm

$r = \frac{20}{2} = 10$ nm = 100 A°

$\because\ r = 0.529 \times \frac{n^2}{Z}$ A° For H atom $Z = 1$

$100 = 0.529 \times n2$ $\quad n = 14$

135. (b) $E_n = -13.6 \times \frac{Z^2}{n^2}$

$E_1(H) = -13.6 \times \frac{1}{1} = -13.6$ eV

$E_2(He^+) = -13.6 \times \frac{4}{4} = -13.6$ eV

$E_3(Li^{2+}) = -13.6 \times = \frac{3^2}{3^2}\ -13.6$ eV

$E_4(Be^{3+}) = -13.6 \times = \frac{4^2}{4^2} -13.6$ eV

$\therefore$ B is the answer.

136. (c) $E = -78.4$ kcal/mol

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

for H atom $Z = 1$ $\quad -78.4 = 313.6 \times \frac{1}{n^2}$

$n^2 = \frac{313.6}{78.4}$ $\quad n = 2$

137. (a) $V_n = 2.188 \times 10^6 \times$ m/sec.

$$\frac{V_3(Li^{2+})}{V_1(H)} = \frac{Z_3/n_3}{Z_1/n_1} = \frac{3/3}{1/1} \qquad V(Li^{2+}) = V$$

138. (a) Let state (A) = n_1
State (B) = n_2

$r_1 - r_2 = 624\ r_0$

$$0.529 \times \frac{n_1^2}{Z} - \frac{0.529 n_2^2}{Z} = 624 \times \frac{0.529 \times 1}{Z}$$

$n_1^2 - n_2^2 = 624$

$n_1 = 25$

$n_2 = 1$

$25 \rightarrow 1$

139. (c)

(a) Energy of ground state
$He^+ = -13.6 \times 4$ eV $= -54.4$ eV

(b) P.E. of first orbit of H-atom $\frac{0.529 \times 1}{Z}$ = 2T.E. = -2×13.6 eV $= -27.2$ eV

(c) Energy of second excited state

$$= -13.6 \times \frac{Z^2}{n^2} = -13.6 \times \frac{(2)^2}{(3)^2}$$

$$= -13.6 \times \frac{4}{9} = -6.03\text{ eV}$$

(d) I.E. $= -E_1 = 21.8 \times 10^{-19} \times 4\text{J} = 8.7 \times 10^{-18}$ J

140. **(d)** For d_{yz}, xy and xz are nodal palne
node = $(n - l - 1) = 6 - 2 - 1 \Rightarrow 3$

141. **(b)**
$$x \longrightarrow y + {}_{2}^{4}\text{He}$$
$$y \longrightarrow {}_{8}\text{O}^{18} + {}_{1}\text{H}^{1}$$
$$y = {}_{9}y^{19}$$
$$x = {}_{11}x^{23}$$
Hence x = Na
Na present in third period
Number of neutron = $23 - 11 \Rightarrow 12$
$$\text{Mole of Na} = \frac{4.6}{23} \Rightarrow 0.2$$
Mole of neutron $\Rightarrow 0.2 \times 12 \Rightarrow 2.4$

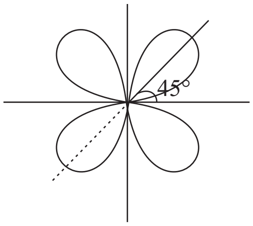
142. **(c)** $E = \dfrac{hc}{\lambda} \Rightarrow \dfrac{1240}{\lambda_{\text{nm}}}\text{eV} \quad E = \dfrac{1240}{31} \Rightarrow 40 \text{ eV}$
$$40 = 12.8 + \text{K.E.}$$
$$\text{K.E.} = 40 - 12.8 = 27.2 \text{ eV}$$
$$\text{K.E.} = 27.2 \times 1.6 \times 10^{-19}$$
$$27.2 \times 1.6 \times 10^{-19} = \frac{1}{2} \times 9.1 \times 10^{-31} \times v^2$$
$$v = 2.18 \times \sqrt{2} \times 10^6 \text{ m/s}$$

143. **(d)** Frequency $= \dfrac{1}{T} \propto \dfrac{v}{r} \propto \dfrac{\cancel{z}/n}{n^2/\cancel{z}}$
$$\text{Frequency} = \frac{1}{T} \propto \frac{\cancel{z}^2}{n^3} \quad T \propto \frac{n^3}{\cancel{z}^2} = \frac{1/4}{8/1} \Rightarrow \frac{1}{32}$$

144. **(a)** s-orbital is spherical hence it is non-directional.

145. **(c)** $\Delta x = 2\Delta p \qquad \Delta x \cdot 2\Delta p = \dfrac{h}{4\pi}$
$$2(\Delta p)^2 = \frac{h}{4\pi} \qquad (\Delta v)^2 = \frac{h}{8\pi m^2}$$
$$\Delta v = \frac{1}{2m}\sqrt{\frac{h}{2\pi}} \qquad \Delta v = \frac{1}{2m}\sqrt{h}$$

146. **(c)**



147. **(c)** $n = 5$
l = 0, 1, 2, 3, 4,
s, p, d, f, g

148. (Theory Based)

149. **(c)** From $(n + l)$ rule

150. **(d)** The value of $l = 0$ to $(n - 1)$
Number of electron for given value of $l = 2(2l + 1)$
$$\text{Hence} \sum_{l=0}^{l=(n-1)} 2(2l+1)$$

LEVEL II

1. **(d)** last e^- enter in 2P subshell
$\therefore \quad l = 1$

2. **(d)**
$$\begin{array}{lccccccccccl} & \text{Pd} & 1s^2 & 2s^2 & 2p^6 & 3s^2 & 3p^6 & 4s^2 & 3d^{10} & 4p^6 & 5s^0 & 4d^{10} \\ \text{(I) } l = 0 & & \downarrow & \downarrow & & \downarrow & & \downarrow & & & \downarrow & \\ & & 2 & 2 & & 2 & & 2 & & & 0 & = 8 \text{ electrons} \end{array}$$
(II) Z is different, therefore, Z_{eff} will be different.
(III) Configuration of ${}_{26}\text{Fe} \rightarrow [\text{Ar}]\, 4s^2\, 3d^5$
Configuration of $\text{Ni}^{+2} \rightarrow [\text{Ar}]\, 3d^8\, 4s^0$
Number of unpaired electrons are different.
(IV) 57 electron (La) $5d^1$
$n = 5$
$l = 2 \qquad \left(\dfrac{l}{n}\right) = 0.4$

3. **(a)** A^{+2} have 22 electron
A has 24 electron / 24 p^+
$n^0 = 26$
(i) Mass number of $A = 50$
Atomic number is 24
$3d^5 4s^1$
(iv) A^{+2} 1 electron is removed from s and 1 from d.

4. **(a)** Ga (31) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}\, 4p^1$
$n = 4$
$l = 1 \quad n + l + m = 6$
$m = 1$

5. **(b)**
(a) Fe^{+3} $[\text{Ar}]3d^5$
Co^{+3} $[\text{Ar}]\ 3d^6$
More the number of unpaired electron, more will be multiplicity.
$$\text{(b)} \left.\begin{array}{l} \text{Ti}^{+3}[\text{Ar}]3\text{d}^1 \\ \text{Cr}^{+}[\text{Ar}]3\text{d}^5 \\ \text{Sc}^{+2}[\text{Ar}]\text{ed}^1 \end{array}\right\} \text{are paramagnetic}$$
(c) Mg [Ne] $3s^2$
$n = 3, l = 0, m = 0$
$\therefore \quad n + l + m = 3$
(d) Cl $(1s^2)\ (2s^2\, 2p^6)\ (3s^2\, 3p^5)$
$\sigma = 6 \times 0.35 + 8 \times 0.85 + 2 \times 1 = 10.9$
$Z_{\text{eff}} = 17 - 10.9 = 7.1$

6. **(a)** Element is Na
$\therefore$ number of neutron = 12
$\therefore$ number of proton and electron = 11
(a) Mg^{24} also has 12 neutrons
(b) $3s^1$ is last electron
(c) H_2O has 10 electrons
(d) Since atoms have 1 unpaired electron $\therefore$ it is paramagnetic.

7. (b)

(a) $_{12}$Mg $1s^2\,2s^2\,2p^6\,3s^2$ (Diamagnetic)

(b) $_{20}$Ca $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2$ (Paramagnetic)

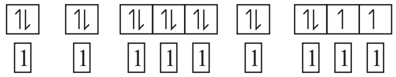
(c) $_{28}$Ni $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$ (Diamagnetic)

(d) $_{30}$Zn $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2$ (Diamagnetic)

8. (a) For 2.84 B.M., 2 unpaired electrons are required.

Fe^{2+}	[Ar]	$3d^5$
Cr	[Ar]	$3d^5{\cdot}4s^1$
Cr^{+3}	[Ar]	$3d^3$
Ti^{+2}	[Ar]	$3d^2$
Mn^{+2}	[Ar]	$3d^5$
V^{+3}	[Ar]	$3d^2$

9. (a) $S = 1s^2 2s^2 2p^6 3s^2 \quad 3p^2$



$S = +1/2$

minimum (7) e^-

$S = +1/2 \qquad [16 - 7] = 9$

Maximum ($9e^-$)

(b) e with $m = 0$ present in s-orbital is not compulsory as the value of n increases m also be 0.

(c) Na^{+1} Mg^{+2} all isoelectronic species have same σ but different Z_{eff}

(d) Number of subshell n^{th} shell is equal to n.

10. (d) $l = 2$

Fe (26) = $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$

Fe^{2+} (24) = $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6$

$l = 2 \Rightarrow d$

Electron present in ($l = 2$) d-orbitals = 6

11. (a) $1s^4 \quad 2s^4 \quad 2p^8 \quad 3s^4 \quad 3p^8 \quad 4s^2$

12. (d) Hint Use $\dfrac{v}{2\pi r}$

13. (b) $\Delta E_{Li^{+2}} = \Delta E_H$

$$13.6 \times 3^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = 13.6 \times 1^2\left[\frac{1}{1^2} - \frac{1}{4^2}\right]$$

$$\left[\frac{1}{\left(\frac{n_1}{3}\right)^2 - \left(\frac{n_2}{3}\right)^2}\right] = \left[\frac{1}{1^2} - \frac{1}{4^2}\right]$$

$\Rightarrow \quad n_1 = 3$

$n_2 = 12$

14. (c) Probability of finding and electron at a particular distance = $4\pi r^2 R^2$

$$P_1 = 4\pi r^2 R^2 = 4\pi r^2 \times \frac{4}{a_0^3} e^{-2r/a_0}$$

at $\quad r = a_0 \quad p_1 = 4\pi a_0^2 \times \dfrac{4}{a_0^3} e^{-2a_0/a_0}$

at $\quad r = a_{0/2} \quad p_2 = 4\pi \dfrac{a_0^2}{4} \times \dfrac{4}{a_0^3} e^{\frac{-2a_0}{2a_0}}$

$$\frac{p_1}{p_2} = \frac{4\pi a_0^2 \times \frac{4}{a_0^3} e^{-a_0/a_0}}{4\pi \frac{a_0^2}{4} \times \frac{4}{a_0^3} e^{-2a_0/2a_0}}$$

$$\frac{p_1}{p_2} = \frac{e^{-2}}{\frac{1}{4} e^{-1}} = \frac{4}{e}$$

15. (a) See graph in theory

16. (b) $\Delta x = 0.0001$ Å

$\Delta P = ?$

$\Delta x \times \Delta p \geq \dfrac{h}{4\pi}; \qquad \Delta P = \dfrac{h}{4\pi \times 0.0001 \text{ Å}}$

$a_0 = 0.529$ Å

$$P = \frac{h}{2\pi \times 0.529 \text{ Å}}$$

$$\frac{\Delta P}{P} = \frac{\frac{h}{4\pi \times 0.0001 \text{ Å}}}{\frac{h}{2\pi \times 0.529 \text{ Å}}}$$

$$\frac{\Delta P}{P} = \frac{2 \times 0.529}{4 \times 0.0001} = 2645$$

17. (c) $\lambda = \dfrac{h}{\sqrt{2m \times e \times V}}$

$$\lambda = \frac{h}{\sqrt{2 \times m' \times 2e \times \frac{V}{8}}}$$

$$m' \times 2e \times \frac{V}{8} = m \times e \times V$$

$m' = 4$ m

18. (a) Maximum KE of Ejected $e^- = \dfrac{1242}{253.7} - 4.65$

$= 0.245$ ev

19. (c) Spherical node : $\Psi^2 = 0$

$\sigma^2 - 4\sigma + 3 = 0; \qquad \sigma^2 - 3\sigma - \sigma + 3 = 0$

$\sigma(\sigma - 3) - 1(\sigma - 3) = 0; \quad (\sigma - 1)(\sigma - 3) = 0$

$\sigma = 1, 3; \qquad \sigma = \dfrac{2Zr}{a_0} = 1, 3$

$$r = \frac{3}{2}\frac{a_0}{Z}, \frac{1}{2}\frac{a_0}{Z}$$

20. (b) Let the orbits are n and $(n + 1)$ $mv_1r_1 = \dfrac{n\,h}{2\,\pi}$ ...(i)

$$mv_2r_2 = \frac{(n+1)h}{2\pi} \qquad \text{...(ii)}$$

The difference in angular momentum will be (ii) – (i)

or $\quad (mv_2r_2 - mv_1r_1) = \dfrac{(n+1)h}{2\pi} - \dfrac{nh}{2\pi} = \left(\dfrac{h}{2\pi}\right)$

21. (a) $\dfrac{1}{\lambda_{\min}} = R \times (1)^2 \times \left(\dfrac{1}{1^2} \times \dfrac{1}{\infty}\right); \lambda_{\min} = 911.7$ Å

22. **(a)** $v_n = \dfrac{2.19 \times 10^6 \times \text{Zm/sec.}}{n}$

For $n = 2$ of hydrogen atom

$$v_2 = \frac{2.19 \times 10^6 \times \text{m/sec}}{2} = 1.09 \times 10^6 \text{m/sec.}$$

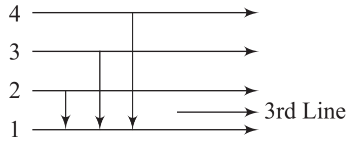
23. **(d)** $n_1 + n_2 = 4$

$$\frac{n_2 - n_1 = 2}{2n_2 = 6}$$

$\therefore \quad n_2 = 3$

For the third line of the same series;

$n_1 = 1$ and $n_2 = 4$



$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = R \times 9\left[\frac{1}{1^2} - \frac{1}{4^2}\right]$$

$\lambda = 1080$ nm

24. **(d)** $\lambda = v \quad \lambda = \dfrac{h}{mv}$

$$\lambda^2 = \Rightarrow \boxed{\lambda = \sqrt{\frac{h}{m}}}$$

25. **(b)** According to Schrodinger's model e^- behave as wave only.

26. **(b)** The maximum probability of finding an electron is described by the orbital, which is denoted by Ψ^2.

27. **(a)** $\lambda_m = \lambda_e \qquad \lambda = \dfrac{h}{mv}$

$$\frac{h}{m_c v_c} = \frac{h}{m_n v_n} \qquad \frac{v_e}{v_n} = \frac{m_n}{m_c}$$

28. **(b)** (Ψ) is the solution of Schrodinger wave equation.

29. **(d)** $2\pi r = n\lambda$ [as per de Broglie theory]

30. **(b)** $m_y = 0.25\ m_x, \qquad v_y = 0.75\ v_x$

$$\lambda = \frac{h}{mv} \qquad \lambda_x = \frac{h}{m_x v_x},\ \lambda_y = \frac{h}{m_y v_y}$$

$$\lambda_y = \frac{h}{0.25 M_x \times 0.75 v_x} \qquad \lambda_y = 5.33\ \text{A}$$

31. **(a)** Orbital angular momentum = $\sqrt{l(l+1)}\,\hbar$

	s	p	d	f
$l =$	0	1	2	3

32. **(c)** $m = (2l + 1) \Rightarrow l = \dfrac{m-1}{2}$

33. **(d)** $Mn^{4+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

↑	↑	↑		

34. **(a)** According to $(n + l)$ rule, after np, $(n + l)$ s always filled.

35. **(b)** $Ti = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

1	1			

$n = 2$

Magnetic moment = $\sqrt{n(n+2)} \Rightarrow \sqrt{2(4)} = \sqrt{8} = 2.83$ BM

36. **(d)** $T \propto \dfrac{n^3}{\cancel{z}^2} \qquad \dfrac{T_1}{T_2} = \dfrac{n_1^3}{n_2^3} = 1/8$

37. **(a)** $E_\infty - E_1 = h\nu_1, \qquad \Rightarrow \quad E_1 \Rightarrow h\nu_1$

$E_2 - E_1 = h\nu_2$

$E_\infty - E_2 = h\nu_3, \qquad \Rightarrow \quad E_2 \Rightarrow h\nu_3$

$-h\nu_3 + h\nu_1 = h\nu_2$

$$\boxed{\nu_2 = \nu_1 - \nu_3}$$

$$\boxed{\nu_3 = \nu_1 - \nu_2}$$

38. **(d)** $E_C - E_B = \dfrac{hc}{\lambda_1}$ ...(i)

$$E_B - E_A = \frac{hc}{\lambda_2} \qquad \text{...(ii)}$$

$$E_C - E_A = \frac{hc}{\lambda_3} \qquad \text{...(iii)}$$

add equations (i) and (ii)

$$E_C - E_A = hc\left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2}\right)$$

put in equation (iii)

$$hc\left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2}\right) = \frac{hc}{\lambda_3}$$

$$\frac{1}{\lambda_3} = \frac{\lambda_1 + \lambda_2}{\lambda_1\lambda_2} \Rightarrow \boxed{\lambda_3 = \frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2}}$$

39. **(d)** $\Delta E = \dfrac{hc}{\lambda}$

$$\Delta E = \frac{hc}{\lambda_1} \qquad \text{(for H atom)}$$

$$\Delta E \times z^2 = \frac{hc}{\lambda_2} \qquad \text{(for He}^+ \text{ ion)}$$

$$\frac{hc}{\lambda_1} \times 4 = \frac{hc}{\lambda_2} \Rightarrow \boxed{\lambda_2 = \frac{\lambda_1}{4}}$$

40. **(b)** First excitation potential

$= E_2 - E_1 \Rightarrow -4 + 16 \qquad \Rightarrow 12$ eV

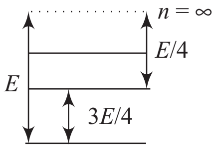
41. **(d)**

$n_2 = 4, \qquad n_1 = 3;$

$n_2 = 5 \qquad n_1 = 4;$

$n_2 = 6 \qquad n_1 = 5;$

$n \to (n - 1) \qquad (n \geq 4)$



42. **(c)** $n_2 = 5, \qquad n_1 = 1$

Total number of spectrum line are $\dfrac{\Delta n(\Delta n + 1)}{2}$

OR $\quad \Sigma(5 - 1) \Rightarrow \Sigma 4$

OR $\quad \Sigma 4 \Rightarrow 4 \quad + 3 \quad + \quad 2 \quad + \quad 1$

lyman Balmer Paschen brackett

Three line in visible reigon.

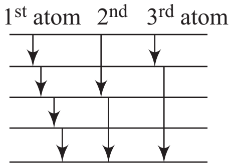
LEVEL III

(Match the Column)

1. [(A) P (B) P, Q, R, S, T (C) Q, R, S (D) P]
2. **A – r.t B-p C-q, s D – q**
3. **A – p B- p C-p, q, r, s D – p**
4. **A – r, p B – r, t C – s D – q** Conceptual
5. **A – r B - q C – p, t D - s**
   (A) for H , radius of second orbit
   $$= 0.53 \times \frac{2^2}{1} = 0.53 \times 4 \text{ Å}$$
6. **(A) → t; (B) → s ; (C) → u ; (D) → q ; (E) → p; (F) → r**
7. **(A) → u ; (B) → s ; (C) → p ; (D) → t ; (E) → q ; (F) → r**
8. **(A) → q ; (B) → p ; (C) → q, r ; (D) → r, s**
9. **(A) → r ; (B) → s; (C) → p; (D) → q**
10. **A → P, B→p, q, s, C→p, r, D → q, s**
    Radial node = $(n - l - 1)$
    Angular node = l
    $4s$, $5p_x$, 6_{dxy} having 3 radial node.
    angular node in all 's' orbital in zero.

Passage-1

11. **(b)**



12. **(b)**
13. **(c)** $\lambda = \sqrt{\frac{150}{V}}$

    $V = 24$ volt ∴ energy of free electron = 24 eV,
    $$\Delta E = 13.6 \times (Z)^2 \left[\frac{1}{6^2} - \frac{1}{\infty}\right]$$
    $$= 1.51 \text{ eV}$$
    Total energy released = 24 – (–1.51) = 25.51
14. **(b)** $(n - 2)$
    $6 - 2 = 4$
15. **(a)** Minimum energy transition for 6 → 5

Passage 3

16. **(c)** Maximum number of electrons in an orbit is $= 2n^2 = 2 \times 3^2 = 18$
17. **(d)** Maximum number of electrons in a subshell $= 2[2l + 1] = 4l + 2 = 4 \times 3 + 2 = 14$
18. **(d)** For $2p$ orbital $n = 2$, $l = 1$

Passage 4

19. **(d)** $\Delta x = 2\Delta p$
    $$\Delta x \times \Delta p = \frac{h}{4\pi}$$
    $$2(\Delta p)^2 = \frac{h}{4\pi}$$
    $$\Delta p = \frac{1}{\sqrt{2} \times 2}\sqrt{\frac{h}{\pi}}$$
    $$\Delta v = \frac{1}{2\sqrt{2}m}\sqrt{\frac{h}{\pi}}$$
20. **(b)** $\Delta v = 0.3$
    $$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.6 \times 10^{-27}}{4 \times 3.14 \times 9.1 \times 10^{-28} \times 0.3} = 1.92 \text{ cm}$$
21. **(d)** When $\Delta x = 0$, $\Delta p = \infty$

Passage 5

22. **(d)** Orbital angular momentum (O.A.M) $= \sqrt{l(l+1)}\frac{h}{2\pi}$
    $n = 5$, So $l = 1,2,3,4$. For maximum
    $$\text{O.A.M} = \sqrt{4(5)}\frac{h}{2\pi} = \sqrt{20}\frac{h}{2\pi}$$
23. **(b)** $m = \sqrt{l(l+1)}\cos\theta \times \frac{h}{2\pi}$
    $l = 1$ for p-orbital
    $$m = \sqrt{1(2)}\cos 45^\circ \times \frac{h}{2\pi}$$
    $$Z - \text{component of O.A.M} = \frac{h}{2\pi}$$
24. **(a)** $\sqrt{8} = \sqrt{n(n+2)}; n = 2$
    Number of unpaired electrons = 2
    $$s = \frac{1}{2} + \frac{1}{2} = 1$$
    $$L_s = \sqrt{s(s+1)}\frac{h}{2\pi} = \sqrt{2}\frac{h}{2\pi}$$
25. **(a)** Lyman series
    $$\frac{1}{\lambda_1} = \bar{v}_1 = R_H \cdot 1^2\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right]$$
    Balmer series
    $$\frac{1}{\lambda_2} = \bar{v}_2 = R_H \cdot 1^2\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$
    For highest energy transition
    For Lyman series $n_2 = \infty$
    For Balmer series $n_2 = \infty$
    $$\therefore \quad \frac{\bar{v}_1}{\bar{v}_2} = \frac{4}{1}$$
26. **(b)** $\frac{1}{\lambda} = \bar{v} = R_H Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

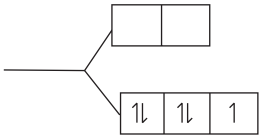
    For lowest energy transition of ion in Lyman series
    $$\bar{v} = R_H 2^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = 3R_H$$

Passage 7

27. **(c)** $Cr^{3+} = 3d^3$ (Valance shell).
$n = 3$ (Unpaired electrons)

$$\mu_s = \sqrt{15}\ \text{BM}$$

28. **(b)**



$Fe^{3+} = 3d^5$ (Valance shell)

$s = \frac{1}{2}$ in strong O_h magnetic field

Spin multiplicity = $2(s) + 1 = 2$

29. **(a)** Momentum = $\sqrt{2mK.E.}$

$$P_e = P_\alpha$$
$$\sqrt{2m_e \cdot \text{K.E.}_e} = \sqrt{2m_\alpha \cdot \text{K.E.}_\alpha}$$
$$m_e\text{K.E.}_e = m_\alpha\text{K.E.}_\alpha$$
$$\frac{\text{K.E.}_e}{\text{K.E.}_\alpha} = \frac{m_\alpha}{m_e}$$

Mass of a particle is more than mass of electron.

Thus, $\frac{m_\alpha}{m_e} > 1$; thus $\frac{\text{K.E.}_e}{\text{K.E.}_\alpha} > 1$

Thus statement 1 is true.
Statement 2 is also true.

30. **(d)** Aufbau principle

31. **(c)** Pairing is favourable when all orbitals are half filled.

32. **(c)** The Balmer series is born of transition of electron into the second orbit from higher orbits.

33. **(b)** Both statements are independently true.

34. **(c)** $Cu^+ = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}$
All the electrons are paried; hence it is paramagnatic.

(b) For energy of second orbit

$$= -13.6 \times \frac{2^2}{2^2} = -13.6 \text{ eV}$$

(c) For radius of fourth orbit $= 0.53 \times \frac{4^2}{4} = 0.53 \times 4$ Å

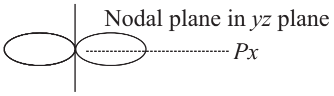
Also, energy of fourth orbit

$$= -13.6 \times \frac{4^2}{4^2} = -13.6 \text{ eV}$$

(d) For, velocity of electron in third orbit $= 2.18 \times 10^8 \times \frac{3}{3} = 2.18 \times 10^8$ Å

Assertion and Reason

35. **(a)**



36. **(a)** Pauli rule

37. **(b)** Lobes = $2l$

38. **(a)** Conceptual

39. **(c)** mass number is the sum of $n + p$

40. **(a)** $\frac{1242}{3.4}$ nm = 365.3 nm

41. **(a)** Hund's Rule

42. **(b)** $(n + l)$ Rule and Hund's Rule

43. **(a)** Spherical nodes = $n - l - 1$
$2 - 1 - 1 = 0$
for p orbital $l = 1$
∴ Spherical node for p orbital = $n - 2$

44. **(b)** Ruther ford's experiment

45. **(e)** concept

46. **(b)** Spherical nodes = $n - l - 1$
angular node = l

47. **(a, b, d)**

(a) $v = 2.18 \times 10^6 \times \frac{Z}{n} \Rightarrow v \propto \frac{Z}{n}$ or $v \propto \frac{1}{n}$

(b) $f = \frac{v}{2\pi r}$ or $f = \frac{v}{r} \propto \frac{Z/n}{n^2/Z}\, f \propto \frac{Z^2}{n^3}$

(c) $r \propto n^2/Z \quad \left[T \propto \frac{n^3}{Z^2}\right]$

(d) $F = \frac{mv^2}{r} \therefore F \propto \frac{v^2}{r} \propto \frac{(Z^2/n^2)}{n^2/Z} \quad F \propto \frac{Z^3}{n^4}$

So ans (A, B, D)

48. **(a, c, d)** B.E. = I.E.
$(\text{I.E.})_{\text{any atom}} = (\text{I.E.})_H \times z^2$

$$\frac{122.4}{13.6} = z^2$$

$z^2 = 9z = 3$

$E_2 - E_1 = 122.4 - 30.6 = 91.8$ eV

49. **[a, b, c, d]** 10 cm^{-1} = 1000 m^{-1}

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

$= 6.66 \times 10^{-34}$ (Js) $\times 3 \times 10^8$ (ms^{-1}) $\times 1000$ (m^{-1})
$= 2 \times 10^{-22}$ J per photon
$= 2 \times 10^{-15}$ ergs per photon
$= 2 \times 10^{-22} \times 6.02 \times 10^{23}$ J mol^{-1}
$= 1.2 \times 10^{-1}$ kJ mol^{-1}
$= 2.9 \times 10^{-2}$ kcal mol^{-1}

50. **[b, c, d]** According to emission photoelectric effect

$$h\nu = h\nu_0 + \frac{1}{2}mV^2$$

E of incident radiation = $\frac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{200 \times 10^{-10}}$$

$$= 9.94 \times 10^{-18}\ \text{J}$$

$$\nu_0 = \frac{5 \times 1.6 \times 10^{-19}}{6.626 \times 10^{-34}} = 1.2 \times 10^{15}\ \text{sec}^{-1}$$

$$\frac{1}{2}mv^2 = 9.94 \times 10^{-18} - 8 \times 10^{-19} = 9.14 \times 10^{-18}$$

$$v = \sqrt{\frac{2 \times 9.14 \times 10^{-18}}{9.1 \times 10^{-31}}} = 4.47 \times 10^{6} \text{ m/sec}$$

51. **(A, D)** Both Fe^{3+} and Mn^{2+} have 5 unpair electrons. Cu_2Cl_2 is colourless because Cu^{+} has no unpair electrons.

MnO_4^- has no unpair electrons in Mn^{+7}, due to charge transfer spectra it is coloured.

$$\mu = \sqrt{n(n+2)}\, BM \text{ and } n = 4$$

for Fe^{+2} and CO^{+3}

52. **(4)** If $m = +3$ (maximum), then $l = 3$ and $n = 4$

Number of waves in an orbit $= n$

53. **(6)** Number of spherical lines produced

$$= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2} = \frac{(5-2)(5-2+1)}{2} = 6$$

54. **(0)** Orbital angular momentum

$$= \sqrt{l(l+1)}\frac{h}{2\pi} = \sqrt{0(0+1)}\frac{h}{2\pi} = 0$$

55. **(2)** $mvr = n\dfrac{h}{2\pi}$

$$\frac{h}{\pi} = n\frac{h}{2\pi},\ n = 2$$

56. **(0)** Number of radial modes $= n - l - 1$

$2 - l - 1 = 0$

57. **(4)** Number of electron $= \dfrac{-6.39 \times 10^{-19}}{-1.60 \times 10^{-19}} = 4$

58. **(3)** Number of waves $= n$

60. **(1)** Number of radial nodes $= n - l - 1 = 2 - 0 - 1 = 1$

61. **(4)** $\sqrt{n(n+2)} = \sqrt{24}$

$n(n + 2) = 24,\ n = 4$

62. **(2)** $\psi 420$ is $4d$ orbital $l = 2$

63. **(2)** $n - l - 1 = 3 - 0 - 1 = 2$

64. **(5)** $l = 2$

Number of d-electrons = 5

65. **(3)** $E_n = -13.6 + 12.09 = -1.51$

$$E_n = \frac{E_1}{n^2} \therefore n^2 = \frac{-13.6}{-1.51} = 9,\ n = 3$$

66. **(0)** Hint: $\mu = \sqrt{n(n+2)} = \sqrt{35}$ BM

$n = 5$

i.e., 5 unpaired e^e are present in $(n - 1)d$ shell of M^{+3} transition metal cation so it is Fe^{+3}

$_{26}Fe \rightarrow [Ar]3d^6 4s^2$

$Fe \rightarrow [Ar]3d^5 4s^0$

67. **(2)** Hint: Number of waves $n = \dfrac{\text{Circumference}}{\text{Wavelength}}$

$$n = \frac{400}{200} = 2 \text{ (or) } n\lambda = 2\pi r$$

$n \times 200 = 400$

$n = 2$

68. **(4)** Hint: $m = 3$, $l = 3$, $n = 4$

For $n = 4$ number of waves will be 4.

69. **(6)** Hint: $n = 4$, $l = 1$ represents $4P$ – subshell containing six electrons. Thus, three will be six elements having $4P^1$ to $4P^6$ electronic configuration.

70. **(0)** Hint: $\mu_l = \dfrac{h}{2\pi}\sqrt{l(l+1)}$ ($l = 0$ for s-orbital)

71. **(5)** Hint: $Cu^{+} = [Ar]3d^{10}4s^{0}$

Five d – electrons have $+\dfrac{1}{2}$ spin

Five d – electrons have $-\dfrac{1}{2}$ spin

72. **(12)** Hint: $n = 4 \quad l = 0 \quad m_e = 0$

$l = 1 \quad m_e = -1, 0, +1$

$l = 2 \quad m_e = -2, -1, 0, +1, +2$

$l = 3 \quad m_e = -3, -2, -1, 0, +1, +2, +3$

There are three orbitals having $m_e = +1$, and three orbitals having $m_e = -1$,

Thus maximum number of electrons in them will be 12.

73. **(1)** Hint: Number of radial nodes

$= n - l - 1 = 3 - 1 - 1$ (for $3P$, $n = 3$, $l = 1$).

74. Distance to be travelled from Mars to Earth

$= 8 \times 10^{7}$ km

$= 8 \times 10^{10}$ m

$\because$ velocity $= 3 \times 10^{8}$ m/sec

$\therefore$ Time = Distance/Velocity $= \dfrac{8 \times 10^{10}}{3 \times 10^{8}}$

$= 2.66 \times 10^{2}$ sec.

75. (a) I.P. $= \underset{1=\infty}{\Delta E} = E_\infty - E_1 = 0 - (-15.6) = 15.6$ l.v.

(b) $n = \infty\ n = 2$

$\Delta E = [0 - (-5.3)] = 5.3$ l.v.

$$\Delta E = \frac{1240}{\lambda(\text{nm})} \quad \lambda = \frac{1240}{5.3} = 233.9 \text{ nm}$$

(c) $|\Delta E_{3 \rightarrow 1}| = |-3.08 - (-15.6)|$

$= 15.6 - 3.08 = 12.52$ e.v.

$$= \frac{1240}{\lambda} = \frac{12.52}{1240} = \frac{1}{\lambda}(\text{n.m})$$

$\lambda = 1.808 \times 10^{7}\ m^{-1}$

(d) (i) $E = -15.6 - (-6) = -15.6 + 6 = -9.6$

(ii) $E = -15.6 - (-11) = -15.6 + 11 = -4.6$

76. $E = \dfrac{nhc}{\lambda}$

$$10^{-17} = \frac{n \times 6.625 \times 10^{-34} \times 3 \times 10^{8}}{550 \times 10^{-9}}$$

$n = 27.67 \quad \therefore \quad 28$

77. $330\ J = n(hn)$

$330\ J = n\,[6.62 \times 10^{-34} \times 5 \times 10^{13}]$

$$\frac{330}{6.62 \times 10^{-34} \times 5 \times 10^{13}} = n = 10^{22}$$

78. $E = \dfrac{nhC}{\lambda}$ $\qquad n = \dfrac{3.15 \times 10^{-14} \times 850 \times 10^{-9}}{6.62 \times 10^{-34} \times 3 \times 10^{8}}$

$n = 134.8 \times 10^{3} \qquad n = 1.35 \times 10^{5}$

79. $\dfrac{1}{\lambda} = R_h Z^2\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

$n_1 = 3$ for paschan

80. $n_2 = 3\ n_1 = 2$ [first line]

$n_2 = 4\ n_1 = 2$ [second line]

$$\frac{1}{\lambda} = R_H\left[\frac{1}{4} - \frac{1}{9}\right]$$

$$\frac{1}{6565}\text{Å} = R_H\left[\frac{1}{4} - \frac{1}{9}\right] \qquad \text{(i)}$$

$$\frac{1}{\lambda} = R_H\left[\frac{1}{4} - \frac{1}{16}\right] \qquad \text{(ii)}$$

$$\frac{\lambda}{6565} = \frac{\frac{5}{36}}{\frac{3}{16}} = \frac{5\times16}{36\times3}\ \lambda = 4863\ \text{Å}$$

81. $3 \to 2$

$$\frac{1}{\lambda_1} = R_H \times Z^2\left[\frac{1}{n_1^2} - \frac{1}{\text{n}_2^2}\right] = R_H \times\left[\frac{1}{4} - \frac{1}{9}\right] \qquad \text{...(i)}$$

$$2 \to 1\ \frac{1}{\lambda_2} = R_H \times 4\left[\frac{1}{1} - \frac{1}{4}\right] \qquad \text{...(ii)}$$

$$(\lambda_1 - \lambda_2) = 133.7\ \text{nm} \qquad \text{...(iii)}$$

We solve the three equations and we get

$R = 1.096 \times 10^7\ \text{m}^{-1}$

82. $\Delta E = 13.6\left[\dfrac{1}{9} - \dfrac{1}{4}\right] \times 96.3368$ kJ/mole

$$= 13.6\left[\frac{4-9}{36}\right] \times 96.368 = 182.074$$

$$= 1.827 \times 10^5\ \text{J/mole}$$

83. IE per mole $= N_A \times \dfrac{hc}{\lambda}$

$$= \frac{6.022\times10^{23}\times6.625\times10^{-34}\times3\times10^8}{854\times10^{-10}}\text{J}$$

$$= 0.14\times10^7 = 14\times10^5\,\text{J} = 1400\ \text{KJ/Mole}$$

84. Radius = 16 × radius of H in ground state = 16 × 0.529

$$16 \times 0529 = 0.0529 \times \frac{n^2}{Z}$$

$$16 = \frac{n^2}{1} \qquad \boxed{n = 4}$$

$$\text{T.E.} = -13.6 \times \frac{Z^2}{n^2}\ \text{e.v.} = -0.85\ \text{e.v.}$$

85. $E_n = \dfrac{-21.7\times10^{-12}}{n^2}$ 1 erg $= 10^{-7}$ Joule

$$E_n = \frac{-21.7\times10^{-12}}{4}$$

$$\text{J.E.} = 0 - \left[\frac{-21.7\times10^{-12}}{4}\right] = \frac{21.7\times10^{-12}}{4}$$

$$= 5.425 \times 10^{-12}\ \text{ergs}$$

(b) $\lambda = \dfrac{6.625\times10^{-34}\times3\times10^8}{5.425\times10^{-19}}$

$$= 3.66 \times 10^{-7}\ \text{meter} = 3.7 \times 10^{-5}\ \text{cm}$$

86. $\underset{2\to1}{\Delta E} = \text{I.E.}\left[\dfrac{1}{4} - \dfrac{1}{1}\right]$

$$2.17 \times 10^{-11}\ \text{erg/atom}\left[\frac{1}{4} - \frac{1}{1}\right] = \frac{hc}{\lambda(m)}$$

$$2.17\times10^{-11}\times10^{-7}\ \text{J}\left[\frac{1}{4} - \frac{1}{1}\right] = \frac{6.626\times10^{-34}\times3\times10^8}{\lambda}$$

$$\lambda = \frac{6.626\times10^{34}\times3\times10^8\times4}{2.17\times10^{-18}\times3} = \frac{6.626\times4\times10^8}{2.17}$$

$$= 12.20 \times 10^{-8}\ \text{m} = 1220\ \text{Å}$$

87. $V_n = 2.18 \times 10^6 \times \dfrac{Z}{n} = \dfrac{2.18\times10^6}{n}$

$$\frac{2.18\times10^6}{n} = \frac{1}{275} = \frac{v}{3\times10^8}$$

$$\frac{2.18\times10^6}{n} = \frac{3\times10^8}{275}$$

$$n = 1.99 \simeq 2$$

88. $Z = 3,\ n_1 = 1,\ n_2 = 3$

$$E_n = 13.6 \times (Z^2)\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = 13.6 \times 9\left[\frac{1}{1} - \frac{1}{9}\right]$$

$$= 13.6 \times 9 \times \frac{8}{9} = 108.8\ \text{eV}$$

89. (i) $E_{n_2\to n_1} = 13.6\times Z^2\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right] = 13.6[1]^2\left[\dfrac{1}{1} - \dfrac{1}{4}\right]$

$$= 13.6 \times 1 \times \frac{3}{4} = 10.2\ \text{eV}$$

(ii) $\dfrac{1}{\lambda} = R_H Z^2\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

$$\frac{1}{3\times10^{-8}} = 1.09 \times 10^7 \times Z^2 \times \frac{3}{4}$$

$$\therefore\ Z = 2$$

90. 1.8 mole = (1.8 N_A) atoms

27% = IIIrd energy level = $1.8 \times N_A \times 0.27 = 0.486\ \text{N}_\text{A}$

15% = IInd energy level = $1.8 \times N_A \times 0.15 = 0.27\ \text{N}_\text{A}$

$$\Delta E = \underset{3\to1}{\Delta E_1} + \underset{2\to1}{\Delta E_2}$$

$$= 1.8 \times N_A \times 0.27 \times \text{IE} + \left[\frac{1}{9} - \frac{1}{1}\right]$$

$$+ 1.8 \times N_A \times 0.15 \times \text{IE}\left[\frac{1}{4} - \frac{1}{1}\right]$$

$$= (0.432\ N_A + 0.20\ N_A) \times \text{IE} = 56.65 \times 10^{11}\ \text{erg.}$$

91. Number of atom in third orbit = 0.5 NA
Number of atom in second orbit = 0.25 NA
Total energy evolve $= 0.5\,N_A(E_3 - E_1) + 0.25N_A(E_2 - E_1)$

92. Angular momentum $= n\left(\dfrac{h}{2\pi}\right)$

$$\left(\frac{hc}{\lambda}\right) = -3.4\text{ eV} \qquad -3.4 = -13.6 \times \frac{(1)^2}{n^2}$$

$$\frac{-3.4}{-13.6} = \frac{1}{n^2} \qquad n^2 = \frac{13.6}{3.4} = 4$$

$$n^2 = 4 \Rightarrow n = 2$$

$$= 2\left(\frac{6.626 \times 10^{-34} \times 7}{2 \times 22}\right) = \frac{h}{\pi} \text{ or } \frac{6.62 \times 10^{-39} \times 7}{2}$$

93. $4.5\text{ eV} = \dfrac{1240}{\lambda(\text{nm})} \qquad \dfrac{1}{\lambda} = \dfrac{4.5}{1240} = 0.0036\text{ nm}^{-1}$

94. $\dfrac{\Delta n(\Delta n + 1)}{2} = 15$

$$\Delta n\,(\Delta n + 1) = 30 = 5 \times 6$$

$\therefore \quad n_1 = 1$ and $n_2 = 6$

$$\frac{1}{\lambda\text{Å}} = R_H \times \left[\frac{1}{1} - \frac{1}{36}\right]$$

$$\frac{1}{x} = \frac{1}{912} \times \frac{35}{36} = \frac{35 \times 2496}{32832}$$

$$\boxed{\lambda = 932\text{ Å}}$$

95. The condition can be met by taking first derivative $P(r)$ w.r.t r and setting the same equal to zero, i.e.,

$$\frac{dP(r)}{dr} = \frac{1}{dr}\left[\left(\frac{1}{\pi a_0^3}\right)^{v_2} e^{-r/a_0}\right] = 0$$

$\therefore \quad r = a_0 \qquad (\because e^{-2r/a_0} \neq 0)$

96. The energy of photon which can cause ejection of electron = kinetic energy of ejected electron + ionisation energy …(i)

Ionisation energy = 13.6 eV

$$= \frac{13.6}{6.24 \times 10^{18}}\text{J} = 2.179 \times 10^{-18}\text{ J} \qquad \text{…(ii)}$$

Here 6.24×10^{18} eV = 1 J

de Broglie wavelength $= \lambda = \dfrac{h}{mv}$

$$\therefore \quad v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 4.7 \times 10^{-10}}$$

$$= 0.15492 \times 10^7\text{ m/sec}$$

$$\text{K.E.} = \frac{1}{2}mv^2$$

$$= \frac{1}{2} \times 9.1 \times 10^{-31} \times (0.15492 \times 10^7)^2$$

$$= 1.092 \times 10^{-18}\text{J} \qquad \text{…(iii)}$$

Now from Eq. (i)

The energy of photon which can cause ejection of electron

$$= 2.179 \times 10^{18} + 1.092 \times 10^{-18}$$
$$= 3.271 \times 10^{-18}\text{J}$$

97. Energy required per molecule in the following process is given as

$$O_2 \xrightarrow{h\nu} O + O^*$$

$$E = \frac{h \times c}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{174 \times 10^{-9}}$$

$$= 11.424 \times 10^{-19}\text{ J/molecule}$$

Energy for O → O* is 3.15×10^{-19} Joule

Thus, energy $O_2 \rightarrow 2O$ will be

$$= 11.424 \times 10^{-19} - 3.1 \times 10^{-19}$$
$$= 8.274 \times 10^{-19}\text{ J/molecule}$$
$$= 8.274 \times 10^{-19} \times 6.023 \times 10^{23} \times 10^{-3}\text{ kJ/mole}$$
$$= 498.3\text{ kJ/mole}$$

98. $V_2 = V_0 \times \dfrac{1}{2} = \dfrac{V_0}{2}$

$$x = v \times t$$

$$x = \frac{V_0}{2} \times 10^{-8}\text{sec} = \left(\frac{V_0 \times 10^{-8}}{2}\right)\text{m}$$

$2\pi r$ distance covered in 1 round

$\therefore \quad \dfrac{V_0 \times 10^{-8}}{2}$ distance covered in $\dfrac{V_0 \times 10^{-8}}{2} \times \dfrac{1}{2\pi r}$

$$r_2 = r_0 \times n_2 = 4r_0$$

so, number of revolutions $= \dfrac{V_0/2 \times 10^{-8}}{2\pi \times 4r_0} = \dfrac{V_0 \times 10^{-8} \times 1}{2 \times 2\pi \times 4r_0}$

$$= \frac{2.18 \times 10^6 \times 10^{-18}}{2 \times 2 \times 3.14 \times 4 \times 0.529}$$

$$= \frac{2.18 \times 10^{-12}}{2.6 \times 10^{-21}} = 0.838 \times 10^{19} = \boxed{8 \times 10^6}$$

99. $v = \dfrac{V}{\lambda}$

E of Ist Bohr orbit = –13.6

$$-13.6 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

or $\quad -13.6 = \dfrac{1240}{\lambda(\text{in nm})}$

$$\lambda = \frac{1240}{136} \times 10$$

$$\lambda = 91.17\text{ (nm)} = 912\text{ Å}$$

$$v = \frac{2.18 \times 10^6 \times \frac{1}{1}}{912 \times 10^{-10}} = 2.3 \times 10^{13}\text{ Hz}$$

100. $\Delta E = 47.2\text{ eV} = 13.6\, Z^2\left(\frac{1}{4}-\frac{1}{9}\right)$

$$\frac{47.2}{13.6}=\frac{5}{36}Z^2$$

$Z^2 = 25$

∴ $Z = 5$

101. $\Delta E = Z^2 \times 10.2\text{ eV} = 4 \times 10.2\text{ eV}$

$$\text{K.E.}=\frac{1}{2}mV^2 = 4\times 10.2 - 13.6\text{ eV}$$

$$\therefore \quad V=\sqrt{\frac{2\times 27.2\times 1.6\times 10^{-19}}{9.1\times 10^{-31}}}=3.09\times 10^{6}\text{ m/sec.}$$

102. B.E. = 180.69 kJ/mole ⇒ $w = h\nu_0$

$$\frac{180.69}{96.368}\text{eV/atom} = h\nu_0$$

$$\frac{180.69}{96.368}\times 1.6\times 10^{-19} = 6.6\times 10^{-34}\times \nu_0$$

$$\nu_0 = 6.626\times 10^{-34}$$

103. $h\nu_1 = h\nu_0 + 2E_1$ and $h\nu_2 = h\nu_0 + E_1$

$h\nu_1 - h\nu_0 = 2E_1$ and $h\nu_2 - w_0 = E_1$

$$2=\frac{h\nu_1 - w_0}{h\nu_2 - w_0} \quad \therefore \quad 2h\nu_2 - 2w_0 = h\nu_1 - w_0$$

$h[2\nu_2 - \nu_1] = w_0$

$w_0 = 6.62 \times 10^{-34}\,(4 \times 10^{15} - 3.2 \times 10^{15})$

$w_0 = 6.62 \times 10^{-34} \times 0.8 \times 10^{15}$

$w_0 = 5.29 \times 10^{-19}$ $\quad w_0 = 318.9$ kJ/mol

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. **(d)** Charge/mass for $n = 0, \alpha = \frac{2}{4}, p = \frac{1}{1}, e = \frac{1}{1/1837}$
   So, order is n, α, p, e
2. **(a)** Isotonic : same number of neutrons
3. **(c)** Conceptual
4. **(c)** $\lambda=\frac{h}{mv}=\frac{6.6\times 10^{-34}}{(0.2)\times 5/(60\times 60)}=2.37\times 10^{-30}\text{m}$
5. **(a)** $Z = 37$, so electronic configuration is $1s^2\, 2s^2\, 2p\, 3s^2\, 3p^6\, 4s^2\, 3s^{10}\, 4p^6\, 5s^1$
   ∴ for outermost electron
6. **(c)** Most electro-negative element is F.
   ∴ electronic configuration: ns^2np^5
7. Average mass = Mass of isotopes × Mole fraction + Mass of isotopes × Mole fraction

   $10.81 = 11.01 \times x + 10.01\,(1 - x)$

   $10.81 = 11.01\, x + 10.01 - 10.01\, x$

   $x = 10.81 - 10.01 = 0.80$

   $\% = 0.80 \times 100 = 80\%$

8. $\Delta E = E_3 - E_2 = \frac{hc}{\lambda}$

   $= -2.41 \times 10^{-12} - (5.42 \times 10^{-12}) = \frac{hc}{\lambda}$

   $= 3.01 \times 10^{-12} \times 10^{-7} = \frac{6.626\times 10^{-34}\times 3\times 10^{8}}{\lambda}$

   $\lambda=\frac{6.626\times 10^{-26}\times 3}{3.01\times 10^{-19}}=\frac{6.626\times 10^{-7}\times 3}{3.01}$

   $= 6603\text{ Å} = 6.603 \times 10^{-7}\text{ m}$

9. $\Delta E = 2.17 \times 10^{-18}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

   $\frac{hc}{\lambda}=2.17\times 10^{-18}\left[1-\frac{1}{4}\right]$

   $\frac{6.62\times 10^{-34}\times 3\times 10^{8}}{\lambda}=2.17\times 10^{-18}\times\frac{3}{4}$

   $\lambda=\frac{4\times 6.62\times 3\times 10^{-26}}{6.51\times 10^{-18}}=12.20\times 10^{-8}\text{m}=1220\text{ Å}$

10. $\Delta E=\frac{2.17\times 10^{-18}}{n^2}\times Z^2=\frac{2.17\times 10^{-18}}{4}=5.42\times 10^{-19}$

    or $\quad 5.42 \times 10^{-12}$ erg

    ∵ $\quad \Delta E=\frac{hc}{\lambda}$

    $\lambda=\frac{6.626\times 10^{-34}\times 3\times 10^{8}}{5.42\times 10^{-19}}=3.67\times 10^{-7}\text{ meter}$

    or $\quad 3.67 \times 10^{-5}$ cm

11. For $n = 3$ and $l = 2$ (i.e., 3*d* orbital), the values of *m* varies from –2 to +2, i.e., –2, –1, 0, +2 and for each '*m*' there are 2 values of '*s*', i.e., +1/2 and –1/2.
    Maximum number of electrons in all the five *d*-orbitals is 10.

12. $E_{3^{\text{rd}}}=\frac{-21.76\times 10^{-19}\times 4}{9}\text{J}$

    $=\frac{87.04}{9}\times 10^{-19}=9.67\times 10^{-19}\text{J}$

    ∴ $\quad \Delta E=\frac{hc}{\lambda}$

    $\lambda=\frac{6.626\times 10^{-34}\times 3\times 10^{8}}{9.67\times 10^{-19}}$

    $= 2.0556 \times 10^{-7}\text{ M} = 2055\text{ Å}$

13. $\lambda=\frac{h}{mu}=\frac{6.62\times 10^{-34}}{0.1\times 100}$

    or $\quad \lambda = 6.62 \times 10^{-35}\text{ m} = 6.62 \times 10^{-25}\text{ Å}$

14. For hydrogen atom, $Z = 1$, $n = 1$

    $V = 2.18 \times 10^{6} \times \frac{Z}{n}\text{ms}^{-1} = 2.18 \times 10^{6}\text{ ms}^{-1}$

    de Broglie wavelength,

$$\lambda = \frac{h}{mv} = \frac{6.26 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18 \times 10^{6}}$$

$= 3.34 \times 10^{-10}$ m = 3.3 Å

For $2p$, $l = 1$

∴ Orbital angular momentum $\sqrt{2}\frac{h}{2\pi}$

15. From $\Delta E = E_f - E_i = \dfrac{hc}{\lambda}$

$$2.18 \times 10^{-18} \times Z^2 \left[\frac{1}{(1)^2} - \frac{1}{(2)^2}\right] = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{3 \times 10^{-8}}$$

or $\quad -2.18 \times 10^{-18} \times Z^2 \times \dfrac{3}{4} = 6.626 \times 10^{-18}$

$$Z^2 = \frac{6.626 \times 10^{-18} \times 4}{2.18 \times 10^{-18} \times 3} \approx 4$$

$Z = 2$

for $\quad He^+$ $Z = 2$

16. $\Delta E_{\text{He}^+} = \Delta E_{\text{H}}$

or $\quad -2.18 \times 10^{-18} \times Z^2 \left[\dfrac{1}{4} - \dfrac{1}{16}\right]$

$$= -2.18 \times 10^{-18} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$4\left[\frac{1}{4} - \frac{1}{16}\right] = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

∴ $\quad n_1 = 1$ and $n_2 = 2$

17. r_n for $H = r_1 \times n^2$

R_3 for $H = 0.529 \times 9 \times 10^{-8}$ cm $= 529 \times 9 \times 10^{-10}$ m

(∵ $r_1 = 0.529$ A°)

Also $\quad u_n = Z\dfrac{u_1}{n}$

∴ $\quad u_3 = \dfrac{2.19 \times 10^8}{3}\text{cm sec}^{-1}\ \dfrac{2.19 \times 10^6}{3}\text{m sec}^{-1}$

(∵ $u_1 = 2.19 \times 10^8$ cm sec^{-1})

∴ Number of waves in one round

$$= \frac{2\pi r_3}{\lambda} = \frac{2\pi r_3}{h/mu_3} = \frac{2\pi r_3 \times u_3 \times m}{h}$$

$$= \frac{2 \times 22 \times 0.529 \times 9 \times 10^{-10} \times 2.19 \times 10^{6} \times 9.108 \times 10^{-31}}{7 \times 3 \times 6.62 \times 10^{-34}} = 3$$

18. Bond energy of I_2 =240 kJ mol^{-1} = 240 ×10^3 J mol^{-1}

$$= \frac{240 \times 10^3}{6.023 \times 10^{23}}\text{J mol}^{-1} = 3.984 \times 10^{-19}\text{ J mol}^{-1}$$

$$\text{Energy absorbed} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\text{Js} \times 3 \times 10^{8}\text{ms}^{-1}}{4500 \times 10^{-10}\text{m}}$$

$= 4.417 \times 10^{-19}$ J

Kinetic energy = Absorbed energy – Bond energy

∴ kinetic energy $= 4.417 \times 10^{-19} - 3.984 \times 10^{-19}$ J

$= 4.33 \times 10^{-20}$ J

∴ kinetic energy of each atom

$$= \frac{4.33 \times 10^{-20}}{2} = 2.165 \times 10^{-20}\text{ J}$$

19. The shortest wavelength transition in the Balmer series corresponds to the transition

$n = 2 \rightarrow n = \infty$. Hence, $n_1 = 2$, $n_2 = \infty$

$$\overline{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = (109677\text{ cm}^{-1}) \times \left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)$$

$= 27419.25$ cm^{-1}

20. As the α particle travelling with velocity, 'u' stops at a distance 10^{-13} m, its K.E. becomes zero and gets converted in to P.E.

$$\frac{1}{2}mu^2 = \frac{1}{4\pi\varepsilon_0} \times \frac{2Ze^2}{r} \text{ or } u^2 = \frac{Ze^2}{\pi\varepsilon_0 \cdot m.r}$$

Here, $Z = 29$ for Cu atom

$$\Rightarrow \quad u^2 = \frac{29 \times (1.6 \times 10^{-19})^2}{3.14 \times 8.85 \times 10^{-12} \times (4 \times 1.672 \times 10^{-27}) \times 10^{-13}}$$

∴ $\quad u = 6.3 \times 10^6$ m sec^{-1}

21. $\dfrac{1}{2}mu^2 = \text{eV}$; also $\lambda = \dfrac{h}{mu}$

$$\therefore \quad \frac{1}{2}\text{m}\frac{h^2}{m^2\lambda^2}\text{eV} \text{ or } V = \frac{1}{2}\frac{h^2}{m\lambda^2 e}$$

$$V = \frac{1 \times (6.62 \times 10^{-34})^2}{2 \times 9.108 \times 10^{-31} \times (1.54 \times 10^{-10})^2 \times 1.602 \times 10^{-19}}$$

= 63.3 volt

22. Determination of number of moles of hydrogen gas,

$$n = \frac{PV}{RT} = \frac{1 \times 1}{0.082 \times 298} = 0.0409$$

The concerned reaction is $H_2 \rightarrow 2H$; $\Delta H = 436$ kJ mol^{-1}. Energy required to bring 0.0409 moles of hydrogen gas to atomic state = 436 × 0.0409 = 17.83 kJ.

Calculation of total number of hydrogen atoms in 0.0409 mole of H_2 gas.

1 mole of H_2 gas has 6.02×10^{23} molecules

$$0.0409 \text{ mole of } H_2 \text{ gas} = \frac{6.02 \times 10^{23}}{1} \times 0.0409$$

Since 1 molecule of H_2 gas has 2 hydrogen atoms, $6.02 \times 10^{23} \times 0.0409$ molecules of H_2 gas $= 2 \times 6.02 \times 10^{23} \times 0.0409 = 4.92 \times 10^{22}$ atoms.

Energy required to excited an electron from the ground state to the next excited state

$$=13.6\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{eV}=13.6\times\left(\frac{1}{1}-\frac{1}{4}\right)$$

$$=13.6\times\frac{3}{4}=10.2\text{ eV}=10.2\times\frac{1.6\times10^{-19}}{1000}\text{KJ}$$

Therefore, energy required to excite 4.92×10^{22} electrons

$= 1.632 \times 10^{-21}\ 4.92 \times 10^{22}$ kJ

$= 8.03 \times 10 = 80.3$ kJ

Therefore, total energy required $= 17.83 + 80.3$

$= 98.17$ kJ

23. For maximum energy, $n_1 = 1$ and $n_2 = \infty$

$$\frac{1}{\lambda}=R_H Z^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

Since R_H is a constant and transition remains the same

$$\frac{1}{\lambda}\propto Z^2;\ \frac{\lambda_{\text{He}}}{\lambda_{\text{H}}}=\frac{\text{Z}_{\text{H}}^2}{\text{Z}_{\text{He}}^2}=\frac{1}{4}$$

Hence, $\lambda_{\text{He}}=\frac{1}{4}\times91.2=22.8\text{ nm}$

24. ψ_{2s}^2 = Probability of finding electron within 2*s* sphere

$\psi_{2s}^2 = 0$ (at node)

($\because$ probability of finding an electron is zero at node)

$$\therefore\quad 0=\left[\frac{1}{4}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r_0}{a_0}\right)^2\times e^{-r_0/a_0}\right]^2$$

$$\Rightarrow\quad\left[2-\frac{r_0}{a_0}\right]=0;\ \therefore\ 2=\frac{r_0}{a_0};\ 2a_0=r_0$$

25. A → r; B → q, C → p, D → s

(a) Potential Energy

$$=-\frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r}\right)=-13.6\times2\frac{z^2}{n^2}\text{ev}$$

Kinetic energy $= +13.6\frac{z^2}{n^2}\text{ev}$

$$K_n=\frac{1}{8\pi\varepsilon_0}\left(\frac{Ze^2}{r}\right)\Rightarrow\frac{V_n}{K_n}=-2(R)$$

(b) $E_n=-\frac{Ze^2}{8\pi\varepsilon_0 r}=-13.6\frac{Z^2}{n^2}\text{ev}\propto r^{-1}\Rightarrow x=-1$

(c) Angular momentum $=\sqrt{l(l+1)}\frac{h}{2\pi}$

$= 0$ in *S* orbital

(d) $r_n=\frac{a_0n^2}{z}=0.529\frac{n^2}{z}\text{Å}$

26. A → q; B → p, q, r, s; C → p, q, r ; D → p, q, r

(a) Orbital angular momentum (L) $=\sqrt{l+(l+1)}\frac{h}{2\pi}$

i.e., depends on azimuthal quantum number only.

(b) To describe a one electron wave function, three quantum numbers *n*, *l* and *m* are needed. Further to abide by Pauli exclusion principle, spin quantum number (s) is also needed.

(c) For shape, size and orientation, only *n*, *l* and *m* are needed.

(d) Probability density (ψ^2) can be determined if *n*, *l* and *m* are known.

Comprehension-Based Questions

27. $\Rightarrow n = 2$, i.e., $S_1 = 2s$ orbital.

28. Ground state energy of electron in H –atom.(E_H)

$$\frac{(E_{\text{Li}^{+2}})S_1}{E_H}=\frac{-13.6\frac{[3]^2}{[2]^2}\text{ev}}{-13.6\times\frac{[1]^2}{[1]^2}\text{ev}}=\frac{9}{4}=2.25$$

29. In S_2 state, E (Li^{2+}) $= k$ (given)

$$E_{\text{Li}^{+2}}=-13.6\frac{(3)^2}{n_2^2}\text{ev}=13.6\times\frac{(1)^2}{(1)^2}\text{ev}$$

$\therefore\quad n_2 = 3 = S_2$

Integer-Type Questions

30. When $n = 3$, $l = 0, 1, 2$, i.e., there are 3*s*, 3*p* and 3*d* orbitals. If all these orbitals are completely occupied as

⇅ ⇅⇅⇅ ⇅⇅⇅⇅⇅

Total 18 electrons, 9 electrons with $s=+\frac{1}{2}$ and 9 with $s=-\frac{1}{2}$.

31. $\therefore\quad E_n=-\frac{13.6}{n^2}\text{eV}$ where, $n = 1, 2, 3$..........

In excited states, $E_2=\frac{-13.6}{4}=-3.4\text{ eV}$

32. **(a)** Given, atomic number of Rb, $Z = 37$

Thus, its electronic configuration is [Kr]$5s^1$. Since, the last electron or valence electron enter is 5*s* subshell. So, the quantum numbers, are $n = 5$, $l = 0$, (for *s*-orbital) $m = 0$ $\because$ $m = +l$ to $-l$, $s = +1/2$ or $-1/2$.

33. **(a)** Given, in the question $E=-2.178\times10^{-18}\text{J}\left[\frac{Z^2}{n^2}\right]$

For hydrogen $Z = 1$,

So, $E_1=-2.178\times10^{-18}\text{J}\left[\frac{1}{n^2}\right]$

$E_2=-2.178\times10^{-18}\text{J}\left[\frac{1}{2^2}\right]$

Now, $E_1 - E_2$ i.e.

$$\Delta E = 2.178\times 10^{-18}\left(\frac{1}{1^2}-\frac{1}{2^2}\right)=\frac{hc}{\lambda}$$

$$2.178\times 10^{-18}\left(\frac{1}{1^2}-\frac{1}{2^2}\right)=\frac{6.62\times 10^{-34}\times 3.0\times 10^{8}}{\lambda}$$

$\therefore\quad \lambda = 1.21\times 10^{-7}$ m

34. **(c)** According to Bohr's model,

$$mvr=\frac{nh}{2\pi}\Rightarrow (mv)^2=\frac{n^2h^2}{4\pi^2r^2}$$

$$\Rightarrow\quad \text{Kinetc Energy}=\frac{1}{2}mv^2=\frac{n^2h^2}{8\pi^2r^2m}$$

Also, Bohr's radius for H-atom is, $r = n^2a_0$

Substituting 'r' in Eq. (i) gives

$$\text{K.E.}=\frac{h^2}{8\pi^2n^2a_0^2m}\ \text{when } n=2,\ \text{K.E.}=\frac{h^2}{32\pi^2a_0^2m}$$

35. **(6) Hint:** This problem is based on correct of quantum number. Follow the following steps to solve this problem. Write all possible orbital's having combination of same principal, azimuthal, magnetic and spin quantum number. Then count the all possible electrons having given set of quantum numbers. For $n = 4$, the total number of possible orbitals are

4*s*	4*p*			4*d*					4*d*						
0	–1	0	+1	–2	–1	0	+1	+2	–3	–2	–1	0	+1	+2	+3

According to question $|m_1| = 1$, i.e. there are two possible values of m_1, i.e. +1 and –1 and one orbital can contain maximum two electrons one having $s = +\frac{1}{2}$ and other having $s = -1/2$.

So, total number of orbitals having $\{|m_1| = 1\} = 6$

Total number of electrons having

$$\left\{|m_1|=1 \text{ and } m_2=\frac{1}{2}\right\}=6$$

36. **(5) Hint:** $\text{K.E.}=\frac{1}{2}MV^2=\frac{3}{2}RT$

$$\therefore\quad m^2v^2 = 2mKE \therefore mv=\sqrt{2mKE}$$

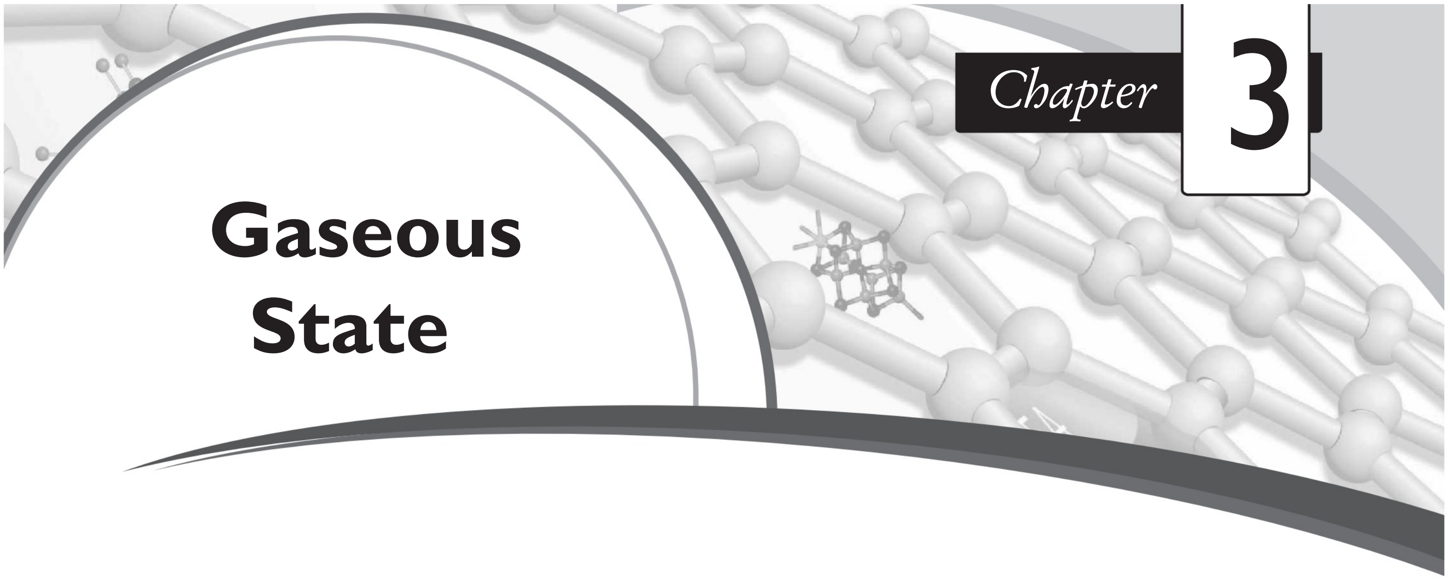
$$\lambda(\text{wavelength}) = \frac{h}{mv}=\frac{h}{\sqrt{2mKE}}\propto\frac{h}{\sqrt{2m(T)}}$$

Where, T = Temperature in Kelvin

$$\lambda(\text{He at } -73°\text{C} = 200\text{ K})=\frac{h}{\sqrt{2\times 20\times 1000}}$$

$$\therefore\quad \frac{\lambda(\text{He})}{\lambda(\text{Ne})}=M=\sqrt{\frac{2\times 20\times 1000}{2\times 4\times 200}}=5$$

Thus, $M = 5$



Chapter 3

Gaseous State

Key Concepts

In this chapter, we will study about physical classification of matter. State in which a matter exists depends upon two factors:

1. **Intermolecular force**: This gives an idea of binding force between constituents particles.
2. **Kinetic energy or thermal or heat**: It gives the idea of velocity of constituent particles.
   These two factors at a given temperature decide the state of aggregate matter.

	Property	**Solid**	**Liquid**	**Gas**
1.	Shape	Fixed	Not fixed	Not fixed
2.	Intermolecular force of attraction	High	Lower than solid	Least
3.	Volume	Fixed	Fixed	Not fixed
4.	Density	High	Intermediate	Low
5.	Kinetic energy	Least	Higher than solid	High
6.	Diffusibility	Less	Medium	High
7.	Compressibility	Low	Medium	High

Gas

	Ideal	**Real**
1.	No intermolecular force of attraction or repulsion	Exist
2.	The volume of gaseous molecules is negligable in comparison to the volume of container eg.	Molecular volume exist
	It is a theoretical concept, there is no ideal gas	For example, all gases around us.

Measurable properties of gases:

1. Number of moles of gases or amount of gas (n)
2. Volume of gas V
3. Pressure of gas P
4. Temperature of gas T

Temperature determines the direction of heat flow.

There are three scales for temperature measurement.

(i) Celcius scale (°C)
(ii) Kelvin scale (K)
(iii) Fahrenheit scale (°F)

$$\boxed{\frac{T_{\text{any scale}} - \text{F.P.}_{(\text{water})}}{(\text{BP} - \text{FP})_{\text{water}}} = \text{constant}}$$

BP = Boiling Point

FP = Freezing Point

This equation is used to convert temperature from 1 scale to another scale.

$(\text{BP})_{\text{water}}$	$°\text{C}_{100}$	K_{373}	F_{212}
$(\text{FP})_{\text{water}}$	0	273	32

$$\boxed{\frac{t^{°\text{C}} - 0}{100 - 0} = \frac{t_k - 273}{373 - 273} = \frac{T_F - 32}{212 - 32}}$$

1. $t°\text{C} = \frac{5}{9}\,[t_f - 32]$
2. $T_k = \frac{5}{9} t_{(f)} + 255.2$
3. $T_k = 273 + °\text{C}$

Pressure : $P = \dfrac{F}{A} = \dfrac{mg}{A}$

It is the force exerted by the gas per unit area on the walls of a container. Pressure exerted because of collision and causing change in momentum assuming no intermolecular force of attraction.

Device:

1. Baromater (Atmospheric pressure)
2. Monometer (Other than atmospheric pressure)

Unit:

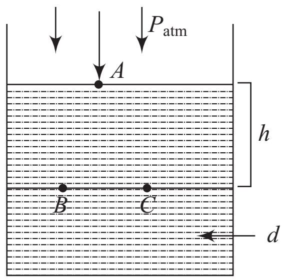
$$\begin{aligned}1 \text{ atm} &= 76 \text{ cm of Hg} = 760 \text{ mm Hg} = 760 \text{ torr}\\ &= 1.013 \times 10^5 \text{ N/m}^2 \text{ or pascal}\end{aligned}$$

EXPERIMENTAL METHOD FOR PRESSURE CALCULATION

$$\begin{aligned}P_B &= P_A + \Delta P\\ &= P_A + \text{Pressure due to ‘}h\text{’ column (liq)}\end{aligned}$$

$$\begin{aligned}P_B &= P_A + \left(\frac{F}{A}\right) = P_A + \frac{mg}{A}\\ &= P_A + \frac{V \times d \times g}{A}\\ &= P_A + \frac{A \cdot h \cdot d \cdot g}{A}\end{aligned}$$

$$\boxed{P_B = P_A + hdg}$$



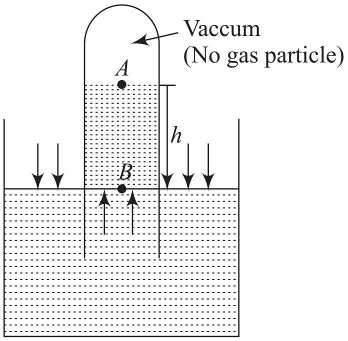
This formula is applicable only when d is constant throughout vertical height.

$P_B = P_C$ because h is same.

Barometer:

Case I

$$\begin{aligned}\therefore\quad P_A &= 0\\ P_B &= P_A + \Delta P\\ P_B &= 0 + hdg\\ d &= 13.6 \text{ gm/cm}^3 = 13.6 \times 9.8\\ g &= 9.8 \text{ m/sec}^2 \text{ and } h = 76 \text{ cm}\\ \therefore\quad P_B &= hdg\\ &= 0.76 \times 13.6 \times 10^3 \times 9.8\\ &= 1.01325 \times 10^5 \text{ pascal}\\ P_B &= 1 \text{ atm}\end{aligned}$$



Hg is preferred in barometer because density is high, length of tube small and non volatile.

For other liquid

Other liquid	Hg
$h_1 d_1 g$	$h_2 d_2 g$

$$\boxed{h_1 d_1 = h_2 d_2}$$

or $hd = \text{constant}$

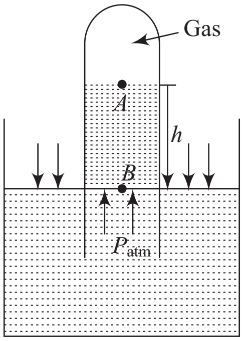
Hg	**H_2O**

$$0.76 \times 13.6 \times 10^3 = h_2 \times 1 \times 10^3$$

$$h_1 = \frac{0.76 \times 13.6}{1} = 10.33 \text{ meter}$$

It means $d\uparrow$ then $h\downarrow$

Case II



$$\boxed{P_{atm} = \underset{\substack{\text{Pressure}\\ \text{of gas}}}{\underset{\downarrow}{P_A}} + \underset{\substack{\text{Pressure}\\ \text{due to column}}}{\underset{\downarrow}{hdg}}}$$

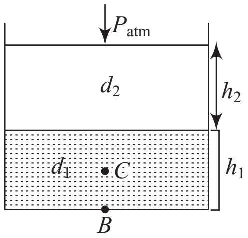
Q.1 (i) An open tank is filled with Hg upto a height of 76 cm. Find pressure at the bottom and middle of the tank. If atmospheric pressure is 1 atm.

(ii) Find the height of water up to which water must be filled to create same pressure at the bottom.

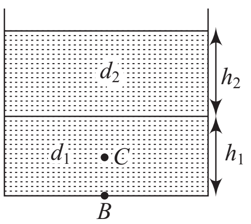
Q.2 What will be the pressure

(i) at the bottom of the tank?

(ii) at middle of the bottom layer? If two immiscible liquids are filled as shown in the above figure.

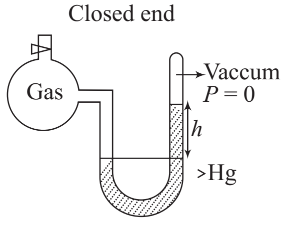


Q.3 What will be the pressure
(i) at the bottom of the tank?
(ii) at $h_1/2$ height from bottom if two completely miscible liquids densities are d_1 and d_2 are filled as shown in the following diagram assuming cross-section area is same.



(Discussed in Solved Examples)

MONOMETER



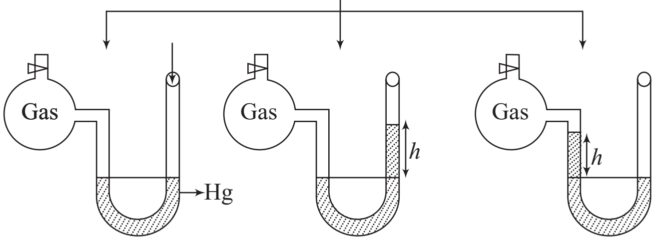
$P = hdg$

$P_{gas} = P_A + hdg$

$P_{gas} = 0 + hdg$

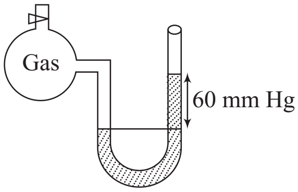
$P_{gas} = hdg$

Open end
There are three posibility



If level of Hg is same in both limb. $P_{gas} = P_{atm}$	$P_{gas} > P_{atm}$ $P_{gas} = P_{atm} + hdg$ $P_{gas} = 1 + h(\text{cm})/76$ atm	$P_{gas} < P_{atm}$ $P_{gas} = P_{atm} - hdg$ $P_{gas} = 1 - h(\text{cm})/76$ atm

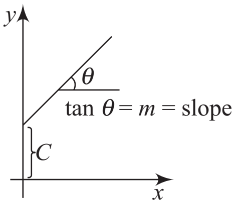
Q4. Find pressure of the gas inside the container if manometer attached to the container show a difference of 60 mm as shown in figure?



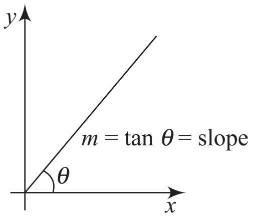
$$P = P_{atm} + \frac{60}{760} = 1 + \frac{6}{76}\text{atm}$$

Common equation for graph

(i) $y = mx + C$

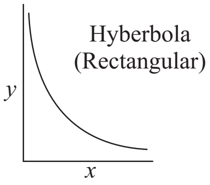


(ii) $y = mx$

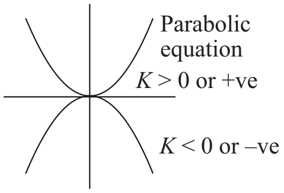


(iii) $yx = \text{constant}$

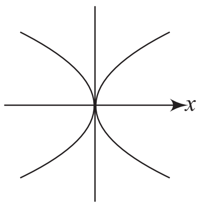
$$y = \frac{\text{constant}}{x}$$



(iv) $y = kx^2$



(v) $x = Ky^2$
If $K < 0$ or –ve
If $K > 0$ or +ve



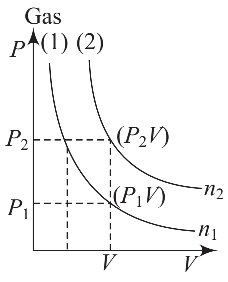
Gas Laws

Assumption

1. All gases are assumed to have no molecular attraction and volume of gas molecule is negligible.
2. In any gas law, relation between any two parameter are studied and other two are kept constant.
3. All gas laws are based on experiment.

Boyle's Law

This law states that for a fixed amount of gas kept at fixed temperature the pressure exerted by gaseous molecule is inversaly proportional to the volume of the gas.



$$P \propto \frac{1}{V} \quad [n \text{ and } T \text{ constant}]$$

$$P = \frac{K}{V}$$

$PV = K$ (1)
$P = y$
$V = x$
$yx = K$ constant.

$PV = nRT = K \qquad \therefore P = \dfrac{K}{V} \qquad P_2 > P_1$

$(nRT)_2 > (nRT)_1 \qquad \left(\dfrac{K}{V}\right)_2 > \left(\dfrac{K}{V}\right)_1$

(i) If $T_1 = T_2$ $\quad \therefore n_2 > n_1$
(ii) If $n_1 = n_2$ $\quad \therefore T_2 > T_1$

Charle's Law

This law states that for a fixed amount of gas at constant pressure, volume occupied by two gases is directly proportional to absolute temperature.

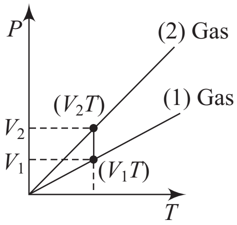
$V \propto T \quad [n \text{ and } p \text{ constant}]$

$$\boxed{\frac{V}{T} = K = \frac{nR}{P}}$$

or

$$\boxed{V = KT}$$

$= y = mx$

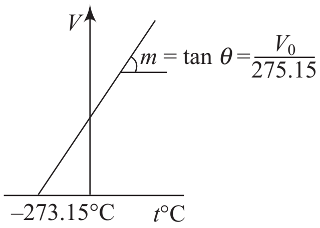


(i) If $n_1 = n_2$ $\quad V_2 > V_1$
$P_1 > P_2$ $\quad (KT)_2 > (KT)_1$

(ii) If $P_1 = P_2$ $\quad K_2 > K_1$ or $\left(\dfrac{nR}{P}\right)_2 > \left(\dfrac{nR}{P}\right)_1$

$\therefore \quad n_2 > n_1$

At constant pressure, the volume of a given amount of a gas increases or decreases by $\dfrac{1}{273.15}$th of volume at 0°C per degree rise or fall of temperature



If V_0 is the volume of gas at 0°C then at t°C

$$V_t^{°C} = \left\{V_0 + \frac{V_0}{273.15}t\right\}$$

$\Rightarrow \qquad y = C + mx$

Note:
Temperature lower than –273.15°C is not possible because volume of gas cannot be negative.

1. Boyle's law: $P \propto \dfrac{1}{V}$ and $[K = nRT]$
2. Charle's law: $V \propto T$ and $\left[K = \dfrac{nR}{P}\right]$
3. Gaylussac law: $P \propto T$ and $\left[K = \dfrac{nR}{V}\right]$
4. Avogadro's law: $V \propto n$ and $\left[K = \dfrac{RT}{P}\right]$

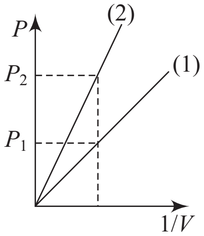
Graph's for Boyl's law

1. $P \text{ V}_\text{S} \dfrac{1}{V}$

$P = \dfrac{K}{V}$

$P = K \cdot \dfrac{1}{V}$

$y = mx$
$P_2 > P_1$



$\left(\dfrac{K}{V}\right)_2 > \left(\dfrac{K}{V}\right)_1 \quad \left\{\dfrac{1}{V}\text{is same}\right\}$

$K_2 > K_1$
$(nRT)_2 > (nRT)_1$

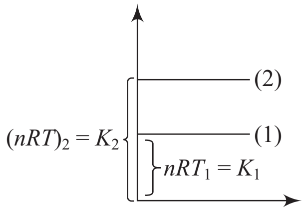
(i) If $n_1 = n_2$ $\quad \therefore \; T_2 > T_1$
(ii) If $T_1 = T_2$ $\quad \therefore \; n_2 > n_1$

2. $PV \text{ V}_\text{S} P$

$y = PV$
$x = P$

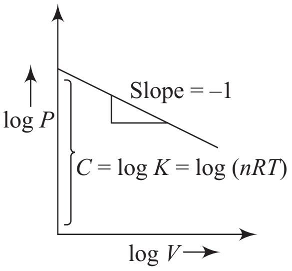
From Boyl's law

$PV = K = y$
$P\uparrow$ then $V\downarrow$
$K_2 > K_1$
$(nRT)_2 > (nRT)_1$



3. $\log P \text{ V}_\text{S} \log V$

$y = \log P$
$x = \log V$



But from Boyl's law

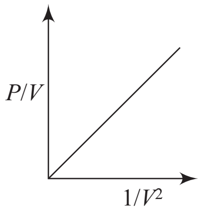
$$PV = K$$
$$\log(PV) = \log K = \log(nRT)$$
$$\log P + \log V = \log K$$
$$\log P = -\log V + \log K$$
$$= y = -mx + C$$

4. $\frac{P}{V}$ Vs $\frac{1}{V^2}$

$$y = \frac{P}{V} \text{ and } x = \frac{1}{V^2}$$

But $PV = K$

$$\therefore \quad \frac{PV}{V^2} = \frac{K}{V^2}$$
$$\frac{P}{V} = \frac{1}{V^2} \times K$$
$$\equiv y = mx$$



5. $\frac{P}{V}$ Vs $\frac{1}{V}$

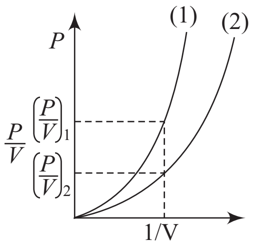
$$y = \frac{P}{V} \text{ and } x = \frac{1}{V}$$

But $PV = K$

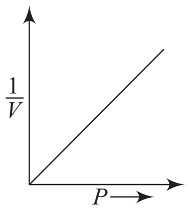
$$\frac{PV}{V^2} = \frac{K}{V^2}$$
$$\frac{P}{V} = K\frac{1}{V^2}$$
$$\equiv y = Kx^2$$

Since

$$\left(\frac{P}{V}\right)_1 > \left(\frac{P}{V}\right)_2$$
$$\left(\frac{K}{V^2}\right)_1 > \left(\frac{K}{V^2}\right)_2$$

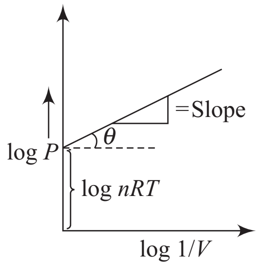


6. $\frac{1}{V}$ Vs P



7. $\log P$ vs $\log\frac{1}{V}$

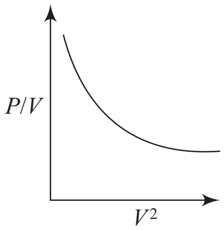
$$y = \log P \text{ and } x = \log\frac{1}{V}$$
$$PV = K = nRT$$
$$\log P + \log V = \log(nRT)$$
$$\log P = -\log V + \log(nRT)$$
$$\log P = \log\left(\frac{1}{V}\right) + \log(nRT)$$



8. $\frac{P}{V}$ vs V^2

From Boyl's law

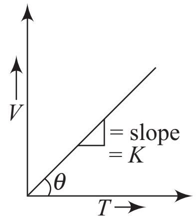
$$PV = \text{constant} = K$$
$$\frac{PV}{V^2} = \frac{K}{V^2}$$
$$\frac{P}{V} = \frac{K}{V^2}$$
$$\frac{P}{V} = y \text{ and } V^2 = x$$
$$y = \frac{K}{x}$$
$$yx = K$$



Special Case for Charle's Law

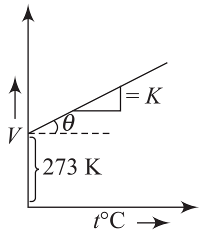
(i) $V \propto T$

$$\frac{V}{T} = K = \frac{nR}{P}$$
$$V = KT$$
$$\equiv y = mx$$



(ii) $V = KT$

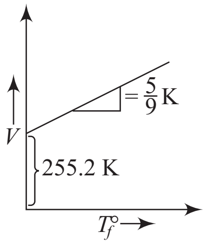
$$= K[t°\text{C} + 273]$$
$$V = Kt°\text{C} + 273 \text{ K}$$



(iii) $V = KT$

$$V = K\left[\frac{5}{9}T_f + 255.2\right]$$
$$V = \left[\frac{5}{9}K\right]T_f + 255.2 \text{ K}$$
$$\equiv y = mx + C$$

hence slope of kelvin and °C scale will be same but in forenheit scale it will be lesser.



Combining Law or Ideal Gas Equation

Ideal gas equation

$$V \propto \frac{1}{P} \qquad \text{Boyle's Law} \qquad (1)$$

$$V \propto T \qquad \text{Charle's Law} \qquad (2)$$

$$V \propto n \qquad \text{Avogadro's Law} \qquad (3)$$

Combining (i), (ii) and (iii)

$$V \propto \frac{nT}{P}$$

$$PV \propto nT$$

$$\boxed{PV = nRT}$$

R = universal gas constant.
$R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$ when P sin Pa or N/m^2
and V in m^3
$R = 0.0821$ atm lit mol^{-1} K^{-1}
P in atm and V in litre
$R = 1.987$ cal/mol K^{-1}
We know

$$PV = nRT$$

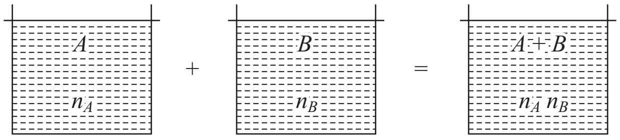
$$PV = \frac{\omega t}{Mwt} RT$$

$$P\,Mwt = \frac{\omega t}{V} RT$$

$$\boxed{PMwt = dRT}$$

or $$\boxed{PM = dRT}$$

Dalton's Law of Partial Pressure



$$P_A = \frac{n_A RT}{V} \quad P_B = \frac{n_B RT}{V} \quad P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V}$$

Partial pressure of gas $A = P_A$ and partial pressure of gas $B = P_B$.

$$P_T \boxed{= P_A + P_B}$$

$$P_A = X_A P_T \text{ and } P_B = X_B P_T$$

This law states that total pressure exerted by the mixture of gas is equal to the sum of partial pressure of each gas.

$$\boxed{P_T = P_A + P_B}$$

Partial pressure of any gas is defined as pressure exerted by moles of that particular gas only in same condition of temperature and volume.

The above law is applied only for non-reacting gas at given condition.

Graham's Law of Diffusion and Effusion

According to this law, rate of diffusion and effusion of any gas is inversaly proportional to the square root of molecular mass of gas.

$$R \propto \frac{1}{\sqrt{M_{\text{mass}}}} \qquad \text{[T.P. and } n \text{ are constant]}$$

$$\frac{R_A}{R_B} = \sqrt{\frac{M_B}{M_A}} \qquad \text{[T.P. } n \text{ are constant]}$$

$$\frac{R_A}{R_B} = \frac{P_A}{P_B}\sqrt{\frac{M_B}{M_A}} \qquad \text{[Dfferent partial pressure]}$$

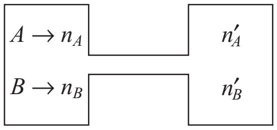
Since mole ∝ Partial pressure

$$\frac{R_A}{R_B} = \frac{n_A}{n_B}\sqrt{\frac{M_B}{M_A}}$$

$$\frac{R_A}{R_B} = \frac{\left(\frac{\Delta V}{\Delta t}\right)_A}{\left(\frac{\Delta V}{\Delta t}\right)_A} = \frac{\left(A \cdot \frac{\Delta L}{\Delta T}\right)_A}{\left(A \cdot \frac{\Delta L}{\Delta t}\right)_B}$$

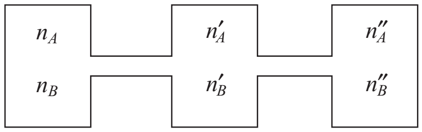
Enrichment of a lighter gas in given gaseous mixture

(i) For single diffusion system



$$\boxed{\frac{n'_A}{n'_B} = \frac{n_A}{n_B}\sqrt{\frac{M_B}{M_A}}}$$

(ii) Double diffusion system



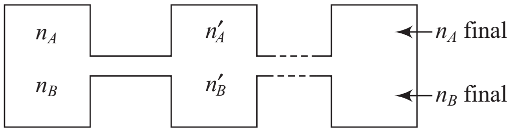
$$\text{for } 1^{\text{st}} \quad \frac{n'_A}{n'_B} = \frac{n_A}{n_B}\sqrt{\frac{M_B}{M_A}} \qquad \text{(i)}$$

$$\text{for } 2^{\text{nd}} \quad \frac{n''_A}{n''_B} = \frac{n'_A}{n'_B}\sqrt{\frac{M_B}{M_A}} \qquad \text{(ii)}$$

$$= \left[\frac{n_A}{n_B}\sqrt{\frac{M_B}{M_A}}\right] \cdot \sqrt{\frac{M_B}{M_A}}$$

$$\frac{n''_A}{n''_B} = \left[\frac{n_A}{n_B}\right]\left\{\sqrt{\frac{M_B}{M_A}}\right\}^2$$

(iii) For multiple diffusion

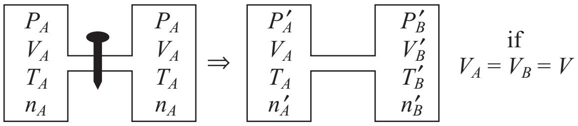


$$\left[\frac{n_A}{n_B}\right]_{\text{final}} = \left[\frac{n_A}{n_B}\right]_{\text{initial}} \left\{\sqrt{\frac{M_B}{M_A}}\right\}^n$$

n is also known as isotopic separation factor or number of diffusion step.

Application of Concept of Gaseous State

Connected Container

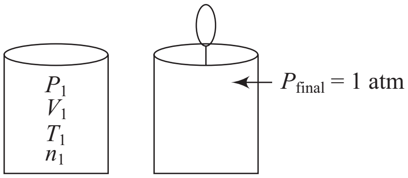


Result:

(i) $P'_A = P'_B$ (ii) $n_A + n_B = n'_A = n'_B$

(iii) $V_A = V'_A$ (iv) $V'_B = V_B$

Cylinder- and Balloon-Type Problem



Rules

1. $P_{\text{final}} = 1\text{atm}$
2. $V_{\text{initial}} = V_{\text{cylinder}}$

   [Because volume of balloon initially = 0]
3. $V_{\text{final}} = V_{\text{cylinder}} + V_{\text{balloons}}$

   $= V_{\text{cylinder}} + n$ [volume of 1 balloon]

> ***Note:***
> 1. In this type of problem, volume of system increases.
> 2. Number of moles of gas present in cylinder at initial position is equal to moles of cylinder and moles of balloon finally.
>
> $$\boxed{n_{\text{initial}} = n_{\text{cylinder}} + n_{\text{balloon}}}$$
>
> $$\boxed{\frac{P_1 V_{\text{cylinder}}}{T_1}} = 1 \times \frac{[V_{\text{cylinder}} + V_{\text{balloon}}]}{T_2}$$

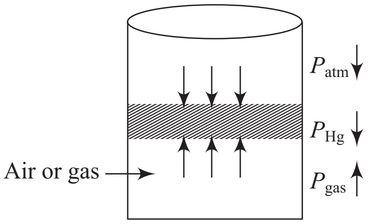
Capillary Tube-Type Problem

Rules

1. In this type of problem, we assume all the forces are balanced at equilibrium position. In other words, we can say total downward force is equal to total upward force.

   Hg always applies force in downward direction whereas atmospheric pressure and pressure of gas is applied on surface of mercury (Hg)

   Total upward directive force = Total downward directive force



$$P_{\text{gas}} = P_{\text{atm}} + P_{\text{Hg}}$$
$$= P_{\text{atm}} + hdg$$
$$= 1 + \left[\frac{h}{1000} \times \frac{13.6 \times 10^3 \times 9.8}{1.01 \times 10^5}\right] \text{atm}$$

$$\boxed{P_{\text{gas}} = 1 + \frac{h}{760}} \text{ atm}$$

h = height of Hg column in mm Hg.

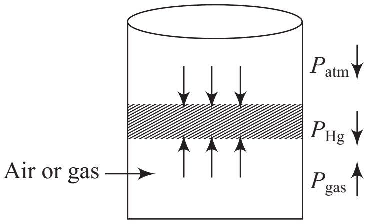
(2) This type of problem obeys Boyle's law

$$\boxed{P_1V_1 = P_2V_2}$$

Case I:

$$P_{\text{gas}} = P_{\text{atm}} + P_{\text{Hg}}$$

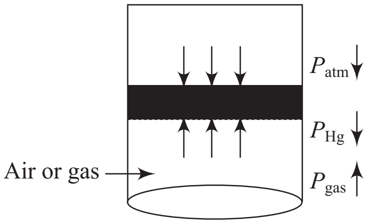
$$\boxed{P_{\text{gas}} = 1 + \frac{h}{760}} \text{ atm}$$



Case II:

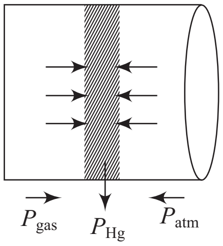
$$P_{\text{gas}} = P_{\text{atm}} - P_{\text{Hg}}$$

$$\boxed{P_{\text{gas}} = 1 - \frac{h}{760}} \text{ atm}$$

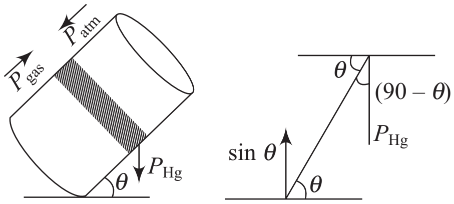


Case III:

$$\boxed{P_{\text{gas}} = P_{\text{atm}} = 1 \text{ tm}}$$



Case IV:



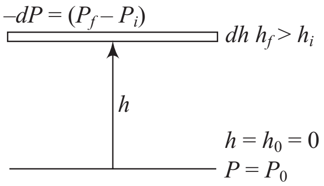
$$P_{gas} = P_{atm} + P_{Hg}\sin\theta$$

$$\boxed{P_{gas} = 1 + \frac{h}{760}\sin\theta}$$

Borometic distribution: To calculate the pressure difference for a vertical height '*h*' for any fluid where density is dependent on pressure.

$$-dp = dh(\rho g) \qquad \text{(i)}$$

Negative sign shows that decrease in pressure with increase in height.



$$PV = nRT$$

or $$PM = dRT = \rho RT$$

$m = M =$ molar mass of air

$$\rho = \frac{PM}{RT} \qquad \text{(ii)}$$

From Eqs. (i) and (ii)

$$-dp = \frac{PMg}{RT}dh$$

$$\frac{dp}{P} = -\frac{mg}{RT}dh$$

$$\int_{P_0}^{P_h}\frac{dP}{P} = -\frac{mg}{RT}\int_0^h dh$$

$$\boxed{\ln\frac{P_h}{P_0} = -\frac{mgh}{RT}}$$

$$\boxed{2.303\log\frac{P_0}{P_h} = \frac{mgh}{RT}} \qquad \text{(iii)}$$

From Eq. (iii)

$$\boxed{\frac{P_h}{P_0} = e^{-\frac{mgh}{RT}}}$$

$$P_h = P_0 e^{-\frac{mgh}{RT}}$$

or $$P_h = P_0 10^{-\frac{mgh}{2.303RT}}$$

Assumption:

1. Composition of air does not change with increase in height.
2. Temperature remains constant through the vertical height.
3. If molar temperature is constant.

$$P_1V_1 = P_2V_2$$

$$P_0V_0 = P_hV_h$$

$$\frac{P_0}{P_h} = \frac{V_h}{V_0} = e^{\frac{mgh}{RT}}$$

$$\therefore \quad V_h = V_0 e^{\frac{mgh}{RT}}$$

$$\boxed{\log\frac{V_h}{V_0} = \frac{Mgh}{2.303RT}}$$

4. Since $P \propto d$ (density)

$$\frac{P_h}{P_0} = \frac{d_h}{d_0} = e^{-\frac{mgh}{RT}}$$

$$d_h = d_0 e^{-\frac{mgh}{RT}}$$

5. $M_{dis.air} = M_{pay.load} + M_{balloon}$

$$\therefore \quad M_{Payload} = V \times d_h - M_{balloon}$$

$$\boxed{M_{Pay\,load} = Vd_0 e^{-\frac{mgh}{RT}} - M_{balloon}}$$

Pay load: It is defined as the maximum weight that can be lifted by a gas filled balloon.

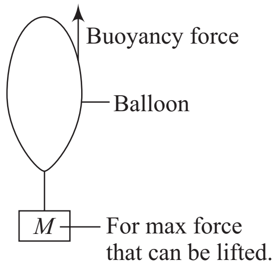
$$F_{Buoyancy} = Mg + m_{balloon}g$$

$$M_{displaced\ air} \times g = W_{Pay\ load} + W_{balloon}$$

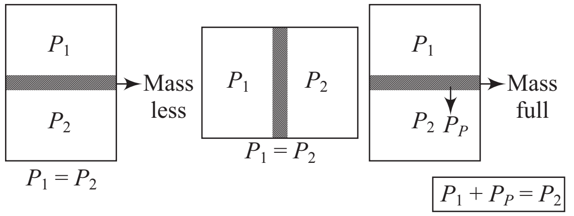
$$[M_{displaced\ air} \times g]$$

$$= [M_{payload} \times g] + [M_{gas} \times g + M_{balloon} \cdot g]$$

$$\boxed{\begin{aligned}&\therefore\ [V_{balloon}\cdot d_{air}\cdot g] = \\ &[M_{pay\,load}\cdot g] + [V_{balloon}\cdot d_{gas}\cdot g + M_{balloon}\cdot g]\end{aligned}}$$



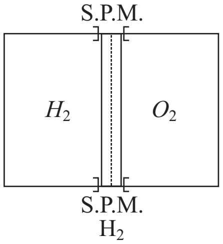
Problems Related with Piston



Final pressure is equal at both sides of movable massless piston.

Semi-permeable membrane (SPM)

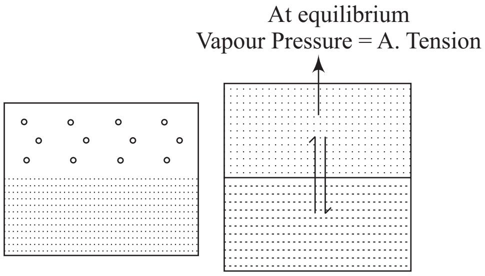
(i)



S.P.M. allows the movement of some particular molecules through itself.

(ii) Partial pressure of diffusable gas is same in non-movable or fixed S.P.M.

HUMIDITY



$$H_2O(l) \rightleftharpoons H_2O_{(vap)}$$

K = equilibrium constant. It depends only on temperature. It does not depend on quantity of water, volume or any other gaseous pressure.

At equilibrium position quantity of water in air is maximum. So we can say equilibrium is a saturation point.

At equilibrium (saturation) point, partial pressure of water is called aqueous tension.

$$\boxed{\text{P.P. of } H_2O \text{ vapour at saturation} = \left[\frac{n_{H_2O}RT}{V}\right]}$$

$$\boxed{\text{Relative humidity} = \frac{\text{P.P. of } H_2O \text{ vapour}}{\text{A.T as same temp.}} \times 100}$$

and

$$P_{\text{total}} = P_{\text{dry air}} + P_{H_2O\,\text{vapour}}$$

R.H. relative humidity

$$\frac{\text{P.P.}_{H_2O}\text{ in air}}{\text{A.T.} = \text{V.P.} = \text{P.P.}_{H_2O}(\text{at equi.})} \times 100$$

if $(\text{P.P.}_{H_2O})_{\text{air}} > \text{A.T.}$ (condensation)

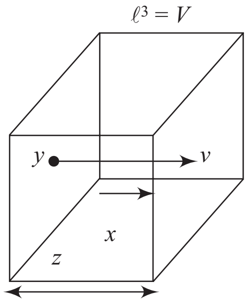
KINETIC THEORY OF GASES

(Microscopic model)

KTG is a theoretical model which can correlate the experimental facts.

Assumptions:

1. Gas consists of small particles (molecules or atoms) identical in size, shape and mass.
2. The volume of molecules itself is considered negligible w.r.t. to the total volume of the gas (total volume of container).
3. There is no force of interaction (attraction or repulsion) in between the gas particles, i.e., each molecule can move independently.
4. The gaseous molecules move in rapid motion and collide randomly with each other as well as the walls of container. (The pressure of gas is due to the collision of molecules with the walls of container.)
5. The collisions are perfectly elastic in nature (no energy loss). Hence there is no net loss of kinetic energy. Kinetic energy is transferred from one molecule to another but it is not converted into any other form of energy such as heat.
6. At any instant, given molecules can have energy range from small to large but the average kinetic energy of the molecules is directly proportional to absolute temperature $\left(\frac{3}{2}RT\right)$.
7. The law of classical mechanics (Newton's law of motion) are applicable to the molecules.



Consider there are total 'N' particles in a cubic container having volume 'V' and side length 'l'.

Consider a particle having velocity 'v' moves on X-direction then momentum of that particle before collision = mv_x.

Momentum of particle after collision = $-mv_x$.

Therefore, change in momentum $mv_x - (-mv_x) = 2mv_x$.

The molecules collide with opposite wall as the time

$$= \frac{l}{v_x}\left[\because v_x = \frac{l}{t}\right]$$

It is the time of one collision.

Total collisions are per unit time = $\frac{1}{T} = \frac{v_x}{l}$

Change in momentum per unit time in x-direction by a single particles is

$$= \boxed{2mv_x \times \frac{v_x}{l} = \frac{2mv_x^2}{l}}$$

Similarly in y-direction and z-direction

$$y = \frac{2mv_y^2}{l}$$

$$z = \frac{2m_2v_z^2}{l}$$

Total rate of change of momentum by single particle in all direction:

$$\frac{2m}{l}(v_x^2 + v_y^2 + y_z^2)$$

$$v = v_x\hat{i} + v_y\hat{j} + v_z\hat{k}$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$= \frac{2m}{l}v^2$$

There are 'N' particles present in a container. Therefore, force exerted by them is equal to

$$= \frac{2m}{l}(N_1v_1^2 + N_2v_2^2 + \dots\dots\dots + N_N v_N^2)$$

$$= \frac{2m}{l}[Nu_{\text{rms}}^2]$$

$$\therefore \qquad \text{Applied pressure} = \frac{\frac{2m}{l}[Nu_{\text{rms}}^2]}{6l^2}$$

$$P = \frac{1}{3l^3}m[Nu_{\text{rms}}^2]$$

$$l^3 = V$$

$$P = \frac{1}{3V}m[Nu_{\text{rms}}^2]$$

for 1 mole m. N. = M mass

$$PV = \frac{1}{3}M_{\text{Mass}}U_{\text{rms}}^2$$

$$\text{K.E.} = \frac{1}{2}mu^2 = \frac{3}{2}PV.$$

$$= \frac{3}{2}nRT$$

for 1 mole KE = $\frac{3}{2}RT$

for 1 molecule KE = $\frac{3}{2}KT$

$$K = \frac{R}{N_A} = 1.38 \times 10^{-23}$$

Boltzmann constant

Calculation of Root, Mean, square velocity Represented as V_{rms} or U_{rms} and C_{rms}

$$V_{\text{rms}} = \sqrt{\frac{N_1v_1^2 + N_2v_2^2 + N_2v_3^2 + N_nv_N^2}{N}}$$

$$PV = \frac{1}{3}MU_{\text{rms}}^2$$

$$U_{\text{RMS}} = \sqrt{\frac{3PV}{M}}$$

$$\boxed{U_{\text{RMS}} = \sqrt{\frac{3RT}{M}}} \Rightarrow \text{for mole gas}$$

$$PV = RT$$

Data in MKS

P = N/m^2

M = kg/mol

R = 8.314

Proof of Various Gas Laws

Boyle's law

$$PV = \frac{1}{3}\text{m}\,C_{\text{rms}}^2$$

if T in Kelvin (Constant)

$$C = \sqrt{\frac{3RT}{M}}$$

$$P \propto \frac{1}{V}$$

$$PV = \frac{2}{3}\cdot\frac{1}{2}MC^2$$

$$= \frac{2}{3} \times \frac{3}{2}\cdot RT$$

$$\boxed{\begin{array}{l} PV = RT \\ PV = nRT \end{array}}$$

Maxwell's distribution of velocities.

According to the kinetic theory of gases velocity of a molecule continuously change as a result of collision with other molecules as well as the walls of container.

Net result cannot comment about the velocity of 'a' single molecule but we consider that the average of velocity of all molecules remains constant at constant temperatures.

Since the observed properties such as volume pressure and temperature of an isolated gaseous sample do not change with time, so it is expected that the same is also true for the distribution of molecular velocities, i.e., the fraction of the total number of molecules having velocity in between any definite range must be constant.

Maxwell gave the expression by the theory of probability:

$$d_{\text{Nu}} = 4\pi N\left(\frac{M}{2\pi RT}\right)^{3/2} U^2 e^{-\frac{Mv^2}{2RT}}\cdot du$$

d_{Nu} → total nmber of molecules in velocity range from u to $(u + du)$

N → total number of particles in collection

M → molar mass of gas (kg/mole)

T → temperature in kelvin

u → starting speed

du → difference of speed

R → gas constant

$$\boxed{\frac{d_{\text{Nu}}}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} u^2 e^{-\frac{Mu^2}{2RT}}\cdot du} \qquad \text{(i)}$$

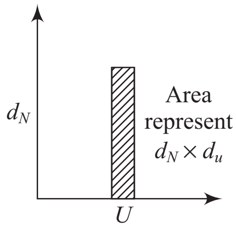
$\frac{d_{\text{Nu}}}{N}$ → fraction of molecules having velocity is between u to $(u + du)$

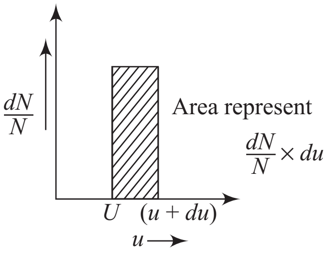
> ***Note:***
> According to Eq. (1)
> $\frac{d_{\text{Nu}}}{N}$ (fraction of molecules) depends only on temperature for a given gas (having molecular mass M)
> Characteristics of Maxwell's distribution

Curve

The parameter which were selected by Maxwell such that the area under the graph (curve) give the value of fraction of molecules between two speeds.

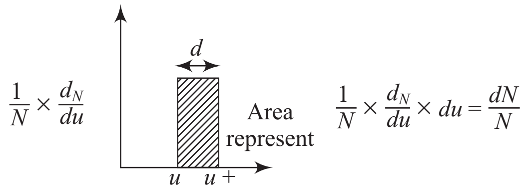
$$\frac{1}{N}\cdot\frac{d_{\text{Nu}}}{du} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\cdot U^2\cdot e^{-\frac{Mu^2}{2RT}}$$

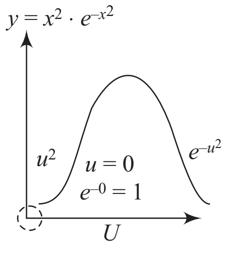




Finally,

$$y = x^2\cdot e^{-x^2}$$





1. **Most probable speed**

   The values of speed for which is $\frac{1}{N}\frac{d_N}{du}$ maximum is called most probable speed, i.e., the speed possessed by maximum number of molecule or maximum fraction of molecules is called the most probable speed. (U_{amp} or v_{mp})

$$\left(\frac{1}{N}\right)\left(\frac{d_N}{du}\right) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}u^2e^{-\frac{Mv^2}{2RT}}$$

$$\frac{d}{du}\left(\frac{1}{N}\frac{d_N}{du}\right) = k\left[2ue^{-\frac{Mv^2}{2RT}} + u^2e^{-\frac{Mv^2}{2RT}}\times(-)\frac{2mv}{2RT}\right]$$

$$K = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}$$

$$= K\times ue^{-\frac{Mv^2}{RT}}\left[2 - \frac{Mv^2}{RT}\right]$$

For maximisation, put $\frac{d}{du}\left(\frac{1}{N}\frac{d_N}{du}\right) = 0$

$$\Rightarrow \qquad 2 = \frac{Mv^2}{RT}$$

$$\boxed{v_{\text{mp}} = \sqrt{\frac{2RT}{M}}}$$

OR

It can be derived by condition of maxima.

$$\frac{d\left[\frac{1}{N}\frac{dNu}{du}\right]}{du} = 0$$

$$= \frac{d}{du}\left[4\pi\left[\frac{M}{2\pi RT}\right]^{3/2}u^2e^{-\frac{Mu^2}{2RT}}\right] = 0$$

$$= 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}}\frac{d}{du}\left[\underset{(i)(ii)}{u^2e^{-\frac{mu^2}{2RT}}}\right] = 0$$

$$= 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}}\left[2ue^{-\frac{mu^2}{2RT}} + u^2e^{-\frac{mu^2}{2RT}}\times(-)\frac{2mu}{2RT}\right]$$

$$= 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}}ue^{-\frac{mu^2}{2RT}}\left[2 - \frac{mu^2}{RT}\right] = 0$$

$$2 - \frac{MV^2}{RT} = 0$$

$$\frac{Mu^2}{RT} = 2$$

$$u_{mp} = \sqrt{\frac{2RT}{M}}$$

M = molecular mass in kg
T = Temperature in Kelvin
$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$

2. **Average molecular speed**

$$u_{\text{av}} = \frac{N_1V_1 + N_2V_2 + N_3V_3 + --}{N_1 + N_2 + N_3 + --}$$

We can also derive this by Maxwell distribution theory.

$$u\left(\frac{dNu}{N}\right) = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} u^3 e^{-\frac{mu^2}{RT}} du.$$

$$= 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} \int_0^\infty u^3 e^{-\frac{mu^2}{RT}} du.$$

$$u_{\text{av}} = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}}\left[2\left(\frac{RT}{M}\right)^2\right]$$

$$u_{\text{av}} = 4\pi\left(\frac{M}{2\pi RT}\right)\left[\sqrt{\frac{M}{2\pi RT}}\right]\left[2\left(\frac{RT}{M}\right)^2\right]$$

$$u_{\text{av}} = \sqrt{\frac{8RT}{\pi M}}$$

3. **Root mean square velocity**

$$u_{\text{rms}} = \sqrt{\frac{M_1V_1^2 + M_2V_1^2 + M_3V_3^2}{M_{\text{total}}}}$$

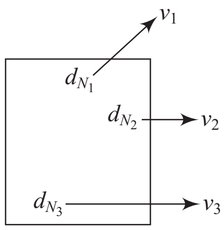
$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Note:
The relative ratio

u_{av}	:	U_{mp}	:	u_{rms}
$\sqrt{\frac{8RT}{\pi M}}$	:	$\sqrt{\frac{2RT}{M}}$	:	$\sqrt{3}$
$\sqrt{\frac{8}{\pi}}$	:	$\sqrt{2}$	:	$\sqrt{3}$
$\sqrt{\frac{56}{22}}$	:	$\sqrt{2}$	:	$\sqrt{3}$

Consequence of Distribution of Speed

It is the average kinetic energy of gas at a given time that is constant.



$$\text{K.E.} = \frac{1}{2}Mv_1^2 \times d_{N_1} + \frac{1}{2}Mv_2^2 d_{N_2} + ... + \frac{1}{2}Mv_n^2 d_N$$

$$= \frac{1}{2}M\sum_{i=1}^{N} v_i^2\left(\frac{d_{Ni}}{N}\right) \qquad \text{(i)}$$

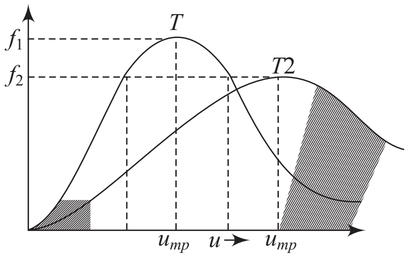
$$d_{\mathbf{N}_1} + d_{N_2} + ... + d_{N_n} = N$$

From Eq. (i)

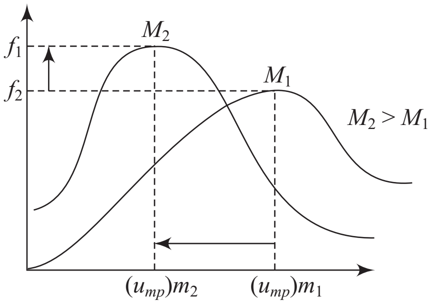
We can say that for a particular gas at constant temprature for fraction, $\frac{d_N}{N}$ is constant. So the average kinetic energy of gas is only and only the function of temperature.

Conclusions

1. The fraction of molecules having very low or very high speed are small in number.
2. Majority of molecules have speed near the most probable speed.
3. Total area under the curve is the major of total number of fraction of molecules (or total number of molecules in collection).
4. Since with increase in temperature kinetic energy of molecules increases by which fraction of molecules have low speed range decreases whereas the fraction of molecules having high speed range increases.



5. With the increase in temperature, U_{mp} also increases but corresponding fraction of molecules will decrease.
6. Speed distribution also depends on molar mass of gas and the gas having high molar mass has higher fraction (corresponding to U_{mp}).



Hence the distribution depends on the value of $\frac{M}{T}$. It means the distribution will be same for gas having '2*M*' molecular mass at 2*T* temperature because $\frac{M}{T}$ ratio remains same.

Example 1. The temperature at which Maxwell distribution curve of SO_2 will be same as O_2 at 300 K.

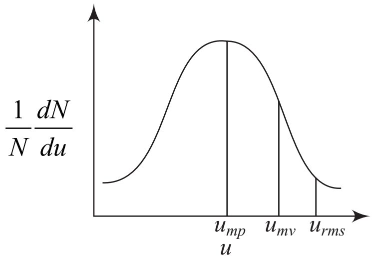
$M_{O_2} = 32$ $\qquad$ $M_{SO_2} = 64$

Mass is double $\qquad$ ∴ temperature is doubled

⇒ $T = 600$ K.

Ratio of speeds

$$u_{\text{mp}} : v_{\text{av}} : v_{\text{rms}} :: \sqrt{2} : \sqrt{\frac{8}{\pi}} :: \sqrt{3} = 1.14 : 1.6 : 1.732$$



If the speeds are written in terms of pressure and volume then number of moles of gas are also required but if temperature is given then number of moles number is not required.

$$PV = \frac{1}{3} m\text{Nu}_{\text{rms}}^2$$

mass of gas = $m \times N$ = total weight and M molar mass

$$nRT = \frac{1}{3} m\text{Nu}_{\text{rms}}^2$$

$$\frac{\text{weight}}{\text{Molar Mass }(M)} RT = \frac{1}{3} m\text{Nu}_{\text{rms}}^2$$

$$\boxed{u_{\text{rms}} = \sqrt{\frac{3RT}{M}}}$$

$$\boxed{\sqrt{\frac{3PV}{nM}} = u_{\text{rms}}}$$

$$\sqrt{\frac{3PV}{\left(\frac{W}{M}\right)M}}$$

$$\boxed{\sqrt{\frac{3P}{d}} = u_{\text{rms}}}$$

Molecular collision

Assumptions

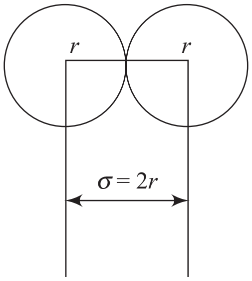
(i) Molecular are considered perfectly rigid and spherical in shape.

(ii) All the particles are moving with u_{avg} speed.

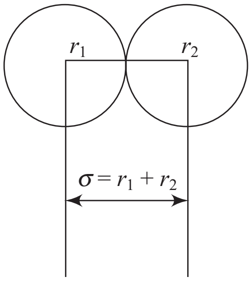
Collision Diameter (σ)

It is the distance between centres of two-diameter colliding particles, i.e. the distance between particles is 2R, the particles will collide.

Same gas

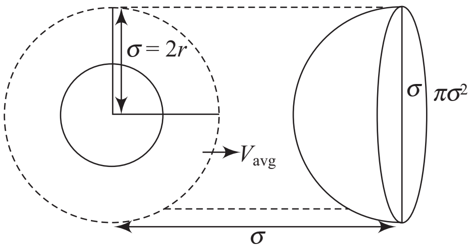


Different gas



Collision cross-section area

It is the cross-sectional area of imaginary sphere surrounding a molecule into which centre of another molecule cannot penetrate.



When the molecules arrive a circumference of $2r$, then the molecules will collide.

Collision frequency

It is equal to the number of collision occuring in per unit volume per unit time under the specific conditions.

Case 1: Consider only one particle is moving and others are stationary

(i) A molecule will collide if centre will lie inside the collision cross has a section.

(ii) If a moving particle speed of u_{avg}, then the imaginary volume swept by moving particle per unit time is equal to $v' = \pi\sigma^2 V_{\text{avg}}$.

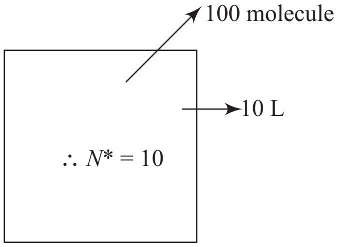
$$v' = \pi\sigma^2 V_{\text{avg}}$$

$$\boxed{v' = A \times \ell}$$

(iii) If N^* is the number of molecules of gas per unit volume, then the total number of molecules within the swept volume is equal to $\pi\sigma^2 v_{\text{avg}} \times N^* = Z$ = collision frequency.

$$N^* = \frac{N}{V}$$

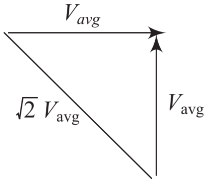
Total number of particles = $N^* \times V'$



Therefore, Z is the number of collisions made by a single moving particle in per unit time, when all others are considered to be stationary.

Case 2: Consider all molecules are moving.

(i) Two particles can collide at angle anywhere 0 to 180°. It means the chances of collision at each angle are same. Therefore, average angle of collision is 90° and the relative velocity = $\sqrt{2}\, v_{\text{avg}}$



$$\boxed{Z_1 = \sqrt{2}\pi\sigma^2 v_{\text{avg}} \times N^*}$$

Z_1 is the number of collisions made by a single molecule in per unit time when all particles are moving.

Bimolecular collision

Case I:

When molecular collision in between two molecules of same gas (Z_{11}).

Bimolecular collision frequency = $\frac{1}{2}$ × (number of particle per unit volume) × (number of collisions made by 1 particle in per unit time)

$$Z_{11} = \frac{1}{2} \times (N^*) \times (Z_1)$$

$$= \frac{1}{2} \times (N^*) \times (\sqrt{2}\,\pi\sigma^2\, v_{\text{avg}}) \times N^*$$

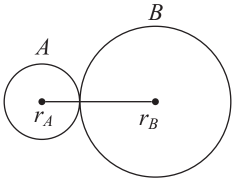
$$\boxed{Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2 v_{\text{avg}} (N^*)^2}$$

Note:

Division by 2 is essential since the simple multiplication of Z_1 by N^* would count every collision twice.

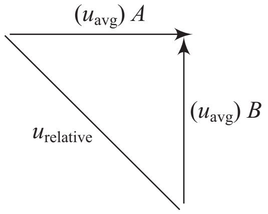
Case 2:

When collision occurs in between the molecules of two different gases (Z_{12}).



$$\sigma_{12} = r_A + r_B$$

$$\boxed{\sigma = \frac{\sigma_A}{2} + \frac{\sigma_B}{2}}$$



$$u_{\text{relative}} = \sqrt{\left(\frac{8}{\pi}RT\right)\left(\frac{1}{M_A} + \frac{1}{M_B}\right)} = \sqrt{(u_{\text{avg}})_A^2 + (u_{\text{avg}})_B^2}$$

$$\boxed{u_{\text{relative}} = \sqrt{\frac{8RT}{\pi M}}}$$

$$\because \quad \boxed{\frac{1}{M} = \frac{1}{M_A} + \frac{1}{M_B}}$$

(i) The volume swept by moving molecule A per unit time is equal to $\pi\sigma^2\, u_{\text{relative}}$.

(ii) If N_B^* is the number of molecules of gas B per unit volume, then the total number of molecules within the swept volume = $\pi\sigma^2\, u_{\text{relative}} \times N_B^*$

(iii) Then the total number of collision made by gas A per unit volume per unit time is equal to

$$\boxed{N_A^* \times N_B^* \times \pi\sigma^2 v_{\text{relative}} = Z_{12}}$$

Mean free path (λ):

It is defined as the average distance travelled by molecules between two successive collissions.

Then distance travelled by 1 molecule in per unit time

$$\boxed{v_{\text{avg}} = \frac{l}{t = 1\,\text{sec.}}}$$

Total collision made by a molecule in per unit time

$Z_1 = \sqrt{2}\,\pi\sigma^2\, u_{\text{avg}} \cdot N^*$

λ distance travelled in one collision.

$\therefore$ 1unit distance travelled in $\frac{1}{\lambda}$ collision.

Then, u_{avg} distance travelled in $\frac{1}{\lambda} \times u_{\text{avg}}$ collision.

$$\boxed{\frac{1}{\lambda} \times u_{\text{avg}} \text{collission} = Z_1}$$

$$\boxed{\lambda = \frac{u_{\text{avg}}}{Z_1}}$$

$$= \frac{u_{\text{avg}}}{\sqrt{2}\pi\sigma^2 u_{\text{avg}} N^*}$$

$$\therefore \quad \boxed{\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}}$$

Effect of temperature, pressure and volume on λ, Z_1, Z_{11}

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*} \qquad \text{(i)}$$

$$Z_1 = \sqrt{2}\,\pi\sigma^2\, u_{\text{avg}}\, N^*$$

$$Z_{11} = \frac{1}{\sqrt{2}}\,\pi\sigma^2\,(N^*)^2\, u_{\text{avg}}$$

$$PV = \left(\frac{N}{N_A}\right)RT$$

$$P = \left(\frac{N}{V}\right)\left(\frac{R}{N_A}\right)T$$

$$P = N^*\, KT$$

$$\boxed{\frac{P}{KT} = N^*}$$

From Eq. (i)

$$\lambda \propto \frac{T}{P}$$

$$Z_1 \propto \sqrt{\frac{8}{\pi}\frac{RT}{M}} \times \frac{P}{kT}$$

$$\boxed{Z_1 \propto \frac{P}{\sqrt{T}}}$$

$$Z_{11} \propto \sqrt{\frac{8}{\pi}\frac{RT}{M}} \times \frac{P^2}{k^2T^2}$$

$$\boxed{Z_{11} \propto \frac{P^2}{(T)^{3/2}}}$$

At constant (T)

$$\lambda \propto \frac{T}{P} \qquad Z_1 \propto \frac{P}{\sqrt{T}} \qquad Z_{11} \propto \frac{P^2}{T^{3/2}}$$

$$\uparrow \lambda \propto \frac{1}{P\downarrow} \quad \uparrow Z_1 \propto P\uparrow \quad Z_{11} \propto P^2$$

At constant (P) $\lambda \propto T \quad Z_1 \propto \frac{1}{\sqrt{T}} \quad Z_{11} \propto \frac{1}{T^{3/2}}$

At constant (V)

$$\lambda \propto \frac{T^*}{T} = K \quad Z_1 \propto \frac{T}{\sqrt{T}} = \sqrt{T} \quad Z_{11} \propto \frac{T^2}{T^{3/2}}$$

$$\boxed{\uparrow P \propto T \uparrow} \qquad \boxed{Z_{11} = \propto \sqrt{T}}$$

λ = constant [when volume is constant]

$$V = \frac{P}{T} = \text{constant}$$

Maxwell distribution in terms of kinetic energy

$$\frac{d_{Nu}}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} U^2 e^{-\frac{MU^2}{2RT}} \cdot du$$

$$KE = E = \frac{1}{2}mu^2$$

$$u = \sqrt{\frac{2E}{M}}$$

$$dE = \frac{1}{2}m \times 2Udu$$

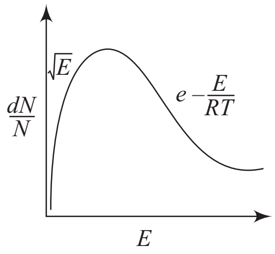
$$= \frac{dE}{MU} = du$$

$$\frac{dE}{M\sqrt{\frac{2E}{M}}} = du \Rightarrow \frac{dE}{\sqrt{2EM}}$$

$$\frac{dN_E}{NdE} = \frac{2\sqrt{E}}{\sqrt{\pi}\,(RT)^{3/2}} e^{-\frac{E}{RT}}$$

$$\boxed{y = \sqrt{x}e^{-x}}$$

$$dE = \left(\frac{dN}{N}\right)$$



REAL GAS

Gases which do not obey ideal gas law is called *real gas*. A real gas is different from ideal gas from 2 factor.

(i) According to K.T.G., the intermolecular attraction negligible for an ideal gas. However in reality, the attraction are significant enough. Therefore, the pressure observed will be less than pressure that would have been obtained under similar condition by an ideal gas. Therefore a correction factor '$P_{\text{C.F.}}$' is to be added.

$$P = P_{\text{obs}} + P_{\text{C.F.}}$$

(ii) According to K.T.G., the volume occupied by particle is negligible hence total free volume for ideal gas is same as volume of container. However for real gas since size of molecule is significant, therefore, free volume available for the moment is less than volume of container.

$$V = V_{\text{obs}} - V_{\text{C.F.}}$$

Gas equation for real gas

$$(P + P_{\text{C.F.}})\,(V - V_{\text{C.F.}}) = RT$$

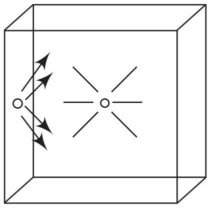
Calculation for correction factor

(1) Calculation of pressure correction:

The pressure correction factor depends on 2 factor.

(i) Number of molecules attracting the striking molecules.

(ii) Number of molecules striking the wall of container.



$$P_{\text{C.F.}} \propto [\text{Attracting molecules}] \times [\text{String molecules}]$$

$$\text{PC.F.} \propto [N^*]\,[N^*] \text{ and } N^* = \frac{N}{V} \text{ and } N = nN_A$$

$$P_{C.F.} \propto \left[\frac{N}{V}\right]\left[\frac{N}{V}\right]$$

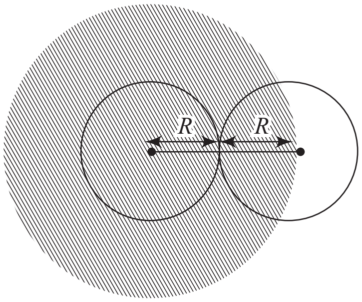
$$P_{\text{C.F.}} \propto \left[\frac{n \times N_A}{V}\right]\left[\frac{n \times N_A}{V}\right]$$

$$\boxed{P_{\text{C.F.}} = a\frac{n^2}{V^2}}$$

$$\boxed{a = \frac{P_{\text{C.F.}}V^2}{n^2}}$$

Unit = atm lit^2 mol^{-2}
a = Vanderwall const.

Correction Factor for Volume



The shaded part show the excluded volume for the pair of particle.

Excluded volume for a pair of molecule $= \frac{4}{3}\pi\,[2R]^3$

$$= \frac{32}{3}\pi R^3$$

$\therefore$ excluded volume for one molecule $= \frac{16}{3}\pi R^3$

$$= 4\left[\frac{4}{3}\pi r^3\right] = 4\,[\text{volume of 1 molecule}]$$

$\therefore$ excluded volume for 1 mole molecule
$= 4\,[\text{Volume of 1 molecule}] \times N_A$
$= 4 \cdot V_1 N_A = b$

$\therefore$ for n mole molecule $= n \times 4V_1N_A = nb$

$$\therefore \quad \left[P + \frac{n^2a}{V^2}\right][V - nb] = nRT$$

This is called Van der wall equation for real gas for n mole.

Physical significance of *a* and *b*

(i) a depends on force of attraction between molecules.
F.A. ∝ (i) At wt. or Mwt.
F.A. ∝ (ii) polarity of compound

F_2 Cl_2 Br_2 I_2 ↓ He Ne Ar ↓ a increases

$\therefore \quad a_{NH_3} > a_{N_2}$

Polar	**Nonpolar**
$\begin{bmatrix}\text{HCl, NH}_3\\ \text{H}_2\text{O}\end{bmatrix}$	$\begin{bmatrix}\text{N}_2, \text{Cl}_2\\ \text{H}_2, \text{O}_2\end{bmatrix}$

(ii) b depends on size of molecules
$b \propto$ size of molecule
So $\quad b_{H_2} < b_{Cl_2}$

Q. One way of writing the equation of state for real gases is

$PV = RT\left[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3}\right]$ where B is a constant.

Derive an expression for 'B' in terms of Van der wall constant.

Ans. We know that Van der wall gas equation for real gas is

$$\left[P + \frac{a}{V^2}\right][V - b] = RT$$

$$\left[P + \frac{a}{V^2}\right] = \frac{RT}{V - b}$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$PV = \frac{RTV}{V - b} - \frac{a}{V}$$

$$PV = RT\left[\frac{V}{V - b} - \frac{a}{VRT}\right]$$

$$PV = RT\left[\frac{1}{1 - \frac{b}{V}} - \frac{a}{VRT}\right]$$

$$PV = RT\left[\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{VRT}\right]$$

We know $(1 - x)^{-1} = 1 + x + x^2 + x^3 + \ldots$
if $\quad x << 1$

$$x = \frac{b}{V} << 1$$

$$PV = RT\left[1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + - \frac{a}{VRT}\right]$$

$$PV = RT\left[1 + \frac{b}{V}\left[b - \frac{a}{RT}\right] + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3\right]$$

This equation is compared by the given equation then we can find the value of 'B'.

$$B = \left[b - \frac{a}{RT}\right] \quad C = b^2\,D = b^3$$

> ***Note:***
> A temperature above which real gases have a ideal gas nature is called Boyle's temperature.

Calculate the Value of Boyle's Temperature

We find

$$PV = RT\left[1 + \frac{1}{V}\left[b - \frac{a}{RT}\right] + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + ...\right]$$

Since $\frac{b}{V} <<< 1$

So we can neglect the heigher value of $\frac{b}{V}$ for eq. $\left(\frac{b}{V}\right)^2, \left(\frac{b}{V}\right)^3$ … etc.

For ideal nature

$$b - \frac{a}{RT} = 0$$

$$\boxed{T = \frac{a}{Rb}} \text{ Boyle's temperature}$$

$$PV = RT$$

Compressibility Factor

It is defined as the ratio of actual volume of gas and volume occupied by ideal gas under similar condition of temperature pressure and mole.

$$\left[Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}\right] \text{ Same condition of } P, T \text{ and } n.$$

$$V_{\text{ideal}} = \frac{nRT}{P}$$

$$Z = \frac{V_{\text{act.}}}{\frac{nRT}{P}}$$

$$Z = \frac{PV_{\text{act}}}{nRT}$$

$$\boxed{PV_{\text{act.}} = Z \cdot nRT} \quad Z = 1 \text{ for ideal gas}$$

For 1 mole

$$\boxed{PV_{\text{act.}} = ZRT}$$

$Z > 1 \Rightarrow$ Less compressible than expected.

$$Z = \frac{PV}{RT}$$

Variation of Compressibility factor with Respect to Pressure

(a) At low pressure

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

At low P volume $V\uparrow$ so $V - b \approx V$

$$\left(P + \frac{a}{V^2}\right)V = RT$$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} + \frac{a}{RVT} = 1$$

$$\frac{PV}{RT} = 1 - \frac{a}{RVT}$$

$$\therefore \quad Z = 1 - \frac{a}{RVT}$$

if $a\uparrow$ $z\downarrow$,

$\rightarrow \quad a_{N_2} < a_{CO_2}$

$\therefore \quad z_{N_2} > z_{CO_2}$

$\rightarrow \quad z_{N_2} < z_{NH_3}$

$\therefore \quad z_{N_2} > z_{NH_3}$

(b) At high pressure

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

The value can be neglected with respect to pressure but at high pressure the volume of gas is low hence '*b*' cannot be neglected with respect to '*V*'.

$$(V - b) = RT$$

$$P[V - b] = RT$$

$$PV - Pb = RT$$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$Z = 1 + \frac{Pb}{RT}$$

Since size of N_2 < size of NH_3

$\therefore \quad bN_2 < bNH_3$

$ZN_2 < NH_3$

if $\quad b\uparrow\ z\uparrow$

For lighter gases like H_2 and He having low value of Molar Mass and both are non-polar gases so that attraction between molecule is much less compared to other gases.

It means we can assume that the value of $a = 0$. [Both for high pressure and low pressure.]

$$\text{So} \quad \left[P + \frac{a}{V^2}\right][V - b] = RT$$

$$P(V - b) = RT$$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

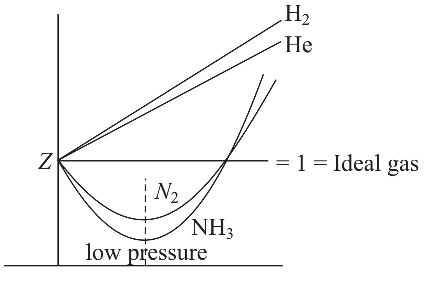
$$Z = 1 + \frac{Pb}{RT}$$

$\therefore \quad Z > 1$

We know $b\uparrow$, $z\uparrow$

$b_{H_2} > b_{H_e}$

So $[Z_{H_2} > Z_{He}]_P$ of constant pressure.

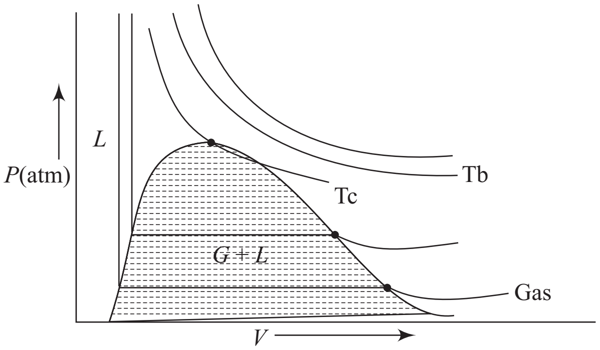


Critical temperature (T_C): Temperature above which gases cannot be liquified by any applied pressure of 'p' is called critical temperature (T_C)

Critical pressure (P_C): Minimum pressure which is required to liquify the gas at critical temperature.

Critical volume (V_C): Volume of 1 mole of gas at critical temperature and pressure is called critical volume (V_C)

Isotherms for gases



We know Van der wall equation

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b)=RT$$

$$(PV_m^2+a)(V_m-b)=RTV_m^2$$

$$PV_m^3-PbV_m^2+aV_m-ab=RTV_m^2$$

$$PV_m^3-V_m^2\,[Pb+RT]+aV_m-ab=0$$

$$V_m^3-V_m^2\left[b+\frac{RT}{P}\right]+\frac{a}{P}V_m-\frac{ab}{P}=0$$

At critical conditions-

$$V_m^3-V_m^2\left[b+\frac{RT_C}{P_C}\right]+\frac{aV_m}{P_C}-\frac{ab}{P_C}=0 \tag{i}$$

Equation (i) should have only one value of volume and should be 'Vc'.

The roots of equation will be

$$(V_m-V_C)\,(V_m-V_C)\,(V_m-V_C)=0$$

or $$V_m^3-3V_m^2V_C+3V_mV_C^2-V_C^3=0 \tag{ii}$$

Equations (ii) and (i) are similar so we can compare their coefficient.

$$\therefore \quad b+\frac{RT_C}{P_C}=3V_C \tag{iii}$$

$$\frac{a}{P_C}=3V_C^2 \tag{iv}$$

$$\frac{ab}{P_C}=V_C^3 \tag{v}$$

$$\frac{(5)}{(4)}=\frac{V_C^3}{3V_C^2}=\frac{ab}{P_C}\times\frac{P_C}{a}$$

$$\frac{V_C}{3}=b$$

$$\therefore \quad \boxed{V_C=3b}$$

By Eq. (iv)

$$\frac{a}{P_C}=3V_C^2$$

$$\frac{a}{P_C}=3[3b]^2$$

$$\therefore \quad \boxed{P_C=\frac{a}{27b^2}}$$

From Eq. (iii)

$$b+\frac{RT_C}{P_C}=3V_C$$

$$b+\frac{RT_C}{\left[\dfrac{a}{27b^2}\right]}=3V_C$$

$$b+\frac{RT_C}{\left[\dfrac{a}{27b^2}\right]}=3[3b]$$

$$\frac{RT_C}{\dfrac{a}{27b^2}}=8b$$

$$\therefore \quad T_C=\frac{8b}{R}\times\frac{a}{27b^2}$$

$$\boxed{T_C=\frac{8a}{27Rb}}$$

The law of corresponding states

P_r = Reduced pressure.

$$P_r=\frac{P}{P_C} \quad T_r=\frac{T}{T_C} \quad V_r=\frac{V_m}{V_C}$$

$$\left(P+\frac{a}{V_m^2}\right)\;(V_m-b)=RT$$

$$\left[P_rP_C+\frac{a}{(V_rV_C)^2}\right][V_rV_C-b]=RT_rT_C$$

$$\left[P_r\frac{a}{27b^2}+\frac{a}{V_r^2(3b)^2}\right][V_r(3b)-b]=RT_r\left[\frac{8a}{27Rb}\right]$$

$$\frac{a}{27b}\left[\frac{P_r}{b}+\frac{3}{V_r^2b}\right]b[3V_r-1]=8T_r\left[\frac{a}{27b}\right]$$

$$\boxed{\left[P_r+\frac{3}{V_r^2}\right][3V_r-1]=8T_r}$$

$$Z=\frac{PV_m}{RT}=\frac{(P_rP_C)(V_rV_C)}{R[T_rT_C]}$$

$$\boxed{Z=\frac{3}{8}\left[\frac{P_rV_r}{T_r}\right]}$$

Molar Heat Capacity

It is the required heat to rise 1°C temperature of 1mole substance.

1. In case of gaseous state molar heat capacity is a function of pressure and volume so that it has two different values C_P and C_V.

   C_P: molar heat capacity at constant pressure:
   It is the required heat to rise 1°C temperature of 1 mole of gas at constant pressure.

   C_V: Molar heat capicity at constant volume:
   It is the required heat to rise 1°C of temperature of 1mole of gas at constant volume.
2. For liquid and solid $C_P = C_V$
3. For ideal gas $C_P - C_V = R$ and $C_P > C_V$
   $R = 2$ cal $\text{mol}^{-1}\text{K}^{-1}$

   and $\gamma = \dfrac{C_P}{C_V}$ = constant = poisson ratio

   $\gamma > 1$
4. Value of C_P and C_V for different gases.

Gas	C_V	$C_P = C_V + R$	$r = \dfrac{C_P}{C_V}$
Monoatomic	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$
Diatomic	$\frac{5}{2}R$	$\frac{7}{R}R$	$\frac{7}{5}$
Triatomic linear (L)	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{9}{7}$
Triatomic non linear (NL)	$3R$	$4R$	$\frac{4}{3}$

5. Normally C_P and C_V are constant and it does not depend on temperature. But in case of high temperature, it is a function of temperature and it varies with temperature.

   $C_V = a + bt + ct^2$

   where a, b and c are constant.

Degree of freedom:

Translational degree of freedom

Movement of molecules in all 3(x, y, z) directions.

Value of translational degree (max.) is 3[for mono, di or triatomic]

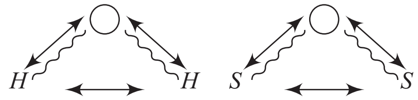
Degree of rotation is possible due to the rotation of atoms in molecule and the value of rotation degree of freedom is

for linear molecules (L) = 2

for non linear molecules (NL) = 3

Vibration degree of freedom:

It is possible due to the vibration in molecules



($3N - 5$) for linear molecule (L)

($3N - 6$) for non-linear molecule (NL).

where N is number of atoms.

Degree of freedom	**Linear (L)**	**Non-linear (NL)**
Translation	3	3
Rotational	2	3
Vibrational	$3N - 5$	$3N - 6$

Q. Determine the various degree of freedom for CH_4

Comp.	Trans.	Rot.	Vib.	Total
CH_4	3	3	9	15

3 × N
- 3tr — $\frac{1}{2}$KT
- 2rot [L] — $\frac{1}{2}$KT
- 3 rot [N.L] — $\frac{1}{2}$KT
- (3n-5) vib[L] – KT
- (3n-6) vib [N.L] – KT

For one molecule of benzene number of atom 12 (Non linear) so total degree of freedom 3 × 12 = 36 = 3 Rotational + 3 Translation + 30 vibrational

∴ Energy of one molecule

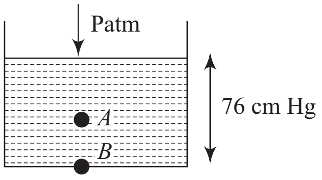
$$\frac{3}{2}\text{KT} + \frac{3}{2}\text{KT} + 30\ \text{KT} = 33\ \text{KT for } C_6H_6$$

Solved Examples

1. (i) An open tank is filled with Hg up to a height of 76 cm. Find pressure at the bottom and middle of the tank, if atmospheric pressure is 1 atm.

(ii) Find the height of water up to which water must be filled to create same pressure at the bottom.

Sol. (i)



$$P_B = P_{\text{atm}} + \frac{h}{76}$$

$$= 1 + \frac{76}{76} = 2\ \text{atm}$$

$$P_A = P_{\text{atm}} + \frac{h}{76}$$

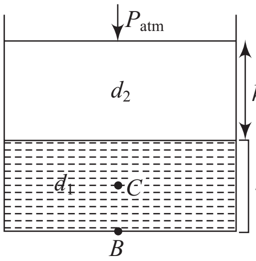
$$= 1 + \frac{38}{76} = 1.5\ \text{atm}$$

(ii) $(h_1 d_1 g)_{H_2O} = (h_2 d_2 g)_{Hg}$

$h_1 \times 1 \times 10^3 = 0.76 \times 13.6 \times 10^3$

$h = 10.33$ meter

2. What will the pressure



(i) at the bottom of the tank?

(ii) at the middle of the bottom layer if two immiscible liquids are filled as shown in figure?

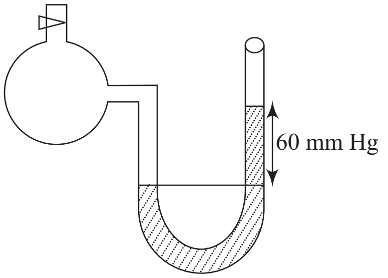
Sol. $P_B = P_{atm}$ + Pressure due to liquid (2) + Pressure due to liquid (1)

$$P_B = P_{atm} + \frac{h_2 d_2 g}{1.013 \times 10^5} + \frac{h_1 d_1 g}{1.013 \times 10^5}$$

If h in metre d in kg/m^3 and g in m/sec^2] or in M.K.S. 1 atm = 1.013×10^5 Pa

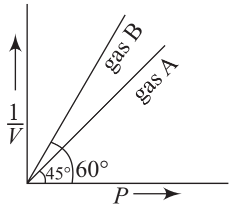
$$P_C = P_{atm} + \frac{h_2 d_2 g}{1.013 \times 10^5} + \frac{\frac{h_1}{2} d_1 g}{1.013 \times 10^5}$$

3. Find the pressure of gas inside the container if manometer attached to the container shows a difference of 60 mm as shown in the figure?



Sol. $P = P_{atm} + \dfrac{60}{760} = 1 + \dfrac{6}{76}$ atm

4. At a constant temperature of 273K, $\dfrac{1}{V}$ vs P is plotted for two ideal gases A and B as shown in the figure. Find out the number of moles of gases A and B.



Sol. $PV = nRT, \quad P = \dfrac{1}{V} nRT$

$$\frac{1}{V} = \frac{1}{nRT} P$$

Comparing by above equation,

$y = mx + C$

$C = 0$

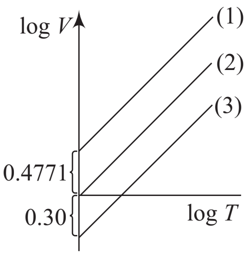
$m = \dfrac{1}{nRT} \qquad (m = \tan\theta)$

$$\tan\theta = \frac{1}{nRT} \quad nA = \frac{1}{RT \tan\theta}$$

$$n_A = \frac{1}{0.0821 \times 273 \times \tan 45°} \Rightarrow n_A = \frac{1}{22.4}\text{mole}$$

$$n_B = \frac{1}{RT \tan 60°} = \frac{1}{22.4\sqrt{3}}\text{mole}$$

5. At constant P of 0.0821 atm log V vs log T graph was plotted for three sample of ideal gases. Calculate the number of moles of each gas.



Sol. $V \propto T$

$$\frac{V}{T} = K = \frac{nR}{P}$$

$\log V = \log T + \log K$

$y = mx + C$

$C = \log K = \log\left(\dfrac{nR}{P}\right)$

$$C = \log\left[n \times \frac{0.0821}{0.0821}\right]$$

For (1) $C = \log n$

$0.4771 = \log n = \log 3$

$n = 3$

For gas (2) $0 = \log n = \log 1$

$n = 1$

For gas (3) $- \log x = 0.30$

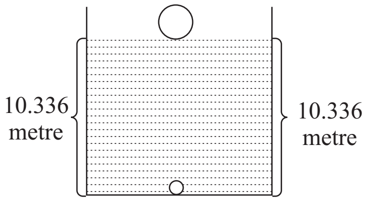
$- \log 2 = \log n$

$-\log 2^{-1} = \log n$

$\log\left[\dfrac{1}{2}\right] = \log n$

$n = \dfrac{1}{2}$ mole

6. Radius of a bubble at the bottom of the tank shown below was found to be 1 cm. Find the radius of the bubble at the surface of water at same temperature.



Pressure at bottom $= P_{atm} + \dfrac{hdg}{1.013 \times 10^5}$

$$= 1 + \frac{10.336 \times 1 \times 10^3 \times 9.8}{1.013 \times 10^5} = 2 \text{ atm}$$

Since temperature is constant and n constant

$$\therefore \quad \frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

$$\therefore \quad P_1 V_1 = P_2 V_2$$

$$2\times\frac{4}{3}\pi(1)^3=1\times\frac{4}{3}\pi r^3$$

$$r=\sqrt[3]{2}\text{ cm}$$

(b) If the absolute temperature at surface is 4 times to that at the bottom. Find the radius of bubble at surface?

Sol. $T_2 = 4T$

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$$

$$\frac{2\times\frac{4}{3}\pi(1)^3}{T}=\frac{1\times\frac{4}{3}\pi r^3}{4T}$$

$$8 = r^3$$

$$r = 2\text{ cm}$$

7. If 2 liter of gas A at 1.5 atm and 3 liter of gas B at 2 atm are mixed in a 5 liter container find the final pressure.

Sol. $n_1 + n_2 = n$

$$\frac{P_1V_1}{RT}+\frac{P_2V_2}{RT}=\frac{PV}{RT}$$

$$P_1V_1 + P_2V_2 = PV$$

$$1.5\times 2 + 2\times 3 = \text{P}\times 5$$

$$P=\frac{9}{5}\text{atm}=1.8\text{ atm}$$

8. Two moles of NH_3 and one mole of HCl gas are taken in a container of capacity 8.21 L at 300 K to produce NH_4Cl. Find total pressure after reaction.

Sol.
$$\begin{array}{ccc} NH_3 + & HCl \longrightarrow & NH_4Cl \\ (g) & (g) & (S) \\ 2 & 1 & O \\ 1 & O & 1 \end{array}$$

$n_g = n_{NH_3} = 1$ mole (after reaction)

$$P=\frac{n_gRT}{v}=\frac{1\times 0.821\times 300}{8.21}=3\text{ atm}$$

9. A closed container containing O_2 and some liquid water was found to exert 740 mm pressure at 27°C.

(a) Calculate the pressure exerted by O_2 if aqueous tension at 27°C is 20 mm of Hg.

(b) What will be the final pressure if volume is reduced to half; assuming volume of liquid water is negligible?

(c) What will be the final pressure when volume is doubled?

Sol. (a) $P_T = P_g + P_{\text{aq.tension}}$

$$740 = P_{\text{gas}} + P_{\text{aq.tension}}$$

$$P_{\text{aq.tension}} = 20\text{ mm Hg}$$

$$\therefore\quad P_{\text{gas}} = 720\text{ mm Hg}$$

Gas law applicable for gas only

(b) ($P_{\text{aq. tension}}$ change with temp. only)

Gas law applicable for gas only

$$P_1V_1 = P_2V_2$$

$$720\times V = P_2\times\frac{V}{2}$$

$$P_2 = 1440 = P_{\text{gas}}$$

$$\therefore\quad P_T = P_g + P_{\text{aq.ten}} = 1440 + 20 = 1460\text{ mm-Hg}$$

(Aqueous tension change with temperature only)

(c) $P_1V_1 = P_2V_2$

$$720\times V = P_2\times 2V$$

$$P_2 = 360$$

$$P_T = P_2 + P_{\text{aq.ten}}$$

$$= 360 + 20 = 380\text{ mm-Hg}$$

10. An iron tank contains helium at a pressure of 3.0 atm at 27ºC. The tank can withstand a maximum pressure of 10 atm. The building in which tank has been placed catches fire. Will the tank blow up first or melt. (Melting point of iron is 1535ºC.)

Sol. $P_1 = 3.0$, $T_1 = 300$ K

$$\frac{P_1}{T_1}=\frac{P_2}{T_2}\quad\Rightarrow\quad\frac{3.0}{300}=\frac{P_2}{1808}$$

$$P_2=\frac{3.0\times 1808}{300}=18.08\text{ atm}$$

Since at melting point, it is greater than the maximum pressure, therefore it will blow up.

11. An open vessel at 27°C is heated until 3/5th of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find

(a) the temperature at which vessel was heated.

(b) the air that escaped if vessel is heated to 900 K.

(c) temperature at which half of the air escaped out.

Sol. Note the fact that on heating a gas in a vessel, the number of moles of gas which go out, the volume of vessel remains constant.

Let initial moles of air at 300 K be 'n'. On heating 3/5 moles of air are escaped out at temperature T.

$\therefore$ moles of air left at temperature $T=\left(n-\frac{3}{5}n\right)=\frac{2n}{5}$

(a) Under simillar conditions of P and V

$$n_1T_1 = n_2T_2$$

$$n\times 300 = \frac{2n}{5}\times T\quad\Rightarrow\quad T = 750\text{ K}$$

(b) On heating vessel to 900 K, let n_1 moles be left again $n_1T_1 = n_2T_2$

$$n_1\times 900 = 300\times n\quad\Rightarrow\quad n_1=\frac{1}{3}n$$

$$\therefore\text{ moles escaped out }= n-\frac{n}{3}=\frac{2}{3}n\text{ moles}$$

(c) Assume $n/2$ moles are escaped at temperature T, then

$$n_1T_1 = n_2T_2$$

$$n/2\times T = n\times 300$$

$$T = 600\text{ K}$$

12. A balloon is inflated to $\frac{7}{8}$ of its maximum volume at 27°C.

(a) Will it burst at 30°C?

(b) Calculate the minimum temperature above which it will brust.

Sol. (a) Balloon will burst if $V' \geq$ maximum volume

Maximum volume = V

Initial volume of balloon = $\frac{7}{8}V$

at 27°C or at 300 K

$$\frac{7}{8}V \times 300 = V^1 \times 303$$

$$V' = \frac{2100}{2424}V$$

∴ ballon will not burst.

(b) $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\frac{7}{8}V/300 = V/T_2$$

$$\frac{7}{9 \times 300} = \frac{1}{T_2}$$

$$T_2 = \frac{2400}{7} = 342.85 \text{ K.}$$

13. An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that

(i) $\frac{1}{3}$ of air measured in the container at 27°C escapes out.

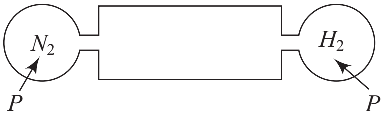
(ii) $\frac{1}{3}$ of air measured in the container if final temperature escapes out.

Sol. **Hint:** $n_i - n_f = n$ expelled

(i) $\frac{PV}{R.300} - \frac{PV}{RT} = \frac{1}{3}\left[\frac{PV}{R.300}\right]$

(ii) and $\frac{PV}{R.300} - \frac{PV}{RT} = \frac{1}{3}\frac{PV}{RT}$

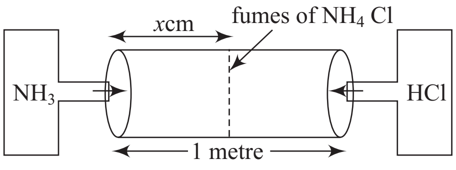
14.



Find $\frac{L_{N_2}}{L_{H_2}}$ = ? If P is same for both gases.

Sol. $$\frac{\frac{\Delta V}{\Delta t}}{\frac{\Delta V}{\Delta t}} = \frac{A \cdot \frac{L_{N_2}}{\Delta t}}{A \cdot \frac{L_{H_2}}{\Delta t}} = \sqrt{\frac{M_B}{M_A}} = \sqrt{\frac{2}{28}}$$

15.



Find x.

Sol. $$\frac{L_{NH_3}}{L_{HCl}} = \sqrt{\frac{M_B}{M_A}} = \sqrt{\frac{36.5}{17}}$$

$$\frac{x}{100 - x} = \frac{6}{4.1}$$

∴ $x = 60$ cm

16. A container consist of H_2 & O_2 gas having same no of moles. If the volume of H_2 gas is collected after half an-hour is 30 ml. Then calculate the volume of O_2 collected under similar condition.

Sol. $$\frac{R_{H_2}}{R_{O_2}} = \sqrt{\frac{\text{MM of } O_2}{\text{MM of } H_2}} = \frac{R_{H_2}}{R_{O_2}} = \sqrt{\frac{32}{2}} = \frac{V_{H_2}}{V_{O_2}} = \frac{30}{V_{O_2}} = 4$$

∴ $V_{O_2} = \frac{30}{4} = 7.5$ ml

In 30 minute V_{O_2} collected = 7.5 ml

> ***Note:***
> In any diffusion and effusion process, the rate of diffusion and effusion do not remain constant throughout the given time interval. (Generally it decreases) However, for solving a problem, the rate is assumed to be constant during specific interval of time and this constant rate of diffusion or effusion is taken as initial rate of diffusion or effusion.

17. A container consists of H_2 and O_2 gases having same number of moles. If the volume of H_2 gas is collected after half an-hour is 30 ml. Then calculate the volume of O_2 collected in 15 minutes taking diffusion rate constant.

Sol. $$\frac{R_{H_2}}{R_{O_2}} = \sqrt{\frac{\text{MM of } O_2}{\text{MM of } H_2}} = \frac{R_{H_2}}{R_{O_2}} = \sqrt{\frac{32}{2}} = \frac{V_{H_2}}{V_{O_2}} = \frac{30}{V_{O_2}} = 4$$

∴ $V_{O_2} = \frac{30}{4} = 7.5$ ml

In 30 minutes V_{O_2} collected = 7.5 mL

In 15 minutes V_{O_2} collected = $7.5 \times \frac{15}{30}$ = 3.75 mL

18. A container consists of H_2 and O_2 in 2 : 1 molar ratio. If the volume of H_2 gas collected after 10 minutes is 15 mL at same T and P. What will be the volume of O_2 gas collected at minute and 20 minute?

Sol. $$\frac{R_A}{R_B} = \frac{V_A}{V_B} = \frac{n_A}{n_B} \times \sqrt{\frac{M_B}{M_A}} = \frac{n_A}{n_B}\sqrt{\frac{32}{2}} = 16$$

$$\frac{V_{H_2}}{V_{O_2}} = \frac{2}{1} \times 4$$

∴ $V_{O_2} = \frac{15}{8}$ at $t = 10$ minute

at $t = 20$ minute

$$\frac{15}{8} \times \frac{20}{10} = \frac{30}{8} \text{mL}$$

19. A container consists of $\frac{1}{20}$ moles of D_2 gas and $\frac{1}{10}$ mole of H_2 is collected through a nozzle to a large container. After 10 minute 0.1 gm of D_2 was collected in the second container, then calculate

(i) initial rate of diffusion of both gases.

(ii) Moles of H_2 obtained in second container after 10 minute.

Sol. (i) $\frac{R_{H_2}}{R_{D_2}} = \frac{n_{H_2}}{n_{D_2}}\sqrt{\frac{4}{2}} = \frac{1}{10} \times \frac{20}{1}\sqrt{2}$

$\therefore \quad R_{H_2} = 2\sqrt{2}\,R_{D_2}$ or $R_{D_2} = \frac{1}{2\sqrt{2}} R_{H_2}$

(ii) $\frac{n'_{H_2}}{n'_{D_2}} = \frac{n_{H_2}}{n_{D_2}}\sqrt{\frac{4}{2}} \Rightarrow \frac{1/10}{1/20} \times \sqrt{2}$

$$\frac{n'_{H_2}}{n'_{D_2}} = 2\sqrt{2}$$

$$n'_{H_2} = 2\sqrt{2}\, n'_{D_2}$$

$$W_{H_2} = 2\sqrt{2} \times \frac{0.1}{4} \times 2$$

$$= 0.1414 \text{ gram}$$

20. A closed container having molar ratio H_2 and N_2 of 1 : 9. After *n* diffusion this ratio changed up to 9 : 1. Calculate what is the value of '*n*'?

Sol. $\left(\frac{n_A}{n_B}\right)_{\text{initial}} = \frac{1}{9}$ and $\left(\frac{n_A}{n_B}\right)_{\text{final}} = \frac{9}{1}$

$$\left(\frac{n_A}{n_B}\right)_{\text{final}} = \left(\frac{n_A}{n_B}\right)_{\text{initial}} \left(\sqrt{\frac{M_B}{M_B}}\right)^n$$

$$9 = \frac{1}{9}\left(\sqrt{\frac{28}{2}}\right)^n$$

$$81 = (14)^{\frac{n}{2}}$$

$$\log (9)^2 = \frac{n}{2}\log (14)$$

$$2 \times 2[\log 3] = \frac{n}{2}[\log 2 + \log 7]$$

$$4[0.4771] = \frac{n}{2}[0.3 + 0.85]$$

$$n = \frac{1.9084 \times 2}{1.15} = 3.31$$

$\therefore$ after 4 diffusion.

21. A sample of $^{235}UF_6$ and $^{238}UF_6$ is present in ratio 3 : 5 motar ratio after *n* diffusion this ratio become 5 : 3 then calculate value of *n*.

Sol. $\left[\frac{n^{235}UF_6}{n^{238}UF_6}\right]_{\text{final}} = \left[\frac{n^{235}UF_6}{n^{238}UF_6}\right]_{\text{initial}} \times \left[\sqrt{\frac{M^{238}UF_6}{M^{235}UF_6}}\right]$

$$\frac{5}{3} = \frac{3}{5}\left[\sqrt{\frac{352}{349}}\right]^n$$

$$\frac{25}{9} = \left[\frac{352}{349}\right]^{\frac{n}{2}}$$

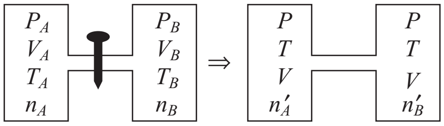
$$\log 25 - \log 9 = \frac{n}{2}\log[1.0086]$$

$$1.397 - 0.954 = \frac{n}{2}[0.0037]$$

$$n = 240$$

22. Given figure shows 2 Identical *A* and *B* with rigid walls containing ideal gas. The pressure, volume and temperature in vessel *A* are T_A, V_A and P_A whereas in second container pressure is P_B, volume is V_B and temperature is T_B. Vessels second are now connected through a narrow tube. Show that the final ratio of '*P*' and temperature *T* satisfy the equation $\frac{P}{T} = \frac{1}{2}\left[\frac{P_A}{T_A} + \frac{P_B}{T_B}\right]$

Sol.



$V_A = V_B = V$

$V_A = V_B = V$ (Same vessel)

$$n_A = \frac{P_A V}{RT_A} \quad n'_A = \frac{PV}{RT}$$

$$n_B = \frac{P_B V}{RT_B} \quad n'_B = \frac{PV}{RT}$$

$$(n'_A + n'_B) = n_A + n_B$$

$$\frac{PV}{RT} + \frac{PV}{RT} = \left[\frac{P_A V}{RT_A} + \frac{P_B V}{RT_B}\right]$$

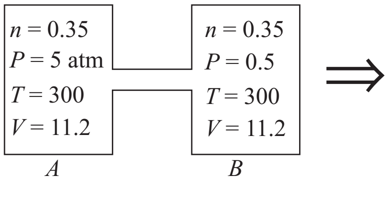
$$\frac{2PV}{RT} = \frac{V}{R}\left[\frac{P_A}{T_A} + \frac{P_B}{T_B}\right]$$

$$\frac{P}{T} = \frac{1}{2}\left[\frac{P_A}{T_A} + \frac{P_B}{T_B}\right]$$

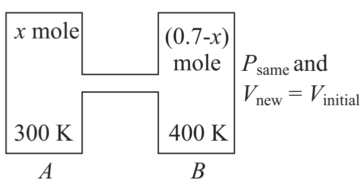
23. Two flasks of equal volume connected by a narrow tube are at 27°C and container has 0.7 moles of H_2 and 0.5 atm. One of the flasks is then emerged into a bath kept at 127°C while the other remains at 27°C. Calculate the final pressure and number of mole of H_2 in each flask.

Sol. $V = \frac{nRT}{P} = \frac{0.35 \times 0.082 \times 300}{0.5} = 11.2 \text{ L}$

Case – I



Case – II



For A $\quad P_{\text{new}}\, V = x \cdot R \times 300 \qquad$ (i)

For B $\quad P_{\text{new}}\, V = (0.7 - x) \cdot R \times 400 \qquad$ (ii)

$$x \cdot R \cdot 300 = (.700 - x) \times R \times 400$$
$$300x = 280 - 400x$$
$$700x = 280$$
$$x = 0.4 \text{ mole}$$

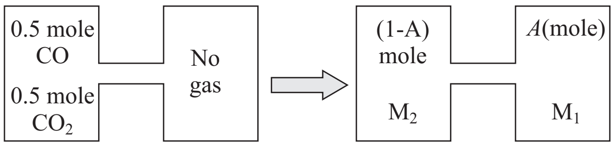
24. A mixture of 0.5 moles of CO and 0.5 moles of CO_2 is taken in a vessel and allowed to effuse in another container which has vacuum. If total 'A' moles have effused out in time 't', show that $M_1A + M_2(1 - A) = 36$ M_1, M_2 are mean molar masses of mixture that are effused out and mixture still remaining.

Sol. Initial mass $= 0.5 \times 28 + 0.5 \times 44 = 36$

$$\text{Final mass} = (1 - A)\, M_2 + AM_1 = 36$$
$$= M_2 - M_2A + AM_1 = 36$$

or

$$M_1A + M_2\,[1 - A] = 36$$



25. A 2 L cylinder has 10 mole at 300 K. This container is connected to a 1 L vaccum container by a narrow tube. If final temperature is remain same, then calculate the final pressure of the system.

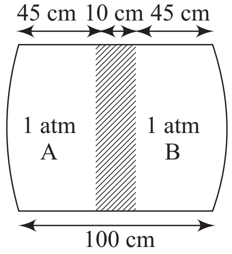
Sol. $P_1V_1 = n_1RT_1$

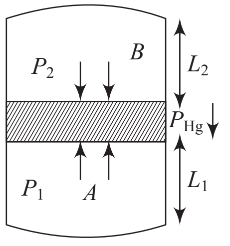
$$P_1 = \frac{10 \times 0.0821 \times 300}{2} \quad \text{and} \quad \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

$$\frac{\left[\dfrac{10 \times 0.0821}{2}\right] \times 2}{nT} = \frac{P_2 \times 3}{n \times T}$$

$$P_2 = \frac{10 \times 0.0821 \times 300}{3} = 82.1 \text{ atm}$$

26.





Calculate L_1 and L_2

Sol. $L_1 + L_2 = 90$ cm (Hg does not expand)

and $\quad P_1 = P_2 + P_{\text{Hg}}$

$$= P_2 + \frac{10}{76}$$

for A $P_iV_i = P_fV_f \qquad$ **for B** $P_iV_i = P_fV_f$

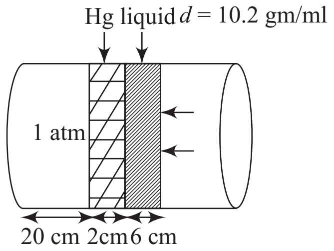
$P_ih_i = P_fh_f \qquad 1 \times 45 = P_2[90 - l_1] \qquad$ (i)

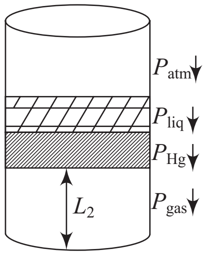
$$1 \times 45 = \left[P_2 + \frac{10}{76}\right]L_1 \qquad \text{(ii)}$$

$$\frac{\text{(ii)}}{\text{(i)}} = \frac{\left(P_2 + \dfrac{10}{76}\right)L_1}{P_2[90 - L_1]} = 1$$

L_1 and L_2 can be calculated.

27. Calculate L_2.





Sol. $P_2 = P_{\text{gas}} = P_{\text{atm}} + P_{\text{Hg}} + P_{\text{liq}}$

$$P_{\text{gas}} = \left[1 + \frac{2}{76} + \frac{\dfrac{6}{100} \times 10.2 \times 10^3 \times 9.8}{1.01 \times 10^5}\right] \text{atm}$$

$P_1 = 1$ atm, $\qquad V_1 = A \times L_1 = A \times 20$

$P_2 = P_{\text{gas}}, \qquad V_2 = A \times L_2$

$P_1V_1 = P_2V_2$

$1 \times 20 = P_{\text{gas}} \times l_2$

$$l_2 = \frac{20}{\left[1 + \dfrac{2}{76} + \dfrac{6}{100}\right]} \text{CM}$$

28. 10 cm column of air is trapped by a column of Hg 8 cm. If capillary tube is fixed horizontally as shown in the figure at 1 atm, calculate the length of air column when the tube is fixed at same temperature.

(a) Vertically with open end up.

(b) Vertically with opened down.

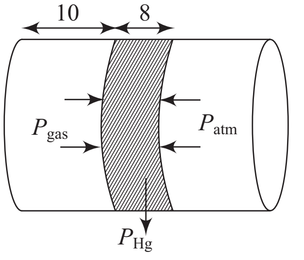
(c) At 45° from horizontal with open end up.

Sol. (a) $P_{\text{gas}} = P_{\text{atm}} = 1$ atm

Let the area be A

$$P_1V_1 = P_2V_2$$

$$P_2 = P_{\text{gas}} + P_{\text{Hg}} = 1 + \frac{8}{76}$$



$$1 \times 10 \times A = \left[1+\frac{8}{76}\right] \times h \times A$$

$h = 9.04$ cm

(b) $P_1 = 1$ atm, $V_1 = 10 \times A$

$$P_2 = \left[P_{\text{gas}} - \frac{h}{76}\right] = \left[1 - \frac{8}{76}\right]$$

$$V_2 = h \times A$$

$$P_1V_1 = P_2V_2$$

$$1 \times 10 \times A = \left[1-\frac{8}{76}\right] \times h \times A$$

$h = 11.18$ cm

(c) $P_1 = 1$ atm, $V_1 = 10 \times A$

$$P_2 = \left[1 + \frac{h}{76}\sin 45°\right]$$

$$V_2 = h \times A$$

$$P_1V_1 = P_2V_2$$

$h = 9.3$ cm

29. Mr. Gupta weights 72.15 kg and wants to fly in the sky with balloon whose weight is 20 kg and each containing 50 moles of H_2 gas at 0.05 atm and 27°C. Density of air at given condition is 1.25 gm/ltr. How many such types of balloon is needed to fly in the sky?

Sol. $M_{\text{Payload}} = M_{\text{dip. air}} - M_{\text{Balloon}}$

$$N[V_{\text{balloon}} \times d_{\text{air}}] - [d_{\text{gas}} \cdot V_{\text{balloon}} + M_{\text{balloon}}] = M_{\text{pay load.}}$$

$$N\left[\frac{nRT}{P}\right] \times 1.25 - N\,[20 \times 10^3 + 100] = 75.15 \times 10^3$$

$$N = \frac{75.15 \times 10^3}{\left[\dfrac{50 \times 0.0821 \times 300 \times 1.25}{0.05}\right] - [20 \times 10^3 + 100]} = 7$$

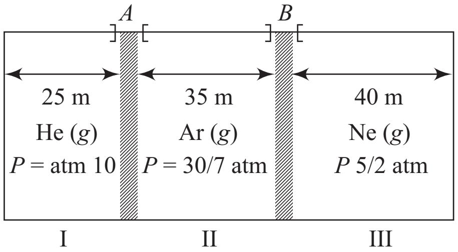
$\therefore \quad N = 7$

30. Figure below shows initial conditions of a uniform cylinder with frictionless piston *A* and *B* held in position by mechanical stoppers. If the mechanical stoppers holding piston *A* and *B* are removed, (assume that temperature remains constant)

(i) What will be the pressure developed in each compartment in final state?

(ii) What will be the final position of piston *A* with respect to for left end of container?

(iii) What will be the final position of piston *B* with respect to for left end of container?



Sol. (i) $n_T = n_{\text{He}} + n_{\text{Ar}} + n_{\text{Ne}}$

$$\frac{P_fV_f}{RT} = \frac{10 \times 25 \times A}{RT} + \frac{\frac{30}{7} \times A \times 35}{RT} + \frac{\frac{5}{2} \times A \times 40}{RT}$$

$$P_f \times A \times 100 = 10 \times 25 \times A + \frac{30}{7} \times A \times 35 + \frac{5}{2} \times 40 \times A$$

$$P_f \times 100 = 250 + 150 + 100$$

$$Pf = \frac{500}{100} = 5 \text{ atm}$$

$$\boxed{P_f = 5 \text{ atm}}$$

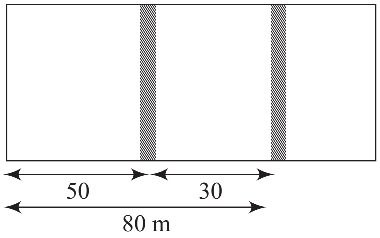
(ii) (a) $P_1V_1 = P_2V_2 \Rightarrow 10 \times 25 = 5 \times l_2$

$$\boxed{l_2 = 50 \text{ m}}$$

(b) $P_1V_1 = P_2V_2$

$$\frac{30}{7} \times 35 = 5 \times l_2$$

$$\boxed{l_2 = 30 \text{ m}}$$



Final position = 80 meter

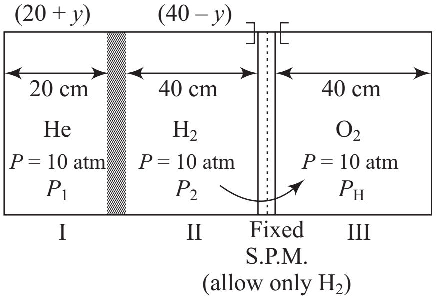
31. Few gases are filled as air in the container as shown in the figure and allowed to attain equilibrium (assuming temperature remains constant) throughout the process. Select the correct option:

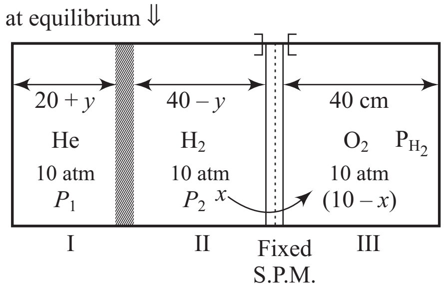
(i) Total moles of gas in compartment III will be 12.

(ii) The moles of hydrogen in compartment II will be 2.

(iii) The length of compartment containing only hydrogen will be after equilibrium is attained?

(iv) Distance of movable piston from left end is 50 cm after equilibrium is attained.





Sol. At S.P.M. compartment II and III

$$P_{H_2} = P_2 = P'_{H_2}$$

Let (x) moles of H_2 are deffused from II → III (By S.P.M.)

P. Pressure of H_2 in II = III

$$\frac{x}{40-y} = \frac{(10-x)}{40}$$

$$P_2 = P'_{H_2}$$

$$\frac{nRT}{V}$$

At Piston in compartment I and II

$$P_1 = P_2$$

$$\frac{10RT}{(20+y)R} = \frac{xRT}{(40-y)A}$$

$$\frac{10}{20+y} = \frac{x}{40-y}$$

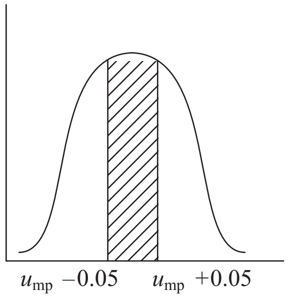
$$\boxed{\begin{array}{l} x = 2 \\ y = 30 \end{array}}$$

32. Calculate V_{rms} speed of oxygen at 300 K.

Sol. $V_{\text{rms}} = \sqrt{\dfrac{3\times 8.314\times 300}{32\times 10^{-3}}}$ = 483.12 m/sec

33. Calculate the fraction of N_2 molecules at 1 atm pressure and 300 K$^-$ whose speeds are in the range of $u_{\text{mp}} \pm 0.005$.

Sol.



∴ du = final velocity – Initial velocity

$= [u_{\text{mp}} + 0.005] - [u_{\text{mp}} - 0.005] = 0.1$

$du = 0.01$

By Maxwell distribution theory

$$\frac{dNu}{N} = 4\pi\left[\frac{M}{2\pi RT}\right]^{3/2} u^2 e^{-\frac{mu^2}{2RT}} du$$

$$= 4\times 3.14\left[\frac{28\times 10^{-3}}{2\times 8.314\times 300\times 3.14}\right]^{\frac{3}{2}}$$

$$\left[\frac{2RT}{M}\right] e^{-\frac{M}{2RT}\times\frac{2RT}{M}} \times 0.01\sqrt{\frac{2RT}{M}}$$

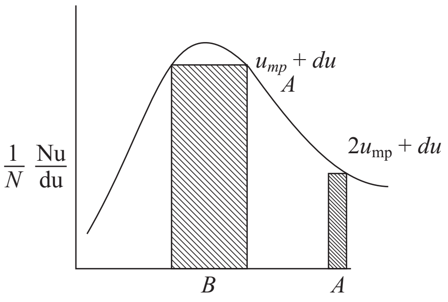
$$= 4\times 3.14\left[\frac{28\times 10^{-3}}{2\times 8.314\times 300\times 3.14}\right]^{\frac{3}{2}}$$

$$\times [422]^2 e^{-1}\times 0.01\times 422$$

$$= 8.303\times 10^{-3}\ \text{Ans}$$

34. What is the ratio of the number of molecules having speeds in the range of 2 u_{mp} and $2u_{\text{mp}} + du$ to the Number of molecules having speed in the range of u_{mp} and $u_{\text{mp}} + du$.

$$\frac{\text{Area of } A}{\text{Area of } B}$$



Sol. $\left(\dfrac{dNu}{N}\right)_A = 4\pi\left[\dfrac{M}{2\pi RT}\right]^{\frac{3}{2}} u_A^2\, e^{-\frac{M}{2RT}u_A^2} du$

$$\left(\frac{dNu}{N}\right)_B = 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} u_B^2 e^{-\frac{M}{2RT}u_B^2} du$$

$$\frac{\left(\frac{dNu}{N}\right)_A}{\left(\frac{dNu}{N}\right)_B} = \frac{u_A^2}{u_B^2}\times\frac{e^{-\frac{Mv_A^2}{2RT}}}{e^{-\frac{Mv_B^2}{2RT}}}$$

$$= \frac{4u_{mP}^2}{u_{mP}^2}\times\frac{e^{-\frac{M}{2RT}\times 4\times\frac{2RT}{M}}}{e^{-\frac{M}{2RT}\times\frac{2RT}{M}}}$$

$$= 4\times\frac{e^{-4}}{e^{-1}} = 4e^{-3} = \frac{4}{e^3} = 0.199$$

35. Calculate v_{rms} speed of H_2 molecule under the following conditions?

(i) 2 moles of H_2 gas at 27°C.

(ii) 3 moles of H_2 gas in 5 l container at 10^5 Pa.

(iii) 4 moles of H_2 having density 1 g/mL at 10^5 Pa.

Sol. We know

$$V_{\text{rms}} = \sqrt{\frac{3RT}{\text{Molar mass in kg}}}$$

$$= \sqrt{\frac{3PV}{\text{Total mass in kg}}} = \sqrt{\frac{3P}{d}}$$

P in Pascal, V in m^3, molar mass in kg and density d or ρ in kg/m^3

(i) $$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 300}{2 \times 10^{-3}}}$$

$$= \sqrt{\frac{3 \times 83.14 \times 3 \times 10^4}{2}} = 19.34 \times 10^2 \text{ m/sec.}$$

(ii) $$\sqrt{\frac{3PV}{nM}} = \sqrt{\frac{3 \times 10^5 \times 5 \times 10^{-3}}{3 \times 2 \times 10^{-3}}} = \sqrt{25 \times 10^4}$$

$$= 500 \text{ m/sec}$$

(iii) $$\sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 10^5}{10^3}} = 17.32 \text{ m/sec.}$$

$$1 \text{ g/ml} = \frac{10^{-3}\text{kg}}{10^{-6}\text{m}^3} = 10^3 \text{ kg/m}^3$$

36. What is the density of moist air with 90% relative humidity under the condition of 1 atm pressure and 21ºC. The vapour pressure of water at 25ºC is 23.7 torr and dry air has 76% N_2 and 24% O_2. Also find the difference in the density of dry air and moist air at the given condition.

Sol. (V.P. of H_2O at 25ºC is 23.7 mm of Hg)

(Mav)dry air = (0.76 × 28) + (0.24 × 32)

= 21.28 + 7.68 = 28.96 g/mol.

$$\because \quad \text{R.H.} = \frac{\text{Partial Pressure of } H_2O}{\text{V.P. of } H_2O} \times 100\,;$$

$$\text{Density } (\rho) = \frac{PM_{\text{air}}}{\text{RT}}$$

$$\therefore \quad P_{H_2O} = 23.7 \times 0.9 = 21.33 \text{ mmHg} = 0.028 \text{ atm.}$$

(Now) Moist air = (28.96 × 0.972) + (18 × 0.028)

= 28.147 + 0.504 = 28.65 gm/mol.

$$\rho_{\text{moist air}} = \frac{PM_{\text{moist air}}}{RT} = \frac{1 \times 28.65}{0.0821 \times 298} = 1.17 \text{ gm/L}$$

$$\Delta\rho = \rho_{\text{dry air}} - \rho_{\text{moist air}}$$

$$= \frac{P}{RT}[M_{\text{dry air}} - M_{\text{moist air}}]$$

$$= \frac{1}{0.0821 \times 298}(28.96 - 28.65) = 0.1267$$

37. Calculate the payload when a balloon of radius 10 meter mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air 1.2 kgm^{-3} and R = 0.083 bar $dm^3k^{-1}mol^{-1}$)

Sol. Volume of balloon

$$= \frac{4}{3}\pi r^3 = \frac{4}{3}\left(\frac{22}{7}\right)(10)^3 = 4190.47 \text{ m}^3$$

$$= 4190.47 \times 10^3 \text{ L}$$

Mass of dry air = $d \times v$ = 1.2 × 4190.47 = 5028.56 kg

$$\text{Mass of the helium} = W = \frac{PV}{RT} \times 4 \times 10^{-3}\text{kg}$$

$$= \frac{1.66 \times 4190.47 \times 10^3 \times 4 \times 10^{-3}}{0.083 \times 300} = 1117.45 \text{ kg}$$

Mass of balloon with helium

= 1117.45 + 100 = 1217.45 kg

Pay load = mass of air displaced – mass of filled balloon = 5028.56 – 1217.45 = 3811 kg

38. The compressibility factor for 1 mole of a Van der Walls gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that volume of a gas molecule is ‘negligible’, calculate the Van der Walls constant ‘a’.

Sol. For 1 mole of the gas $Z = \frac{PV}{RT}$

$$0.5 = \frac{100 \times V}{0.0821 \times 273}$$

$$V = 0.112\ L$$

Neglecting b, the equation is $\left(P + \frac{a}{V^2}\right)V = RT$

or $PV + \frac{a}{V} = RT$, $a = 1.25L^2$ atm mol^{-2}

39. Calculate the pressure exerted by 22 g of carbon dioxide in 0.5 dm^3 at 298 15 K using:

(a) the ideal gas law and

(b) Van der waals equation.

Given: [a = 363.76 kPa dm^6 mol^{-2} and b = 42.67 cm^3 mol^{-1}]

Sol. (a) $$P = \left(\frac{22}{44}\right) \times \frac{0.0821 \times 298.15}{0.5} \text{atm} = 2.479 \times 10^3 \text{kPa}$$

(b) $$\left(P + \frac{\left(\frac{1}{2}\right)^2 \times 363.76}{(0.5)^2}\right) \times \left(0.5 - \frac{1}{2} \times \frac{42.67}{1000}\right)$$

$$= \frac{1}{2} \times 8.3187 \times 298.15 \text{ kPa}$$

$$P = 2225.55 \text{ kPa}$$

40. The Van der waals, constants for gases A, B and C are as follows:

Gas	a/dm^6 kPa mol^{-2}	b/dm^3 mol^{-1}
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

Which gas has

(i) the highest critical temperature,

(ii) the largest molecular volume, and

(iii) most ideal behaviour around STP?

Sol. (i) find $T_C = \dfrac{8a}{27Rb}$ $\therefore$ gas B

(ii) Large value of b α largest molecular volume. $\therefore$ gas C

(iii) Least value of a and b $\therefore$ gas A

41. A commercial cylinder contains 6.91 m^3 of O_2 at 15.18 M Pa and 21°C. The critical constants for O_2 are $T_C = -118.4°C$, $P_C = 50.1$ atm. Determine the reduced pressure and reduced temperature for O_2 under these conditions.

Sol. Reduced pressure. $P_r = \dfrac{P}{P_C} = 2.99$

Reduced temperature $T_r = \dfrac{T}{T_C} = 1.90$

42. Calculate the volume occupied by 14.0 g N_2 at 200 K and 8.21 atm pressure if $\dfrac{P_C V_C}{RT_C} = \dfrac{3}{8}$ and $\dfrac{P_r V_r}{Tr} = 2.2$.

Sol. 14 g $N_2 \rightarrow 0.5$ mole

$T = 200$ k, $\quad P = 8.21$ atm

$$\frac{P_C V_C}{RT_C} = \frac{3}{8}, \qquad \frac{P_r V_r}{T_r} = 2.2$$

$$P_r = \frac{P}{P_c}, \qquad V_r = \frac{V}{V_c}, \qquad T_r = T/T_c \text{ so,}$$

$$\frac{(P_c P_r)(V_c V_r)}{R(T_c T_r)} = \frac{3}{8} \times 2.2 \Rightarrow \frac{PV}{RT} = \frac{3}{2} \times 2.2$$

$$V = \frac{3}{8} \times \frac{2.2 \times 0.0821 \times 200}{8.21} = 1.65 \text{ L}$$

so volume of 0.5 mole $N_2 = 1.65 \times 0.5 = 0.825$ L

43. The critical temperature and pressure of CO_2 gas are 304.2 K and 72.9 atm respectively. What is the radius of CO_2 molecule assuming it to behave as Van der Waal's gas?

Sol. $T_C = 304.2$ K $\qquad P_C = 72.9$ atm

$$T_C = \frac{8a}{27Rb} \qquad P_C = \frac{a}{27b^2}$$

$$\therefore \quad \frac{T_C}{P_C} = \frac{\dfrac{8a}{27Rb}}{\dfrac{a}{27b^2}} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$$

$$\text{or} \quad b = \frac{RT_C}{8P_C} = \frac{1}{8} \times \frac{0.082 \times 304.2}{72.9}$$

$$= 0.04277 \text{ lit mol}^{-1} = 42.77 \text{ cm}^3\text{/mole}$$

$$b = 4\, N_A \times \frac{4}{3}\pi r^3 = 42.77 \text{ cm}^3$$

$$\therefore \quad 4 \times N_A \times \frac{4}{3}\pi r^3 = 42.77$$

$$\text{or} \quad r^3 = r^3 = \frac{3 \times 42.77 \times 10^{-23}}{16 \times 6.023 \times 3.14}$$

or $r^3 = 0.424 \times^{-23} = 4.24 \times^{-24}$

or $r = (4.24)^{1/3} \times^{-8}$ cm $= 1.62 \times^{-8}$ cm

$\therefore$ radius of CO_2 molecule = 1.62 Å

Exercise

LEVEL I

1. Pressure of 1g of an ideal gas A at 27° C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at the same temperature, the pressure becomes 3 bar. Find the relationship between their molecular masses.

(a) $M_A = 4M_B$ (b) $M_B = 4M_A$
(c) $M_A = 2M_B$ (d) $M_B = 2M_A$

2. Density of a gas is found to be 5.46 g/dm^3 at 27°C at 2 bar pressure. What will be its density at STP?

(a) 6 gm/l (b) 8 gm/l (c) 3 gm/l (d) 1.5 gm/l

3. Calculate the temperature of 4.0 mole of a gas occupying 5 dm^3 at 3.32 bar. (R = 0.83 bar dm^3 K^{-1} mol^{-1}).

(a) 100 K (b) 50 K (c) 150 K (d) 200 K

4. Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. $R = 0.083$ bar $LK^{-1}mol^{-1}$.

(a) 10.1 ltr (b) 8.0 ltr
(c) 2.0 ltr (d) 5.05 ltr

5. 380 mL of a gas at 27°C, 800 mm of Hg weights 0.455 g. The molecular weight of gas is

(a) 27 (b) 28 (c) 29 (d) 30

6. At what temperature will be the rate of effusion of N_2 be 1.625 times the rate of effusion of SO_2 at 500°C?

(a) 273 K (b) 830 K (c) 110 K (d) 173 K

7. What is the ratio of the rate of diffusion of O_2 and H_2 at same P and T?

(a) 1 : 4 (b) 1 : 8 (c) 1 : 16 (d) 4 : 1

8. Equal weights of methane and oxygen are mixed in an empty container at 25°C. What is the fraction of the total pressure exerted by oxygen?

(a) $\dfrac{1}{3}$ (b) $\dfrac{1}{2}$ (c) $\dfrac{2}{3}$ (d) $\dfrac{1}{3} \times \dfrac{273}{298}$

9. What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1 L vessel at 27°C?

(a) 4 bar (b) 1.8 bar
(c) 0.9 bar (d) 3.6 bar

10. Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm^3 at 27°C. $R = 0.083$ bar dm^3 K^{-1} mol^{-1}.

(a) 28.5 bar (b) 56.025 bar
(c) 112.5 bar (d) 14.25 bar

11. 2.9 g of gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C, at the same pressure. What is the molar mass of the gas?

(a) 120 g mol^{-1} (b) 20 g mol^{-1}
(c) 80 g mol^{-1} (d) 40 g mol^{-1}

12. The average velocity of an ideal gas molecule at 27°C is 0.3 m/sec. What will be the average velocity at 927°C?

(a) 0.6 m/sec (b) 0.3 m/sec
(c) 0.9 m/sec (d) 3.0 m/sec

13. The root mean square velocity of one mole of a monoatomic gas having molar mass M is Ur.m.s. What is the relation between the average kinetic energy (E) of the gas and Ur.m.s.?

(a) $u_{\text{r.m.s.}} = \sqrt{\frac{3E}{2M}}$ (b) $u_{\text{r.m.s.}} = \sqrt{\frac{2E}{3M}}$

(c) $u_{\text{r.m.s.}} = \sqrt{\frac{2E}{M}}$ (d) $u_{\text{r.m.s.}} = \sqrt{\frac{E}{3M}}$

14. The compressibility of a gas is less than unity at STP. Therefore,

(a) Vm > 22.4 ltr (b) Vm < 22.4 ltr
(c) Vm = 22.4 ltr (d) Vm = 44.8 ltr

15. In Van der Waals equation of state for a non-ideal gas, what is the term that accounts for intermolecular forces?

(a) $(V - b)$ (b) RT

(c) $\left(P + \frac{a}{V^2}\right)$ (d) $(RT)^{-1}$

16. 4.0 g of argon has pressure P at temperature T K in a vessel. On keeping the sample at 50° higher temperature, 0.8 g gas was given out to maintain the pressure P. What was the original temperature?

(a) 73 K (b) 100 K (c) 200 K (d) 510 K

17. The temperature of an ideal gas is increased from 140 K to 560 K. If at 140 K the root mean square velocity of the gas molecules is u, at 560 K it becomes

(a) $5u$ (b) 2u (c) $u/2$ (d) $u/4$

18. 40 mL of mixture of H_2 and O_2 was placed in a gas burette at 18°C and 1 atm. A spark was produced so that the formation of water was complete. The remaining pure gas had a volume of 10 mL at 18°C and 1 atm. If the remaining gas was H_2, what was the initial mole % of H_2 in mixture?

(a) 75% (b) 25% (c) 60% (d) 45%

19. A flask of capacity of 1 ltr contains NH_3 at 1 atm and 25°C. A spark is passed through until all the NH_3 is decomposed into N_2 and H_2. Calculate the pressure of gases left at 25°C.

(a) 2 atm (b) 0.5 atm (c) 1.5 atm (d) 1 atm

20. The density of CO_2 at 100°C and 800 mm Hg pressure would be

(a) 1.212 g ltr^{-1} (b) 1.5124 g ltr^{-1}
(c) 2.1124 g ltr^{-1} (d) 1.012 g ltr^{-1}

21. Pressure remaining the same, the volume of given mass of an ideal gas increases for every degree centigrade rise in temperature by definite fraction of its volume at

(a) 0°C (b) its critical temperature
(c) absolute zero (d) its Boyle temperature

22. If 20 cm^3 gas at 1 atm is expanded to 50 cm^3 at constant T, then what is the final pressure?

(a) $20 \times \frac{1}{50}$ (b) $50 \times \frac{1}{200}$

(c) $1 \times \frac{1}{20} \times 50$ (d) None of these

23. The volume of 1 g each of methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) was measured at 350K and 1 atm. What is the volume of butane?

(a) 495 cm^3 (b) 600 cm^3
(c) 900 cm^3 (d) 1700 cm^3

24. A sample of gas occupies 100 mL at 27°C and 740 mm pressure. When its volume is changed to 80 mL at 740 mm pressure, what will be the temperature of gas?

(a) 21.6°C (b) 240°C
(c) –33°C (d) 89.5°C

25. At S.T.P., the density of nitrogen monoxide is?

(a) 3.0 gL^{-1} (b) 30 gL^{-1}
(c) 1.34 gL^{-1} (d) 2.68 gL^{-1}

26. The rate of effusion of a gas is proportional to?

(a) $\frac{P}{\sqrt{d}}$ (b) $\frac{P}{d}$

(c) $\sqrt{\frac{P}{d}}$ (d) $\frac{\sqrt{P}}{d}$

27. If 4 g of oxygen diffuse through a very narrow hole, how much hydrogen would have diffused under identical conditions?

(a) 16 g (b) 1 g (c) 1/4 g (d) 64 g

28. The rate of diffusion of SO_2 and O_2 are in the ratio

(a) $1 : \sqrt{2}$ (b) 1 : 32 (c) 1 : 2 (d) 1 : 4

29. A cylinder is filled with a gaseous mixture containing equal masses of CO and N_2. The partial pressure ratio is

(a) $P_{N_2} = P_{CO}$ (b) $P_{CO} = 0.875\ P_{N_2}$

(c) $P_{CO} = 2\ P_{N_2}$ (d) $P_{CO} = 1/2\ P_{N_2}$

30. Which of the following is correct relation for root mean square velocity?

(a) $V_{\text{rms}} = \sqrt{\dfrac{8RT}{\pi M_w}}$ (b) $V_{\text{rms}} = \sqrt{\dfrac{3RT}{M_w}}$

(c) $V_{\text{rms}} = \sqrt{\dfrac{2RT}{M_w}}$ (d) $V_{\text{rms}} = \sqrt{\dfrac{3RT}{M_w}}$

31. The average velocity of gas molecules is equal to

(a) $\left(\dfrac{8RT}{M_w}\right)^{\frac{1}{2}}$ (b) $\left(\dfrac{3RT}{M_w}\right)^{\frac{1}{2}}$

(c) $\left(\dfrac{8RT}{\pi M_w}\right)^{\frac{1}{2}}$ (d) $\left(\dfrac{8RT}{\pi M_w}\right)$

32. A gas occupies 300 mL volume at 27°C temperature and 730 mm pressure. Its volume at STP is

(a) 162.2 mL (b) 262.2 mL
(c) 362.2 mL (d) 462.2 mL

33. A truck having oxygen cylinders is coming from Shrinagar. The gas in cylinder is at –23°C temperature and 3 atm pressure when truck passes from Madras. What will be the pressure of oxygen gas when temperature is 30°C?

(a) 2.64 atm (b) 1.64 atm
(c) 1 atm (d) 3.64 atm

34. Find out the density of CO_2 at 100°C temperature and 400 mm Hg pressure.

(a) 0.75 g L^{-1} (b) 2.5 g L^{-1}
(c) 0.5 g L^{-1} (d) 0.2 g L^{-1}

35. The density of a gas at –23°C temperature and 780 torr pressure is 1.40 g L^{-1}. Identify the gas.

(a) CO_2 (b) SO_2 (c) Cl_2 (d) N_2

36. Calculate the weight of CH_4 gas when the applied pressure is 16 atm, temperature is 27°C and its volume is 9 litre ($R = 0.08$ L atm K^{-1}).

(a) 96 g (b) 86 g (c) 80 g (d) 90 g

37. The density of SO_2 at STP is

(a) 2.86 g L^{-1} (b) 1.76 g L^{-1}
(c) 1.86 g L^{-1} (d) None of these

38. The volume occupied by 7 g N_2 gas at 27°C temperature and 750 mm Hg pressure is

(a) 6.3 ltr (b) 7.3 ltr
(c) 6.8 ltr (d) 5.3 ltr

39. 5 g XeF_4 gas is filled in a 6 ltr vessel at 80°C temperature, the applied pressure on gas is

(a) 0.21 atm (b) 0.31 atm
(c) 0.11 atm (d) 0.41 atm

40. 5.75 g of gas at 55°C temperature and 0.940 atm pressure occupies 3.5 ltr volume. Identify the molecular weight of gas.

(a) 45 (b) 47 (c) 49 (d) 51

41. 28 g of a N_2 gas occupies 10 ltr volume at 2.46 atm pressure. Identify the temperature.

(a) 300 K (b) 320 K
(c) 340 K (d) 280 K

42. A gas occupies 1.5 ltr, volume at 75 cm Hg pressure. At the same temperature, what will be the volume of gas at 50 cm, Hg pressure?

(a) 1.25 ltr (b) 3.25 ltr
(c) 4.25 ltr (d) 2.25 ltr

43. A mixture of gases at 760 mm Hg contains 65% N_2, 15% O_2 and 20% CO_2 by volume, then partial pressure of each gas in mm is

(a) 494, 114, 252 (b) 494, 224, 152
(c) 494, 114, 152 (d) None of these

44. 0.45 g of a gas having mole weight is 60 and 0.22 g of another gas has 44 mole weight. The total pressure on these gases is 75 cm Hg, then partial pressure of another gas is

(a) 30 cm of Hg (b) 20 cm of Hg
(c) 10 cm of Hg (d) 40 cm of Hg

45. If the density of a gas A is 1.5 times that of B then the molecular mass of A is M. The molecular mass of B will be

(a) 1.5 M (b) $\dfrac{M}{1.5}$

(c) 3M (d) $\dfrac{M}{3}$

46. A certain mass of a gas occupies a volume of 2 ltr at STP. Keeping the pressure constant at what temperature would the gas occupy a volume of 4 ltr?

(a) 546°C (b) 273°C
(c) 100°C (d) 50°C

47. 8.2 L of an ideal gas weighs 9.0 g at 300 K and 1 atm pressure. The molecular mass of gas is

(a) 9 (b) 27 (c) 54 (d) 81

48. One litre of an unknown gas weighs 1.25 g at N.T.P. Which of the following gas pertains to the above data?

(a) CO_2 (b) NO_2 (c) N_2 (d) O_2

49. If pressure of a gas contained in a closed vessel is increased by 0.4% when heated by 1°C, what is its initial temperature?

(a) 250 K (b) 250°C
(c) 2500 K (d) 25°C

50. A football bladder contains equimolar proportions of H_2 and O_2. The composition by mass of the mixture effusing out of punctured football is in which ratio ($H_2 : O_2$)?

(a) 1 : 4 (b) $2\sqrt{2}:1$ (c) $1:2\sqrt{2}$ (d) 4 : 1

51. At low pressure compressibility factor is equal to:

(a) $\left(1-\dfrac{a}{RTV}\right)$ (b) $\left(1-\dfrac{RTV}{a}\right)$

(c) $\left(1+\dfrac{a}{RTV}\right)$ (d) $\left(1+\dfrac{RTV}{a}\right)$

52. If a mixture containing 3 moles of hydrogen and 1 mole of nitrogen is converted completely into ammonia, what will be the ratio of initial and final volume under the same temperature and pressure?

(a) 3 : 1 (b) 1 : 3 (c) 2 : 1 (d) 1 : 2

53. SO_2 at STP contained in a flask was replaced by O_2 under identical conditions of pressure, temperature and volume. Then the weight of O_2 will be ______ of SO_2?
(a) half (b) one fourth
(c) twice (d) four times

54. According to Charle's law,
(a) $\left(\frac{dV}{dT}\right)_P = k$ (constant) (b) $\left(\frac{dV}{dT}\right)_P = P$
(c) $\left(\frac{dV}{dT}\right)_P = V$ (d) $\left(\frac{dV}{dT}\right) = T$

55. A sample of gas at 35°C and 1 atm pressure occupies a volume of 3.75 ltr. At what temperature should the gas be kept if it is required to reduce the volume to 3 ltr at the same pressure?
(a) –26.6°C (b) 0°C
(c) 3.98°C (d) 28°C

56. Equal weights of methane and hydrogen are mixed in an empty container at 25°C. The fraction of total pressure exerted by hydrogen is
(a) 1/2 (b) 8/9 (c) 16/19 (d) 1/9

57. The best vaccum so far attained in laboratory is 10^{-10} mm of Hg. The number of molecules of gas remain per cm^3 at 20°C in this vaccum is
(a) 3.29×10^4 molecules
(b) 3.29×10^5 molecules
(c) 3.29×10^6 molecules
(d) 3.29×10^7 molecules

58. A hydrocarbon contains 10.5 g of carbon per gm of H. One litre vapours of hydrocarbon at 127°C and 1 atm pressure weighs 2.8 g. The molecular formula of hydrocarbon is
(a) C_6H_8 (b) C_7H_8 (c) C_5H_{12} (d) C_8H_4

59. A 0.5 dm^3 flask contains gas A and 1 dm^3 flask contains gas B at the same temperature. If density of $A = 3$ g/dm^3 and that of $B = 1.5$ g/dm^3 and the molar mass of $A = 1/2$ of B, the ratio of pressure exerted by gases is
(a) $\frac{P_A}{P_B} = 2$ (b) $\frac{P_A}{P_B} = 1$
(c) $\frac{P_A}{P_B} = 4$ (d) $\frac{P_A}{P_B} = 3$

60. 120 g of an ideal gas of molecular weight 40 are confined to a volume of 20 ltr at 400 K. What is the pressure of gas is?
(a) 490 atm (b) 4.92 atm
(c) 2236 atm (d) 22.4 atm

61. A cylinder contains acetylene gas at 27°C and 4.05 M Pa. The pressure in the cylinder after half the mass of gas is used up and the temperature that has fallen to 12°C will be
(a) 4.05 M Pa (b) 2.025 M Pa
(c) 3.84 M Pa (d) 1.92 M Pa

62. The weight of 350 mL of a diatomic gas at 0°C and 2 atm pressure is 1 g. The weight in g of one atom at NTP is
(a) 2.64×10^{-23} g (b) 2.64×10^{-22} g
(c) 5.28×10^{-23} g (D) 0.82×10^{-22} g

63. Oxygen is present in a litre flask at a pressure of 7.6×10^{-10} mm of Hg. The number of oxygen molecules in the flask at 0°C is
(a) 2.7×10^9 molecules (b) 2.7×10^{10} molecules
(c) 2.7×10^{11} molecules (d) 2.7×10^{12} molecules

64 The r.m.s. velocity of hydrogen at 27°C, $R = 8.314$ J mol^{-1} K^{-1} is
(a) 1.934 m/s (b) 19.34 m/s
(c) 193.4 m/s (d) 1934 m/s

65. Temperature at which R.M.S. speed of O_2 is equal to that of neon at 300 K is
(a) 280 K (b) 480 K
(c) 680 K (d) 180 K

66. The most probable velocity of a neutron at 20°C is nearby
(a) 220 m/s (b) 2200 m/s
(c) 22200 m/s (d) 22 m/s

67. The R.M.S. speed of the molecules of a gas of density 4 kg m^{-3} and pressure 1.2×10^5 N m^{-2} is
(a) 120 m s^{-1} (b) 300 m s^{-1}
(c) 600 m s^{-1} (d) 900 m s^{-1}

68. The R.M.S. velocity of a gas whose each molecule weighs 10^{-12} g and at temperature 27°C is
(a) 0.70 cm/s (b) 0.35 cm/s
(c) 0.35 m/s (d) 0.70 m/s

69. The average speed of an ideal gas molecule at 27°C is 0.3 m sec^{-1}. The average speed at 927°C is
(a) 0.15 m sec^{-1} (b) 0.6 m sec^{-1}
(c) 1.2 m sec^{-1} (d) 0.6 cm sec^{-1}

70. The temperature at which CO_2 has the same R.M.S. speed to that of O_2 at S.T.P. is/are
(a) 375.38 K (b) 102.38 °C
(c) 275.38 K (d) 202.38 °C

71. The temperature at which the most probable speed of CO_2 molecules be twice as that of 50°C is
(a) 200°C (b) 1292 K
(c) 100°C (d) 646 K

72. What is the total translational and rotational energy of 1 mole of oxygen at 300 K?
$R = 8.314$ J mol^{-1} K^{-1}:
(a) 6235.5 J (b) 623.25 J
(c) 62.325 J (d) 6.2325 J

73. The kinetic energy of N molecules of O_2 is x Joule at –123°C. Another sample of O_2 at 27°C has a kinetic energy of 2 x. The later sample contains ________ molecules of O_2.
(a) N (b) N/2 (c) 2 N (d) 3 N

74. The average kinetic energy in joules of molecules in 8.0 gm of methan at 27°C is

(a) 6.21×10^{-20} J/molecule
(b) 6.21×10^{-21} J/molecule
(c) 6.21×10^{-22} J/molecule
(d) 3.1×10^{-22} J/molecule

75. The ratio of rates of diffusion of CO_2 and SO_2 at the same pressure and temperature is
(a) $4 : \sqrt{11}$ (b) $11 : 4$
(c) $1 : 4$ (d) $1 : 6$

76. 20 L of SO_2 diffuses through a porous partition in 60 seconds. Volume of O_2 diffuse under similar conditions in 30 seconds will be
(a) 12.14 L (b) 14.14 L
(c) 18.14 L (d) 28.14 L

77. Three footballs are respectively filled with nitrogen, hydrogen and helium. If the leaking of the gas occurs with time from the filling hole, then the ratio of the rate of leaking of gases $(r_{N_2} : r_{H_2} : r_{He})$ from three footballs (in equal time interval) is
(a) $(1 : \sqrt{14} : \sqrt{7})$ (b) $(\sqrt{14} : \sqrt{7} : 1)$
(c) $(\sqrt{7} : 1 : \sqrt{14})$ (d) $(1 : \sqrt{7} : \sqrt{14})$

78. NH_3 and SO_2 gases are being prepared in two corners of a laboratory. The gas that will be detected first in the middle of the laboratory is
(a) NH_3 (b) SO_2
(c) Both at the same time (d) Cannot determine

79. 10 mL of gaseous hydrocarbon on combustion gives 40 mL of CO_2 and 50 mL of H_2O. The hydrocarbon is
(a) C_4H_6 (b) C_4H_8 (c) C_8H_{10} (d) C_4H_{10}

80. The volume of oxygen required for complete oxidation of 2 ltr of methane at NTP is
(a) 12.25 L (b) 4 L
(c) 1 L (d) 3 L

81. LPG is a mixture of *n*-butane and iso-butane. The volume of oxygen needed to burn 1 kg of LPG at NTP would be
(a) 2240 L (b) 2510 L
(c) 1000 L (d) 500 L

82. The viscosity of a which liquid is the maximum?
(a) Water (b) Glycol
(c) Acetone (d) Ethanol

83. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by methane is
(a) 1/3 (b) 1/2
(c) 2/3 (d) (1/3) (273/298)

84. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is
(a) Two times that of a hydrogen molecules
(b) Same as that of a hydrogen molecules
(c) Four times that of a hydrogen molecules
(d) Half that of a hydrogen molecules

85. The compressibility of a gas is more than unity at STP. Therefore,
(a) $V_m > 22.4$ L (b) $V_m < 22.4$ L
(c) $V_m = 22.4$ L (d) $V_m \geq 44.8$ L

86. If two moles of an ideal gas at 546 K occupies a volume of 44.8 ltr, the pressure must be
(a) 2 atm (b) 3 atm (c) 4 atm (d) 1 atm

87. At STP, the order of root mean square velocity of molecules of H_2, N_2, O_2 and HBr is:
(a) $H_2 > N_2 > O_2 > HBr$ (b) $HBr > O_2 > N_2 > H_2$
(c) $HBr > H_2 > O_2 > N_2$ (d) $N_2 > O_2 > H_2 > HBr$

88. The density of a gas at 27°C and 1 atm is *d*. Pressure remaining constant at which of the following temperatures will its density become 0.75 d?
(a) 20°C (b) 30°C (c) 400 K (d) 300 K

89. At 27°C the ratio of R.M.S velocities of ozone to oxygen is
(a) $\sqrt{3/5}$ (b) $\sqrt{4/3}$
(c) $\sqrt{2/3}$ (d) 0.25

90. A real gas most closely approaches the behaviour of an ideal gas at
(a) 15 atm and 200 K (b) 1 atm and 273 K
(c) 0.5 atm and 500 K (d) 15 atm and 500 K

91. At STP, 2.8 ltr of hydrogen sulphide were mixed with 1.6 ltr of sulphur dioxide and the reaction occurred according to the equation,

$$2H_2S\,(g) + SO_2\,(g) \longrightarrow 2H_2O\,(l) + 3S\,(s)$$

Which of the following shows the volume of the gas remaining after the reaction?
(a) 0.2 ltr of SO_2 (g) (b) 0.4 ltr of H_2 (g)
(c) 1.2 ltr of H_2S (g) (d) 1.2 ltr of SO_2 (g)

92. The rates of diffusion of SO_3, CO_2, PCl_3 and SO_2 are in the following order:
(a) $PCl_3 > SO_3 > SO_2 > CO_2$
(b) $CO_2 > SO_2 > PCl_3 > SO_3$
(c) $SO_2 > SO_3 > PCl_3 > CO_2$
(d) $CO_2 > SO_2 > SO_3 > PCl_3$

93. A closed vessel contains equal number of nitrogen and oxygen molecules at pressure of P mm. If nitrogen is removed from the system, then the pressure will be
(a) P (b) $2P$ (c) $P/2$ (d) P^2

94. The rate of diffusion of methane at a given temperature is twice that of gas X. The molecule weight of X is
(a) 64.0 (b) 32.0 (c) 4.0 (d) 8.0

95. The ratio, $\dfrac{\text{R.M.S velocity of } SO_2}{\text{R.M.S velocity of He}}$, of sulphur dioxide and helium gases at 30°C is equal to
(a) 4 (b) 0.25 (c) 0.10 (d) 8

96. A certain volume of argon gas (Mol. Wt. 40) requires 45 s to effuse through a hole at a certain pressure and temperature. The same volume of another gas of unknown molecular weight requires 60 s to pass through the same hole under the same conditions of temperature and pressure. The molecular weight of the gas is
(a) 53 (b) 35 (c) 71 (d) 120

97. A chemist has synthesised a greenish yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36°C and 2.88 atm. Then the molecular formula of the compound will be

(a) ClO_3 (b) ClO_2 (c) ClO (d) Cl_2O_2

98. When a gas is expanded at constant temperature,

(a) the pressure decreases.
(b) the kinetic energy of the molecules remains the same.
(c) the kinetic energy of the molecules decreases.
(d) the number of molecules of the gas decreases.

99. At what temperature will the total K.E. of 0.3 mol of He be the same as the total K.E. of 0.40 mol of Ar at 400 K

(a) 533 K (b) 400 K (c) 346 K (d) 300 K

100. If molecules of the gas are spherical of radius 1 Å, the volume occupied by the molecules in 1 mol of a gas is:

(a) 22400 mL (b) 22.4 L
(c) 2.52 mL (d) 4.22 mL

LEVEL II

1. The drain cleaner, Drainex contains small bits of aluminum which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and one bar will be released when 0.15g aluminum reacts?

(a) 200.4 mL (b) 102.5 mL
(c) 101.25 mL (d) 405.0 mL

2. A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.

(a) 0.8 bar (b) 0.4 bar (c) 1.6 bar (d) 3.2 bar

3. How much time would it take to distribute one Avogadro number of wheat grains, if 10^{10}grains are distributed in each second?

(a) 4×10^2 year (b) 9×10^6 year
(c) 6×10^4 year (d) 2×10^6 year

4. What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27°C?

(a) 8.314 Pa (b) 8.314×10^2 Pa
(c) 2×10^2 Pa (d) 8.314×10^4 Pa

5. 34.05 mL of phosphorus vapour weighs 0.0625 g at 546 °C and 0.1 bar pressure. What is the molar mass of phosphorus?

(a) 1247.7 g (b) 1147.0 g
(c) 1047 g (d) None of these

6. A student forgot to add the reaction mixture to the round bottom flask at 27°C but instead he/she placed the flask on the flame. After a lapse of time, he realised his mistake and using a pyrometer he found the temperature of the flask was 477°C. What fraction of air would have been expelled out?

(a) 5/3 (b) 5/6 (c) 3/5 (d) 6/5

7. The circulation of blood in human body supplies O_2 and releases CO_2. The concentration of O_2 and CO_2 is variable but on the average, 100 mL blood contains 0.02 g of O_2 and 0.08 g of CO_2. The volume of O_2 and CO_2 at 1 atm and at body temperature of 37°C, assuming 10 ltr blood in human body, would be

(a) 2 ltr, 4 ltr (b) 1.5 ltr, 4.5 ltr
(c) 1.59 ltr, 4.62 ltr (d) 3.82 ltr, 4.62 ltr

8. When 2 g of a gas '*A*' is introduced into an evacuated flask kept at 25°C, the pressure is found to be 1 atm. If 3 g of another gas '*B*' is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of molar masses $M_A : M_B$

(a) 1 : 3 (b) 1 : 4 (c) 4 : 1 (d) 3 : 1

9. 5 mL of a gaseous hydrocarbon was exposed to 30 mL of O_2. The resultant gas, on cooling is found to measure 25 mL, of which 10 mL was absorbed by NaOH and the remainder by pyrogallol. All measurements are made at constant pressure and temperature. The molecular formula of the hydrocarbon is

(a) C_2H_2 (b) C_3H_8 (c) C_2H_4 (d) C_2H_6

10. A gaseous compound X contained 44.4% C, 51.9% N and 3.7% H. Under like conditions 30 cm^3 of X diffused through a pinhole in 25 sec and the same volume of H_2 diffused in 4.81 sec. The molecular formula of X is

(a) C_2H_2N (b) $C_2H_4N_2$
(c) $C_2H_2N_2$ (d) $C_4H_2N_21_2$.

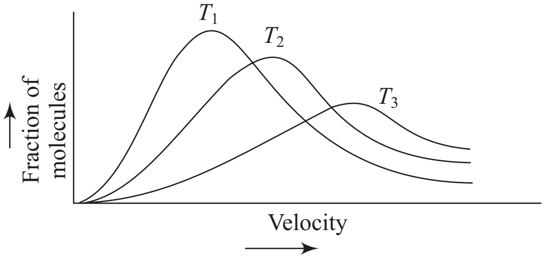
11. The density of the gaseous mixture (He and N_2) is $\frac{10}{22.4}$ g/ltr at NTP. What is the percentage composition of He and N_2 by volume in this mixture respectively?

(a) 75%, 25% (b) 25%, 75%
(c) 30%, 70% (d) 40%, 60%

12. A gas bulb containing air is connected to an open limb manometer at 27°C and at 750 mm Hg. Assuming that initially the level of Hg in the both limbs were same. The bulb was heated to 77°C, what will be difference in the levels of Hg in two limbs? (Assuming the volume difference of the gas produced is negligible at higher temperature).

(a) 7.5 cm Hg (b) 8 cm Hg
(c) 6 cm Hg (d) 12.5 cm Hg

13. In the following graph of Maxwell-Boltzmann distribution of molecular velocities



Which of the following is the correct order of temperature?

(a) $T_1 < T_2 < T_3$ (b) $T_3 < T_2 < T_1$
(c) $T_2 < T_1 < T_3$ (d) None of these

14. CH_4 gas is collected over water vapour having total pressure = 735 torr and temperature = 29°C. If the pressure of water vapour is 30 at 29°C temperature, the applied pressure of dry methane gas is

(a) 605 torr (b) 205 torr
(c) 405 torr (d) 705 torr

15. What is the density of oxygen gas at 1.0 atm. pressure and 27°C temperature?

(a) 0.8 g L^{-1} (b) 1.3 g L^{-1}
(c) 1.8 g L^{-1} (d) 2.3 g L^{-1}

16. The van der Waal's constant 'b' of a gas is $4\pi \times 10^{-4}$ L/mol. How near can the centres of the two molecules approach each other?
[Use : $N_A = 6 \times 1023$]

(a) 10^{-7} m (b) 10^{-10} m
(c) 10^{-11} m (d) 10^{-9} m

17. A box of 1L capacity is divided into two equal compartments by a thin partition which are filled with 2 g H_2 and 16g CH_4 respectively. The pressure in each compartment is recorded as P atm. The total pressure when partition is removed will be

(a) P (b) $2P$ (c) $P/2$ (d) $P/4$

18. A 2.24 L cylinder of oxygen at N.T.P. is found to develop a leakage. When the leakage was plugged, the pressure dropped to 570 mm of Hg. The number of moles of gas that escaped will be

(a) 0.025 (b) 0.050
(c) 0.075 (d) 0.09

19. An open vessel containing air is heated from 27°C to 127°C. The fraction of air originally present which goes out of it is

(a) 3/4 (b) 1/4 (c) 2/3 (d) 1/8

20. At a constant pressure, what should be the percentage increase in the temperature in Kelvin for a 10% increase in volume

(a) 10% (b) 20% (c) 5% (d) 50%

21. Assuming that O_2 molecule is spherical in shape with radius 2Å, the percentage of the volume of O_2 molecules to the total volume of gas at S.T.P. is

(a) 0.09% (b) 0.9% (c) 0.009% (d) 0.045%

22. The mass of molecule A is twice that of molecule B. The root mean square velocity of molecule A is twice that of molecule B. If two containers of equal volume have same number of molecules, the ratio of pressure P_A/P_B will be

(a) 8 : 1 (b) 1 : 8 (c) 4 : 1 (d) 1 : 4

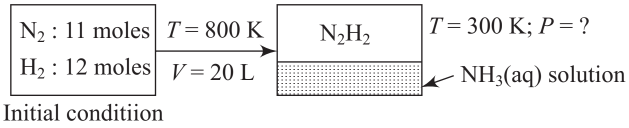
23. Calculate the compressibility factor for CO_2, if one mole of it occupies 0.4 ltr at 300 K and 40 atm. Comment on the result.

(a) 0.40, CO_2 is more compressible than ideal gas.
(b) 0.65, CO_2 is more compressible than ideal gas.
(c) 0.55, CO_2 is more compressible than ideal gas.
(d) 0.62, CO_2 is more compressible than ideal gas.

24. On the surface of the Earth at 1 atm pressure, a balloon filled with H_2 gas occupies 500 mL. This volume 5/6 of its maximum capacity. The balloon is left in air. It starts rising. The height above which the balloon will burst if temperature of the atmosphere remains constant and the pressure decreases 1 mm for every 100 cm rise of height is

(a) 120 m (b) 136.67 m
(c) 126.67 m (d) 100 m

25. 11 moles N_2 and 12 moles of H_2 mixture reacted in 20 litre vessel at 800 K. After equilibrium was reached, 6 mole of H_2 was present. 3.58 ltr of liquid water is injected in equilibrium mixture and resultant gaseous mixture suddenly cooled to 300 K. What is the final pressure of gaseous mixture? Negative vapour pressure of liquid solution. Assume (i) all NH_3 dissolved in water, (ii) no change in volume of liquid and (iii) no reaction of N_2 and H_2 at 300 K.



(a) 18.47 atm (b) 60 atm
(c) 22.5 atm (d) 45 atm

26. Two closed vessel A and B of equal volume containing air at pressure P_1 and temperature T_1 are connected to each other through a narrow open tube. If the temperature of one is now maintained at T_1 and other at T_2 (where $T_1 > T_2$) then what will be the final pressure?

(a) $\dfrac{T_1}{2P_1T_2}$ (b) $\dfrac{2P_1T_2}{T_1+T_2}$

(c) $\dfrac{2P_1T_2}{T_1-T_2}$ (d) $\dfrac{2P_1}{T_1+T_2}$

27. A balloon containing 1 mole air at 1 atm initially is filled further with air till pressure increases to 4 atm. The initial diameter of the balloon is 1 m and the pressure at each stage is proportion to diameter of the balloon. How many number of moles of air added to change the pressure from 1 atm to 4 atm?

(a) 80 (b) 257 (c) 255 (d) 256

28. What is the density of wet air with 75% relative humidity at 1 atm and 300 K? Given : vapour pressure of H_2O is 30 torr and average molar mass of air is 29 g mol^{-1}.

(a) 1.614 g/L (b) 0.96 g/L
(c) 1.06 g/L (d) 1.164 g/L

29. Calculate minimum number of balloons each of volume 82.1 L required to lift a mass of 1 kg to a height of 831 m. Given : molar mass of air = 29 g/mol, temperature is constant at 290 K and mass of each balloons is 40 g. [Use $e^{-0.1} = 0.9$, pressure at sea level = 1 atm, acceleration due to gravity (g) = 10 m/s^2].

(a) 10 (b) 20 (c) 25 (d) 50

LEVEL III

1. Match the columns:

Column I		Column II	
(A)	T_c/P_c	(P)	Z
(B)	T_c/V_c	(Q)	a/Rb
(C)	T_B	(R)	$8b/R$
(D)	T_i/T_B	(S)	$8a/81Rb^2$

2. Four different gases and their Van der Waal's constant are given below.

Gas	a in atm L^2mol^{-2}	b in L/mol
A_2	1.5	0.05
B_2	2.0	0.08
C_2	4.2	0.025
D_2	5.0	0.1

Column I		Column II	
(A)	Gas having highest intermolecular force of attraction.	(P)	A_2
(B)	Gas having smallest size of molecules.	(Q)	B_2
(C)	Gas that can't be liquefied at 90 K.	(R)	C_2
(D)	Gas resembles with ideal gas at the boiling point of water	(S)	D_2

3.

Column I		Column II	
(A)	At definite volume and temperature total pressure of gas.	(P)	Changes with the change in temperature.
(B)	The ratio of densities of moist air to the density of dry air at the definite temperature and pressure.	(Q)	Changes with change in number of moles.
(C)	The value of $\dfrac{p_{H_2O}}{p^\circ_{H_2O}}$.	(R)	Ideal gases
(D)	Dalton's law of partial pressures.	(S)	Lesser than one.

4.

Column I		Column II	
(A)	He	(P)	Greatest u_{rms} at temperature T
(B)	H_2	(Q)	Lowest u_{rms} at temperature T
(C)	CO_2	(R)	Highest value of C_P/C_V at temperature T
(D)	SO_2	(S)	Vibrational energies equal to $4RT$ per mole at temperature T

Comprehension

Passage # 1 (Ques. 5 to 7)

Measuring the molar mass of gases is an important application of the ideal gas law. Before the development of mass spectroscopy, the molar mass of many substances were determined using the ideal gas law. The ideal gas law is used to calculate the number of moles in a sample of known mass then molar mass can be found.

5. What is the molar mass of a gas if 0.495 g sample of the gas occupies 127 mL at 754 torr pressure and 98°C temperature?
(a) 120 (b) 160 (c) 190 (d) 200

6. Calculate the molar mass of the gas that has a density of 0.714 g/L at STP
(a) 12 (b) 16 (c) 20 (d) 26

7. A 3 ltr container is rated to hold a gas at a pressure not higher than 100 atm. What is the maximum number of moles of the gas that container can hold at 27°C?
(a) 13.6 (b) 11.4 (c) 12.2 (d) 15.8

Passage # 2 (Qus. 8 to 10)

Real gas obey the equation of state $PV = nRT$ under conditions of low pressure and high temperature. In general, the most easily liquefiable gases, like CO_2, SO_2 and ammonia show much longer deviations from ideal behaviour than gases like H_2, N_2, Or, O_2. This can be seen from the compressibility factor (Z) – pressure diagram for various gases. The deviation from ideal behaviour is attributed to two factors: (i) The volume occupied by gas molecules is not negligible in comparison to the total volume of gas and (ii) The intermolecular forces between gas molecules are significant. To account for these deviation, the Van der Waals equation has been proposed.

8. The Van der Waals constant "a" for SO_2, ethylene, HCl and CO_2 are 6.71, 4.47, 13.67 and (3.59) L^2 atm mol^{-2} respectively. The order of liquefaction of the gases in increasing order will be:
(a) $CO_2 < HCl < C_2H_4 < SO_2$
(b) $SO_2 < C_2H_4 < HCl < CO_2$
(c) $C_2H_2 < SO_2 < CO_2 < HCl$
(d) $HCl > SO_2 > C_2H_4 > CO_2$

9. The critical compressibility factor Z_C for O_2 is 0.308 and its critical pressure and critical volume are 50.1 atm and 7.8×10^{-2} ltr mol^{-1} respectively. The Boyle temperature of O_2 is (in deg K)
(a) 348.6 (b) 215.4 (c) 154.5 (d) 521.4

10. At extremely low pressures, the Van der Waals equation for one mole of a gas may be expressed as

(a) $PV = RT - \frac{a}{V}$ (b) $P(V - b) = RT$

(c) $(P + a)(V - b) = RT$ (d) $PV = 1.2RT$

Integer-Types Questions

11. One mole of nitrogen gas at 0.8 atm takes 38 seconds to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine XeFx at 1.6 atm takes 57 seconds to diffuse through the same hole. Find out the value of *x*.

12. 9 mL of a gaseous mixture consisting of a gaseous compound A and just sufficient amount of oxygen required for complete combustion, yielded on burning, 4 mL of CO_2, 6 mL of water vapour and 2 mL of N_2, all volumes measured at the same temperature and pressure. If compound A contained only C, H and N, how many volumes of oxygen are required for complete combustion.

13. 0.9 gm of an organic compound (Mol. wt. = 90) contains carbon, hydrogen and oxygen requires 224 mL of oxygen at STP for complete combustion. After the combustion, the gases occupy 556 mL at STP. On passing it through KOH solution, the volume reduced to 112 mL. If the compound has formula $C_XH_XO_{2X}$, then find out the value of *X*.

14. At 400 K, the root mean square (rms) speed of a gas *X* (Mol. wt. = 40) is equal to the most probable speed of gas *Y* at 60 K. What is the molecular weight of the gas *Y*?

15. Two flasks *A* and *B* have equal volumes. A is maintained at 300 K and *B* at 600 K. While *A* contains H_2 gas, *B* has an equal mass of CH_4 gas. Assuming ideal behaviour for the both gases, find the ratio of $(u_{av})A : (u_{av})B$.

16. A flask of capacity of 1 L containing NH_3 at 1atm and 25°C. A spark is passed through until all the NH_3 is decomposed in N_2 and H_2. Calculate the pressure of gases left at 25°C after the reaction.

17. A compound exists in the gaseous phase both as monomer (A) and dimer (A_2). The atomic weight of A is 48. In an experiment 96 g of compound was confined in vessel of volume 33.6 L and heated to 273°C. Calculate the pressure developed if the compound exists as dimer to the extent of 50% by weight under these conditions.

18. The compressibility factor for nitrogen at 330 K and 800 atm is 1.90 and at 570 K and 200 atm is 1.10 A certain mass of N_2 occupies a volume of 1 dm^3 at 330 K and 800 atm. Volume occupied by same quantity of N_2 gas at 750 K and 200 atm in litre is

19. If the slope of *Z* (compressibility factor) v/s *p* curve is constant (slope = $\pi/492.6\ atm^{-1}$) at a particular temperature (300 k) and very high pressure, then calculate diameter of the molecules in Å, (Given $N_A = 6.0 \times 10^{23}$, $R = 0.0821$ atm lit $mol^{-1}\ K^{-1}$)

20. Two moles of a gas are confined to a 5 ltr flask at 27°C. Calculate its pressure using Van der Waals equation. For ammonia $a = 6.25$ atm $lit^{-2}\ mol^{-2}$ and $b = 0.037$ lit mol^{-1}.

21. What will be the temperature difference needed in a hot air balloon to lift 1.0 kg weight? Assume that the volume of balloon is 100 m^3, the temperature of atmosphere is 25°C and pressure is 1.0 atm. Average molar mass of air is 29 amu.

22. 4 g of an ideal gas was introduced into a bulb of volume of 0.821 dm^3 at certain pressure, *P* and temperature *T*. The above bulb was placed in a thermostat maintained at temperature (*T* + 125) K of 0.8 gm of the gas was left off to keep the original pressure. Calculate the pressure in atmospheres. [Molecular weight of the gas is 40 g $mole^{-1}$ and R value is 0.0821 lit-atm- K^{-1} mol.

23. Pressure in a bulb dropped from 2000 to 1500 mm in 47 minute when the oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in molar ratio 1:1 at a total pressure of 4000 mm was introduced. Find the molar ratio of two gases remaining in the bulb after a period of 74 minute.

24. The composition of the equilibrium mixture, ($Cl_2 \rightleftharpoons 2Cl$) which is attained at 1200°C, is determined by measuring the rate of effusion through a pinhole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast a krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. (At. wt. of Kr = 84).

25. A mixture of ethane and ethene occupies 40 ltr at 1.00 atm and at 400 K. The mixture reacts completely with 130 gm of O_2 to produce CO_2 and H_2O. Assuming ideal behavior, calculate the mole fraction of C_2H_4 and C_2H_6 in the mixture?

26. The total pressure of a mixture of H_2 and O_2 is 1.00 bar. The mixture is allowed to react to form water which is completely removed to leave only pure at a pressure of 0.35 bar. Assuming ideal gas behavior and that all pressure measurements we made under the same conditions of temperature and volume, calculate the composition of the original mixture.

27. The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. Assuming ideal behavior of all gases, calculate the density of equilibrium mixture at 400 K and 1.0 atm. (P = 31, Cl = 35.5)

28. The pressure exerted by 12 gm of an ideal gas at t°C in a vessel of volume *v* ltr is one atm. When the temperature is increased by 10°C at the same volume the pressure increased by 10%. Calculate the temperature *t* and volume *v*? (Mol. Wt. = 120)

29. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

Determine (i) molecular weight, (ii) molar volume, (iii) compression factor (Z) of the vapour and (iv) which forces among the gas molecules are dominating: the attractive or the repulsive?

30. At 27°C, H_2 gas is leaked through a tiny hole into a vessel for 20 mts. Another unknown gas, at the same temperature and pressure, as that of H_2, is leaked through the same hole for 20 mts. After the effusion of the gases the mixture exerts a pressure of 6 atm. If H_2 is 0.7 mol and volume of vessel is 3 ltr, calculate molecular weight of the unknown gas.

31. 1 ltr flask contains O_2 at 0°C and 7.6×10^{-10} mm Hg. Calculate the number of molecules of O^2 present.

32. Assuming that N2 molecules is spherical and its radius is 2×10^{-10} metre, calculate the empty space in one mole of N2 gas at NTP.

33. A glass bulb of 1 ltr contains 2×1021 molecules of nitrogen exerting pressure of 7.57×103 Nm^{-2}. Calculate (a) the root mean square velocity and temperature of the gas molecules and (b) Umpv of gas molecules at this temperature.

34. Two grams of gas A are introduced in an evacuated flask at 25°C. The pressure of the gas is 1 atm. Now 3 g of another gas B is introduced in the same flask, the total pressure becomes 1.5 atm. Calculate (a) the ratio of molecular mass MA and MB and (b) volume of the vessel, if A is O^2.

35. 1 ltr O^2 and 1 ltr H^2 are taken in a vessel of 2 ltr at STP. These gases are made to react to form water. Calculate (a) moles and weight of water formed (b) amount of gas left in the vessel and (c) total pressure of the gas at 100°C.

36. A long rectangular box is filled with chlorine (at.wt. 35.45) which is known to contain only ^{35}Cl and ^{37}Cl. If the box can be divided by a partition and the two types of chlorine molecules put in the two compartiments respectively, calcualte where should the partition be made if the pressure on both side are to be equal.

37 3.6 g of an ideal gas was injected into a bulb of internal volume of 8 L at pressure *P* atm and temp *T* K. The bulb was then placed in a thermostat maintained at (*T* + 15)K 0.6 g of the gas was let off to keep the original pressure. Find *P* and *T* if molecular weight of is 44.

38. A toy balloon originally held 1.0 g of He gas and had a radius 10 cm. During the night, 0.25 g of the gas effused from the balloon. Assuming ideal gas behaviour, under these constant *P* and *T* conditions, what was the radius of the balloon the next morning?

39. If a scuba diver is to remain submerged for 1 hr, what pressure must be applied to force sufficient air into the tank to be used. Assume 0.5 dm^3 of air per breath at standard atmospheric pressure, a respiration rate of 38 breaths per minute, and a tank capacity of 30 dm^3.

40. While resting, the average human male uses 0.2 dm^3 of O_2 per hour at STP for each kg of body mass. Assume that all this O_2 is used to produce energy by oxidising glucose in the body. What is the mass of glucose required per hour by a resting male having mass 60 kg. What volume, at STP of CO_2 would be produced?

41. 12 g N_2, 4 g H_2 and 9 g O_2 are put into a 1 ltr container at 27°C. What is the total pressure?

42. 1.0×10^{-2} kg of hydrogen and 6.4×10^{-2} kg of oxygen are contained in a 10×10^{-3} m^3 flask at 473 K. Calculate the total pressure of the mixture. If a spark ignities the mixture, what will be the final pressure?

43. At room temperature, NH_3 gas at one atm and HCl gas at "P" atm are allowed to effuse through identical pin holes to the opposite ends of a glass tube 1 m long and uniform cross section. A white deposit is observed at a distance of 60 cm from the HCl end. What is P.

44. A gas mixture contains equal number of molecules of N_2 and SF_6, some of it is passed through a gaseous effusion apparatus. Calculate how many molecules of N_2 are present in the product gas for every 100 molecules of SF_6.

45. Two gases NO and O_2 were introduced at the two ends of a 1 mtr long tube simultaneously (tube of uniform cross section). At what distance from NO gas end, brown fumes will be seen?

46. At 20°C two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg N_2 and other with 1 kg H_2. The N_2 balloon leaks to a pressure of $\frac{1}{2}$ atm in one hour. How long will it take for H_2 balloon to leak to a pressure of $\frac{1}{2}$ atm?

47. Pure O_2 diffuses through an aperture in 224 sec, whereas mixture of O_2 and another gas containing 80% O_2 diffuses from the same in 234 sec. What is molecular weight of the gas?

48. A space capsule is filled with neon gas 1.00 atm and 290 K. The gas effuses through a pin - hole into outer space at such a rate that the pressure drops by 0.3 torr/sec.

(a) If the capsule were filled with ammonia at the same temperature and pressure, what will be the rate of pressure drop?

(b) If the capsule were filled with 30.0 mol % helium, 20.0 mol% oxygen and 50.0 mol% nitrogen at a total pressure of 1.00 atm and a temperature of 290 K, what will be the corresponding rate of pressure drop?

49. Show that the height at which the atmospheric pressure is reduced to half its value is given by $h = \frac{0.693RT}{Mg}$.

50. Calculate the pressure of a barometer on an aeroplane which is at an altitude of 10 km. Assume the pressure to be 101.325 kPa at sea level and the mean temperature 243 K. Use the average molar mass of air (80% N_2, 20% O_2).

51. An iron cylinder contains helium at a pressure of 250 kPa and 27°C. The cylinder can withstand a pressure of 1×10^6 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it metls or not. [Melting point of cylinder = 1800 K]

52. Determine the molar mass of a gas if its pressure is to fall to one-half of its value in a vertical distance of one metre at 298 K.

53. The time taken for a given volume of gas E to effuse through a hole is 75 sec. Under identical conditions, the same volume of a mix of CO and N_2 (containing 40% of N_2 by volume) is effused in 70 sec. Calculate

(i) the relative molecular mass of *E*, and

(ii) the R.M.S velocity (in ms^{-1} units) of *E* at 0°C.

54. At what temperature in °C, the Urms of SO_2 is equal to the average velocity of O_2 at 27°C?

55. The density of CO at 273 K and 1 atm is 1.2504 kg m^{-3}. Calculate (a) root mean square speed, (b) the average speed and (c) most probable speed.

56. Calculate the temperature values at which the molecules of the first two members of the homologous series C_nH_{2n+2} will have the same R.M.S speed as CO_2 gas at 770 K. The normal b.p. of *n*-butane is 273 K. Assuming ideal gas behaviour of *n*-butane up to this temperature, calculate the mean velocity and the most probable velocity of its molecules at this temperature.

57. Calculate the temperature at which the root mean square velocity, average velocity and most probable velocity of oxygen gas are all equal to 1500 ms^{-1}.

58. The compressibility factor for N_2 at –50°C and 800 atm pressure is 1.95 and at 100°C and 200 atm, it is 1.10. A certain mass of nitrogen occupied 1 ltr at –50°C and 800 atm. Calculate the volume occupied by the same quantity of N_2 at 100°C and 200 atm.

59. At 273.15 K and under a pressure of 10.1325 MPa, the compressibility factor of O_2 is 0.927. Calculate the mass of O_2 necessary to fill a gas cylinder of 100 dm^3 capacity under the given conditions.

60. The Van der Waals constant for O_2 are $a = 1.36$ atm L^2 mol^{-2} and $b = 0.0318$ L mol^{-1}. Calculate the temperature at which O_2 gas behaves, ideally for longer range of pressure.

61 Show that at low densities, the Van der Waals equation

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

and the Dieterici's equation $P(V_m - b) = RT \exp(-a/RTV_m)$ given essential the same value of *p*.

62. Calculate from the Van der Waal's equation, the temperature at which 192 g of SO_2 will occupy a volume of 10 dm^3 at 15 atm pressure. [$a = 6.7$ atm L^2 mol^2, $b = 0.0564$ L mol^{-1}]

63. Calculate the pressure of 15 mol neon at 30°C in a 12 ltr container using

(i) the ideal gas equation

(ii) the Vander Waal's equation

[$a = 0.2107$ atm L^2 mol^2, $b = 0.0171$ L mol^{-1}]

64. What will be the temperature difference needed in a hot air balloon to lift 1.0 kg of mass? Assume that the volume of balloons is 100 m^3, the temperature of ambient air is 25°C, the pressure is 1 bar, and air is an ideal gas with an average molar mass of 29 g mol^{-1} (hot and cold both).

65. One mole of a non-linear triatomic gas is heatted in a closed rigid container from 500°C to 1500°C. Calculate the amount of energy required if vibrational degree of freedom become effective only above 1000°C.

66. The respiration of a suspension of yeast cells was measured by determining the decrease in pressure of the gas above the cell suspension. The apparatus was arranged so that the gas was confined to a constant volume, 16 cm^3 and the entire pressure change was caused by uptake of oxygen by the cells. The pressure was measured in a monometer, the fluid of which had density of 1.034 g/cm^3. The entire apparatus was immersed in a thermostat at 37°C. In a 30 mts observation period, the fluid in the open side of the manometer dropped 37 mm. Neglecting the solubility of oxygen in the yeast suspension, compute the rate oxygen consumption by the cells in mm3 of O_2 (STP) per hour.

67. In a basal metabolism measurement timed at 6 mts, a patient exhaled 52.5 L of air measured over water at 20°C. The vapour pressure of water at 20°C is 17.5 torr. The barometric pressure was 750 torr. The exhaled air analysed 16.75 volume % oxygen and the inhald air 20.32 volume % oxygen. Both on a dry basis neglecting any solubility of the gases in water and any difference in the total volumes of inhaled and exhaled air, calculate the rate of oxygen consumption by the patient in mL (STP) per minute.

68. The temperature and the relative humidity of air are 20°C and 80% on a certain day. Find the fraction of the mass of water vapour that will condense if the temperature falls to 5°C. Saturation vapour pressures at 20°C and 5°C are 17.5 mm and 6.5 mm of Hg respectively.

69. 6.0 g of He having average velocity 4×10^2 ms^{-1} is mixed with 12.0 g of Ne^{20} having the same average velocity. What is the average kinetic energy per mole in the mixture?

70. Molar volume of He at 10.1325 MPa and 273 K is 0.011075 times its molar volume at 101.325 kPa. Calculate radius of He atom assuming negligible 'a'.

71. The viral equation for ethane gas is given by $PV = RT + BP$. At 0°C, $B = -0.1814$ L/mol. Calculate volume of one mole of ethane at 10 atm, and 'a'.

72. Pressure of He gas confined in a steel chamber drops from 4.0 to 1.0 atmosphere in 4 hrs due to diffusion through a pin hole in the steel chamber. If an equimolar mixture of He and methane gas at 20 atmosphere and the same temperature are confined in the same chamber, what will be the parital pressure of He and methane after 1 hr. Assume rate of diffusion to be linear function of gas pressure and inverse function of square root of molar masses.

73. A 1 ltr flask containing NH_3 (g) at 2.0 atmoshpere and 300 K is connected to another 800 mL flask containing HCl (g) at 8.0 atmosphere and 300 K by means of a narrow tube of negligible volume and gases were allowed to react quantitatively as

$NH_3\,(g) + HCl\,(g) \longrightarrow NH_4Cl\,(s)$; DH = – 43 kJ/mol

If heat capacity of HCl (g) CV is 20 JK^{-1} mol^{-1}, determine final pressure inside the flask assuming negligible heat capacity of flask and negligible volume of solid NH_4Cl.

74. Calculate the value of σ, λ, Z_1 and Z_{11} for nitrogen molecules at 25°C and at pressure of 10^{-3} mm Hg. Given that b for nitrogen is 39.1 cm^3 mol^{-1}.

75. The mean free path of the molecule of a certain gas at 300 K is 2.6×10^{-5} m. The collision diameter of the molecule is 0.26 nm. Calculate

(a) pressure of the gas, and
(b) number of molecules per unit volume of the gas.

76. There are two vessels of same consisting same number of moles of two different gases at same temperature. One of the gas is CH_4 and the other is unknown X. Assuming that all the molecules of X are under random motion whereas in CH_4 except one all are stationary. Calculate Z_1 for X in terms of Z_1 of CH_4. Given that the collision diameter for both gases are same and $(U_{\text{rms}})x$ $= \frac{1}{\sqrt{6}}(U_{\text{av}})_{CH_4}$.

77. A mixture of CH_4 and O_2 is used as an optimal fuel if O_2 is present in thrice the amount required theoretically for combustion of CH_4. Calculate number of effusion steps required to convert a mixture containing one part of CH_4 in 193 parts mixture (parts by volume). If calorific value (heat evolved when 1 mole is burnt) of CH_4 is 100 cal/mole and if after each effusion 90% of CH_4 is collected, find out what initial mole of each gas in initial mixture required for producing 1000 cal of energy after processing?

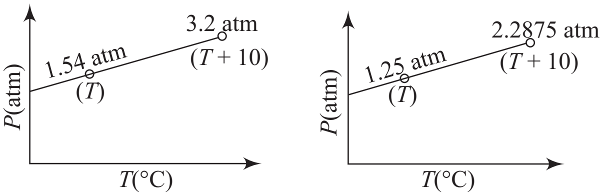
[Given $(0.9)^5 = 0.6$]

78. A closed vessel of known volume containing known amount of ideal gaseous substance 'A' was observed for variation of pressure with temperature. The expected graph was to be like (i) However actual observations revealed the graph to be like. (ii) The deviation was attributed to polymerisation of gas molecules as

$nA(g) \rightleftharpoons An(g)$. If it is known that the above reaction gave only 50% yield,

(a) calculate the ratio of $\frac{n_{\text{experiment}}}{n_{\text{theoritical}}}$ (where nexp.= Total number of gaseous mole actually present ntheoritical = Total number of mole original taken)

(b) Find the value of n to which the gas A is being polymerised into.



(i) Expected (ii) Actual

79. During one of his adventures, Chacha Chaudhary got trapped in an underground cave which was sealed 200 yrs back. The air inside the cave was poisonous, having some amount of carbon monoxide in addition to O_2 and N_2. Sabu, being huge could not enter into the cave, so in order to save Chacha Choudhary he started sucking the poisonous air out of the cave by mouth. Each time, he filled his lunge with cave air and exhaled it out in the surroundings. In the mean time, fresh air from surrounding effused into the cave till the pressure was again one atmosphere. Each time Sabu sucked out some air, the pressure in the cave dropped to half of its initial value of one atmosphere.

If the initial sample of air from the cave contained 5% by volume CO. If the safe level of CO in the atmosphere is less than 0.001% by volume, how many times does Sabu need to such out air in order to save Chacha Choudhary.

80. A closed vertical cylinder is divided into two parts by a frictionless piston, each part contains 1 mole of air. At 27°C, the volume of the upper part is four times than that of the lower part. Calculate the temperature when volume of the upper part will be three times that of the lower part.

81. A water gas mixture has the composition by volume of 50% H_2, 40% CO and 5% CO_2.

(i) Calculate the volume in litres at STP of the mixture which on treatment with excess steam will contain 5 ltrs of H_2. The stoichiometry for the water gas shift reaction is

$CO + H_2O \rightarrow CO_2 + H_2$

(ii) Find the density of the water gas mixture in kg/m^3.

(iii) Calculate the moles of the absorbants KOH, $Ca(OH)_2$ and ethanolamine.

$HO - CH_2 - CH_2 - NH_2$ required respectively to collect the CO_2 gas obtained.

82. A gas present in a container connected to frictionless, weightless piston operating always at one atmosphere pressure such that it permits flow of gas outside (with no adding of gas). The graph of n vs T (Kelvin) was plotted and was found to be a straight line with coordinates of extreme points as (300, 2) and (200, 3). Calculate:

(i) relationship between n and T
(ii) relationship between V and T
(iii) Maxima or minima value of 'V'

83. Find the critical constant (Pc, Vc and Tc) in terms of A and B. Also find compressibility factor (z) for the following equation of state:

$$PV = RT - \frac{A}{V} + \frac{2B}{V^2}$$

where A and B are constant, P = pressure and V = molar volume.

84. Calculate the mass of mercury in a uniform column 760 mm high and 1.00 cm^2 in cross-sectional area. Is there any change in
(a) mass and
(b) pressure of column of same height but with 2.00 cm^2 cross-sectional area is taken?
(Density of Hg = 13.6 g/cm^3)

85. The diameters of a bubble at the surface of a lake is 4 mm and at the bottom of the lake is 1 mm. If atmospheric pressure is 1 atm and the temperature of the lake water and the atmosphere are equal, what is the depth of the lake? (The density of lake water and Hg are 1 gm/mL and 13.6 gm/mL respectively. Also neglect the contribution of pressure due to surface tension).

86. At room temperature, following reaction goes to completion:

$$2NO + O_2 \longrightarrow 2NO_2 \longrightarrow N_2O_4$$

Dimer N_2O_4 at 262 K is solid. A 250 mL flask and a 100 mL flask are separated by a stop cock. At 300 K, the nitric oxide in the large flask exerts a pressure of 1.053 atm and the smaller one contains O_2 at 0.789 atm. The gases are mixed by opening the stop cock and after the end of the reaction, the flasks are cooled to 220 K. Neglecting the vapour pressure of dimer. Find out the pressure and composition of gas remaining at 220 K (Assume gases behave ideally).

87. 1 mole of N_2 and 3 moles of H_2 are mixed in 8.21 ltr container at 300 K to form NH_3. If equilibrium average molecular mass was found to be 34/3 gram then find partial pressure of each component.

88. One litre flask contains air, water vapour and a small amount of liquid water at a pressure of 200 mm-Hg. If this is connected to another 1 ltr evacuated flask, what will be the final pressure of the gas mixture at equilibrium? Assume the temperature to be 50°C. Aqueous tension at 50°C = 93 mm-Hg.

89. A 500 mL bulb is filled with CH_4 at a pressure of 1 atm and oxygen at a pressure of 4 atm at 27ºC. The mixture is then exploded, when the reaction $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O\ (l)$ occurs. Calculate the pressure if the final temperature is 27ºC. Aqueous tension at 27ºC is 26.7 mm.

90. What is the difference in the density of dry air at 1 atm and 25ºC and moist air with 50% relative humidity under the same condition? The vapour pressure of water at 25ºC is 23.7 Torr and dry air has 75.5% N_2 and 24.5% O_2.

91. A sample of butane gas C_4H_{10} of unknown mass is contained in a vessel of unknown volume V at 25ºC and a pressure of 760 mm-Hg. To this vessel, 8.6787 g of neon gas is added in such a way that no butane is lost from the vessel. The final pressure in the vessel is 1920 mm-Hg at the same temperature. Calculate the volume of the vessel and the mass of butane.

92. A mixture of CO and CO_2 is found to have a density of 1.50 g/ltr at 30ºC and 730 mm. Calculate the composition of mixture.

93. The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 minutes.

94. 1 mole of CCl_4 vapours at 77ºC occupies a volume of 35.0 L. If vander waal's constants are $a = 20.39$ L^2 atm mol^{-2} and $b = 0.1383$ L mol^{-1}, calculate compressibility factor Z under, (a) low pressure region and (b) high pressure region.

94. One mole of nitrogen gas at 0.8 atm takes 38 sec to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 sec to diffuse through the same hole. Determine the molecular formula of the compound.

95. Which of the following statements is correct?
(a) He diffuses at a rate of 8.65 times as much as CO does
(b) He escapes at a rate of 2.65 times as fast as CO does
(c) He escapes at a rate of 4 times as CO_2 does
(d) He escapes at a rate 4 times as fast as SO_2 does

96. The pressure of an ideal gas is increased isothermally at 298 K in a 5 L vessal from 1 bar to 2 bar. The correct option (s) is /are
(a) $\Delta G = 2.7$ kJ/mol (b) $\Delta G = 1.7$ kJ/mol
(c) $\Delta S_{gas} < 0$ (d) $\Delta S_{surroundings} = 0$

97. One mole triatomic vapours of an unknown substance effuses $\frac{4}{3}$ times faster than 1 mole O_2 under same conditions. If the density of unknown vapours at pressure P and temperature T is d, which of the following holds true for the unknown substance?
(a) $d_{N.T.P} = 0.8035$ g/l
(b) Z(atomic number) = 6
(c) Z(compress ibility factor) = $\frac{18P}{dRT}$
(d) Vapour density = 9

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. The number of moles per litre in the equation $PV = nRT$ is expressed by **[AIEEE-02]**

(a) $\frac{P}{RT}$ (b) $\frac{PV}{RT}$

(c) $\frac{RT}{PV}$ (d) None of these

2. The correct value of R is **[AIEEE-02]**

(a) $R = 0.082$ litre atm

(b) $R = 8.314 \times 10^7$ erg –K^{-1} mol^{-1}

(c) $R = 2K^{-1}$ mol^{-1}

(d) None of the above

3. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by factor of which of the following ? **[AIEEE-04]**

(a) 1/2 (b) $\sqrt{(313/293)}$

(c) 313/293 (d) 2

4. In Van der Waal's equation of state of the gas law, the constant b is a measure of **[AIEEE-04]**

(a) intermolecular repulsions

(b) intermolecular attraction

(c) volume occupied by the molecules

(d) intermolecular collisions per unit volume

5. The ratio between the R.M.S. velocity of H_2 at 50 K and that of O_2 at 800 K is **[JEE 1996]**

(a) 4 (b) 2

(c) 1 (d) 1/4

6. X mL H_2 gas effuses through a hole in a container in 5 sec. The time taken for the effusion of the same volume of the gas specified below under identical conditions is **[JEE 1996]**

(a) 10 sec, He (b) 20 sec, O_2

(c) 25 sec, CO (d) 55 sec, CO_2

7. One mole of N_2O_4 (g) at 300 K is kept in a closed container under 1 atm. It is heated to 600 K when 20% by mass of N_2O_4 (g) decomposes to NO_2 (g). The resultant pressure is **[JEE 1996]**

(a) 1.2 atm (b) 2.4 atm

(c) 2.0 atm (d) 1.0 atm

8. One way of writing the equation for state for real gases is, $P\overline{V} = RT\left[1+\frac{B}{\overline{V}}+.........\right]$ where B is constant. **[JEE 1997]**

Derive an approximate expression for 'B' in terms of Van der Waals constant 'a' and 'b'.

9. According to Graham's law, at a given temperature the ratio of the rates of diffusion $\frac{r_A}{r_B}$ of gases A and B is given by **[JEE 1997]**

(a) $\frac{P_A}{P_B}\left(\frac{M_A}{M_B}\right)^{1/2}$ (b) $\left(\frac{M_A}{M_B}\right)\left(\frac{P_A}{P_B}\right)^{1/2}$

(c) $\frac{P_A}{P_B}\left(\frac{M_B}{M_A}\right)^{1/2}$ (D) $\frac{M_A}{M_B}\left(\frac{P_B}{P_A}\right)^{1/2}$

10. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g /mL and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas.

11. Using Van der Waals equation, calculate the constant "a" when 2 moles of a gas confined in a 4 ltr flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of "b" is 0.05 ltr mol^{-1}. **[JEE 1998]**

12. One mole of N_2 gas at 0.8 atm takes 38 sec to diffuse through a pin hole, whereas one mole of an unknown compound of Xenon with F at 1.6 atm takes 57 sec to diffuse through the same hole. Calculate the molecular formula of the compound. **[JEE 1999]**

13. A gas will approach ideal behaviour at **[JEE 1999]**

(a) low temperature and low pressure

(b) low temperature and high pressure

(c) low pressure and high temperature

(d) high temperature and high pressure

14. The compressibility of a gas is less than unity at STP. Therefore **[JEE 2000]**

(a) $V_m > 22.4$ L (b) $V_m < 22.4$ L

(c) $V_m = 22.4$ L (d) $V_m = 44.8$ L

15. The R.M.S. velocity of hydrogen is $\sqrt{7}$ times the R.M.S. velocity of nitrogen. If T is the temperature of the gas, **[JEE 2000]**

(a) $T(H_2) = T(N_2)$ (B) $T(H_2) > T(N_2)$

(c) $T(H_2) < T(N_2)$ (D) $T(H_2) = \sqrt{7}\, T(N_2)$

16. Calculate the pressure exerted by one mole of CO_2 gas at 273 K, if the Van der Waals constant $a = 3.592$ dm^6 atm mol^{-2}. Assume that the volume occupied by CO_2 molecules is negligible. **[JEE 2000]**

17. The compression factor (compressibility factor) for one mole of a Van der Waals gas at 0°C and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the Van der waals constant 'a'. **[JEE 2001]**

18. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 Kg m^{-3}. The vapour effuse through a small hole at a rate of 1.33 times faster than oxygen under the same condition. **[JEE 2002]**

(a) Determine

(i) Molecular weight ; (ii) Molar volume ; (iii) compressibility factor (z) of the vapour

(iv) Which forces among the gas molecules are dominating the attractive or the repulsive?

(b) If the vapour behaves ideally at 1000 K, determine the average translational K.E. of a molecule.

19. The average velocity of gas molecules is 400 m/sec. Calculate its (R.M.S) velocity at the same temperature. **[JEE 2003]**

20. Positive deviation from ideal behaviour takes place because of **[JEE 2003]**

(a) molecular interaction between atoms and $\frac{PV}{nRT} > 1$

(b) molecular interaction between atoms and $\frac{PV}{nRT} < 1$

(c) finite size of atoms and $\frac{PV}{nRT} > 1$

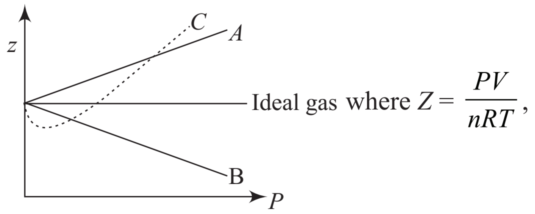
(d) finite size of atoms and $\frac{PV}{nRT} < 1$

21. For a real gas obeying Van der Waal's equation a graph is plotted between PV_m (y-axis) and P(x-axis) where V_m is molar volume. Find y-intercept of the graph. **[JEE 2005]**

22. The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be **[JEE 2005]**

(a) 4 (b) 2 (c) 1 (d) 0.5

23.



a = Van der Waal's constant for pressure correction
b = Van der Waal's constant for volume correction
Pick the incorrect statement only. **[JEE 2006]**

(a) For gas A, if $a = 0$, the compressibility factor is directly proportional to pressure.

(b) For gas B, if $b = 0$, the compressibility factor is directly proportional to pressure.

(c) For gas C, $a \neq 0$, $b \neq 0$, it can be used to calculate a and b by giving lowest P value and its intercept with $Z = 1$.

(d) Slope for all three gases at high pressure (not shown in graph) is positive.

Answer Key

LEVEL I

1. (b)	2. (c)	3. (b)	4. (d)	5. (b)	6. (b)	7. (a)	8. (a)	9. (b)	10. (b)
11. (d)	12. (a)	13. (c)	14. (b)	15. (c)	16. (c)	17. (b)	18. (a)	19. (a)	20. (b)
21. (a)	22. (a)	23. (a)	24. (c)	25. (c)	26. (a)	27. (b)	28. (a)	29. (a)	30. (b)
31. (c)	32. (b)	33. (d)	34. (a)	35. (d)	36. (a)	37. (a)	38. (a)	39. (c)	40. (b)
41. (a)	42. (d)	43. (c)	44. (a)	45. (b)	46. (b)	47. (b)	48. (c)	49. (a)	50. (a)
51. (a)	52. (c)	53. (a)	54. (a)	55. (a)	56. (b)	57. (c)	58. (b)	59. (c)	60. (b)
61. (d)	62. (a)	63. (b)	64. (d)	65. (b)	66. (a)	67. (b)	68. (b)	69. (b)	70. (a)
71. (b)	72. (a)	73. (a)	74. (b)	75. (a)	76. (b)	77. (a)	78. (a)	79. (d)	80. (b)
81. (b)	82. (b)	83. (c)	84. (b)	85. (a)	86. (a)	87. (a)	88. (c)	89. (c)	90. (c)
91. (a)	92. (d)	93. (c)	94. (a)	95. (b)	96. (c)	97. (b)	98. (a)	99. (a)	100. (c)

LEVEL II

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

LEVEL III

1. (A) → r; (B) → s; (C) → q; (D) → p 2. (A) → s; (B) → r; (C) → p, q; (D) → p, q
3. (A) → q; (B) → s; (C) → p, s; (D) → p, q, r 4. (A) → r; (B) → p; (C) → s; (D) → q
5. (a) 6. (b) 7. (c) 8. (d) 9. (d) 10. (d) 11. (6) 12. (7 ml) 13. (2) 14. (4)
15. (2) 16. (2 atm) 17. (2 atm) 18. (4) 19. (5 Å) 20. (9) 21. (3) 22. (5 atm) 23. (1.236) 24. (0.138)
25. ($X_{C_2H_6} = 0.66$) 26. ($X_{H_2} = 0.78$) 27. (4.46 g/L) 28. (100 K and 0.82 L)
29. (i) [$M = 18.1$], (ii) [50.27×10^{-3} m^3], (iii) [1.225], (iv) [$Z > 1$ repulsive] 30. ($M = 1033$ g Mol^{-1})

31. (2.68×10^{10}) 32. (99.9%) 33. (494.2 m/sec. and 405.26 m/sec.) 34. (a) 1/3 (b) (1.53 lit.)
35. (a) [0.803 gram], (b) [0.71 gram], (c) [1.02 atm] 36. [3.44 : 1] 37. [0.062 atm, 75 K]
38. [r = 9.0856 cm] 39. [P = 38 atm] 40. [11.999 L] 41. [66.74 atm] 42. [19.66×10^5 N/m^2]
43. [P = 2.1979atm] 44. [x = 228] 45. [50.8 cm] 46. [16 min] 47. [46.6]
48. (a) [3.25 torr/sec.] (b) [0.3387 torr/sec.] 49. [Conceptual] 50. [25.027 kPa] 51. [Blow Up]
52. [M = 175.133 kg mole^{-1}] 53. (i) [32.1428 gm/mole], (ii) [460.28 m/s] 54. [236.29°C]
55. (a) [493.03 m/s] (b) [454.259356] (c) [403 m/s] 56. [Conceptual]
57. [2886 K, 3399 K,4330 K for rms, average, most probable]
58. [3.77 L] 59. [15.40 kgm] 60. (Conceptual) 61. [Derivation] 62. T = 350.5°C
63. (i) [31.1 atm] (ii) [31.4 atm] 64. [Conceptual] 65. [4500 R] 66. [0.104 cm^3/m]
67. [280 mL/min.] 68. [0.509] 69. [807.84 J] 70. [134 pm]
71. [α = 3.77 bar L^{2}mol^{-2}] 72. [8.4 atm] 73. [10.3 atmosphere]
74. [314 pm, 7.05 cm, 6739.4 sec^{-1}, 1.09×10^{17} cm^{-3} sec^{-1}] 75. [530.3 Pa, 1.281×10^{23} m^{-3}]
76. ($Z_1(x) = Z_1(CH_4)$ 77. [5333.3 mole O_2 and 28.78 mole CH_4] 78. (a) [0.625] (b) [n = 4] 79. [n = 13]
80. [421.9 K] 81. (i) [V = 5.263 L], (ii) [ρ = 0.7 g/L], (iii) [0.2349 Mole]

82. (i) $\left[n = \frac{-T}{100} + 5\right]$ (ii) $\left[V = -\frac{RT^2}{100} + 5RT\right]$, (iii) [51.3125 L]

83. $$\left[P_C = \frac{A^3}{108B^2}, V_C = \frac{6B}{A}, T_C = \frac{A^2}{6RB} \text{ and } Z = \frac{1}{3}\right]$$

84. (i) [2067.2 g] (ii) This mass would rest on twice the area and exert the same pressure.]
85. [65116.8 cm] 86. [P_{NO} (left) = 0.221 atm] 87. [P_{N2} = 1.5 atm, P_{H2} = 4.5 atm]
88. [146.5 mm-Hg] 89. [3.0513 atm] 90. [0.007 kg m^{-3}] 91. [6.85 L and 6.24 g]
92. [mole % of CO_2 ,CO = 67.81%, 32.19%] 93. [1.236 : 1] 94. (a) [0.98], (b) [1.004]
95. (b,d) 96. (a, c, d) 97. (a, c, d)

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (a) 2. (b) 3. (c) 4. (c) 5. (c) 6. (b) 7. (b) 8. $B = b - \frac{a}{RT}$ 9. (c)
10. [123] 11. (6.46 atm ltr^2 mol^{-2}]) 12. [XeF$_6$] 13. (c) 14. (b) 15. (c) 16. [0.9922 atm]
17. [1.253 atm L^2 mol^{-2}]
18. (a) (i) [18.09] (ii) [41.05 L] (iii) [1.224] (iv) [repulsive force] (b) [2.07×10^{-20} J molecule^{-1}]
19. [434 m/s] 20. (a) 21. [intercept = RT] 22. (b) 23. (b)

Hints and Solutions

LEVEL I

1. (b) P_A = 2 bar $P_{\text{Total}} = P_A + P_B$ $PV = nRT$
P_{Total} = 3 bar P_B = 3 – 2 = 1 bar PV = W/M RT

$$\frac{P_AM_A}{W_A} = \frac{P_BM_B}{W_B} \text{ or } \frac{2 \times M_A}{1} = \frac{1 \times M_B}{2} \text{ or } \frac{M_A}{M_B} = \frac{1}{4}$$

or $M_B = 4M_A$

2. (c) $P = \left(\frac{w}{v}\right)\frac{RT}{M}$

$$\frac{P_1M_1}{d_1T_1} = \frac{P_2M_2}{d_2T_2} \ (\because M_1 = M_2)$$

$$\frac{2}{5.46 \times 300} = \frac{1}{d_2 \times 273}$$

$$d_2 = \frac{5.46 \times 300}{2 \times 273} = 3 \text{ gm/dm}^3$$

3. (b) $\because PV = nRT$

$$T = \frac{PV}{nR} = \frac{3.32 \times 5}{4 \times 0.083} = 50 \text{ K}$$

4. (d) $PV = nRT$

$$V = \frac{nRT}{P} = \frac{wRT}{MP} = \frac{8.8 \times 0.083 \times 304.1}{44 \times 1} = 5.05 \text{ ltr}$$

5. **(b)** From $PV = \frac{w}{M}RT = \frac{800}{760}\times\frac{380}{1000} = \frac{0.455}{M} \times 0.0821 \times 300$

$$= \frac{800}{760}\times\frac{380}{1000} = \frac{0.455}{M}\times 0.0821\times 300$$

6. **(b)** $\frac{r_{SO_2}}{r_{N_2}} = \sqrt{\frac{M_{N_2}}{M_{SO_2}}\times\frac{T_{SO_2}}{T_{N_2}}}$ or $\frac{x}{1.625x} = \sqrt{\frac{28}{64}\times\frac{773}{T_{N_2}}}$

or $\quad T_{N_2} = \sqrt{\frac{28}{64}}\times 773\times 1.625$

$$= \sqrt{7}\times\frac{773\times 1.625}{4} = 830\text{ K}$$

7. **(a)** $\frac{r_{O_2}}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} = \sqrt{\frac{2}{32}} = \frac{1}{4}$

8. **(a)** $\frac{n_{\text{methane}}}{n_{O_2}} = \frac{w_{CH_4}}{w_{O_2}}\times\frac{M_{O_2}}{M_{CH_4}} = \frac{32}{16} = 2$

$$x_{CH_4} = \frac{2}{3} x_{O_2} = \frac{1}{3}$$

$\therefore \quad P_{O_2} = x_{O_2}\times P_{\text{total}} = \frac{1}{3}P_{\text{total}}$

9. **(b)** For H_2

$P_1V_1 = P_2V_2$

$0.8\times 0.5 = P_3\times 1$

$\therefore \quad P_3 = 0.40$ bar

For O_2

$P_1V_1 = P_4\times 1$

$0.7\times 2 = P_4\times 1$

$P_4 = 1.4$ bar

$\therefore \quad P_T = P_3 + P_4 = (0.4 + 1.4)$ bar $= 1.8$ bar

10. **(b)** $P_TV = nRT$

$$P_T = \frac{n_TRT}{V} \qquad n_T = n_{O_2} + n_{H_2} = \frac{8}{32} + \frac{4}{2} = 2.25$$

$$= \frac{2.5\times 0.083\times 300}{1} = 56.025\text{ bar}$$

11. **(d)** For gas $V_{\text{gas}} = \frac{nRT}{P}$ (i)

For H_2 $V_{H_2} = \frac{n_{H_2}RT_{H_2}}{P_{H_2}}$ (ii)

From Eqs. (i) and (ii)

$\frac{2.9\times 368}{M_{\text{gas}}} = \frac{0.184\times 290}{2}$ (since volume and pressure of both gases are same)

$M_{\text{gas}} = 40\text{ g mol}^{-1}$

12. **(a)** $U_{\text{av}}\propto\sqrt{T}$ or $\frac{U_1}{U_2} = \sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{300}{1200}} = \frac{1}{2}$

$U_2 = 2\times U_1 = 2\times 0.3 = 0.6$ m/sec

13. **(c)** Since K.E. $= \frac{1}{2}Mu_{\text{rms}}^2 \therefore u_{\text{rms}} = \sqrt{\frac{2E}{M}}$

14. **(b)** $Z < 1$ then $V_m < 22.4$

Since, PV = ZRT or $V = \frac{ZRT}{P}$

15. **(c)** Pcorection $= \frac{an^2}{V^2}$ $\quad P_{\text{ideal}} = \left(P + \frac{an^2}{V^2}\right)$

for 1 mole $P_{\text{ideal}} = \left(P + \frac{a}{V^2}\right)$

responsible for intermolecular force.

16. **(c)** At constant P and V, $n_1T_1 = n_2T_2$

$4\times T_1 = 3.2\times(T_1 + 50)$

On solving,

$T_1 = 200$ K

17. **(b)** The ratio of V_{rms} of gas at two different temperatures is given by

$$\frac{(V_{\text{rms}})_2}{(V_{\text{rms}})_1} = \sqrt{\frac{T_2}{T_1}};\ (V_{\text{rms}})_2$$

$$= \sqrt{\frac{560}{140}}\times V = 2V \because (V_{\text{rms}})_1 = V$$

18. **(a)** Let the volume of O_2 is the mixture be x mL

	H_2	+	$1/2O_2$	$\longrightarrow$	H_2O (l)
Initial volume	$(40 - x)$		x		
Final volume	$(40 - 3x)$		0		

Final volume of H_2 = 10 mL (Given)

$\therefore \quad 40 - 3x = 10;\ x = 10$ mL

$\therefore$ initial volume of H_2 = 30 mL ; Initial mole % of $H_2 = \frac{30}{40}\times 100 = 75\%$

19. **(a)** Ammonia decomposes into N_2 and H_2 completely when a spark is passed through it.

	$NH_3(g) \longrightarrow$	$\frac{1}{2}N_2g\ +$	$\frac{3}{2}H_2g$
Initial	1	0	0
Final	0	$\frac{1}{2}$	$\frac{3}{2}$

The total pressure of N_2 and H_2 after complete decomposition is given by

$P_T = P_{N_2} + P_{H_2} = 0.5 + 1.5 = 2$ atm

20. **(b)** Given: $P = (800/760)$ atm

$T = 100 + 273 = 373$ K; $m_{CO_2} = 44$

$PV = (w/m)$ RT

$w/V = d = (Pm/RT)$

$$d = \frac{800\times 44}{760\times 0.0821\times 373} = 1.5124\text{ g litre}^{-1}$$

21. **(a)** $V_{t^\circ} = V_0 + \frac{V_0}{273.15}t$

For every 1°C increase in temperature, the volume of a given mass of an ideal gas increases by a definite fraction $\frac{1}{273.15}$ of V_0.

22. **(a)** $P_1V_1 = P_2V_2$ or $1 \times 20 = P_2 \times 50$

or $P_2 = 20 \times \frac{1}{50}$ atm

23. **(a)** $PV = nRT = \frac{w}{M_w}RT$

or $V = \frac{wRT}{PM_w} = \frac{1 \times 0.0821 \times 350}{1 \times 58} = 0.495 \text{ L} = 495 \text{ mL}$

24. **(c)** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ or $\frac{740 \times 100}{300} = \frac{740 \times 80}{T_2}$

or $T_2 = 240 \text{ K} = -33°\text{C}$

25. **(c)** $d = \frac{w}{V} = \frac{P \cdot M}{RT} = \frac{1 \times 30}{.0821 \times 273} = 1.34 \text{ gm/L}$

26. **(a)** Rate of effusion $\propto \frac{1}{\sqrt{d}} \propto P$

$\therefore$ rate of effusion $\propto \frac{P}{\sqrt{d}}$

27. **(b)** $\frac{r_{O_2}}{r_{H_2}} = \frac{V_{O_2}}{V_{H_2}}$

$$\frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{Mw_{H_2}}{Mw_{O_2}}}$$

or $\frac{4/32}{w/2} = \sqrt{\frac{2}{32}}$ or $\frac{1}{4w} = \frac{1}{4}$ or $w = 1$ g

28. **(a)** $\frac{r_{SO_2}}{r_{O_2}} = \sqrt{\frac{M_w \text{ of } O_2}{M_w \text{ of } SO_2}} = \sqrt{\frac{32}{64}} = \sqrt{\frac{1}{2}} = \frac{1}{\sqrt{2}}$

29. **(a)** Let weight of CO = Weight of N_2 = w g,

$\therefore$ $n_{CO} = \frac{w}{28}$ and $n_{N_2} = \frac{w}{28}$, Hence $P_{N_2} = P_{CO}$]

30. **(b)** $V_{rms} = \sqrt{\frac{3RT}{M}}$

31. **(c)** $V_{avg} = \sqrt{\frac{8RT}{\pi M}}$

32. **(b)** Given: $T_1 = 300$ K, $T_2 = 273$ K (STP)

$V_1 = 300 \text{ mL} = \left(\frac{300}{1000}\right)$ ltr,

$P_2 = 1$ atm, $P_1 = \left(\frac{730}{760}\right)$ atm, $V_2 = ?$

$\because$ $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \cdot \frac{730 \times 300}{760 \times 1000 \times 300} = \frac{1 \times V_2}{273}$

$\because$ $V_2 = 0.2622$ ltr = 262.2 mL

33. **(d)** $P_1 = 3$ atm, $P_2 = ?$,

$T_1 = -23 + 273 = 250$ K,

$T_2 = 273 + 30 = 303$ K

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{3}{250} = \frac{P_2}{303} \Rightarrow P_2 = \frac{3 \times 303}{250} = 3.64 \text{ atm.}$$

34. **(a)** Given: $P = \left(\frac{400}{760}\right)$ atm, $T = 100 + 273 = 373$ K

$$d = \frac{PM_w}{RT} \Rightarrow d = \frac{400 \times 44}{760 \times 0.0821 \times 373} = 0.75 \text{ g L}^{-1}$$

35. **(d)** $d = \frac{PM_w}{RT} \Rightarrow 1.40 = \frac{\frac{780}{760} \times M_w}{0.0821 \times 250}$

$\Rightarrow$ $M_w = 28$ $\therefore$ gas is N_2

36. **(a)** Given: $P = 16$ atm, $V = 9$ ltr, $T = 300$ K, $M_{w_{CH_4}} = 16$, $R = 0.08$ atm K^{-1}

$$PV = \frac{w}{M_w} \times R \times T$$

$$16 \times 9 = \frac{w}{16} \times 0.08 \times 300, \quad w = 96 \text{ g}$$

37. **(a)** Molecular weight of SO_2 = 64
Volume occupied by 1 mole SO_2 gas = 22.4 ltr

Density of $SO_2 = \frac{64}{22.4} = 2.86 \text{ g L}^{-1}$

38. **(a)** Given : $W_{N_2} = 7$ g,

$P = \left(\frac{750}{760}\right)$ atm. $M_{w_{N_2}} = 28$,

$T = 300$ K

$\because$ $PV = \left(\frac{w}{M_w}\right)RT \Rightarrow$

$\therefore$ $\frac{750}{760} \times V = \frac{7}{28} \times 0.0821 \times 300$

$\Rightarrow$ $V = 6.29 \approx 6.3$ ltr

39. **(c)** $PV = \frac{\text{weight}}{M_w}RT$ or $P \times 6 = \frac{5}{207.3} \times 0.0821 \times (273 + 80)$

or $P = \frac{5 \times 0.0821 \times 353}{6 \times 207.3} = 0.11 \text{ atm}$

40. **(b)** Using gas equation

$$M_w = \frac{wRT}{PV} = \frac{5.75 \times 0.0821 \times (273 + 55)}{0.940 \times 3.5} = 47.0$$

41. **(a)** Given: $w_{N_2} = 28$ g, $P = 2.46$ atm, $M_{w_{N_2}} = 28$, $V = 10$ ltr

$\because$ $PV = \left(\frac{w}{M_w}\right)RT$

or $2.46 \times 10 = \left(\frac{28}{28}\right) \times 0.0821 \times T$

or $T = 300$ K

42. **(d)** According to Boyle's law

$P_1V_1 = P_2V_2$ or $1.5 \times 75 = 50 \times V_2$

or $V_2 = \frac{1.5 \times 75}{50} = 2.25$ ltr

43. **(c)** $P'_{N_2} = 760 \times \dfrac{65}{100} = 494$ mm,

$P'_{O_2} = 760 \times \dfrac{15}{100} = 114$ mm,

$P'_{CO_2} = 760 \times \dfrac{20}{100} = 152$ mm,

44. **(a)** Moles of first gas $= n_1 = \dfrac{w_1}{m_1} = \dfrac{0.45}{60} = 0.0075$

Moles of second gas $= n_2 = \dfrac{w_2}{m_2} = \dfrac{0.22}{44} = 0.0050$

So the total moles $= n_1 + n_2 = 0.0075 + 0.0050 = 0.0125$

So partial pressure of second gas $P_2 = \dfrac{0.0050}{0.0125} \times 75$

$= 30$ cm of Hg

45. **(b)** $d_A = 1.5\, d_B$

$$d = \frac{PM_w}{RT}$$

$$\frac{d_A}{d_B} = \frac{M_{w_A}}{M_{w_B}} = 1.5 = \frac{M}{M_{w_B}}$$

or $M_{w_B} = \dfrac{M}{1.5}$

46. **(b)** $\dfrac{V_2}{V_1} = \dfrac{T_2}{T_1}$

or $\dfrac{4}{2} = \dfrac{T_2}{273}$

or $T_2 = 2 \times 273$ K

or $T_2 = 273°\text{C}$

47. **(b)** $PV = \dfrac{\text{wt.}}{M_w} RT$

$$1 \times 8.2 = \frac{9}{M_w} \times 0.0821 \times 300$$

or $M_w = 27$

48. **(c)** N.T.P. means

$T = 0°\text{C} = 273$ K

$P = 1$ atm.

$$PV = \frac{\text{wt.}}{M_w} RT$$

or $M_w = \text{wt.} \times \dfrac{RT}{PV} = \dfrac{1.25 \times 0.0821 \times 273}{1 \times 1}$

$M_w = 28$ gm mol^{-1}

So gas is N_2

49. **(a)** $P_1 = P$

$P_2 = P + 0.004\,P = (1.004)P$

$T_1 = T$ K

$T_2 = (T + 1)$K

$$\frac{T_2}{T_1} = \frac{P_2}{P_1}$$

or $\dfrac{T+1}{T} = \dfrac{1.004P}{P} = 1.004\,4$

or $T = 250$ K

50. **(a)** $\dfrac{r_{H_2}}{r_{O_2}} = \sqrt{\dfrac{M_{w_{O_2}}}{M_{w_{H_2}}}} = \dfrac{n_{H_2}}{n_{O_2}} = \dfrac{w_{H_2}/2}{w_{O_2}/32}$

or $\sqrt{\dfrac{32}{2}} = 4 = \dfrac{w_{H_2}}{w_{O_2}} \times \dfrac{32}{2}$

or $\dfrac{w_{H_2}}{w_{O_2}} = \dfrac{4}{16} = 1:4$

51. **(a)** at low pressure

$$\left(P + \frac{a}{V^2}\right)V = RT$$

$$PV + \frac{a}{V} = RT$$

$$Z + \frac{a}{VRT} = 1$$

$$\therefore \quad Z = 1 - \frac{a}{VRT}$$

52. **(c)**

$$\begin{array}{lcccc} N_2 & + & 3H_2 & \longrightarrow & 2NH_3 \\ 1 & & 3 & & \\ 0 & & 0 & & 2 \end{array}$$

$$\frac{V_{\text{initial}}}{V_{\text{final}}} = \frac{4}{2} \Rightarrow \frac{2}{1}$$

53. SO_2 replaced by O_2

$P, V, T \Rightarrow$ same

$n \Rightarrow$ constant $\quad n_{O2} = n_{SO2}$

$\dfrac{w_{O_2}}{32} = \dfrac{w_{SO_2}}{64} \quad w_{O_2} = \dfrac{1}{2} w_{SO_2}$

54. At constant pressure $V \propto T$

55. **(a)** $V \propto T \quad \therefore \quad \dfrac{V_2}{V_1} = \dfrac{T_2}{T_1}$

$$T_2 = \frac{3}{3.75} \times 3.8 \times 3.8 \Rightarrow 246.4 \text{ K} \; T_2 = -26.6°\text{C}$$

56. **(b)** $P_{n2} \propto n_{H2} \quad P_{\text{total}} \propto (n_{H2} + n_{CH4})$

$$\frac{P_{H_2}}{P_{\text{total}}} = \frac{w/2}{w/2 + w/16} \Rightarrow \frac{8}{9}$$

57. $PV = nRT \quad n = \dfrac{10^{-10}}{760} \times \dfrac{10^{-3}}{0.082 \times 293}$

Number of molecules

$$= \frac{10^{-10} \times 10^{-3}}{760 \times 0.082 \times 293} \times 6.023 \times 10^{23} = 3.29 \times 10^{6}$$

58. **(b)** $PV = \dfrac{w}{M_w} RT$

$$M_w = \frac{wRT}{PV} \Rightarrow \frac{2.8 \times 0.082 \times 400}{1 \times 1}$$

$M_w = 91.84 = 92 \qquad C_7H_8$

59. $V_A = 0.5\ \text{dm}^3,\quad V_B = 1\ \text{dm}^3$

$d_A = 3\ \text{g/dm}^3,\quad d_B = 1.5\ \text{g/dm}^3$

$$M_A = \frac{1}{2}M_B \qquad P_A = \frac{d_A RT}{M_A},\ P_B = \frac{d_B RT}{M_B}$$

$$\frac{P_A}{P_B} = \frac{d_A}{d_B} \times \frac{M_B}{M_A} \Rightarrow \frac{3}{1.5} \times 2 = 4$$

60. **(b)** $P = \frac{3 \times 0.082 \times 400}{20}\quad \therefore\ P = 4.92\ \text{atm}$

61. **(d)** $PV = \frac{w}{M_w}RT \qquad \frac{P}{wT} = \text{constant}$

$$\frac{P_1}{w_1T_1} = \frac{P_2}{w_2T_2} \qquad \frac{4.05}{w \times 300} = \frac{P_2}{\frac{w}{2} \times 285}$$

$P_2 = 1.92$ MPa

62 **(a)** $PV = \frac{w}{M_w}RT$

$$M_w = \frac{wRT}{PV} \Rightarrow \frac{1 \times 0.082 \times 273}{2 \times 0.350} = 32$$

The mass of one atom

= 16 amu ⇒ 2.64×10^{-23} g

63. **(b)** $PV = nRT$

$$n = \frac{PV}{RT} \Rightarrow \frac{7.6 \times 10^{-10}}{760} \times \frac{1}{0.082 \times 273}$$

$n \Rightarrow 0.0446 \times 10^{-12}$

The no. of oxygen molecule $= 0.0446 \times 10^{-12} \times N_A$

$= 2.7 \times 10^{10}$

64. **(d)** $U_{\text{rms}} = \sqrt{\frac{3RT}{M_w}} \Rightarrow \sqrt{\frac{3 \times 8.314 \times 300}{2 \times 10^{-3}}}$

$U_{\text{rms}} = 1934$ m/sec.

65. **(b)** $(V_{\text{rms}})_{O_2} = (V_{\text{rms}})_{\text{Ne}}$

$$\left(\frac{\sqrt{3RT}}{M}\right)_{O_2} = \left(\frac{\sqrt{3RT}}{M}\right)_{\text{Ne}}$$

$$\frac{T}{32} = \frac{300}{20}\quad \therefore\ T = 480\ \text{K}$$

66. $U_{\text{mp}} = \sqrt{\frac{2RT}{M}}$

$$= \sqrt{\frac{2 \times 8.314 \times 293}{1.67 \times 10^{-27} \times 6.023 \times 10^{23}}} = 220\ \text{m/sec.}$$

67. **(b)** $U_{\text{rms}} = \sqrt{\frac{3\text{PV}}{\text{M}}} = \sqrt{\frac{3\text{P}}{\text{d}}}$

$$= \sqrt{\frac{3 \times 1.2 \times 10^5}{4}} = 300\ \text{m/sec.}$$

68. **(b)** $U_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 300}{10^{-15} \times 6.023 \times 10^{23}}}$

$$U_{\text{rms}} = \frac{3.52}{10^3}\text{m/sec.} \Rightarrow \frac{3.52}{10}\text{cm/sec.}$$

⇒ 0.352 cm/sec.

69. **(b)** $U_{\text{Avg.}} = \sqrt{\frac{8RT}{\pi M}}\ \frac{U_{\text{Avg.}}}{0.3} = \sqrt{\frac{1200}{300}}$

$U_{\text{Avg.}} = 0.6$ m/sec.

70. $U_{\text{rms}} = \sqrt{\frac{3RT}{M}}\quad T \propto M$

$$\left(\frac{T}{M}\right)_{CO_2} = \left(\frac{T}{M}\right)_{O_2}$$

$$\frac{T}{44} = \frac{273}{32}\quad \therefore\ T = 375.37\ \text{K}$$

71. $U_{\text{mp}} = \sqrt{\frac{2RT}{M}}$

$$\frac{u_1}{u_2} = \sqrt{\frac{T_1}{T_2}}$$

$$\frac{1}{(2)^2} = \frac{273 + 50}{T_2}$$

$T_2 = 4 \times 323 = 1292$ K

72. **(a)** $E_T = \frac{3}{2}RT,\ E_R = RT$

$$E_{\text{total}} = \frac{3}{2}RT + RT = \frac{5}{2}RT = \frac{5}{2} \times 300 \times 8.314$$

$= 6235.5$ J

73. **(a)** K.E. $= \frac{3}{2}nRT \qquad x = \frac{3}{2} \times \frac{N}{N_A} \times 150 \times R$

$$2x = \frac{3}{2} \times \frac{N'}{N_A} \times 300 \times R \quad \therefore \quad N' = N$$

74. **(b)** K.E. $= \frac{3}{2}nRT$

$$\frac{\text{K.E}}{\text{Molecule}} = \frac{3}{2} \times \frac{8}{16} \times \frac{300 \times 8.314}{N_A}$$

$= 6.21 \times 10^{-21}$ J/molecule

75. $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{64}{44}} = \frac{4}{\sqrt{11}}$

76. **(b)** $\frac{V_1}{V_2} \times \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$

$$\frac{20}{\text{V}_1} \times \frac{30}{60} = \sqrt{\frac{32}{64}}$$

$V_2 = 14.14$ ltr

77. **(a)** $r \propto \frac{1}{\sqrt{M}}$

$$r_{N_2} : r_{H_2} : r_{\text{He}} :: \frac{1}{\sqrt{28}} : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{4}} :: \frac{1}{\sqrt{14}} : \frac{1}{\sqrt{1}} : \frac{1}{\sqrt{2}}$$

$$r_{N_2} : r_{H_2} : r_{\text{He}} :: 1 : \sqrt{14} : \sqrt{7}$$

78. Rate of diffusion $\propto \dfrac{1}{\sqrt{\text{molecular mass}}}$

79. (d)

$$C_xH_y + (x + y/4)O_2 \longrightarrow xCO_2 + y/2\ H_2O$$

$1.0 \qquad 10x \qquad 5y$

$10x = 40 \qquad 5y = 50$

$x = 4 \qquad y = 10$

C_4H_{10}

80. $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

81. (b) $C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$

58 gm $\frac{13}{2} \times 32$

58 g CH_4 required volume of O_2 at

NTP = $\frac{13}{2} \times 22.4$ lit

1000 g CH_4 required volume of O_2 at NTP

$= \frac{13}{2} \times \frac{22.4}{58} \times 1000 = 2510$ ltr

82. Extent of intermolecular hydrogen bonding increasing the viscosity.

83. (a) $P_{\text{total}} = \frac{3W}{32}\frac{RT}{V} \quad P_{CH_4} = \frac{W}{16}\frac{RT}{V} \cdot \frac{P_{CH_4}}{P_{\text{total}}} \Rightarrow \frac{2}{3}$

84. K.E. $\propto T$

85. (b) $Z = \frac{PV_m}{PV} \cdot \frac{V_m}{22.4} > 1 \quad V_m > 22.4$ L

86. (a) $PV = nRT \; P = \frac{2 \times 0.82 \times 546}{44.8} P = 2$ atm

87. $U_{\text{rms}} = \sqrt{\frac{3RT}{M_w}}$

88. (c) $P = \frac{dRT}{M_w}$

$dT = \text{const } d_1T_1 = d_2T_2$

$d \times 300 = 0.75\, d \times T_2$

$T_2 = 100 \times 4 \Rightarrow 400$ K

89. (c) $U_{\text{rms}} = \sqrt{\frac{3RT}{M_w}} \cdot \frac{(U_{\text{rms}})_{O_3}}{(U_{\text{rms}})_{O_2}} = \sqrt{\frac{32}{48}} \Rightarrow \sqrt{\frac{2}{3}}$

90. Lowest pressure and highest temperature.

91. $2H_2S\,(g) + SO_2\,(g) \longrightarrow 2H_2O\,(l) + 3S\,(s)$

$2.8 \qquad 1.6$

H_2S is limiting reagent

SO_2 remaining = 1.6 – 1.4 ⇒ 0.2 ltr

92. Rates of diffusion $\propto \dfrac{1}{\sqrt{\text{Molar Mass}}}$

93. (c) $PV = nRT \; P'V = \frac{n}{2}RT \quad P' = \frac{P}{2}$

94. (a) $r \propto \frac{1}{\sqrt{M}} \quad r_{CH_4} = 2r_x$

$$\frac{r_{CH_4}}{r_x} = \sqrt{\frac{M_x}{M_{CH_4}}} \cdot 4 = \frac{M_x}{16}$$

$M_x \Rightarrow 64$

95. (b) $\frac{(U_{\text{rms}})_{SO_2}}{(U_{\text{rms}})_{He}} = \sqrt{\frac{M_{He}}{M_{SO_2}}} = \sqrt{\frac{4}{64}} = \frac{1}{4} = 0.25$

96. (c) $r \propto \frac{1}{\sqrt{M}} \quad \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$

$$\frac{60}{45} = \sqrt{\frac{X}{40}} \Rightarrow \sqrt{\frac{X}{40}} = \frac{4}{3} \Rightarrow \frac{X}{40} = \frac{16}{9}$$

$x = 71.11$

97. (b) $P = \frac{dRT}{M_w} \quad M_w = \frac{7.71 \times 0.082 \times 309}{2.88}$

$M_w = 67.83$ Molecular formula = ClO_2

98. $P \propto \frac{1}{V}$

if n and T constant.

99. (a) K.E. = $\frac{3}{2}nRT \qquad nT = \text{constant}$

$0.3 \times T = 0.4 \times 400 \quad T = 533.33$ K

100. (c) $V = \frac{4}{3}\pi r^3$

$V_m = \frac{4}{3} \times \pi \times (10^{-10})^3 \times 6.023 \times 10^{23}$

$V_m = 2.52 \times 10^{-6}\ m^3$

V_m 2.52 mL

LEVEL II

1. (a) $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2 \uparrow$

According to the reaction

2×27 g of Al releasing = 3 moles of H_2

0.15 g of Al releasing = $\frac{3 \times 0.15}{2 \times 27}$ moles of H_2

From $PV = nRT$

$$V = \frac{nRT}{P} = \frac{3 \times 0.15 \times 0.082 \times 293}{2 \times 27}$$

$V = 200.4$ mL

2. (a) Let the weight of mixture = 100 g

$$P_{H_2} = P_{\text{total}} \cdot X_{H_2} = P_{\text{total}} \times \frac{n_{H_2}}{n_{H_2} + n_{O_2}}$$

$$= 1 \times \frac{20/2}{\frac{20}{2} + \frac{80}{32}} \text{ bar} = 0.8 \text{ bar}$$

3. **(d)** $\because$ time taken to be distributed the 10^{10} Wheat grains = 1 sec

$\therefore$ time taken to distributed the 6.023×10^{23}

$$= \frac{1 \times 6.022 \times 10^{23}}{10^{10}}$$

$$= 6.022 \times 10^{13} \text{ sec.}$$

$$= \frac{6.022 \times 10^{13}}{60 \times 60 \times 24 \times 365} \text{years}$$

$$= 1.90956 \times 10^{6} \text{ year}$$

4. **(d)** $\because PV = nRT \quad \therefore \quad n_T = n \text{ Methane} + n\text{CO}_2$

$$\therefore \quad P = \frac{n_T RT}{v} = \frac{3.2}{16} + \frac{4.4}{44} = 0.3$$

$$= \frac{0.3 \times 8.314 \times 300}{9 \times 10^{-3}} = 8.2 \times 10^{4} \text{Pa}$$

5. **(a)** $\because PV = nRT$

$$\text{or} \quad P = \frac{n}{V}RT = \frac{W}{M \times V}RT \quad [M = \text{Molar mass of } P]$$

$$\therefore \quad M = \frac{WRT}{PV} = \frac{0.0625 \times 0.082 \times 819}{0.1 \times 34.05 \times 10^{-3}}$$

$M = 1247.7$ g

6. **(c)** Let initially x moles are present at 27°C.

$P_1V_1 = n_1RT_1$ (Initially) (i)

$P_2V_2 = n_2RT_2$ (Finally) (ii)

from Eqs. (i) and (ii)

$$\frac{T_1}{T_2} = \frac{n_2}{n_1} \qquad [\because V_1 = V_2, P_1 = P_2]$$

$$\frac{300}{750} = \frac{n_2}{x}$$

$$\therefore \quad n_2 = \frac{2}{5}x$$

$\therefore$ fraction of air which have been expelled out

$$= \left(x - \frac{2}{5}x\right)/x = \frac{3}{5}$$

7. **(c)** Number of moles of O_2 in 10 L blood

$$= \frac{0.02 \times 10}{0.1 \times 32} = \frac{1}{16}$$

Number of moles of CO_2 in 10 L blood $= \dfrac{0.08 \times 10}{0.1 \times 44} = \dfrac{2}{11}$

Volume of O_2 at 1 atm and 37°C $= \dfrac{0.0821 \times 310}{16 \times 1} = 1.59$ L

Volume of CO_2 at atm and 37°C

$$= \frac{2 \times 0.0821 \times 310}{11 \times 1} = 4.63 \text{ L}$$

8. **(a)** Partial pressure of gas A in the mixture = 1 atm

Partial pressure of gas B in the mixture = 0.5 atm

We know that

$$\frac{P_A}{P_B} = \frac{X_A}{X_B} = \frac{n_A}{n_B}$$

$$\therefore \quad \frac{1}{0.5} = \frac{2 \times M_B}{M_A \times 3}; \frac{M_A}{M_B} = \frac{0.5 \times 2}{3} = \frac{1}{3}$$

$\therefore \quad MA : MB = 1 : 3$

9. **(c)** Let the formula of hydrocarbon be CxHy. Its combustion reaction is given as

$$\text{CxHy(g)} + \left(x + \frac{y}{4}\right)\text{O}_2\text{(g)} \rightarrow x\text{CO}_2\text{(g)} + \frac{y}{2}\text{H}_2\text{O(l)}$$

Initial	5	30	0	0
Final	0	$30 - \left(x + \frac{y}{4}\right)5$	$5x$	0

Out of 25 mL of resultant gas, 10 mL was CO_2 (absorbed by NaOH) and the remaining 15 mL was oxygen (absorbed by pyrogallol).

$\therefore \quad 5x = 10 ; x = 2$

$$30 - \left(x + \frac{y}{4}\right)5 = 15$$

On solving, $y = 4$

$\therefore$ formula of gaseous hydrocarbon is C_2H_4.

10. **(c)**

Element	Mass %	Mole %	Relative molar ratio
C	44.4	3.7	1
N	51.9	3.7	1
H	3.7	3.7	1

$\therefore$ empirical formula of X = CNH

Ratio of rate of diffusion of X and that of H_2 is given by

$$\frac{r_x}{r_{H_2}} = \frac{30 \times 4.81}{25 \times 30} = \sqrt{\frac{2}{M}}$$

On solving, $M = 54$

$\therefore$ molecular formula of x is $C_2H_2N_2$

11. **(a)** $\because M_{\text{mix}} = \dfrac{10}{22.4} \times 22.4 = 0$

$\therefore$ let the volume of He = V_1 mL

Let the volume of $N_2 = V_2$ mL

$\therefore \quad V_1 + V_2 = 100 \quad \because \quad n \propto V$

$$\therefore \quad 10 = \left(\frac{V_1}{100}\right) \times 4 + \frac{V_2}{100} \times 28$$

$$10 + \frac{V_1}{100} \times 4 + \left(\frac{100 - V_1}{100}\right) \times 28$$

Solving, $V_1 = 75\%$

12. **(d)** $\because \dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$

$$\frac{750}{300} = \frac{P_2}{350}$$

$\therefore \quad P_2 = 875$ mm Hg

$\therefore$ difference in height = 875 – 750 = 125 mm

Hg = 12.5 cm of Hg

13 **(a)** As the peak of the curve decreases, temperature increases.

14. **(D)** $P_{total} = P_{dry} + P_{water\ vapour}$

$735 = P_{dry} + 30$

so $P_{dry} = 735 - 30 = 705$ torr

15. **(B)** $d = \dfrac{PM_w}{RT}$

$$d = \frac{1 \times 32}{0.0821 \times 300} = 1.3 \text{ g L}^{-1}$$

16. $b = 4 \times \dfrac{4}{3} \times \pi r^3 \times N_A;$

$= 4 \times \pi \times 10^{-4} \times 1000$

$= 4 \times \dfrac{4}{3} \times \pi \times r^3 \times 6 \times 10^{23}$

$r = 5 \times 10^{-9}$ cm

Distance of closest approach = $2r = 10^{-8}$ cm $= 10^{-10}$ m

17.

First	Second
2 gmH_2	16 gm CH_4
P atm.	P atm.
0.5 lit.	0.5 lit.

$n_{H_2} = \dfrac{2}{2} = 1$ mol

and $n_{CH_4} = \dfrac{16}{16} = 1$ mol

$n_{H_2} = n_{CH_4}$

$P_{mix}\ V_{mix} = P_1V_1 + P_2V_2$

or $P_{mix}\ (0.5 + 0.5) = P \times 0.5 + P \times 0.5$

$= P \times 0.5 \times 2$

or $P_{mix} \times 1 = P \times 1$

or $P_{mix} = P$

18. **(A)** $PV = nRT$ at NTP

$1 \times 2.24 = n_i \times 22.4$

or $n_i = 0.1$ mol

$\dfrac{P_2}{P_1} = \dfrac{n_2}{n_1}$ or $\dfrac{570/760}{1} = \dfrac{n_2}{0.1}$

Remaining moles = $n_2 = \dfrac{5.7}{76}$ mol

Escaped moles = $n_1 - n_2 = 0.1 - \dfrac{5.7}{76} = 0.025$ mol.

19. **(B)** $n_1T_1 = n_2T_2$

or $n_1 \times 300 = n_2 \times (400)$

or $\dfrac{n_2}{n_1} = \dfrac{3}{4}$

or $\dfrac{n_1 - n_2}{n_1} = \dfrac{4-3}{4} = \dfrac{1}{4}$

20. **(A)**

$V_1 = V$

$V_2 = V + 0.1\text{ V} = 1.1\text{ V}$

$\dfrac{T_2}{T_1} = \dfrac{V_2}{V_1} = \dfrac{1.1\text{ V}}{V} = \dfrac{1.1}{1}$

$$\%\left(\frac{T_2 - T_1}{T_1}\right) = \left(\frac{1.1 - 1}{1}\right) \times 100 = 10\%$$

21. **(A)** $\dfrac{\text{Volume of } O_2 \text{ molecule}}{\text{Volume of } O_2 \text{ molecule at STP}} \times 100$

$$\Rightarrow \frac{\frac{4}{3}\pi \times 8 \times 10^{-30} \times 10^3 \times N_A \times 100}{22.4} = 0.09\%$$

22. **(A)** $M_A = 2M_B$, $(U_{rms})_A = (U_{rms})_B$

$U_{rms} = \sqrt{\dfrac{3PV}{M}} \quad U_{rms} \propto \sqrt{\dfrac{P}{M}}$

$\dfrac{(U_{rms})_A}{(U_{rms})_B} = \sqrt{\dfrac{P_A}{P_B} \times \dfrac{M_B}{M_A}} \cdot 4 = \dfrac{P_A}{P_B} \times \dfrac{1}{2}$

$\dfrac{P_A}{P_B} = 8:1$

23. **( )** $Z = \dfrac{PV}{RT} \Rightarrow \dfrac{40 \times 0.4}{300 \times 0.082}$

$Z = 0.65$

24. **(C)** $P_1V_1 = P_2V_2 \qquad 1 \times 550 = P_2 \times 600$

$P_2 = \dfrac{5}{6}$atm $P_2 = \dfrac{5}{6} \times 760 \Rightarrow P_2 = 633.33$ mm

Pressure decrease $\Rightarrow 760 - 633.33 \Rightarrow 126.67$ mm

25. **(C)**

$$\begin{array}{ccccc} N_2 & + & 3H_2 & \longrightarrow & 2NH_3 \\ 11 & & 12 & & \\ 9 & & 6 & & 4 \end{array}$$

Volume remaining after injected water

$= 20 - 3.58 = 16.42$

All NH_3 dissolve in water PV = nRT

$P \times 16.42 = 15 \times 0.0821 \times 300$

$P = 22.5$ atm

26. **(B)** Let $T_1 > T_2$; final pressure will be same. Let x mole transfer from A to B vessel.

$\therefore \quad P_AV = (n - x)\ RT_1 \qquad$ (A)

and $\quad P_AV = (n + x)\ RT_2 \qquad$ (B)

$\therefore \quad x = \dfrac{n(T_1 - T_2)}{T_1 + T_2}$

Finally $P_1 \times 2\text{V} = 2nRT_1$; $V = \dfrac{nRT_1}{P_1}$ put eq. (A)

$$\therefore \quad P_A \times \frac{nRT_1}{P_1} = \left(n - \frac{n(T_1 - T_2)}{(T_1 + T_2)}\right)RT_1$$

$$P_A = \frac{2P_1T_2}{T_1 + T_2}$$

27. **(D)** $P \propto d$; $P = kd$ and $k = \dfrac{1\text{ atm}}{1\text{ metre}}$

$$PV = nRT\ ;\ kd \times \left(\frac{4}{3}\pi\left(\frac{d}{2}\right)^3\right) = nRT$$

$$\frac{d_1^4}{d_2^4} = \frac{n_1}{n_2};\ \frac{1}{4^4} = n_1/n_2\ ;\ n_2 = 256$$

$\therefore$ Number of moles of air added = 255 moles

28. **(D)** % relative humidity

$$= \frac{\text{Partial pressure of } H_2O}{\text{Vapour pressure of } H_2O} \times 100$$

$$75 = \frac{P_{H_2O}}{30} \times 100 \quad \Rightarrow \quad P_{H_2O} = 22.5 \text{ torr ;}$$

$$\text{\% of } H_2O \text{ vapour in air} = \frac{(22.5)}{760} \times 100 = 2.96$$

$$\text{molar mass of wet air} = \frac{29 \times 97.04 + 2.96 \times 18}{100}$$

$$= \frac{2814.16 + 53.28}{100} = 28.67$$

$$\text{Density of wet air} = \frac{PM}{RT} = \frac{1 \times 28.67}{0.0821 \times 300} = 1.164 \text{g/L}$$

29. **(B)** Density of air at sea level,

$$d_0 = \frac{29 \times 1}{0.0821 \times 290} = \frac{1}{0.821} \text{g/L}$$

density at 831 m = d

$$d_0 e^{-Mgh/RT} = \frac{1}{0.821} \times e^{-\left(\frac{29 \times 10^{-3} \times 10 \times 831}{8.31 \times 290}\right)}$$

$$\Rightarrow \quad \frac{1}{0.821} \times e^{-0.1} = \frac{.9}{0.821} \text{g/L}$$

Let x be the number of balloons

$$\therefore \quad 10^3 \times g + x \times 40g = hdg$$

$$= \frac{0.9}{0.821} \times 8.21 \times g \times x = 20 \text{ balloons.}$$

$$\therefore \quad x = 20 \text{ balloons}$$

LEVEL III

(Match the Column)

1. **[A → R, B → S, C → Q, D → P]**

A → R;

$$T_c = \frac{8a}{27bR}, P_c = \frac{a}{27b^2}$$

$$\frac{T_c}{P_c} = \frac{8a}{27bR} \times \frac{27b^2}{a} = \frac{8b}{R}$$

B → S;

$$\frac{T_c}{V_c} = \frac{8a}{27bR \times 3b} = \frac{8a}{81Rb^2}$$

C → Q;

$$T_B = \frac{a}{bR}$$

D → P;

$$\frac{T_i}{T_B} = \frac{2a}{bR} \times \frac{bR}{a} = 2.$$

2. **[A → S; B → R; C → P, Q, R, S ;D → P,Q]**

Gas	T_c	T_b
A_2	108.4 K	365 K
B_2	90.33 K	304.8 K
C_2	607 K	2048.6 K
D_2	180.67 K	607.7 K

3. $PV = nRT$

When V and T are constant then $P \propto n$

(A) ⟶ (Q)

(B) $d = \frac{PM}{RT}$ $\quad \therefore \quad \frac{d_{\text{moist}}}{d_{\text{dry}}} = \frac{M_{\text{moist}}}{M_{\text{dry}}} < 1$

(B) ⟶ (S)

(C) $p^\circ_{H_2O} > p_{H_2O}$, hence $\frac{p_{H_2O}}{p^\circ_{H_2O}} < 1$ and

$p^\circ_{H_2O}$ is also a function of temperature.

(C) ⟶ (P, S)

Dalton's law of partial pressures are applicable for only ideal gases.

(D) ⟶ (P, Q, R)

4. (A) ⟶ R

Since He is monoatomic, therefore, $C_P/C_V = 5/3 = 1.66$

(B) ⟶ (P)

Since Molecular weight of H_2 is least.

(C) ⟶ (S)

Since CO_2 is a linear triatomic molecule, therefore, vibrational energy = (3N – 5) RT = (9 – 5) RT = 4RT

(D) ⟶ (Q)

Since Molecular weight of SO_2 is highest.

Comprehension

Passage 1 (For Q. 5-7)

5. **(a)**

$$P = 754 \text{ torr} = \frac{754}{760} = 0.992 \text{ atm}$$

$PV = nRT$

$0.992 \times 0.127 = n \times 0.0821 \times 371$

$$n = 4.14 \times 10^{-3} \text{ mole} \Rightarrow n = \frac{\text{Weight}}{\text{Molar mass}}$$

$$\text{Molar mass} = \text{Weight}/n = \frac{0.495}{4.14 \times 10^{-3}} = 120 \text{ g/mol}$$

6. **(b)**

$PV = nRT$

$1 \times 1 = n \times 0.0821 \times 273 \Rightarrow n = 4.46 \times 10^{-2}$ mol

$$\text{Mole} = \frac{\text{Weight}}{\text{Molar mass}}$$

$$\therefore \quad \text{Molar mass} = \frac{\text{weight}}{\text{No. of mole}} = \frac{0.714}{4.46 \times 10^{-2}}$$

$$= 16 \text{ g/mole}$$

7. **(c)**

$PV = nRT$

$100 \times 3 = n \times 0.0821 \times 300$

$n = 12.2$ mol

Passage 2 (For Q. 8-10)

8. (d)

Greater the 'a', more easily liquefiable is the gas.

9. (d)

$$Z_C = \frac{P_C V_C}{RT_C} \quad \therefore \; T_C = \frac{P_C V_C}{Z_C R}$$

$$= \frac{50.1 \times 0.078}{0.308 \times 0.0821} = 154.5 \text{ K}$$

$$T_B = \left(\frac{27}{8}\right) \cdot T_C = \frac{27}{8} \times 154.5 = 521.4 \text{ K}$$

10. (d)

At very low pressure, $\frac{a}{V}$ will be very small in the term $\left[P + \frac{a}{V^2}\right]$. Similarly b will be small compared to v in the term $(V - b)$

$\therefore$ Van der Waal equation reduce to $PV = RT$.

Integer-Types Questions

11. $\frac{P_{N_2}}{P_{gas}} = \frac{57}{38} = 57/38$

$$\Rightarrow \quad \frac{0.8}{21.6}\sqrt{\frac{N_{gas}}{28}} = \frac{57}{38}$$

$N_{gas} = 9 \times 28 = 252$

XeFx = 131 + 19x = 252

19x = 252 – 131 = 121

$$x = \frac{121}{19} \approx 6.5 \qquad x = 6$$

XeF^6

12. Suppose the compound A is CxHyNz.

(i) CxHyNz	+ $O_2 \longrightarrow$	CO_2	+ H_2O (vapour)	+ N_2
(9 – v) mL.	v. mL.	4 mL	6 mL	2 mL
or (9 – v) moles for O atoms.	v moles	4 moles	6 moles	2 moles

$2 \times$ moles of $O_2 = 2 \times$ moles of $CO_2 + 1 \times$ moles of H^2O

$2v = 2 \times 4 + 1 \times 6 = 14$; $v = 7$ mL

13. Let formula in $C_xH_yO_z$.

$$C_xH_yO_z + \frac{1}{2}\left(2x + \frac{y}{2} - z\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

Volume of CO_2 = 556 – 112 = 448 mL

Moles = 0.02

Moles of $C_xH_yO_z = \frac{0.9}{90} = 0.01$

$x = 2$ (1)

$y = 2$; $z = 4$

Formula $C_2H_2O_4$

14. $U_{rms} = \sqrt{\frac{3RT}{M}}\, U_{mp} = \sqrt{\frac{2RT}{M}}$

$\therefore$ from questions $\sqrt{\frac{3R \times 400}{40}} = \sqrt{\frac{2R \times 60}{M}} = 4 \text{ gmol}^{-1}$

$M = 4$

15. Since $(u_{av})_A = (u_{av})_A = \sqrt{\frac{8RT_A}{\pi M_A}} = \sqrt{\frac{8R(300\text{ K})}{\pi(0.002\text{ kg mol}^{-1})}}$

$$(u_{av})_B = \sqrt{\frac{8RT_B}{\pi M_B}} = \sqrt{\frac{8R(600\text{ K})}{\pi(0.016\text{ kg mol}^{-1})}}$$

Therefore, $\frac{(u_{av})_A}{(u_{av})_B} = \sqrt{\frac{300}{2}} \times \sqrt{\frac{16}{600}} = 2$

16. $2NH_3 \longrightarrow N_2 + 3H_2$

Since number of moles after reaction (n_2)
= 2 × number of moles before reaction (n_1)
at same T and V, $P \propto n$

$$\therefore \quad \frac{P_1}{P_2} = \frac{n_1}{n_2} = \frac{1}{2}$$

Hence pressure after reaction = 2 atm.

17. Since A and A_2 are two states in gasoues phase having their weight ratio 50%, i.e., 1 : 1

$$\therefore \quad \text{mole of } A = \frac{96}{2} \times \frac{1}{48} = 1\left(n = \frac{w}{m}\right)$$

$$\text{mole of } A_2 = \frac{96}{2} \times \frac{1}{96} = \frac{1}{2}$$

$$\therefore \quad \text{total mole of } A \text{ and } A_2 \text{ are} = 1 + \frac{1}{2} = \frac{3}{2}$$

Thus, from $PV = nRT$

$$P \times 33.6 = \frac{3}{2} \times 0.0821 \times 546$$

$P = 2$ atm

18. $z = \frac{PV}{nRT}$, $n_{330K} = \frac{1 \times 800}{1.90 \times R \times 330}$,

$n_{570K} = \frac{V \times 200}{1.10 \times R \times 570}$, by equalising the two, we get

$V = 4$

19. $z = 1 + \frac{pb}{RT}$ at high pressure, slope $= \frac{b}{RT} = \frac{\pi}{492.6}$,

$b = \frac{\pi}{492.6} \times 0.0821 \times 30$ and

$$b = \frac{4}{3}\pi r^3 \times 4N_A$$

$R = 2.5A0$, $d = 5A0$

20. $P = \frac{nRT}{V - nb} - \frac{an^2}{v^2} = 10^{-1} = 9$

21. $\Delta m = m_{cold} - m_{hot} = (n_{cold} - n_{hot})$

$$M = \frac{PVM}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right], T_2 - T_1 = 3$$

22. Initial number of moles $= \dfrac{4}{40} = 0.1$

Final number of moles $= \dfrac{3.2}{40} = 0.08$

Since P and V are constant

$n_1T_1 = n_2T_2$

$0.1T_1 = 0.07T_1 + 125$

$T_1 = 500$ K

From $PV = nRT$

$$P = \frac{0.1 \times 0.082 \times 500}{0.821} = 5 \text{ atm.}$$

23. $R_{O_2} = \dfrac{2000 - 1500}{47} = \dfrac{500}{47} \text{mm min}^{-1}$

$$\frac{R_{O_2}}{R_{gas}} = \sqrt{\frac{79}{32}} = 1.57 \; R_{gas} = R_{O_2}/1.57$$

Change in pressure of gas in 74 min $= \dfrac{500}{47} \times \dfrac{74}{1.57} = 501.92$

Change in pressure of $O_2 = \dfrac{500 \times 74}{47} = 787.234$

$$\frac{V_{gas}}{V_{O_2}} = \frac{P_{gas}}{P_{O_2}} = \frac{2000 - 80/42}{2000 - 787.234} = 1.236$$

24. $\dfrac{R_{mix}}{R_{kr}} = 1.16 = \sqrt{\dfrac{84}{M_{mix}}}$

$R_{mix} = 62.43$

$Cl_2 \rightleftharpoons 2Cl$

$t = 0$ 1 mole 0

$1 - x$ $2x$

$nT = 1 + x$

$$x = \frac{M_T - M_O}{M_O} = \frac{71 - 62.4}{62.4} = 0.138$$

25. $C_2H_6 + \dfrac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$

x $7/2x$ $2x$ $3x$

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

$40 - x$ $3x$ $2(40 - x)$ $2(40 - x)$

$$n_{O_2} = \frac{65}{16} \text{mole}$$

$$V = \frac{nRT}{P} = \frac{\frac{65}{16} \times 0.0821 \times 400}{1 \text{ atm}} \text{L}$$

$$\frac{7}{2}x + 3x = \frac{65 \times 0.0821 \times 400}{16}$$

Calculate x and find the ratio $x_{C_2H_6} = 0.66$.

26. $2H_2 + O_2 \longrightarrow 2H_2O$

$(1 - x)$ x 0

$-2x$ $-x$ 1

$1 - 3x$ 0 0

$X_{O_2} = 0.217 » 22$

$X_{H_2} = 0.78$

27. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

a 0 0

teq. $0.6a$ $0.4a$ $0.4a$

$nT = 1.4a$

$$V = \frac{1.4a \times R \times 420}{P}$$

$$\text{Mass} = 0.6a \times \frac{0.4a \times 137.5 + 0.4a \times 71}{208.5}$$

$$d = \frac{m}{V} = \frac{208.5a \times 208.5g}{a[1.4 \times 0.821 \times 420]} = 4.46 \text{ g/L}$$

28. Case – I $P = 1$ atm $w = 12$ gm $T = (t + 273)$K
$V = v$ ltr

Case – II $T = (t + 283)$K $P = 1 + \dfrac{10}{100} = 1.1$ atm
$w = 12$ gm $V = v$ litre

For case I – $PV = nRT$

$$V = \frac{12}{m}R(t + 273)$$

for Case II $1.1\,V = \dfrac{12}{m} \times R(t + 283)$

for cases (I) and (II)

$$\frac{1.1}{1} = \frac{t + 283}{t + 273}$$

$1.1t + 300.3 = t + 283$

$t = -1730C = 100$ K

Using case I $V = \dfrac{12}{120} \times 0.082 \times 100 = 0.82$ ltr

29. $P = 1$ atm. $T = 500$ K $d = 0.36$ kg/m^3

$$\frac{r_{O_2}}{r_{gas}} = \sqrt{\frac{M_{gas}}{M_{O_2}}} = \sqrt{\frac{M}{32}} = \frac{1}{1.33}$$

(i) $M = \dfrac{32}{(1.33)^2}$

(ii) Molar volume

$$= \frac{\text{Molecular weight}}{\text{Density}} = \frac{18.1 \text{ gm}}{360 \text{ g/m}^2} = 50.27 \times 10^{-3}$$

(iii) $Z = \dfrac{PV}{RT} = \dfrac{1 \text{ atm} \times 50.27}{0.0821 \times 500 \text{ K}} = 1.225$

(iv) $Z > 1$ repulsive

30. Mole of gaseous mixture,

$\therefore$ nH_2 + unknown gas $= \dfrac{PV}{RT} = \dfrac{6 \times 3}{0.0821 \times 300} = 0.7308$ mole

$\therefore$ n(unknown gas) $= 0.7308 - 0.7 = 0.0308$ mole

$$\frac{\text{Mole of } H_2 \text{ leaked}}{\text{Mole of unknown gas leaked}} = \sqrt{\frac{M_{(\text{unknown})}}{M_{H_2}}}$$

$$\frac{0.7}{0.0308} = \sqrt{\frac{M}{2}}$$

$M = 1033 \text{ g mol}^{-1}$

31. $PV = nRT$

$$P = \frac{7.6 \times 10^{-10}}{760} \text{ atmosphere}$$

$= 10^{-12}$ atmosphere

$V_1 = 1$ ltr $n = ?$

$R = 0.082$ ltr L atm $K^{-1}mol^{-1}$, $T = 273$ K

$\therefore$ $10^{-12} \times 1 = n \times 0.082 \times 273$

$n = 4.46 \times 10^{-12}$ moles

Molecules $= 4.46 \times 10^{-14} \times 6.02 \times 10^{23} = 2.68 \times 10^{10}$

32. Volume of one molecule of $N_2 = \frac{4}{3}\pi r^3$

$$= \frac{4 \times 3.14(2 \times 10^{-10})^3}{3}$$

$= 3.35 \times 10^{-29} m^3 = 3.35 \times 10^{-23} cm^3$

Volume of one mole molecules $= 6.02 \times 10^{23} \times 3.35 \times 10^{-23}$ $cm^3 = 20.167$ cm^3

Volume of one mole N2 at NTP = 22400 cc.

Hence empty space = 22400 – 22379.833 cm^3

$$\% \text{ empty space} = \frac{22379.833 \times 100}{22400} = 99.9\%$$

33. We will calculate the temperature of the gas from the given data.

$PV = nRT$

All values are to be taken in MKS system.

$P = 7.57 \times 10^3 \text{ N m}^{-2}$

$V = 1 \text{ L} = 1 \times 10^{-3} \text{ m}^3$

$$n = \frac{2 \times 10^{21}}{6.02 \times 10^{23}} \text{ moles}, R = 8.31 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$7.57 \times 103 \times 10^{-3} = \frac{2 \times 10^{21} \times 8.31 \times T}{6.02 \times 10^{23}}$$

$T = 274.2$ K

$$\text{Now, } U_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

All the values are to be taken in MKS system,

$R = 8.31$, $M = 28 \times 10^{-3}$ kg for N2

$T = 274.2$ K

$$U_{\text{rms}} = \sqrt{\frac{3 \times 8.31 \times 274.2}{28 \times 10^{-3}}} = 494.2 \text{ metre/sec.}$$

Again, $U_{\text{mp}} = 0.82 \times U_{\text{rms}}$

$= 494.2 \times 0.82$

$= 405.26$ metre/sec.

34. For gas A : Its mass = 2 g; $PA = 1$ atm $T = 298$ K

For gas B : Its mass = 3 g, $PB = 0.5$ atm. $T = 298$ K

According to Dalton's law of partial pressure

$P = PA + PB$

$1.5 = 1 + PB$

$PB = 0.5$ atm

$$\text{Now, } PV = \frac{wRT}{m}$$

For gas A : $P_A = 1$ atm, $m = M_A$, $w = 2$ g

$$1 \times V = \frac{2 \times RT}{M_A} \quad \text{(i)}$$

for gas B : $P_B = 0.5$ atm, $m = M_B$, $w = 3$ g

$$0.5 \times V = \frac{3 \times RT}{M_B} \quad \text{(ii)}$$

Dividing Eqs. (i) and (ii)

$$0.5 = \frac{3 \times M_A}{2\,M_B} \text{ or } \frac{M_A}{M_B} = \frac{1}{3}$$

(B) If A is $T = 298$ K, $V = ?$

Put these values in Eq. (i)

$$V = \frac{2 \times 0.0821 \times 298}{32} = 1.53 \text{ litres}$$

35. $2H_2 + O_2 = 2H_2O$

Volume before reaction (L)	1	1	0
Volume after reaction (L)	0	0.5	1

(a) For : H_2O $PV = nRT$

At STP $P = 1$ atm, $V = 1$ litre,

$\therefore$ moles of $H_2O(n) = 4.46 \times 10^{-2}$

Weight of $H_2O = 4.46 \times 10^{-2} \times 18 = 0.803$ gram

(b) Gas left in the vessel = 0.5 ltr of O2 at STP

22.4 ltr at STP weigh 32 g

0.5 ltr at STP weigh = 0.71 g

(c) Moles of H_2O formed $= 4.46 \times 10^{-2}$

Moles left = 0.5 ltr of O_2 at STP $= 2.23 \times 10^{-2}$

Total moles in the vessel = Moles of H_2O + moles of O_2 left $= 6.69 \times 10^{-2}$

$PV = nRT$

$P = ?$, $V = 2$ ltr,

$n = 6.69 \times 10^{-2}$, $T = 373$ K

$P \times 2 = 6.69 \times 10^{-2} \times 0.0821 \times 373$

$P = 1.02$ atm

36. $$\frac{35n_1 + 37n_2}{n_1 + n_2} = 35 - 45$$

where n_1 and n_2 are the number of moles of ^{35}Cl and ^{37}Cl respectively.

$$\therefore \quad \frac{n_1}{n_2} = 3.44 : n_1 : n_2 = 3.44 : 1$$

$\therefore$ ratio of the lengths is 3.44 : 1.

37. $$P \times 8 = \left(\frac{3.6}{M}\right) \times R \times T \quad \text{(i)}$$

From Eq. (i)/(ii)

$$P \times 8 = \left(\frac{3.0}{M}\right) \times R\,(T + 15) \qquad \text{(ii)}$$

$$3.6 \times T = 3\,(T + 15)$$

$$= 3T + 45 \Rightarrow T = \frac{45}{0.6} = 75\text{ K}$$

$$\Rightarrow \quad P = \frac{3.6}{44} \times \frac{0.0821 \times 75}{8} = 0.062\text{ atm}$$

38. $P \times \frac{4}{3}\pi(10)^3 = \left(\frac{1}{4}\right)R \times T \qquad \text{(i)}$

From Eq. (i)/(ii)

$$P \times \frac{4}{3}\pi r^3 = \frac{0.75}{4} \times RT \qquad \text{(ii)}$$

$$\frac{(10)^3}{r^3} = \frac{1}{0.75} = \frac{4}{3} \Rightarrow r = 3\sqrt{\frac{3}{4}} \times 10$$

$r = 9.0856$ cm

39. $P \times 30 = 0.5 \times 38 \times 60 \times 1 \qquad P = 38$ atm

40. $C_6H_{12}O_6 \quad + \quad 6O_2 \quad \longrightarrow \quad 6CO_2 + 6H_2O$

0.08928 mole $\left(\frac{0.2}{22.4}\right) \times 60$ mole 0.53568 mole

= 16.071 gm = 11.999 lit

41. $P \times 1 = \left(\frac{12}{28} + \frac{4}{2} + \frac{9}{32}\right) \times 0.0821 \times 300 = 66.74$ atm

$P = 66.74$ atm

42. $P \times 10 = \left(\frac{10}{2} + \frac{64}{32}\right) \times 0.0821 \times 473$

$$\Rightarrow \quad P = 27.1833\text{ atm}$$
$$= 27.54 \times 10^5\text{ N/m}^2$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(l)$$

5 2

(5–4) – 4

$$P \times 10 = 5 \times 0.0821 \times 473$$
$$P \times 19.4166\text{ atm} = 19.66 \times 10^5\text{ N/m}^2$$

43. $\frac{60}{40} = \frac{P}{1}\sqrt{\frac{17}{36.5}} \Rightarrow P = 2.1979$ atm

44. $\frac{x}{100} = \sqrt{\frac{(32 + 6 \times 19)}{28}} \Rightarrow x \simeq 228$ **Ans.**

45. $\frac{d_{NO}}{100 - d_{NO}} = \sqrt{\frac{32}{30}} \Rightarrow d_{NO} = 50.8$ cm

46. $\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{2}{28}} \Rightarrow t_2 = 0.2672$ hr $\simeq 16$ min

47. $\frac{234}{224} = \sqrt{\frac{M_{mix}}{32}} \Rightarrow M_{mix} = 34.92 = \frac{100}{\frac{80}{32} + \frac{20}{M}}$

$M = 46.6$ **Ans.**

48. **(a)** $\frac{0.3}{(dP/dt)} = \sqrt{\frac{17}{20}} \Rightarrow \frac{dP}{dt} = 3.25$ torr/sec.

(b) $M_{avg} = 0.30 \times 4 + 0.2 \times 32 + 0.5 \times 28 = 21.6$

$$\frac{dP}{dt} = 0.3\sqrt{\frac{21.6}{17}} \Rightarrow \frac{dP}{dt} = 0.3387\text{ torr/sec.}$$

49. Hint : $P = P_0 e^{-\mathrm{Mgh/RT}}$

50. $P = (101.325)\ e^{-\frac{28.8 \times 10^{-3} \times 9.8 \times 10 \times 10^3}{8.314 \times 243}} = 25.027$ kPa

51. If it melts then $T > 1800$ K

$$n = \frac{250 \times \mathrm{V}}{R \times 300} = \frac{P \times V}{R \times 1800} \Rightarrow P = 1800 \times \frac{250}{300}$$

$P = 1500$ kPa

1500 kPa > 10^6 Pa (or 10^3 kPa)

so it will blow up before melting.

52. $\frac{P_0}{2} = P_0 e^{-\frac{M \times 9.8 \times 1}{8.314 \times 298}}$

$M = 175.133$ kg mole^{-1}

53. (i) $\frac{75}{70} = \sqrt{\frac{M}{28}} \Rightarrow M = 32.1428$ gm/mole.

(ii) $v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 273}{32.1428 \times 10^{-3}}} = 460.28$ m/s

54. $\sqrt{\frac{3RT}{64 \times 10^{-3}}} = \sqrt{\frac{8R \times 300}{\pi \times 32 \times 10^{-3}}}$

$$T = \frac{8 \times 300 \times 64}{3 \times 32 \times \pi} = 509.29\text{ K} = 236.29°\text{C}$$

55. **(a)** $u_{rms} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 1.01325 \times 10^5}{1.2504}} = 493.03$ m/s

(b) $u_{avg} = \sqrt{\frac{8}{\pi} \times \frac{1.01325 \times 10^5}{1.2504}} = 454.259356$

(c) $u_{mp} = 403$ m/s

56. Use the results:

57. $\sqrt{\frac{3RT_1}{M}} = \sqrt{\frac{8RT_2}{\pi M}} = \sqrt{\frac{2RT_3}{M}} = 1500$ m/s

$$\begin{cases} T_1 = 2886\text{ K} & \text{rms} \\ T_2 = 3399\text{ K} & \text{avg.} \\ T_3 = 4330\text{ K} & \text{m.p.} \end{cases}$$

58. $1.95 = \frac{800 \times 1}{nR \times 223} \qquad \text{(i)}$

$$1.10 = \frac{200 \times V}{nR \times 373} \qquad \text{(ii)}$$

$$\Rightarrow \quad \frac{1.95}{1.10} = \frac{800}{200} \times \frac{1}{V} \times \frac{373}{223} \quad V = 3.77\text{ lit}$$

59. $0.927 = \dfrac{10.1325 \times 10^5 \times 100 \times 10^{-3}}{n \times 8.314 \times 273.15}$

$w = n \times 32 = 15.40 \times 10^3$ gm = 15.40 kgm

60. Hint : At critical temperature (T_C) and critical pressure (P_C), O_2 will behave ideally.

61. Hint : low density ⇒ High molar volume (V_m)

$$V_m \underset{\rightarrow}{\lim} \infty$$

62. $\left(15 + \dfrac{9 \times 6.7}{(10)^2}\right)(10 - 3 \times 0.0564) = 3 \times 0.0821 \times T$

⇒ $T = 623.$ K ⇒ $T = 350.5°$

63. (i) $P \times 12 = 15 \times 0.0821 \times (273 + 30)n$

$P = 31.1$ atm

(ii) $\left(P + \dfrac{(15)^2 \times 0.2107}{(12)^2}\right)(12 - 15 \times 0.0171)$

$= 15 \times 0.0821 \times (273 + 30)$ $P = 31.4$ atm

64. $1000 \times g = e\left(\dfrac{nRT_2}{P} - \dfrac{nRT_1}{P}\right)g$

$$\frac{nR \times M}{RT_1}(T_2 - T_1)$$

65. $Q = C_{V1}(1000 - 500) + C_{V2}(1500 - 1000)$

$$= \left(\frac{3R}{2} + \frac{3R}{2}\right) \times 500 + \left(\frac{3R}{2} + \frac{3R}{2} + 3R\right)(500)$$

$= 1500\,R + 3000\,R = 4500\,R$

66. $\rho_1 h_1 = \rho_2 h_2$,

In one hour $h_1 = 37 \times 2 = 74$ mm

$1.034 \times 74 = 13.6 \times h_2$

$h_2 = 5.626$ mm of Hg

$P = \dfrac{5.626}{760}$ atm/hr. $PV = nRT$

$\dfrac{5.626}{760} \times 0.016 = n \times 0.821 \times 310$

$n = 4.653 \times 10^{-3}$ mole/hr.

Rate of O_2 consumption $= n \times 22400$ cm^3 = 0.104 cm^3/m

$O_2 = 104$ mm^3/hr.

67. $P = 750 - 17.5 = 732.5$ torr

$T = 20°C = 293$ K

Inhaled $O_2 = 52.5 \times 0.2032$

Exhaled $O_2 = 52.5 \times 0.1675$

so at STP $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

$$\frac{732.5 \times 52.5(0.2032 - 0.1675)}{293} = \frac{760 \times V}{273}$$

⇒ $V = 1.683$ L for 6 min.

Oxygen consumption per min $= \dfrac{1.683}{6} = \dfrac{0.28\text{ L}}{\text{min}} = 280$ mL/min.

68. Let moles of water vapour initially $= n_1$

Let moles of water vapour finally $= n_2$

$$n_1 = \frac{17.5 \times 0.8 \times V}{R \times 293} \Rightarrow n_2 = \frac{6.5 \times V}{R \times 277}$$

$$\frac{n_1}{n_2} = 2.036$$

$$\frac{n_2}{n_1} = 0.491$$

So fraction of water vapour condensed

$$= 1 - \frac{n_2}{n_1} = 0.509$$

69. Average velocity $= \sqrt{\dfrac{8RT}{\pi M}} = 4 \times 10^2$

⇒ $\dfrac{RT}{\pi M} = 2 \times 10^4 \Rightarrow RT = 2\ 2\pi M \times 10^4$

Total K.E. of He

$= \dfrac{6}{4} \times \dfrac{3}{2}RT = \dfrac{9}{4}RT = \dfrac{9}{4} \cdot 2\pi \times 4 \times 10^{-3} \times 10^4 = 180$ πJ

Total K.E. of Ne

$= \dfrac{12}{20} \times \dfrac{3}{2}RT = \dfrac{9}{10}RT = \dfrac{9}{10} \times 2\pi \times 20 \times 10^{-3} \times 10^4$

$= 360\ \pi$J

Average K.E. per mol $= \dfrac{(360 + 180)\pi}{1.5 + 0.5} = 807.84$ J

70. $V - b = RT = 100\ (0.011075\ V - b) = 1.1075$

$V - 100b \Rightarrow V = \dfrac{99b}{0.0175} = 921$ b

⇒ $920\ b = RT$

⇒ $b = 24.33$ cm^3 mol^{-1} $= 4 \times \dfrac{4}{3}\pi r^3 \times 6.023 \times 10^{23}$

⇒ $r = 13.4 \times 10^{-9}$ cm = 134 pm

71. $V = \dfrac{RT}{P} + B = 2.058$ L. Also, for the given equation

$$Z = 1 + \frac{PB}{RT} = 1 + \frac{10(-0.1814)}{0.082 \times 273} = 0.918$$

From Van der Waal's equation, for $Z < 1$, Z

$$Z = 1 - \frac{a}{VRT}$$

⇒ $\dfrac{a}{VRT} = 0.082 \Rightarrow a = 3.77$ bar L^2 mol^{-2}

72. $\dfrac{-dP}{dt} = \dfrac{KP}{\sqrt{M}} \Rightarrow \displaystyle\int_{P_0}^{P} \dfrac{-dP}{P} = \dfrac{K}{\sqrt{M}}\int_0^t dt$

⇒ $\ln\left(\dfrac{P_0}{P}\right) = \dfrac{Kt}{\sqrt{M}} \Rightarrow \ln 4 = \dfrac{4\text{K}}{\sqrt{4}} = 2\text{K}$

$\ln\dfrac{10}{P} = \dfrac{K}{2}$ ⇒ $p_{He} = 7.07$ atm

Also, $\ln\left(\dfrac{P_0}{P}\right)_{He} = \dfrac{Kt}{2}$ and $\ln\left(\dfrac{P_0}{P}\right)_{CH_4} = \dfrac{Kt}{4}$

$$\Rightarrow \quad \left(\frac{P_0}{P}\right)_{\text{He}} = \left(\frac{P_0}{P}\right)^2_{\text{CH}_4} \Rightarrow \frac{10}{7.07} = \frac{100}{P^2_{\text{CH}_4}}$$

$\Rightarrow \quad P_{\text{CH}_4} = 8.4$ atm

73.

	$NH_3(g)$ +	$HCl(g) \longrightarrow$	$NH_4Cl(s)$
Moles	0.08	0.26	0
	0	0.18	0.08

$\Rightarrow \quad Q = 0.08 \times 4300 = 3440$ J

Also, $Q = nC_v\Delta T \Rightarrow \Delta T = \dfrac{3440}{0.18 \times 20} = 955.55$

$T_{\text{final}} = 1255.55$ K

$P_{\text{final}} = \dfrac{0.18 \times 0.082 \times 1255.55}{1.8}$

= 10.3 atmosphere

74. $b = 39.1\text{cm}^3\text{mole}^{-1} = 39.1 \times 10^{-6}\text{m}^3\ \text{mole}^{-1} = 4\text{V} \times N_A$

$39.1 \times 10^{-1} = 4 \times \frac{4}{3}\pi r^3 \ \ 6.023 \times 10^{23}$

$r = 1.57 \times 10^{-10}$ m

$\sigma = 2r = 3.14 \times 10^{-10}$ m = 314 pm

$$\mu_{\text{avg.}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 298}{3.14 \times 28 \times 10^{-3}}} = 474.8 \text{ m/sec.}$$

$$N^* = \frac{P}{kT} = \frac{10^{-3} \times 101325}{760 \times 1.38 \times 10^{-23} \times 298} = 3.24 \times 10^{19}$$

$$\lambda_1 = \frac{1}{\sqrt{2}\pi\sigma^2 N^*} = \frac{Z_1 N^*}{2}$$

$$= \frac{1}{\sqrt{2} \times 3.14 \times (3.14 \times 10^{-10})^2 \times 3.24 \times 10^{19}}$$

= 0.0705 m = 7.05 cm

$Z_1 = \sqrt{2}\ \pi\sigma^2\text{UN}^* \ \sqrt{2} \times 3.14 \times (3.14 \times 10^{-10})^2$
$\times 474.8 \times 3.24 \times 10^{19} = 6739.4 \text{ sec}^{-1}$

$$Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2 UN^* = \frac{Z_1 N^*}{2} = \frac{6739.4 \times 3.24 \times 10^{19}}{2}$$

$= 1.09 \times 10^{23}\text{m}^{-3}\text{sec}^{-1} = 1.09 \times 10^{17} \text{ cm}^{-3} \text{ sec}^{-1}$

75. $\lambda = 2.6 \times 10^{-5}$ m, $\quad \sigma = 0.26$ nm $= 2.6 \times 10^{-10}$ m

$T = 300$ K

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

$$2.6 \times 10^{-5} = \frac{1}{\sqrt{2} \times 3.14 \times (2.6 \times 10^{-10})^2 \times N^*}$$

$N^* = 1.281 \times 10^{23}\ \text{m}^{-3}$

$N^* = \dfrac{P}{KT}$

$P = 1.281 \times 10^{23} \times 1.38 \times 10^{-23} \times 300$

$P = 530.3$ Pa

76. $V, n, T \rightarrow$ same so $P \rightarrow$ also same

$\sigma \rightarrow$ same

Given $(v_{\text{rms}})\ x = \dfrac{1}{\sqrt{6}}(v_{\text{avg.}})_{\text{CH4}}$

and $\quad v_{\text{rms}} = \sqrt{\dfrac{3\pi}{8}}\ (v_{\text{avg.}})$ so

$$\sqrt{\frac{3\pi}{8}}\ (v_{\text{avg.}})_x = \frac{1}{\sqrt{6}}(v_{\text{avg.}})\text{CH}_4$$

$$\frac{(v_{\text{avg.}})x}{(v_{\text{avg.}})_{\text{CH}_4}} = \sqrt{\frac{8}{3\pi}} \cdot \frac{1}{\sqrt{6}} = \frac{2}{3\sqrt{\pi}}$$

For $X : Z_1 = \sqrt{2}\pi\sigma^2\ (v_{\text{avg.}})_x N^*$

For $CH_4 : Z_1 = \pi\sigma^2\ (v_{\text{avg.}})_{\text{CH4}} N^*$

Since T, P, v, n are same, N^* will also be same.

$$\frac{Z_1(x)}{Z_1(\text{CH}_4)} = \sqrt{2}\frac{(v_{\text{avg.}})_x}{(v_{\text{avg.}})_{\text{CH}_4}} = \sqrt{2} \cdot \frac{2}{3\sqrt{\pi}}$$

$Z_1(x) = Z_1(\text{CH}_4)$.

77. $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

Initially $\dfrac{n_{\text{CH}_4}}{n_{\text{O}_2}} = \dfrac{1}{192}$

Finally $\dfrac{n_{\text{CH}_4}}{n_{\text{O}_2}} = \dfrac{1}{6}$

$$\frac{1}{6} = \frac{1}{192}\left(\sqrt{\frac{32}{16}}\right)^n$$

$32 = 2^{n/2}$

$5 = n/2 \Rightarrow n = 10$ steps

Let initial moles of $CH_4 \rightarrow x$ so after 10 steps

$x\ (0.9)^{10} \times 100 = 1000$

$x = \dfrac{10}{0.36} = 28.78$ mole

Moles of O_2 initially

$= 192 \times 27.78 = 5333.3$ moles

78. (a) Slope of P and T graph is $\dfrac{nR}{V}$

so $\quad \dfrac{n_{\text{Th.}}R}{V} = 3.2 - 1.54 = 1.66$

$\dfrac{n_{\text{exp.}}R}{V} = 2.2875 - 1.25 = 1.0375$

so $\quad \dfrac{n_{\text{exp.}}}{n_{\text{Th.}}} = \dfrac{1.0375}{1.66} = 0.625$

(b) $nA \rightleftharpoons A_n$ with 50% yield

Theoretical increase in pressure with temperature should be 1.66 atm but actually it is 1.0375 only so.

$$1.66 - 1.66 \times 0.5 + \frac{1.66 \times 0.5}{n} = 1.0375$$

$$0.83 + \frac{0.83}{n} = 1.0375 \Rightarrow n = 4$$

79. Each time Sabu sucks air, volume of CO becomes half so

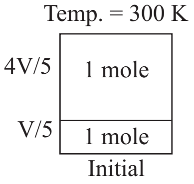
$$5\left(\frac{1}{2}\right)^n < 0.001 \qquad 5(0.5)^n < 0.001$$

$$\log 5 + n \log 0.5 < \log 10^{-3}$$

$$\log 5 - 0.3\,n < -3 \qquad 0.3n > 3 + \log 5$$

$$n > 12.3 \qquad n = 13$$

80. $P_{\text{lower}} = P_{\text{upper}} + P_{\text{piston}}$



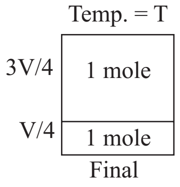
$$5 \times \frac{R \times 300}{V} = \frac{5R \times 300}{4} + P_{\text{piston}}$$

$$\frac{15}{4} \times \frac{R \times 300}{V} = P_{\text{piston}} \qquad \text{(i)}$$

$$P_{\text{lower}} = P_{\text{upper}} + P_{\text{piston}}$$

$$\frac{4RT}{V} = \frac{4RT}{3} + P_{\text{piston}}$$

$$\frac{8RT}{V} = P_{\text{piston}} \qquad \text{(ii)}$$



From Eqs. (i) and (ii)

$$\frac{15}{4} \times \frac{R \times 300}{V} = \frac{8RT}{V} \Rightarrow T = \frac{4500}{32} = 421.9 \text{ K}$$

81. (i) Let initial volume of mixture be V L, then

$H_2 \rightarrow 0.5$ V, CO $\rightarrow 0.45$ V, $CO_2 \rightarrow 0.05$ V

On reaction with excess steam

$$CO \quad + \quad H_2O \rightarrow \quad CO_2 \quad + \quad H_2$$

0.045V – 0.05 V 0.95 V

– – 0.5 V 0.95 V

$0.95\,V = 5$

$V = 5.263$ L

(ii) Molecular mass of initial mixture

$M = 0.5 \times 2 + 0.45 \times 28 + 0.05 \times 44 = 15.8$

$PM = \rho RT$

$1 \times 15.8 = \rho \times 0.0821 \times 273$

$\rho = 0.7$ g/L

(iii) Volume of $CO_2 = 0.5$ V $= 0.5 \times 5.263 = 2.6315$ L

$$\text{Moles of } CO_2 = \frac{2.6315}{22.4} = 0.1174$$

Moles of KOH required = 0.1174 × 2 = 0.2349

Moles of $Ca(OH)_2$ required = 0.1174

Moles of $OH - CH_2 - CH_2 - NH_2$ required

= 0.1174 × 2 = 0.2349

82. (i) Let $n = mT + C$

$2 = 300\,T + C$ and $3 = 200\,T + C$

$$\text{On solving } m = -\frac{1}{100},\ C = 5$$

$$\text{So} \qquad n = \frac{-T}{100} + 5$$

(ii) $$PV = nRT \Rightarrow 1 \times V = \left(\frac{-T}{100} + 5\right)RT$$

$$\Rightarrow \qquad V = -\frac{RT^2}{100} + 5RT$$

(iii) For Maximum volume

$$\frac{dv}{dT} = 0 \Rightarrow \frac{-2RT}{100} + 5R = 0,\ T = 250$$

$$V = \frac{-R(250)^2}{100} + 5 \times 250 \text{ R} = -625 \text{ R} + 1250$$

$R = 625$ R $= 625 \times 0.0821$ L $= 51.3125$ L

83. $$PV = RT - \frac{A}{V} + \frac{2B}{V^2}$$

$$V^3 - \frac{RTV^2}{P} + \frac{A}{P}V - \frac{2B}{P} = 0$$

At critical point $(V - Vc)^3 = 0$

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0$$

so on comparision

$$3V_c^2 = A/P \qquad \text{(i)}$$

$$3V_c = RT/P \qquad \text{(ii)}$$

$$V_c^3 = 2B/P \qquad \text{(iii)}$$

$$\text{On } \frac{\text{(iii)}}{\text{(i)}} \Rightarrow \frac{V_c}{3} = \frac{2B}{A}$$

$= V_c = 6\text{B/A}$

from Eq. (i)

$$3\left(\frac{6B}{A}\right)^2 = AP_c \quad \Rightarrow \quad P_c = \frac{A^3}{108B^2}$$

$$\text{From Eq. (ii) } T_c = \frac{3P_cV_c}{R} = \frac{3}{2}\left(\frac{A^3}{108B^2}\right)\left(\frac{6B}{A}\right)$$

$$T_c = \frac{A^2}{6RB} \Rightarrow Z = \frac{P_cV_c}{RT_c} = \frac{\dfrac{A^3}{108B^2} \cdot \dfrac{6B}{A}}{R \cdot \dfrac{A^2}{6RB}} = \frac{1}{3}$$

84. 760 mm = 76 cm

∴ $V = 76 \times 1 = 76 \text{ cm}^3$

∴ Mass $= V \times d = 76 \times 13.6 = 1033.6$ g

(a) If area of cross section is 2 cm^2 (doubled) then volume is also doubled hence,

$\therefore$ mass = 76 × 2 × 13.6 = 2067.2 g

(b) This mass would rest on twice the area and exert the same pressure.

85. The pressure on the bubble = 1 atm (when it is at the surface.)

The pressure on the bubble = P atm (say) (when it is at the bottom.)

The volume of the bubble = $\frac{1}{6}\pi(0.1)^3$

$$P \times \frac{1}{6}\pi \times (0.1)^3 = 1 \times \frac{1}{6}\pi\,(0.4)^3$$

or $P = 64$ atm. Thus the pressure due to water is 63 atm ($\therefore$ atmospheric pressure = 1 atm)

Now, consider the depth of lake is h cm

$\therefore$ $63 \times 76 \times 13.6 \times g = h \times 1 \times g$

or $h = 63 \times 76 \times 13.6$ cm = 65116.8 cm.

86. For NO gas

$$n\text{NO} = \frac{PV}{RT} = \frac{1.053 \times 250}{0.0821 \times 300 \times 1000} = 1.069 \times 10^{-2}$$

For O_2 gas :- $n_{O_2} = \dfrac{0.789 \times 100}{0.0821 \times 300 \times 1000} = 0.32 \times 10^{-2}$

Now, $2NO + O_2 \longrightarrow N_2O_4$

Mole before reaction: 1.069×10^{-2} 0.32×10^{-2} 0

Mole after reaction: $1.069 \times 10^{-2} - 2 \times 0.32 \times 10^{-2}$ 0 0.32×10^{-2}

$= 0.429 \times 10^{-2}$

Moles of NO left = 4.29×10^{-3}

$P_{NO} \times V = nRT$ Given $T = 220$ K

$$V = \frac{250 + 100}{1000} = \frac{350}{1000}\text{litre}$$

$$P_{NO} \times \frac{350}{1000} = 4.29 \times 10^{-3} \times 0.821 \times 220$$

P_{NO} (left) = 0.221 atm.

87.

	N_2	$+$	$3H_2$	$\rightleftharpoons$	$2NH_3$
Initially	1		3		0
at equilibrium	$(1 - x)$		$3\,(1 - x)$		$2x$

Total moles = $1 - x + 3 - 3x + 2x = (4 - 2x)$ moles

Given Average molecular mass = $\frac{34}{3}$

$$\frac{34}{3} = \frac{28(1-x) + 2(3-3x) + 17(2x)}{(4-2x)}$$

$$\frac{34}{3}(4 - 2x) = 34 \Rightarrow 4 - 2x = 3 \Rightarrow x = 1/2$$

So total number of moles = 3

$$PV = nRT \Rightarrow \frac{nRT}{V} = \frac{3 \times 0.821 \times 300}{8.21} = 9 \text{ atm}$$

$$p_{N_2} = \frac{1-x}{3} \times P = \frac{0.5}{3} \times 9 = 1.5 \text{ atm}$$

$$p_{H_2} = \frac{3-3x}{3} \times P = \frac{1.5}{3} \times 9 = 4.5 \text{ atm}$$

88. The aqueous tension remains same in both the flask. Also flasks are at same temperature.

$\therefore$ $P_1V_1 = P_2V_2$

where $P_1 = 200 - 93 = 107$ mm

$V_1 = 1$ ltr

$V_2 = 2$ ltr

$\therefore$ $107 \times 1 = P \times 2$

$P = 53.5$ mm

Since aqueous tension is also present in flask, it is equivalent to 93 mm.

$\therefore$ pressure of gaseous mixture = 93 + 53.5 = 146.5 mm-Hg.

89. Partial pressure of CH_4, (p_{CH_4}) = 1 atm

Partial pressure of O_2, (p_{O_2}) = 4 atm

$$\therefore \quad \text{moles of } CH_4 \text{ present, } (n_{CH_4}) = \frac{1 \times 0.5}{RT} = \frac{0.5}{RT}$$

$$\therefore \quad \text{moles of } O_2 \text{ present } (n_{O_2}) = \frac{4 \times 0.5}{RT} = \frac{2}{RT}$$

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l)$$

Initially	$\frac{0.5}{RT}$	$\frac{2}{RT}$	
Finally	–	$\frac{1}{RT}$	$\frac{0.5}{RT}$

After the reaction, moles of residual O_2

$$= \frac{2}{RT} - \frac{1}{RT} = \frac{1}{RT}$$

After the reaction, moles of CO_2 produced = $\frac{0.5}{RT}$

Hence total number of moles of O_2 and CO_2 = $\frac{1.5}{RT}$

$\therefore$ total pressure due to O_2 and $CO_2 = \dfrac{1.5}{RT} \times \dfrac{RT}{0.5} = 3$ atm

$\therefore$ pressure exerted by the entire gaseous components

$$= 3 + \frac{26.7}{760} = 3 + 0.03513 = 3.0513 \text{ atm}$$

90. M (dry air)

$$= \frac{M_1(O_2)X_1(\%\text{ of } O_2) + M_2(N_2)X_2(\%\text{ of } N_2)}{X_1 + X_2}$$

$$= \frac{32 \times 24.5 + 28 \times 75.5}{100} = 28.98 \text{ g mol}^{-1}$$

$$d\text{ (dry air)} = \frac{PM_{(\text{air})}}{RT} = \frac{1 \times 28.98}{0.0821 \times 298}$$

$$= 1.184 \text{ g L}^{-1} = 1.184 \text{ kg m}^{-3}$$

$$\left(\because 1\text{ g } L^{-1} = \frac{10^{-3}\text{kg}}{10^{-3}\text{m}^3} = 1 \text{ kg m}^{-3}\right)$$

Relative humidity (50%)

$$= \frac{\text{Partial pressure of } H_2O \text{ in air}}{\text{Vapour pressure of } H_2O}$$

$\therefore \quad P(H_2O) = 0.50 \times 23.7$ Torr

$$= 11.85 \text{ torr} = \frac{11.85}{760} \text{ atm} = 0.0156 \text{ atm}$$

$$\% \text{ of } H_2O \text{ vapour in air} = \frac{0.0156 \times 100}{1} = 1.56\%$$

% of N_2 and O_2 in air = 98.44%

M (wet air)

$$= \frac{28.98 \times 98.44(\text{air}) + 18 \times 1.56 \text{ (water vapour)}}{100}$$

$= 28.81 \text{ g mol}^{-1}$

$$d \text{ (wet air)} = \frac{PM_{(\text{wet air})}}{RT} = \frac{1 \times 28.81}{0.0821 \times 298}$$

$$= 1.177 \text{ g L}^{-1} = 1.177 \text{ kg m}^{-3}$$

Difference = 1.184 – 1.177 = 0.007 kg m^{-3}

91. Partial pressure of C_4H_{10} $(p_1) = 760$ mm Hg

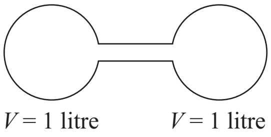
By Dalton's law of partial pressure, $P_{\text{total}} = p_1 + p_2$

$1920 = 760 + p_2$ or $p_2 = 1160$ mm Hg

$p_2 = x_2 \times p_{\text{total}}$

where x_2 = mole fraction of Ne

$$x_2 = \frac{p_2}{P_{\text{total}}} = \frac{1160}{1920} = 0.60;$$



$$\text{Moles of Ne} = \frac{8.6787}{20.2} = 0.43$$

$$x_2 = \frac{n_2}{n_1 + n_2}; \; 0.60 = \frac{0.43}{0.43 + n_1} \Rightarrow n_1 = 0.28$$

Molecular weight of C_4H_{10} = 48 + 10 = 58.

So, amount of C_4H_{10} = n1 × 58 = 16.24 g

Again for C_4H_{10}

$PV = \text{n1RT}$; $T = 273 + 25 = 298$ K,

$$P = \frac{760}{760} \text{atm} = 1 \text{ atm}$$

$$V = \frac{n_1RT}{P} = \frac{0.28 \times 0.0821 \times 298}{1} = 6.85 \text{ L}$$

92. For mixture, $P = (730/760)$ atm,

$T = 303$ K, $\quad d = 150$ g litre^{-1}

$\therefore \quad PV = nRT = (w/M)\, RT \Rightarrow P(w/VM)\, RT$

$$\Rightarrow \quad P = \frac{d}{M} RT$$

$$\therefore \quad \frac{730}{760} = \frac{1.50}{M} \times 0.0821 \times 303$$

$\therefore \quad M = 38.85$

Let $n1$ moles of CO and $(100 - n_1)$ moles of CO_2 be present in 100 moles.

$\therefore$ average molecular weight (M)

$$= \frac{n_1 \times 28 + (100 \times n_1) \times 44}{100} = 38.85 \Rightarrow n1 = 32.19$$

$\therefore$ mole % of CO = 32.19, and mole % of CO_2 = 67.81.

93. The molar ratio of oxygen and the other gas in the evacuated bulb is 1 : 1 and the total pressure of the gas mixture is 4000 mm. Hence the partial pressure of each gas is 2000 mm.

The drop in the pressure of oxygen after 74 minutes,

$$= \frac{(2000 - 1500) \times 74}{47} = 787.2 \text{ mm of Hg}$$

$\therefore$ after 74 minutes, the pressure of oxygen = 2000 – 787.2 = 1212.8 mm of Hg.

Let the rate of diffusion of other gas be r_n, then

$$\frac{r_n}{r_{O_2}} = \sqrt{\frac{32}{79}}$$

$\therefore$ drop in pressure for the other gas = $787.2 \times \sqrt{\frac{32}{79}}$ = 501.01 mm of Hg.

$\therefore$ pressure of the other gas after 74 minutes = 2000 – 501.01 mm = 1498.99 mm of Hg.

$$\text{Molar ratio} = \frac{\text{Moles of unknown gas}}{\text{Moles of } O_2} = \frac{1498.99}{1212.8}$$

$= 1.236 : 1$

94. **(a)** Under low pressure region, V is high

$\therefore \quad (V - b) \approx V$

$$\left(P + \frac{a}{V^2}\right)V = RT$$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} + \frac{a}{RTV} = 1$$

$$Z = \frac{PV}{RT} = \left(1 - \frac{a}{RTV}\right) = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

(b) Under high pressure region, P is high,

$$\left(P + \frac{a}{V^2}\right) \approx P$$

$\therefore \quad P(V - b) = RT$

$PV - Pb = RT$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\therefore \quad Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}\left(\because \frac{PV}{RT} = 1, \text{ or } \frac{P}{RT} = \frac{1}{V}\right)$$

$$Z = 1 + \frac{b}{V} = 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004$$

95. **(b, d)**

$$\frac{\gamma_{He}}{\gamma_{CO}} = \sqrt{\frac{M_{CO}}{M_{He}}} = \sqrt{\frac{28}{4}} = \sqrt{7} = 2.65$$

$$\frac{\gamma_{He}}{\gamma_{SO_2}} = \sqrt{\frac{64}{4}} = \sqrt{16} = 4$$

96. **(a, c, d)**

$$\Delta G = RT \ln \frac{P_2}{P_1}$$

$$= 8.314 \times 298 \times 2.303 \log \frac{2}{1}$$

$$\Delta S = -R \ln \frac{P_2}{P_1} < 0$$

97. **(a, c, d)**

$$\frac{r_{vap.}}{l_{O_2}} = \sqrt{\frac{32}{M_{vap.}}} \Rightarrow \left(\frac{4}{3}\right)^2 = \frac{32}{M_{vap.}}$$

$$M_{vap.} = 18$$

$$\Rightarrow \quad \text{V.D} = 9 \Rightarrow \text{Density} = \frac{18}{22.4} \text{ gram/ltr}$$

$$= 0.8035 \text{ gram/ltr}$$

Now,

$$Z = \frac{PV}{nRT} = \frac{P}{\frac{W}{MV}RT} = \frac{PM}{dRT} \Rightarrow Z = \frac{18P}{dRT}$$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. $PV = nRT$ (number of moles $= nV$)

   $\therefore \quad n/V = P/RT$

2. Value of gas constant

   $(R) = 0.0821\ L \text{ atm } K^{-1}\text{mol}^{-1}$

   $= 8.314 \times 10^7 \text{ ergs } K^{-1}\text{mol}^{-1}$

   $= 8.314 \text{ JK}^{-1}\text{mol}^{-1} = 1.987 \text{ cal } K^{-1}\text{mol}^{-1}$

3. $$\frac{\text{K.E. of neon at } 40°\text{C}}{\text{K.E. of neon at } 20°\text{C}} = \frac{\frac{3}{2}K \times 313}{\frac{3}{2}K \times 293} = \frac{313}{293}$$

4. In van der waal's equation, '*b*' is for volume correction.

5. The expression of root mean square speed is

   $$U_{rms} = \sqrt{\frac{3RT}{M}}$$

   Hence,

   $$\frac{U_{rms}(H_2)}{U_{rms}(O_2)} = \left[\frac{3R(50\text{ K})/(2\text{g mol}^{-1})}{3R(800\text{ K})/(32\text{g mol}^{-1})}\right]^{1/2} = 1$$

6. Under identical condition, $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

   As rate of diffusion is also inversely proportional to time, we will have, $\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$

   (a) This, for He, $t_2 = \sqrt{\frac{4}{2}}(5\text{s}) = 5\sqrt{2}\text{ s} \neq 10\text{ s}$

   (b) For O_2, $t_2 = \sqrt{\frac{32}{2}}(5\text{s}) = 20\text{ s}$

   (c) For CO, $t_2 = \sqrt{\frac{28}{2}}(5\text{s}) \neq 25\text{ s}$

   (d) For CO_2, $t_2 = \sqrt{\frac{44}{2}}(5\text{s}) \neq 55\text{ s}$

7. $$\begin{array}{lcl} N_2O_4 & \rightleftharpoons & 2NO_2 \\ 1 - 0.2 & & 2 \times 0.2 \\ 0.8 \text{ mole} & & 0.4 \text{ mole} \end{array}$$

   $n_T = (0.8 + 0.4)$ mole $= 1.2$ mole

   $$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ at 300 K}$$

   $$\frac{1}{300} = \frac{P_2}{600}$$

   $\therefore \quad P_2 = 2 \text{ atm} = P_{N_2O_4}$ at 600 K

   or Pressure of 1 mole N_2O_4

   $\therefore$ Pressure of 1.2 mole gas (N_2O_4 and NO_2)

   $= 1.2 \times 2 = 2.4$ atm

8. $B = b - \frac{a}{RT}$

   Derivation of Boyles Temperature.

9. According to Graham's law of diffusion, for two gases undergoing diffusion at different pressures throught same hole

   $$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \times \frac{P_A}{P_B}$$

   $$\left(r \propto P \times \sqrt{\frac{1}{M}} \text{ At constant temperature}\right)$$

10. Weight of gas = 50.5 – 50

    $$\therefore \quad V = \frac{148 - 50}{0.98} = 100 \text{ ml}$$

    Using, $PV = nRT = \frac{w}{m}RT$

    $$\frac{760}{760} \times \frac{100}{1000} = \frac{0.5}{\text{m}} \times 0.082 \times 300 \left[n = \frac{0.5}{m}\right]$$

    $\therefore \quad$ molecular weight of gas (m) = 123

11. Van der Waal's equation for *n* moles of gas is

    $$\left[P + \frac{n^2a}{V^2}\right][V - nb] = nRT$$

Given: $V = 4$ ltr; $P = 11.0$ atm, $T = 300$ K;
$b = 0.05$ ltr mol^{-1}, $n = 2$

Thus, $\left[11+\frac{2^2 a}{4^2}\right]$ $[4 - 2 \times 0.5] = 2 \times 0.082 \times 300$

$\therefore \quad a = 6.46$ atm ltr^2 mol^{-2}

12. We know that

$$\frac{r_1}{r_2}=\sqrt{\frac{M_2}{M_1}}\times\frac{P_1}{P_2} \text{ or } \frac{n_1}{t_1}\times\frac{t_2}{n_2}=\sqrt{\frac{M_2}{M_1}}\times\frac{P_1}{P_2}$$

$$\text{or} \quad \frac{1}{38}\times\frac{57}{1}=\sqrt{\frac{M}{28}}\times\frac{0.8}{1.6}$$

$\therefore \quad M = 252$

$$\left[\begin{array}{l}\mathrm{Xe}+(\mathrm{F})_x=252\\ 131+19x=252;\therefore x=6\end{array}\right.$$

Thus compound of xenon with fluorine is XeF_6.

13. For an ideal gas behaviour, the molecules of a gas should be far apart. The factors favouring this condition are high in temperature and low in pressure.

14. Compressibility factor of ideal gas $(Z) = \frac{PV}{nRT}$
For one mole of ideal gas at STP,

$$Z=\frac{P\times 22.4}{RT}$$

For given gases $Z < 1$ and $Z=\frac{P\times V_m}{RT}$

$\therefore \quad Vm < 22.4$ ltr

Alternate solutions

$(PV)_{\text{Observed}}/(PV)_{\text{Ideal}} < 1$

$\Rightarrow \quad V_{\text{obs}} < V\text{ideal}, V\text{obs} < 22.4$ ltr

15. We know

$$U_{\text{rms}}=\sqrt{\frac{3RT}{M}}$$

$$\sqrt{\frac{3RT_{H_2}}{2}}=\sqrt{7}\sqrt{\frac{3RT_{N_2}}{28}}$$

$\therefore \quad T_{N_2}=2T_{H_2} \quad$ or $\quad T_{N_2}>T_{H_2}$

16. Van der Waal's equation for one mole of a gas is

$$\left[P+\frac{a}{V^2}\right](V-b)=RT \qquad \text{(i)}$$

Given that volume occupied by CO_2 molecules, 'b' = 0

Hence, Eq. (i) becomes

$$\left[P+\frac{a}{V^2}\right]V=RT \quad \text{or} \quad P=\frac{RT}{V}-\frac{a}{V^2}$$

Using $R = 0.082$, $T = 273$ K, $V = 22.4l$ for 1 mole of an ideal gas at 1 atm pressure

$$\therefore \quad P=\frac{0.082\times 273}{22.4}-\frac{3.592}{(22.4)^2}=0.9922 \text{ atm}$$

17. We know that, compressibility factor, $Z=\frac{PV}{RT}$

$$0.5=\frac{100\times V}{0.082\times 273}$$

$\therefore \quad V = 0.1119$ L

> **Note:** Further when volume of a gas molecule is negligible, Van der Waal's equation becomes
>
> $$\left(P+\frac{a}{V^2}\right)(V-0)=RT$$
>
> or $PV = RT - \frac{a}{V}$ or $a = RTV - PV^2$
>
> Substituting the values,
>
> $a = (0.082 \times 0.1119 \times 273)$
> $- (100 \times 0.1119 \times 0.1119)$
> $= 1.253$ and L^2 mol^{-2}

18. (a) $d = 0.36$ kgm^{-3} = 0.36 g/L

(i) From Graham's law of diffusion

$$\frac{r_v}{r_{O_2}}=\sqrt{\frac{M_{O_2}}{M_v}};1.33=\sqrt{\frac{32}{M_v}}$$

$$\therefore \quad M_v=\frac{32}{(1.33)^2}=18.09$$

where $Mv = MW$ of the vapour

(ii) Thus, 0.36 g = $\frac{0.36}{18.09}$ mol

$\frac{0.36}{18.09}$ mol occupies 1 L volume, so 1 mole occupies

$$\frac{18.09}{0.36}\text{L} = 40.25 \text{ L}$$

Thus, molar volume of vapour = 50.25 L.
Assuming ideal behaviour the volume of the vapour can be calculated by

$$\frac{V_1}{T_1}=\frac{V_2}{T_2}\Rightarrow V_2=22.4\times\frac{500}{273}=41.05 \text{ L}$$

(iii) Compressibility factor (Z)

$$=\frac{(PV)_{\text{obs}}}{(PV)_{\text{ideal}}}=\frac{1\times 50.25}{1\times 41.025}=1.224$$

(iv) Z is greater than unity, hence it is the short range repulsive force that would dominate.
($\because$ actual density is less than given density.)

(b) $E=\frac{3}{2}KT=\frac{3}{2}\times\frac{8.31}{6.02\times 10^{23}}\times 1000$
$= 2.07 \times 10^{-20}$ J per molecule
($\because$ K, Boltzmann constant = R/NA)

19. TIPS/Formulae:

$$V_{\text{rms}} = \sqrt{\frac{3RT}{M}}, C_{\text{av}} = \sqrt{\frac{8RT}{\pi M}}$$

$$\frac{V_{\text{rms}}}{V_{\text{av}}} = \sqrt{\frac{3RT}{M}} \times \sqrt{\frac{\pi M}{8RT}} = \sqrt{\frac{3\pi}{8}} = 1.085$$

$$V_{\text{rms}} = 1.085 \times C_{\text{av}} = 1.085 \times 400 = 434 \text{ ms}^{-1}$$

20. For positive deviation : $PV = nRT + nPb$

$$\Rightarrow \quad Z = 1 + \frac{Pb}{RT}$$

Thus, the factor nPb is responsible for increasing the PV value. Above ideal value, b is actually the effective volume of molecule. So, it is the finite size of molecules that leads to the origin of b and hence positive deviation at high pressure.

21. The Van de Waal equation (for one mole) of a real gas is

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT$$

$$PV_m = RT + Pb - \frac{a}{V_m} + \frac{ab}{V_m^2} \qquad \text{(i)}$$

Note:
To calculate the intercept $P \rightarrow 0$, hence $V_m \rightarrow \infty$ due to which the last two terms on the right side of the equation (I) can be neglected.

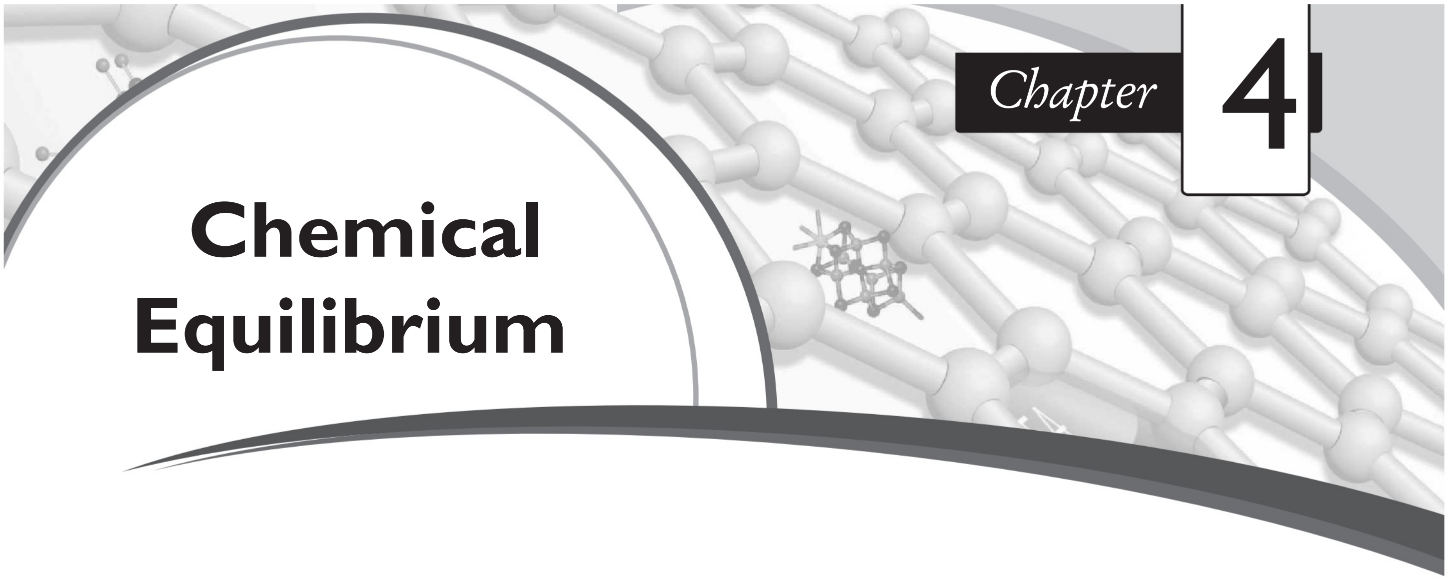
$\therefore \qquad PV_m = RT + Pb$

When $P = 0$, intercept $= RT$

22. TIPS/Formulae:
Using Grahms' law of diffusion,

$$\frac{r_{\text{He}}}{r_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} = \sqrt{\frac{16}{4}} = 2$$

23. For gas A, $a = 0$, $Z = 1 + \frac{Pb}{RT}$ implies Z varies linearly with pressure.
For gas B, $b = 0$, $Z = 1 - \frac{a}{VRT}$. Hence, Z does not vary linearly with pressure.



Chapter 4

Chemical Equilibrium

Key Concepts

DEPENDENCY OF EQUILIBRIUM CONSTANT ON TEMPERATURE

$$K_{\text{eq}} = \frac{K_f}{K_b} = \frac{A_f e^{-\frac{E_{af}}{RT}}}{A_b e^{-E_{ab}/RT}}$$

Arrhenius Equation

$K = Ae^{-Ea/RT}$

K = Rate constant or Velocity constant or Specific reaction rate

A = Arrhenius constant or Frequency Factors or Preexponential factor **Ea** = activation energy

Significance of A

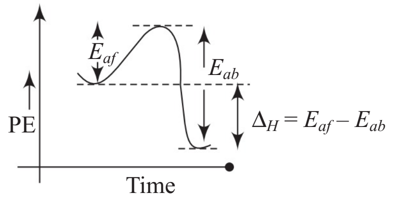
A gives us number of reactant molecules colliding in unit time in unit volume.

'A' for a particular reaction is constant and is independent of temperature.

For a particular reaction E_a is constant and is independent of temperature.

$$\boxed{K = f(T) \text{ only}}$$

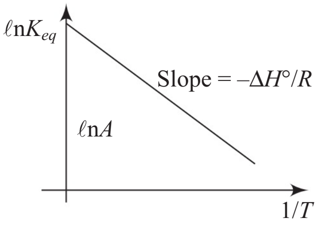
$$K_{\text{eq}} = Ae^{-\frac{1}{RT}(E_{af} - E_{ab})}$$



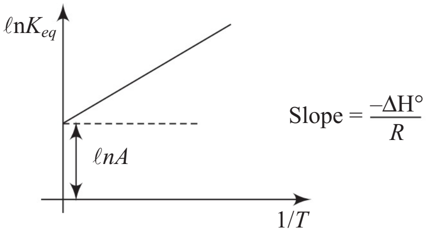
$$\boxed{K_{\text{eq}} = Ae^{-\frac{\Delta H^\circ}{RT}}} \quad \text{...(1)}$$

$$\boxed{\ell n\ K = \ell nA - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T}} \quad \text{...(2)}$$

If $\Delta H^\circ > 0$



If $\Delta H^\circ < 0$



Equation (2) is known as Van't Hoff Equation (Integral)
Differentiate equation (2) with respect to temperature.

$$\frac{d(\ell nK_{\text{eq}})}{dT} = \frac{+\Delta H^\circ}{R} \cdot \frac{1}{T^2}$$

$$\ell n\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Thermodynamics of Equilibrium constant

$$\Delta G = \Delta H - T\Delta S$$

$$-nFE \text{ cell}$$

$$= -W \text{ useful}$$

$$\boxed{\Delta G = \Delta G^\circ + RT\ell n\, Q} \qquad ...(1)$$

$\Delta G < 0 \Rightarrow$ Spontaneous or Irreversible

$\Delta G = 0 \Rightarrow$ Reversible at equilibrium

$\Delta G > 0 \Rightarrow$ Non-Spontaneous

At equilibrium

$$\Delta G = 0$$

$$Q_{\text{eq}} = K_{\text{eq}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad ...(2)$$

$$= -nFE^\circ$$

$$= -RT \ln K_{\text{eq}} \qquad ...(3)$$

If $\mathbf{\Delta G^\circ > 0} \Rightarrow \ln K_{\text{eq}} < 0 \Rightarrow K_{\text{eq}} < 1 \Rightarrow K_f < K_b$

$\mathbf{\Delta G^\circ = 0} \Rightarrow \ln K_{\text{eq}} = 0 \Rightarrow K_{\text{eq}} = 1 \Rightarrow K_f = K_b$

$\mathbf{\Delta G^\circ < 0} \Rightarrow \ln K_{\text{eq}} > 0 \Rightarrow K_{\text{eq}} = 1 \Rightarrow K_f > K_b$

Equating Equations (2) and (3);

$$-RT \ln K_{\text{eq}} = \Delta H^\circ - T\Delta S^\circ$$

$$\boxed{\ell n\, K_{\text{eq}} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}} \qquad ...(4)$$

Calculation of Equilibrium Constant

	$PCl_5(g)$	$\rightleftarrows$ $PCl_3(g)$	$+Cl_2(g)$
Initial moles:	a	—	—
At Equilibrium	$(a-x)$	x	x
Equi.[Conc] =	$\frac{\text{moles}}{v}\ \frac{(a-x)}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{(x/v)(x/v)}{\left(\frac{a-x}{v}\right)}$$

$$K_C = \frac{x^2}{v(a-x)}$$

(b)

	$PCl_5(g)$	$\rightleftarrows$ $PCl_3(g)$	$+Cl_2(g)$
Initial moles :	a	–	–
At Equilibrium	$a(1-\alpha)$	$a\alpha$	$a\alpha$
Concentration	$\frac{a(1-\alpha)}{v}$	$\frac{a\alpha}{v}$	$\frac{a\alpha}{v}$

α = degree of dissociation

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{\left(\frac{a\alpha}{v}\right)\left(\frac{a\alpha}{v}\right)}{\left(\frac{a(1-\alpha)}{v}\right)}$$

$$K_C = \frac{a\alpha^2}{v(1-\alpha)}$$

$$K_P = K_C(RT)^1$$

	PCl_5	$\rightleftharpoons$ PCl_3	$+\ Cl_2$
Initial Pressure	P_0	—	—
At equilibrium	$P_0(1-\alpha)$	$P_0\alpha$	$P_0\alpha$

$$P_t = P_{\text{eq}} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2}$$

$$P_t = P_{\text{eq}} = P_0(1+\alpha)$$

$$P_0 = \frac{P_{\text{eq}}}{(1+\alpha)}$$

$$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{P_{0\alpha}\cdot P_{0\alpha}}{P_0(1-\alpha)} = \frac{\alpha^2}{(1-\alpha)}\cdot P_0$$

$$K_P = P_{\text{eq.}}\cdot\frac{\alpha^2}{1-\alpha^2}$$

	$PCl_5(g)$	$\rightleftharpoons$ $PCl_3(g)$	$+\ Cl_2(g)$
Initial moles	a	–	–
At Equilibrium	$(a-x)$	x	x
Mole Fraction	$\frac{(a-x)}{a+x}$	$\frac{x}{a+x}$	$\frac{x}{a+x}$
Partial Pressure	$\frac{(a-x)}{(a+x)}\cdot P_T$	$\frac{x}{(a+x)}\cdot P_T$	$\frac{x}{(a+x)}\cdot P_T$

$$K_P = \frac{\left(\frac{x}{a+x}P_T\right)^2}{\left(\frac{a-x}{a+x}\right)P_T}$$

$$= \frac{x^2}{a^2-x^2}\cdot P_T$$

$$K_P = \frac{\alpha^2}{1-\alpha^2}\cdot P_T$$

Degree of Dissociation (α) and Equilibrium Vapour Density (d)

	$An(g)$	$\rightleftharpoons$ $nA(g)$
Initial concentration	C	0
Equilibrium concentration	$C(1-\alpha)$	$nC\alpha$

D_0 = Initial vapour density, d = Equilibrium vapour density or vapour density of mixture of An and A at equilibrium

$$\text{Vapour Density} \propto \frac{1}{\text{number of moles}}$$

$$\therefore \quad \frac{D_0}{d} = \frac{n_{\text{eq}}}{n_0} = \frac{c(1-\alpha+n\alpha)}{c}$$

$$\frac{D_0}{d} = 1-\alpha+n\alpha$$

$$\alpha = \frac{\frac{D_0}{d}-1}{n-1}$$

* $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$$D_0 = \frac{\text{Molar Mass of PCl}_5}{2} = \frac{208.5}{2} = 104.25\ n = 2$$

* $SO_3 \rightleftharpoons SO_3 + \frac{1}{2}O_2$

$$D_0 = \frac{\text{Molar Mass of SO}_3}{2} = \frac{80}{2} = 40;\ n = \frac{3}{2}$$

* $2NH_3 \rightleftharpoons N_2 + 3H_2$

$$D_0 = \frac{17}{2};\ n = \frac{4}{2} = 2$$

Degree of Association (α) and Equilibrium Vapour Density (d)

	$nA(g)$	$\rightleftharpoons$	$An(g)$
Initial moles	C		—
at Equilibrium	$C(1-\alpha)$		$\frac{C\alpha}{n}$

$$\frac{D_0}{d} = \frac{C(1-\alpha+\alpha/n)}{C}$$

$$\alpha - \frac{\alpha}{n} = 1 - \frac{D_0}{d}$$

$$\alpha = \frac{\left(1-\frac{D_0}{d}\right)}{\left(1-\frac{1}{n}\right)} = \frac{D_0 - d}{\left(\frac{1}{n}-1\right)d}$$

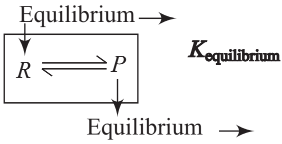
* $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ ($n = 2$)
* $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($n = 2$)
* $2SO_2 + O_2 \rightleftharpoons 2SO_3$ ($n = 3/2$)

Le Chatelier's Principle

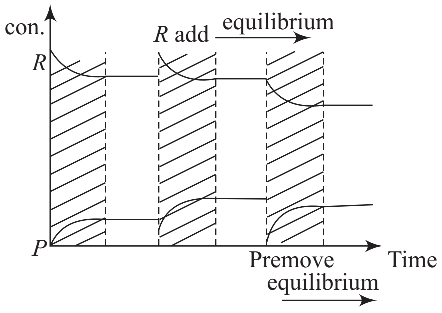
According to *Le Chatelier's* principle when any equilibrium is subjected to change in pressure, temperature, concentration then, equilibrium shifts in a direction so as to nullify the effect.

(i) Effect of Concentration Change

When reactant concentration is increased or product concentration is decreased at equilibrium then, equilibrium always move in the forward direction and vice versa.



$$K_{\text{equilibrium}} = \frac{[P]}{[R]}$$



Addition of inert substance or in active substance has no effect on the equilibrium.

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	$K_{eq} = [CO_2]$
CO_2 Add	– equilibrium shift in backward
$CaCO_3$ add	– no effect
CaO add	– no effect
He/N_2 add	– no effect
(at constant volume)	

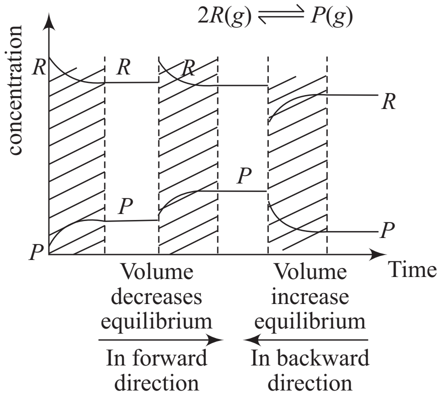
(ii) Effect of Pressure

$$2R(g) \rightleftharpoons P(g)$$

$$P_T = n_T \frac{RT}{V}$$

For gaseous reaction having different gaseous moles on the Left Hand Side and Right Hand Side, if volume is decreased at constant temperature or in other words, pressure is increases then, equilibrium shift in a direction where total number of gaseous moles are less.

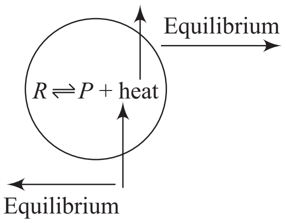
$$2R(g) \rightleftharpoons P(g)$$



(iii) Effect of Temperature

Case (i)

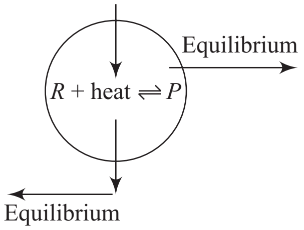
On decreasing temperature exothermic reaction proceed in forward direction



On increasing temperature exothermic reaction proceed in backward direction

Case (ii)

On decreasing temperature endothermic reaction proceed in backward direction



On increasing temperature endothermic reaction proceed in forward direction

(iv) Addition of the Inert Gas at Equilibrium

Case (i) Addition of the inert gas at equilibrium at constant pressure:-

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial mole	1		0		0
at equilibrium	(1-α)		α		α

$$K_C = \frac{\alpha^2}{V(1-\alpha)}$$

where α is the degree of dissociation.
Since V increases and thus to keep K_C constant, α must increases i.e., degree of dissociation of PCl_5 increases or $[PCl_3]$ and $[Cl_2]$ increases at equilibrium and the $[PCl_5]$ decreases at equilibrium

Case (ii) Addition of the inert gas at equilibrium at constant volume:-

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial mole	1		0		0
at equilibrium	(1-α)		α		α

$$K_C = \frac{\alpha^2}{V(1-\alpha)}$$

where α is the degree of dissociation.

Since Volume remains constant during the change and the addition of inert gas at constant volume will also have no influence on the equilibrium concentrations for this type of equilibria

Simultaneous Equilibrium

When two or more than two equilibrium are established together in the same container then, such equilibrium are referred as *simultaneous equilibrium* provided they have atleast one active component common.

Example 1.

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \quad KP_1 = P_{CO_2} = (P_1 + P_2)$
$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g) \quad KP_2 = P_{CO_2} = (P_1 + P_2)$

Example 2.

N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
(P_1)		(P_2)		0
$P_1 - x - y$		$P_2 - 3x - 2y$		$2x$
N_2	+	$2H_2$	$\rightleftharpoons$	N_2H_4
$P_1 - x - y$		$P_2 - 3x - 2y$		y

Example 3.

N_2O_5	$\rightleftharpoons$	N_2O_3	+	O_2
a		0		0
$a - x$		$x - y$		$x + y$
N_2O_3	$\rightleftharpoons$	N_2O	+	O_2
$x - y$		y		$x + y$

$$KP_1 = \frac{x^2 - y^2}{a - x}$$

$$P_{O_2} = x + y, P_{N_2O_3} = x - y$$

Example 4.

$x(s)$	$\rightleftharpoons$	A	+	C	$K_{P_1} = x(x+y)$	...(i)
		x		$x + y$		
$y(s)$	$\rightleftharpoons$	B	+	C	$K_{P_2} = y(x+y)$	...(ii)
		y		$x + y$		

$$\therefore \quad \frac{n_A}{n_B} = \frac{P_A}{P_B} = \frac{x}{y}$$

and $\quad P_T = P_A + P_B + P_C$
$\quad = x + y + (x + y) = 2(x + y)$

Ex. When NO and NO_2 are introduced in a container following equilibrium is simultaneously obtained.

$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad K_P = 6.8 \text{ atm}^{-1}$
$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$

In an experiment NO and NO_2 are mixed in the molar ratio. 1 : 2, the total final pressure was 5.05 atm and the partial pressure of N_2O_4 at equilibrium was 1.7 atm. Calculate the equilibrium P_{NO_2} and Calculate K_P for 2nd reaction.

Sol. $2NO_2(g) \rightleftharpoons \quad N_2O_4(g)$
$2P_0 \quad —$
$(2P_0 - x - y) \quad x/2 \quad \frac{x}{2} = 1.7 = x = 3.4$

$NO + \quad NO_2 \rightleftharpoons \quad N_2O_3$
$(P_0 - y) \quad (2P_0 - x - y) \quad y$

$$K_P = 6.8 = \frac{P_{N_2O_4}}{(P_{NO_2})^2}$$

$$\Rightarrow \quad (P_{NO_2}) = \sqrt{\frac{1.7}{6.8}} = 0.5$$

$(2P_0 - 3.4 - y) = 0.5$
$\Rightarrow \quad 5.7 - 3.4 - y = 0.5 \Rightarrow y = 1.8$
$P_T + P_{NO_2} + P_{NO} + P_{N_2O_3} + P_{N_2O_4}$

$5.05 = 0.5 + (P^o - y) + y + 1.7$

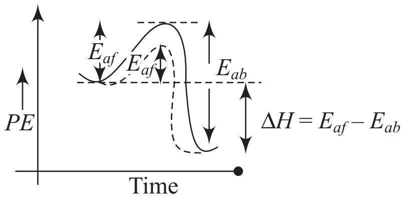
$P_0 = 2.85$

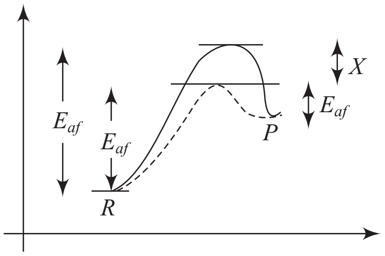
$$K_{P_2} = \frac{y}{P_{NO} \times P_{NO_2}} = \frac{1.8}{1.05 \times 0.5} = 3.43 \text{ atm}^{-1}$$

Effect of Catalyst on the Equilibrium

1. Catalyst alters the reaction mechanism and in the new path activation energy is lowest than the previous one.
2. Catalyst increases the rate of forward and back reaction by same extent.
3. Since, catalyst increases the rate of forward as well as backward reaction, it does not alter the equilibrium concentration of reactants and products.

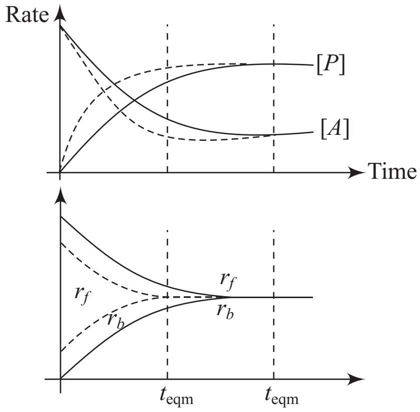
4. Catalyst does not changes the ΔH for the reaction.
5. Catalyst does not affect the equilibrium constant because both K_f and K_b increases.
6. Catalyst reduces the time taken in establishment of equilibrium.





$$K = A^{-E_0/RT} \quad [K' > K]$$

$$K' = Ae^{-(Ea - x)RT}$$



Note: ……………………………

Line in above figure Represent change due to presnce of catalyst.

Kinetic and Equilibrium constant

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$

$$\frac{-d[A]}{df} = \text{rate of disappearance of } A = K_f[A] - k_b[B]$$

at equilibrium

$$\frac{-d[A]}{df} = 0 \quad \Rightarrow \quad K_f[A] = K_b[B]$$

$$\Rightarrow \quad \frac{K_f}{K_b} = \frac{[B]}{[A]} = K_{\text{eq}}$$

$$\frac{+d[B]}{dt} = K_f[A] - K_b[B]$$

rate of formation of B at equilibrium

$$\frac{d[B]}{dt} = 0$$

$$K_f[A] = K_b[B]$$

THREE PHASE DIAGRAM

$$dG = Vdp - SdT$$

for chemical reaction

$$d(\Delta G) = \Delta V \cdot dp - \Delta S \cdot dT$$

at equilibrium: $\Delta G = 0$

$$\Delta V\, dp = \Delta S\, dT$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \longrightarrow \text{Claussius Claperpron Equation}$$

$$H_2O(R) \rightleftharpoons H_2O(g)$$

(1) $H_2O(l) + \text{heat} \rightleftharpoons H_2O(g)$

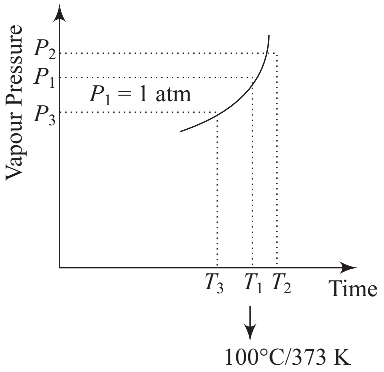
(a) On increasing temperature reaction proceed in forward direction. On decreasing temperature reaction proceed in back ward direction.

(b) On increasing pressure reaction proceed in backward direction. On decreasing temperature reaction proceed in forward direction.

BOILING POINT

The temperature at which vapour pressure of any liquid is equal to external pressure (surrounding pressure) is known as boiling point.

If external pressure is 1 atm then, boiling point is known as normal boiling point. (See figs.)



Pressure ∝ Boiling Point

THRIPLE POINT

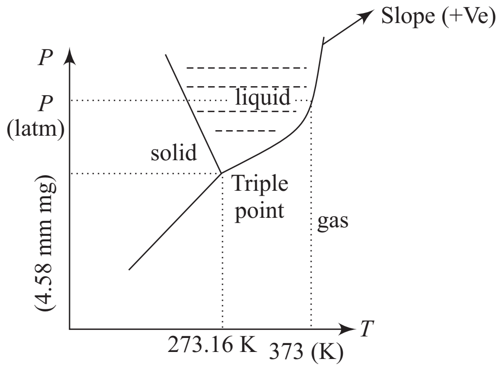
$$\frac{dP}{dt} = \frac{\Delta S}{\Delta V}\frac{(+Ve)}{(+Ve)}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H}{T}$$

$$\Delta V = V_g - V_1 \simeq Vg = \frac{ngRT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T} \times \frac{P}{n_g RT} = \frac{\Delta H_m \cdot P}{RT^2}$$



On separting variables;

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_m}{R} \int_{T_1}^{T_2} \frac{1}{T^2} \cdot dT$$

$$\ell n \frac{P_2}{P_1} = \frac{\Delta Hm}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

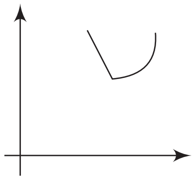
TROUTON'S RULE

1. For majority of the liquids, molar entropy change of vapours.

$$\Delta S_m \simeq 10.5R$$
$$\simeq 88 \text{ J/K-mole}$$

$$\Delta S_m = \frac{\Delta H_m}{T_B}$$

2. $H_2O(S) + \text{heat} \rightleftharpoons H_2O(l)$
   On increasing pressure to a physical equilibrium, equilibrium always shifts in a direction where density increases.
   On increasing Pressure melting point of ice decreases
   becaus slope $= \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{(+\text{ve})}{[V_l - V_s]^{\rightarrow(-\text{ve})}} \Rightarrow (-\text{ve})$
3. $Na(S) + \text{heat} \rightleftharpoons Na(l)$
   $$\frac{dP}{dT} = \frac{\Delta S\,(+\text{ve})}{\Delta V\,(+\text{ve})}$$
   On increasing pressure, melting point will increase.
4. $H_2O(S) + \text{heat} \rightleftharpoons H_2O(g)$
   $$\frac{dP}{dT} = \frac{\Delta S\,(+\text{ve})}{\Delta V\,(+\text{ve})}$$



5. $KOH(S) + H_2O(l) \rightleftharpoons KOH\ (aq.) + \text{Heat}$
   on increasing temperature
   Solubility of KOH decreases
6. $NaCl(S) + H_2O(l) + \text{heat} \rightleftharpoons NaCl(aq.)$
   on increasing temperature
   Solubility of NaCl increases
7. $A(g) + \text{Solvent} \rightleftharpoons A(\text{Solution}) + \text{heat}$
   ($\Delta H < 0$) or Exothermic on increasing temperature solubility of gas decreases on increasing pressure solubility of gas increases

Solved Examples

1. For the reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 300 K, equilibrium constant is 100. If 2 moles of H_2 and 2 moles of I_2 are taken in a 10 L vessel. Calculate the equilibrium concentration of each.

Sol.

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initial moles:	2		2		–
Equ. moles:	$(2-x)$		$(2-x)$		$2x$
Equ. [ ] :	$\frac{(2-x)}{10}$		$\frac{(2-x)}{10}$		$\frac{2x}{10}$

$$K_C = \frac{[HI]^2}{[H_2][I_2]} \quad \text{or}$$

$$100 = \frac{(2x/10)^2}{(2-x/10)(2-x/10)}$$

$$10 = \frac{(2x/10)}{(2-x/10)}$$

$$20 - 10x = 2x$$

$$\therefore \quad x = \frac{5}{3}$$

$$[H_2] = [I_2] = \frac{2-x}{10} = \frac{1}{30}\text{M}$$

$$[HI] = \frac{2x}{10} = \frac{1}{3}\text{M}$$

2. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the equilibrium moles of N_2O_4 and $2NO_2$ are 2 and 1 respectively, in a 10 L container at 300 K. Calculate K_C, K_P.

Sol.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Equ. moles	2		1
Equ. [ ]	$\frac{2}{10}$		$\frac{1}{10}$

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(1/10)^2}{(2/10)} = \frac{1}{20}\text{moles}$$

$$K_P = K_C(RT) = \frac{1}{20}\times(0.0821\times 300)\text{atm} = \frac{24.6}{20}\text{atm}$$

3. For the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ K_C = 100 at any temperature (T). If at equilibrium on same temperature T equilibrium concentration of SO_2 and SO_3 are same in a 10 litre vessel. Calculate equilibrium moles of O_2.

Sol. $$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$[O_2] = \frac{1}{K_C} = \frac{1}{100}$$

Number of moles of O_2 = $\frac{10}{100}$ = 0.1 mole

4. For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ at 400 K and 1 atm; $\alpha = 0.4$. Calculate the density of equilibrium. mixture under given condition in gram per litre.

Sol. $$\alpha = \frac{\frac{D_0}{d} - 1}{n-1}$$

$$\alpha = \frac{\frac{104.25}{d} - 1}{2-1} \quad \Rightarrow \quad 0.4 = \frac{104.25}{d} - 1$$

5. For the reaction : $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ $K_C = 25$. If we take 2 moles of each gases in a 40 litre L vessel. What will be the equilibrium concentration of B.

Sol.

$A(g)$	+	$B(g)$	$\rightleftharpoons$	$C(g)$	+	$D(g)$
2		2		2		2
$2-x$		$2-x$		$2+x$		$2+x$

$$25 = \frac{\left(\frac{2+x}{V}\right)^2}{\left(\frac{2-x}{V}\right)^2}$$

$$5 = \frac{2+x}{2-x}$$

$10 - 5x = 2 + x$

$8 = 7x$

$$x = \frac{8}{7}\text{mole}$$

$$[B] = \frac{2 - \frac{8}{7}}{40} = \frac{6}{280}\text{M}$$

6. Find Kp for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ if initial pressure P_0 and degree of dissociation for reaction is α.

Sol.

$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
P_0		0
$P_0(1-\alpha)$		$2P_0\alpha$

$P_T = P_0(1 + \alpha)$

$$K_P = \frac{(2P_0\alpha)^2}{P_0(1-\alpha)} = \frac{4P_0\alpha^2}{1-\alpha} = 4P_T\frac{\alpha^2}{1-\alpha^2}$$

7. Calculate mole % of Cl at equilibrium for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $K_P = 0.2$ under a total pressure of 2 atm.

Sol.

PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
P_0		–		–
$P_0(1-\alpha)$		$P_0\alpha$		$P_0\alpha$

$$K_P = \frac{P_0\alpha^2}{1-\alpha} = P_T\frac{\alpha^2}{1-\alpha^2}$$

$$X_{Cl_2} = \frac{P_{Cl_2}}{P_T} = \frac{P_0\alpha}{P_0(1+\alpha)} = \frac{\alpha}{(1+\alpha)}$$

mole % of Cl = $(X_{Cl_2}\times 100)$ = 23.07 %

8. Calculate the equilibrium concentration of PCl_3 in a 10 L rigid container if 1 mole of PCl_5 is taken to be certain equilibrium according to the following reaction:

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$K_C = 10^{-5}$

Sol.

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial	1		–		–
at eq. moles	$1-x$		x		x
active mass	$\frac{1-x}{10}$ $\approx\frac{1}{10}$		$\frac{x}{10}$		$\frac{x}{10}$

$$\text{Since}\ \frac{Kc}{\text{Concentration}} < 10^{-3} \therefore 1-x=1$$

$$K_C = 10^{-5} = \frac{(x/10)^2}{(1-x/10)} \Rightarrow 10^{-5} = \frac{x^2}{10}$$

$$x^2 = 10^{-4} = x = 10^{-2}$$

$$[PCl_3] = \frac{x}{10} = 10^{-3}\text{ M}$$

9. Calculate the equilibrium concentration of PCl_3 in a 10 L rigid container if 1 mole of PCl_5 is taken to be certain equilibrium according to the following reaction:

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

If $K_{\text{eqm}} = 10^{-2}$

Sol.

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial	1		–		–
at eq. moles	$1-x$		x		x
active mass	$\frac{1-x}{10}$		$\frac{x}{10}$		$\frac{x}{10}$

$$10^{-2} = \frac{x^2}{10(1-x)}$$

$$x = 0.96$$

$$[PCl_3] = \frac{x}{10} = 0.096\text{ M}$$

10. 23 g of $N_2O_4(g)$ was placed in a 1 L container at 400 K and allowed to attain equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. The total pressure at equilibrium was found to be 11.6 bar, then what will be the partial pressure of NO_2 at equilibrium?

(a) 9.15 bar (b) 4.98 bar
(c) 6.6 bar (d) 8.3 bar

Sol. (c)

$$P = \frac{nRT}{V} = \frac{1}{4} \times 0.083 \times 400 = 8.3 \text{ bar}$$

$$\begin{array}{lll} \therefore & N_2O_4(g) \rightleftharpoons & 2NO_2(g) \\ & 8.3 - x & 2x \\ & 8.3 + x = 11.6 & \\ \therefore & x = 3.3 & \\ \therefore & P_{NO_2} = 2x = 6.6 \text{ bar} & \end{array}$$

11. What is the expression of K_P for the following equilibrium $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$; if initially '$a$' mole of NH_3 is present and at equilibrium 'x' mole of it decomposed and total equilibrium pressure is p?

(a) $\dfrac{27p^2x^4}{16(a-x)^2(a+x)^2}$ (b) $\dfrac{9px^2}{8(a-x)(a+x)}$

(c) $\dfrac{3px^2}{4(a-x)^2}$ (d) $\dfrac{3p^2x^2}{8(a^2-x^2)^2}$

Sol. (a)

$$\begin{array}{lccc} & 2NH_3(g) \rightleftharpoons & N_2(g) & + \quad 3H_2(g) \\ \text{Initially:} & a \text{ mole} & 0 & 0 \\ \text{At equilibrium:} & (a-x) \text{ mole} & \frac{x}{2} \text{ mole} & \frac{3x}{2} \text{ mole} \\ \text{Partial pressure} & \frac{(a-x)}{(a+x)} \times P & \frac{x}{2(a+x)} \times P & \frac{3x}{2(a+x)} \times P \end{array}$$

$$K_P = \frac{(p_{N_2})^1 \times (P_{H_2})^3}{(p_{NH_3})^2} = \frac{27p^2x^4}{16(a-x)^2(a+x)^2}$$

12. $2lCl_{(g)} \rightleftharpoons l_{2(g)} + Cl_{2(g)}$; $K_c = 0.14$

The initial concentration of lCl is 0.78 M. What will be the equilibrium concentration of l_2?

(a) 0.18 M (b) 0.21 M
(c) 0.39 M (d) 0.78 M

Sol. (b)

$$\begin{array}{lccc} 2lCl & \rightleftharpoons \; l_2 & + & Cl_2 \\ 0.78 & 0 & & 0 \\ 0.78 - 2x & x & & x \end{array}$$

$$K = \frac{x \times x}{(0.78 - 2x)^2}$$

$$0.14 = \frac{x^2}{(0.78 - 2x)^2}$$

$$x = 0.21 \text{ M}$$

13. $A + 3B \rightleftharpoons 2C + D$

For this hypothetical reaction, initial moles of A is twice that of B. If at equilibrium moles of B and C are equal then percent of B reacted is:

(a) 10% (b) 20% (c) 40% (d) 60%

Sol. (d)

$$\begin{array}{lccccc} & A & + \; 3B & \rightleftharpoons & 2C & + \; D \\ \text{Initially} & 2a & a & & 0 & 0 \\ \text{At eq}^m & 2a - x & a - 3x & & 2x & x \end{array}$$

and $a - 3x = 2x \quad \therefore \; x = \dfrac{a}{5}$

$$\text{Moles of } B \text{ reacted} = \frac{3x}{a} \times 100 = \frac{3}{5} \times 100 = 60\%$$

14. 2.0 mol of PCl_5 were introduced in a vessel of 5.0 L capacity at a particular temperature. At equilibrium, PCl_5 was found to be 35% dissociated into PCl_3 and Cl_2. The value of K_c for the reaction is

(a) 1.89 (b) 0.377
(c) 0.75 (d) 0.075.

Sol. (c)

$$\text{Moles of } PCl_5 \text{ dissociated} = \frac{2 \times 35}{100} = 0.7$$

Moles of PCl_5 left undissociated = 2 – 0.7 = 1.3 mol

$$[PCl_5] = \frac{1.3}{5} \text{ M}, [PCl_3] = \frac{0.7}{5} \text{ M}, [Cl_2] = \frac{0.7}{5} \text{ M}$$

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{0.7}{5}\right)\left(\frac{0.7}{5}\right)}{\left(\frac{1.3}{5}\right)} = 0.75$$

15. HI was heated in sealed tube at 400°C till the equilibrium was reached. HI was found to be 22% decomposed. The equilibrium constant for $2HI \rightleftharpoons H_2 + I_2$ is

(a) 1.99 (b) 0.0199
(c) 0.0796 (d) 0.282

Sol. (b)

$$\begin{array}{lccc} 2HI & \rightarrow \; H_2 & + & I_2 \\ 1 & 0 & & 0 \\ 1 - x & & & \\ 1 - 0.22 = 0.78 & 0.11 & & 0.11 \end{array}$$

$$x = 22\% \text{ of 1 mole} = \frac{22}{100} \times 1 = 0.22$$

$$K = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.11 \times 0.11}{(0.78)^2} = 0.0199$$

Exercise

LEVEL I

1. The equilibrium constant of a reaction is 20.0. At equilibrium, the rate constant of forward reaction is 10.0. The rate constant for backward reaction is

(a) 0.5 (b) 2.0
(c) 10.0 (d) 200.0

2. At a given temperature, the equilibrium constant for the reactions

$NO\ (g) + \frac{1}{2}\ O_2\ (g) \rightleftharpoons NO_2\ (g)$ and $2\ NO_2\ (g) \rightleftharpoons 2\ NO\ (g) + O_2\ (g)$ are K_1 and K_2 respectively. If K_1 is 4×10^{-3}, then K_2 will be

(a) 8×10^{-3} (b) 16×10^{-3}
(c) 6.25×10^{4} (d) 6.25×10^{6}

3. Equilibrium constant for the reaction : $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl\ (g)$; is correctly given by the expression

(a) $K = \dfrac{[2NOCl]}{[2NO]\,[Cl_2]}$ (b) $K = \dfrac{[NOCl]^2}{[NO]^2\ [Cl_2]}$

(c) $K = \dfrac{[NO]^2\,[Cl]^2}{[NO]^2 + [Cl_2]}$ (d) $K = \dfrac{[NO]^2 + [Cl]^2}{[NOCl]}$

4. Molar concentration of 96 g of O_2 contained in 2 L vessel is

(a) 16 mol L^{-1} (b) 1.5 mol L^{-1}
(c) 4 mol L^{-1} (d) 24 mol L^{-1}

5. In which of the following reactions $K_P > K_C$?

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(c) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

6. At 1000 K, the value of K_P for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 20R, then K_C will be

(a) 0.04 (b) 0.02 (c) 0.01 (d) 0.03

7. For the reaction $N_2O_4 \rightleftharpoons 2NO$, degree of dissociation is α. The number of moles at equilibirum will be

(a) $(1 - \alpha)^2$ (b) $(1 + \alpha)$
(c) 3 (d) 1

8. 4 mole of A are mixed with 4 mole of B, when 2 mole of C are formed at equilibrium according to the reaction, $A + B \rightleftharpoons C + D$. The equilibrium constant is

(a) 4 (b) 1 (c) $\sqrt{2}$ (d) $\sqrt{4}$

9. At a certain temperature, $2HI \rightleftharpoons H_2 + I_2$ only 50% HI is dissociated at equilibrium. The equilibrium constant is

(a) 1.0 (b) 3.0 (c) 0.5 (d) 0.25

10. One mole of ethyl alcohol was treated with one mole of acetic acid at 25°C. 2/3 of the acid changes into ester at equilibrium. The equilibrium constant for the reaction of hydrolysis of ester will be

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

11. For the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressures of CO_2 and CO are 2.0 and 4.0 atm respectively at equilibrium. The K_P for the reaction is

(a) 0.5 (b) 4.0 (c) 8.0 (d) 32.0

12. At 250°C the vapour density of PCl_5 is 100 calculate the degree of dissociation at this temperature

(a) 4 (b) .04 (c) .02 (d) 2

13. 6 gram hydrogen reacts with 9.023×10^{23} chlorine molecules to form HCl. If total pressure of the reaction is 800 mm then what will be the partial pressure of HCl?

(a) 400 mm (b) 533 mm
(c) 600 mm (d) 153.3 mm

14. 20% part of N_2O_4 is dissociated in NO_2 at 1 atmospheric pressure. What is the value of K_p?

(a) 0.29 (b) 16.0
(c) 1.60 (d) None of these

15. In the reaction, $A + B \rightleftharpoons C + D$, the equilibrium constant K is determined by taking 1 mole of A and 1 mole of B as initial amounts. If 2 moles of A and three moles of B are taken, then the equilibrium constant will be

(a) 2 times (b) 3 times
(c) 6 times (d) Unchanged

16. Vaporisation of one mole of PCl_5 is done in a 1 L container. If 0.2 mole Cl_2 is formed at equilibrium, then what will be the value of equilibrium constant?

(a) 0.15 (b) 0.05 (c) 1.78 (d) 0.2

17. $C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$
What will be the effect of pressure on the above equilibrium process?

(a) Remains unaffected
(b) It will go in backward direction
(c) It will go in forward direction
(d) Unpredictable

18. If pressure is increased in the following reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $\Delta H = -22.4$ kcal then the equilibrium will

(a) Be stable
(b) Shift towards left side
(c) Shift towards right side
(d) Shift first towards left side, then right side

19. In which case does the reaction go farthest to completion:

(a) $K = 1$ (b) $K = 10^{10}$
(c) $K = 10^{-10}$ (d) 10^{4}

20. The equilibrium constant K_c for $A_{(g)} \rightleftharpoons B_{(g)}$ is 1.1. means

(a) [A]eq > [B]eq (b) [Aeq] < [B]eq
(c) [Aeq] = 1.1 M (d) [Beq] = 1.1 M

21. 0.1 mole of $N_2O_{4(g)}$ was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of $NO_{2(g)}$ present, if the equilibrium $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, ($K_p = 0.14$) is reached after some time.

(a) 0.34 mole (b) 0.034 mole
(c) 0.14 mole (d) 0.10 mole

22. What concentration of CO_2 be in equilibrium with 2.5 $\times 10^{-2}$ mol L^{-1} of CO at 100°C for the reaction
$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$; $K_C = 5.0$

(a) 0.125 M (b) 12.5 M
(c) 0.125 mole (d) 2.5 M

23. What is the % dissociation of H_2S if 1 mole of H_2S is introduced into a 1.10 litre vessel at 1000 K? K_C for the reaction: $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$ is 1×10^{-6}?

(a) 1.3% (b) 5%
(c) 10% (d) 0.1%

24. In the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts, calculate K_P for reaction.

(a) 12 atm (b) 8 atm
(c) 16 atm (d) 4 atm

25. When $\alpha - D$ glucose is dissolved in water, it undergoes a partial conversion to $\beta - D$ glucose to exhibit mutarotation. This conversion stops when 63.6% of glucose is in β from. Assuming that equilibrium has been attained, calculate K_C for mutarotation.

(a) 1.747 (b) 2.4
(c) 3.0 (d) 1.1

26. For the reaction, $A_{(g)} + 2B_{(g)} \rightleftharpoons 2C_{(g)}$, the rate constants for the forward and the reverse reactions are 1×10^{-4} and 2.5×10^{-2} respectively. The value of equilibrium constant, K for the reaction will be

(a) 1×10^{-4} (b) 2.5×10^{-2}
(c) 4×10^{-3} (d) 2.5×10^{2}

27. At a certain temperature, the equilibrium constant K_c is 16 for the reaction, $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$. If 1.0 mol each of all the four gases is taken in a 1 L container the concentration of NO_2 at equilibrium will be

(a) 1.6 mol L^{-1} (b) 0.8 mol L^{-1}
(c) 0.4 mol L^{-1} (d) 0.6 mol L^{-1}

28. The following reactions are known to occur in the body:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^{-1}$$

If CO_2 escapes from the system

(a) pH will decrease
(b) Hydrogen ion concentration will diminish
(c) H_2CO_3 concentration will remain unchanged
(d) The forward reaction will be favoured

29. For which of the following reactions, the degree of dissociation cannot be calculated from the vapour density data?

I. $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$
II. $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$
III. $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$
IV. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

(a) I and III (b) II and IV
(c) I and II (d) III and IV

30. In the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ the value of the equilibrium constant depends on

(a) volume of the reaction vessel
(b) total pressure of the system
(c) the initial concentration of nitrogen and hydrogen
(d) the temperature

31. In the equilibrium reaction involving the dissociation of $CaCO_{3.}CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (g) the equilibrium constant is given by

(a) $\dfrac{P_{CaO} \times P_{CO_2}}{P_{CaCO_3}}$ (b) $C_{CaO} \times \dfrac{P_{CO_2}}{C_{CaCO_3}}$
(c) $\dfrac{P_{CaO}}{P_{CaCO_3}}$ (d) P_{CO_2}

32. Consider the reaction, PCl_5 (g) $\rightleftharpoons$ PCl_3 (g) + Cl_2(g) in a closed container at equilibrium at a fixed temperature. What will be the effect of adding more PCl_5 on the equilibrium concentration of Cl_2(g)?

(a) It decreases
(b) It increases
(c) It remains unaffected
(d) It cannot be predicted without the value of K_p.

33. In which of the following options does the reaction go almost to completion?

(a) $K = 10^6$ (b) $K = 10^3$
(c) $K = 10^{-6}$ (d) $K = 10^{-12}$.

34. XY_2 dissociates as $XY_2(g) \rightleftharpoons XY(g) + Y(g)$. When the initial pressure is 600 mm of Hg, the total pressure at equilibrium developed is 800 mm of Hg. Therefore pressure of Y at equilibrium is

(a) 200 (b) 50 (c) 100 (d) 150

35. For the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ the concentration of each substance is $[SO_2] = 0.60$M, $[O_2] = 0.82$M and $[SO_3] = 1.90$M, the K_c is

(a) 1.2229 mol L^{-1} (b) 12.229 mol L^{-1}
(c) 6.1145 mol L^{-1} (d) 18.22 mol L^{-1}

36. Find out the value of K_C for each of the following equilibria from the value of K_P:

(i) $2NOCl$ (g) $\rightleftharpoons$ 2NO (g) + Cl_2 (g); $K_P = 1.8 \times 10^{-2}$ at 500 K
(ii) $CaCO_3$ (s) $\rightleftharpoons$ CaO(s) + CO_2(g); K_p= 167 at 1073 K

The value of K_c are respectively

(a) 4.4×10^{-4} and 1.90 (b) 8.8×10^{-4} and 3.8
(c) 4.4×10^{4} and 1.90 (d) 8.8×10^{4} and 3.8

37. For the following equilibrium, $K_C = 6.3 \times 10^{14}$ at 1000 K

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_C, for the reverse reaction?

(a) 15.9×10^{-15} (b) 1.59×10^{-15}
(c) 5×10^{-15} (d) 9×10^{-15}

38. At 450 K, $K_P = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is K_C, at this temperature?

(a) 7.48×10^{11} L mol^{-1} (b) 7.48×10^{-11} L mol^{-1}
(c) 3.78×10^{-11} L mol^{-1} (d) 3.74×10^{11} L mol^{-1}

39. A sample of HI(g) is placed in a flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI(g) is 0.04 atm. What is K_p for the given equilibrium?

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

(a) 6 (b) 16 (c) 4 (d) 2

40. A mixture of 1.57 mol of N_2, 1.92 mol of H_2, and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_C for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2. Is the reaction mixture at equilibrium?
If not, what is the direction of the net reaction?

(a) Not at equilibrium, forward shift
(b) Not at equilibrium, backward shift
(c) Cannot be predicted
(d) In equilibrium

41. The equilibrium constant expression for a gas reaction is, $K_C = \dfrac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$

The balanced chemical equation corresponding to this expression is

(a) $4NO(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 5O_2(g)$
(b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
(c) Both (a) and (b)
(d) None of these

42. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-10} mol L^{-1}. If value of K_C is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(a) 0.08 M (b) 0.04M
(c) 0.2 M (d) 0.02 M

43. Equilibrium constant, K_C for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \text{ at 500 K is 0.061}$$

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium and if not in which direction does the reaction tend to proceed to reach equilibrium?

(a) At equilibrium
(b) Not at equilibrium, backward shift
(c) Not at equilibrium, forward shift
(d) Can not be predicted

44. Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium,

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

for which $K = 32$ at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

(a) 3×10^{-4} (b) 1×10^{-4}
(c) 1.5×10^{-4} (d) 6×10^{-4}

45. What are the values of ΔG^0 and the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

where $\Delta G_f^0 NO_2 = 52.0$ kJ/mol

$\Delta G_f^0 NO = 87.0$ kJ/mol

$\Delta G_f^0 (O_2) = 0$ kJ/mol

(a) 35 kJ mol^{-1} and 1.365×10^6
(b) –35 kJ mol^{-1} and 1.365×10^{-6}
(c) –350 kJ mol^{-1} and 1.3×10^6
(d) –35 kJ mol^{-1} and 1.365×10^6

46. A reaction mixture containing H_2, N_2 and NH_3 has partial pressures 2 atm, 1 atm and 3 atm, respectively at 725 K. If the value of K_p for the reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 4.28×10^{-5} atm^{-2} at 725 K, in which direction the net reaction will go?

(a) Forward
(b) Backward
(c) No net reaction
(d) Direction of reaction cannot be predicted.

47. 2.0 mol of PCl_5 were introduced in a vessel of 5.0 L capacity at a particular temperature. At equilibrium, PCl_5 was found to be 35% dissociated into PCl_3 and Cl_2. The value of K_c for the reaction is

(a) 1.89 (b) 0.377 (c) 0.75 (d) 0.075.

48. In the reversible reaction $A + B \rightleftharpoons C + D$, initially 1 M of A and B taken the concentration of each C and D at equilibrium was 0.8 mole/L^{-1}, then the equilibrium constant K_c will be

(a) 6.4 (b) 0.64 (c) 1.6 (d) 16.0

49. 4 moles of A are mixed with 4 moles of B. At equilibrium for the reaction
$A + B \rightleftharpoons C + D$, 2 moles of C and D are formed. The equilibrium constant for the reaction will be

(a) 1/4 (b) ½ (c) 1 (d) 4

50. On a given condition, the equilibrium concentration of HI, H_2, I_2 are 0.80, 0.10 and 0.10 mole L^{-1}. The equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ will be

(a) 64 (b) 12 (c) 8 (d) 0.8

51. In which of the following, the reaction proceeds towards completion?

(a) $K = 10^3$ (b) $K = 10^{-2}$
(c) $K = 10$ (d) $K = 1$

52. A reversible chemical reaction having two reactants in equilibrium. If the concentration of the reactants are doubled, then the equilibrium constant will

(a) Also be doubled (b) Be halved
(c) Become one-fourth (d) Remain the same

53. The equilibrium constant in reversible reaction at a given temperature
(a) depends on the initial concentration of the reactants.
(b) depends on the concentration of the products and reactants at equilibrium.
(c) does not depend on the initial concentrations.
(d) it is not characteristic of the reaction.

54. Pure ammonia is placed in a vessel at temperature where its dissociation constant (A) is appreciable. At equilibrium
(a) *Kp* change with pressure.
(b) *Kp* does not change with pressure.
(c) Concentration of NH_3 does not change with pressure.
(d) Concentration of H_2 is less than that of N_2.

LEVEL II

1. For the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ the concentration of each substance is $[SO_2] = 0.60M$, $[O_2] = 0.82M$ and $[SO_3] = 1.90$ M, the K_C is for $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$
(a) 1.2229 (b) 3.5
(c) 6.1145 (d) 18.22

2. For the reaction, $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ H_2 is introduced into a five litre flask at 327°C, containing 0.2 mole of CO (g) and a catalyst till the pressure is 4.92 atmosphere. At this point 0.1 mole of $CH_3OH(g)$ is formed. Calculate K_P.
(a) 0.115 atm^{-2} (b) 1.15 atm^{-2}
(c) 2 atm^{-2} (d) 3.15 atm^{-2}

3. If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O according to the reaction $2N_{2g} + O_{2g} \rightleftharpoons 2N_2O_g$ at a temperature for which $K_C = 2.0 \times 10^{-37}$
The composition of equilibrium mixture are
(a) $N_2 = 0.482$ mol/L, $O_2 = 0.0933$ mol/L, $N_2O = 6.6 \times 10^{-21}$ mol/L
(b) $N_2 = 0.482$ mol/L, $O_2 = 0.933$ mol/L, $N_2O = 6.6 \times 10^{-21}$ mol/L
(c) $N_2 = 0.0482$ mol/L, $O_2 = 0.0933$ mol/L, $N_2O = 6.6 \times 10^{-21}$ mol/L
(d) $N_2 = 0.0482$ mol/L, $O_2 = 0.0931$ mol/L, $N_2O = 8.8 \times 10^{-21}$ mol/L

4. When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. The equilibrium amount of NO and Br_2 are:
(a) NO = 0.352 mol, $Br_2 = 0.0178$ mol
(b) NO = 0.0352 mol, $Br_2 = 0.178$ mol
(c) NO = 0.352 mol, $Br_2 = 0.178$ mol
(d) NO = 0.0352 mol, $Br_2 = 0.0178$ mol

5. At 450 K, $K_P = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ What is K_C for $2SO_3 \rightleftharpoons 2SO_2 + O_2$
(a) $\dfrac{1}{7.47 \times 10^{11}}$ (b) $\dfrac{1}{7.47 \times 10^{12}}$
(c) $\dfrac{1}{7.47 \times 10^{14}}$ (d) $\dfrac{1}{7.47 \times 10^{8}}$

6. A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI(g) is 0.04 atm. What is K_C for the given equilibrium at 427°C

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

(a) 6 (b) 16 (c) 4 (d) 2

7. In equilibrium reaction, *x* moles of the reactant *A* decompose to give 1 mole each of *C* and *D*. If the fraction of *A* decomposed at equilibrium is independent of initial concentration, then the value of *x* will be
(a) 1 (b) 2 (c) 3 (d) 4

8. One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium, 40% of water (by mass) reacts with CO according to the equation,

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

What is the value of equilibrium constant (K_c) for the reaction?
(a) 44 (b) 4.4 (c) 0.44 (d) 2.22

9. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of $PC1_5$ was found to be 0.5×10^{-1} mol L^{-1}. If value of K_C is 8.3×10^{-3}, what are the concentrations of $PC1_3$ and $C1_2$ at equilibrium?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(a) 0.08 M (b) 0.04 M
(c) 0.2 M (d) 0.02 M

10. $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ $K_C = 16 \times 10^{-6}$
Find the equilibrium pressure of H_2 gas if 10.0 bar of HBr is introduced into a sealed container at 1024 K.
(a) 2.8×10^{3} (b) 5.2×10^{-3}
(c) 2.5×10^{-3} (d) 2×10^{-3}

11. $X_2 + X^- \rightleftharpoons X_3^-$ (x = iodine)
This reaction is set up in aqueous medium. We start with 1 mol of X_2 and 0.5 mol of X^- in 1 L flask. After equilibrium is reached, excess of $AgNO_3$ gave 0.25 mol of yellow ppt. equilibrium constant is
(a) 1.33 (b) 2.66 (c) 2.00 (d) 3.00

12. 0.15 mole of CO taken in a 2.5 litre flask is maintained at 750 K alongwith a catalyst so that the following reaction can take place.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate K_p.

(a) 0.05 atm^{-2} (b) 2.15 atm^{-2}
(c) 2 atm^{-2} (d) 0.005 atm^{-2}

13. ΔG° for the dissociation of the dimer ($A_2 \rightleftharpoons 2A$) in benzene solution at 27°C is 6.909 kcal/mol. If 8 moles of A is dissolved in 10 litre of benzene at 27°C, then what is the equilibrium concentration of dimer (A_2)? (Given : $R = 2$ Cal/mol K)?

(a) 2×10^{-3} (b) 0.4
(c) 0.04 (d) 0.02

14. When C_2H_5OH and CH_3COOH are mixed in equivalent proportion, equilibrium is reached when 2/3 of acid and alcohol are used. How much ester will be present when 2g molecule of acid were to react with 2g molecule of alcohol?

(a) 1.33 g molecule (b) 1.5 g molecule
(c) 2 g molecule (d) 1.8 g molecule

15. When sulphur in the form of S_8 is heated at 900 K, the initial pressure of one atm falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2. Find the value of equilibrium constant for the reaction $S_{8g} \rightleftharpoons S_{2g}$.

(a) 1.16 atm^3 (b) 0.71 atm^3
(c) 2.55 atm^3 (d) 5.1 atm^3

16. In a system, $A(s) \rightleftharpoons 2B(g) + 3C(g)$. If the concentration of C at equilibrium is increased by a factor 2, it will cause the equilibrium concentration of B to change to

(a) two times of its original value.
(b) one-half of its original value.
(c) $2\sqrt{2}$ times of its original value.
(d) $\frac{1}{2\sqrt{2}}$ times of its original value.

17. For the equilibrium:

$$\text{LiCl. }3NH_3(s) \rightleftharpoons \text{LiCl. }NH_3(s) + 2NH_3(g)$$

$$K_p = 9 \text{ atm}^2$$

at 40°C. A 5 litre vessel contains 0.1 mole of LiCl. NH_3. How many mole of NH_3 should be added to the flask at this temperature to derive the backward reaction for completion?

(a) 0.7837 mole (b) 1.7837 mole
(c) 3.2 mole (d) 2.00 mole

18. For the reaction $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2\,CN^-$, the K_C at 25°C is 4×10^{-19}. Calculate $[Ag^+]$ in solution which was originally 0.1 M in KCN and 0.03 M in $AgNO_3$.

(a) 0.75×10^{-18} M (b) 0.50×10^{-10} M
(c) 0.20×10^{-15} M (d) 0.25×10^{-20} M

19. $\Delta G^\circ = 77.77$ kJ mol^{-1} at 1000 K for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$. What is the partial pressure of NO under equilibrium at 1000 K for air at 1 atm pressure containing 80% N_2 and 20% O_2 by volume ?

(a) 3.47×10^{-5} atm (b) 2.47×10^{-8} atm
(c) 4.45×10^{-15} atm (d) 0.44×10^{-20} atm

20. At 700 K, equilibrium constant for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700 K, what are the concentration of $H_2(g)$ and $I_2(g)$, assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700 K?

(a) 0.068 M (b) 0.034 M
(c) 0.136 M (d) 0.68 M

21. What is the equilibrium concentration of each of the substances of RHS in the equilibrium when the initial concentration of ICl was 0.78 M?

$$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g);\ K_C = 0.14$$

(a) 0.21 M (b) 0.42 M (c) 4.2 M (d) 2.1 M

22. $K_P = 0.04$ atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

(a) 7.24 atm (b) 3.62 atm
(c) 1 atm (d) 1.5 atm

23. One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and CO_2. $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$; $K_P = 0.265$ atm at 1050K. What are the equilibrium partial pressures of CO and CO_2 respectively at 1050 K if the initial partial pressures are: $p_{CO} = 1.4$ atm and $P_{CO_2} = 0.80$ atm?

(a) $[P_{CO}] = 1.739$ atm and $P_{CO_2} = 0.461$ atm
(b) $[P_{CO}] = 17.39$ atm and $P_{CO_2} = 0.461$ atm
(c) $[P_{CO}] = 4.79$ atm and $P_{CO_2} = 0.46$ atm
(d) $[P_{CO}] = 2.739$ atm and $P_{CO_2} = 1.461$ atm

24. The equilibrium constant for the following reaction is 25 at 1024 K

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Find the equilibrium pressure of H_2 gas if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

(a) 10/7 (b) 4.9
(c) 7/10 (d) 5/16

25. The heat of reaction for an endothermic reaction in equilibrium is 1200 cal more than at constant pressure at 300 K. Calculate the ratio of equilibrium constants K_P and K_C.

(a) 1.648×10^{-3} (b) 2.47×10^{-8}
(c) 4.45×10^{-5} (d) 4.4×10^{-3}

26. For the reaction,

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The degree of dissociation (α) of HI(g) is related to equilibrium constant, K_p by the expression

(a) $\dfrac{1 + 2\sqrt{K_p}}{2}$ (b) $\sqrt{\dfrac{1 + 2K_p}{2}}$

(c) $\sqrt{\dfrac{2K_p}{1 + 2K_p}}$ (d) $\dfrac{2\sqrt{2K_p}}{1 + 2\sqrt{K_p}}$

27. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction, $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ with degree of dissociation α, which is small compared with unity. The expression for K_P, in terms of α and the total pressure, P_T is

(a) $\frac{P_T\alpha^3}{2}$ (b) $\frac{P_T\alpha^2}{3}$ (c) $\frac{P_T\alpha^3}{3}$ (d) $\frac{P_T\alpha^2}{2}$

28. The value of K_P is 1×10^{-3} atm^{-1} at 25°C for the reaction: $2NO + Cl_2 \rightleftharpoons 2NOCl$. A flask contains NO at 0.02 atm and at 25°C. Calculate the mole of Cl_2 that must be added if 1% of the NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 mole gas Produce 1 atm pressure at 25°C. (Ignore Probable association of NO to N_2O_2).

(a) 0.02042 (b) 2.01049
(c) 0.01021 (d) 0.04042

LEVEL III

1. Match the reactions of Column I with the relations in Column II.

Column I		Column II	
(a)	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(p)	$K_p = K_c(RT)$
(b)	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(q)	$K_p = K_c(RT)^2$
(c)	$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(r)	$K_p = K_c(RT)^{-2}$
(d)	$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$	(s)	$K_p = K_c$
		(t)	$K_p = K_c(RT)^{-1}$

2. Match Column I with Column II.

Column I		Column II	
(a)	$Q = K$	(p)	Reaction is nearer to completion.
(b)	$Q < K$	(q)	Reaction is not at equilibrium.
(c)	$Q > K$	(r)	Reaction is fast in forward direction.
(d)	$K >> 1$	(s)	Reaction at equilibrium.
		(t)	Rate of forward reaction = rate of back ward reaction.

3. Match **Column I** with **Column II** and select the answers from the given codes:

Column I (Mixture)		Column II (pH)	
(a)	$K_{eq} < 1$	(p)	Affected by temperature
(b)	Degree of dissociation	(q)	Affected by pressure
(c)	Equilibrium constant	(r)	$K_f < K_b$
(d)	Melting of ice	(s)	$K_f > K_b$
		(t)	K_f/K_b

4. Match the chemical reaction in equilibrium (**Column I**) with the pressure dependent of degree of dissociation of the reaction (**Column II**):

Column I		Column II	
(a)	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(p)	$x \propto \sqrt{P}$
(b)	$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	(q)	$x \propto \sqrt{\frac{1}{P}}$
(c)	$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(r)	$x \propto P$
(d)	$N_2 + O_2 \rightleftharpoons 2NO$	(s)	$x \propto P^0$
		(t)	$K_p = K_c$

5. Match the following:

Column I		Column II	
(a)	$N_{2g} + 3H_{2g} \rightleftharpoons 2NH_{3g}$	(p)	$\Delta n_g > 0$
(b)	$PCl_{5g} \rightleftharpoons PCl_{3g} + Cl_{2g}$	(q)	$k_p < k_c$
(c)	$2SO_{3g} \rightleftharpoons 2SO_{2g} + O_{2g}$	(r)	k_p not defined
(d)	$CH_3COOC_2H_5\, l + H_2O\, l \rightleftharpoons CH_3COOH_l + C_2H_5OH_l$	(s)	$k_p > k_c$
(Assume temperature = 25°C)			

Assertion and Reason

Code:

(a) Statements 1 and 2 are True. Statement 2 **is** the correct explanation for Statement 1.
(b) Statement 1 and 2 are True. Statement 2 **is NOT** the correct explanation for Statement 1.
(c) Statement 1 is True, Statement 2 is False.
(d) Statement 1 is False, Statement 2 is True.

6. Statement 1: A catalyst does not alter the equilibrium constant of a reaction.

Statement 2: The catalyst forms a complex with the reactants and provides an alternate path with lower energy of an activation for the reaction. The forward and reverse reaction are affected to the same extent.

7. Statement 1: Haber's synthesis of NH_3 is carried out in the presence of catalyst.

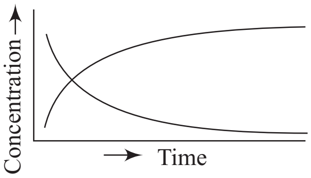
Statement 2: The catalyst shifts the position of the equilibrium of the reaction.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ to the product side.

8. Statement 1: Addition of a non-reacting gas at constant volume and constant temperature to a container containing gas (X), does not change the partial pressure of gas (X).

Statement 2: Addition of non-reacting gas to a container at constant volume and constant temperature results in increase in total pressure of the container.

9. **Statement 1:** The graph between concentration and time is as follows:



Its graph shows a reversible reaction.

Statement 2: In a reversible reaction the concentration of reactants and products becoming constant after a certain time.

10. **Statement 1:** Addition of an inert gas at constant pressure to dissociation equilibrium of $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ favours forward reaction.

Statement 2: $K_c = \dfrac{\alpha^2 V}{1-\alpha}$ for dissociation equilibrium of PCl_5, where α is degree of dissociation of PCl_5

11. **Statement 1:** The reaction: $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ is favoured in the forward direction with increase in pressure.

Statement 2: When pressure is increased then the equilibrium shifts in those direction where V or number of moles decreases.

12. **Statement 1:** Addition or removal of solid reactant/products does not alter the existing equilibrium.

Statement 2: Concentration of solid substances remains constant.

13. **Statement 1:** A catalyst does not affect the equilibrium constant.

Statement 2: Equilibrium constant depends on temperature.

14. **Statement 1:** The equilibrium constant for a reaction having positive $\Delta H°$ increase with increase of temperature.

Statement 2: The temperature dependence of the equilibrium constant is related to $\Delta H°$ and not $\Delta S°$ for the reaction.

15. **Statement 1:** $\Delta G = \Delta G° + 2.303\ RT \log_{10} Q$, where Q is reaction quotient.

Statement 2: Q may be greater or lesser than K or equal to K if $\Delta G = 0$.

16. **Statement 1:** A catalyst increased the equilibrium constant at any fixed temperature.

Statement 2: By the uses of catalyst, the rate of the reaction increases.

17. **Statement 1:** In the Haber process,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3;\ \Delta H = -ve$$

Then concentration of NH_3 increases by decreasing the temperature and increasing the pressure.

Statement 2: For an exothermic reaction, equilibrium constant increases by increasing the temperature.

18. **Statement 1:** For the reaction $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$, the unit of K_p will be atm.

Statement 2: Unit of K_p is $(\text{atm})^{\Delta n}$

19. **Statement 1:** $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} + \text{heat}$

Forward reaction is favoured at high temperature and low pressure.

Statement 2: Reaction is exothermic in forward direction.

Comprehension I

For the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, K_P(1000 K) = 0.059 and K_P (1100 K) = 0.08. Exactly 10 g of $CaCO_3$ is placed in a 10 L container at 1000 K. The equilibrium is reached. Assume that air contains 10% by volume of CO_2.

20. The mass of $CaCO_3$ which remains unreacted at 1000 K is

(a) 1.485 g (b) 0.325 g (c) 9.282 g (d) 4.56 g

21. The ratio of degree of dissociation of $CaCO_3$ at 1100°K and 1000 K is

(a) 4.256 (b) 1.356 (c) 5.286 (d) 3.456

22. The temperature at which $CaCO_3$ dissociates freely in air is

(a) 415°C (b) 913.2°C
(c) 8, 05. 4°C (d) 43°C

23. The value of ΔH is

(a) 6699 cal (b) 2399 cal
(c) 4599 cal (d) 2499 cal

Comprehension II

Let $\Delta G°$ be the difference in free energy of the reaction when all the reactants and products are in the standard state (1 atmospheric pressure and 298 K) and K_C and K_P be the thermodynamic equilibrium constant of the reaction. Both are related to each other at temperature T by the following relation:

$$\Delta G° = -2.303\ RT \log K_C$$

and $\Delta G° = -2.303\ RT \log K_P$ (incase of ideal gas)

This equation represents one of the most important results of thermodynamics and relates to the equilibrium constant of a reaction to a thermodynamic property.

It is sometimes easier to calculate the free energy in a reaction rather than to measure the equilibrium constant.

Standard free energy change can be thermodynamically calculated as

$$\Delta G° = \Delta H° - T\Delta S°$$

Here $\Delta H°$ = standard enthalpy change
$\Delta S°$ = standard entropy change.

24. Which of the following statement is correct for a reversible process in state of equilibrium?

(a) $\Delta G = -2.303\ RT \log K$
(b) $\Delta G = 2.303\ RT \log K$
(c) $\Delta G° = -2.303\ RT \log K$
(d) $\Delta G° = 2.303\ RT \log K$

25. At 490°C, the value of equilibrium constant; K_P is 45.9 the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Calculate the value of $\Delta G°$ for the reaction at that temperature?

(a) –3.5 kcal (b) 3.5 kcal
(c) 5.79 kcal (d) –5.79 kcal

26. Calculate the equilibrium concentration ratio of C to A if 2.0 mol each of A and B were allowed to come to equilibrium at 300 K.

$$A + B \rightleftharpoons C + D \qquad \Delta G^\circ = 460 \text{ Cal}$$

(a) 1.0 (b) 0.5 (c) 0.8 (d) 0.679

Comprehension III

If the composition of the system does not change with time, the system is said to be in chemical equilibrium. It is the state in which net reaction of a system is zero. In other words, we can say that in reversible reactions, a stage is reached when the rate of transformation of reactants into products equals the rate of transformation of products into reactants. At this stage, the composition of reactants and products does not change with time. This does not mean that the reaction has ceased, as both reverse and forward reactions are still taking place but with equal place. Such equilibria are called dynamic equilibria.

Let us consider a reaction of the type,

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

$$K_C = \frac{[C][D]}{[A][B]}$$

where K_C is equilibrium constant when the ratio of the concentrations of the product to reactants.

$$K_P = \frac{P_C \times P_D}{P_A \times P_B}$$

where K_P is the equilibrium constant for the ratio of partial pressure and of products to reactants. The relation between K_P and K_C is as follows:

$$K_P = K_C(RT)^{\Delta n}$$

27. The mass ratio of steam and hydrogen is found to be 1 : 2 at equilibrium.

$$3 \text{ Fe (s)} + 4 \text{ H}_2\text{O(g)} \rightleftharpoons \text{Fe}_3\text{O}_4\text{(s)} + 4 \text{ H}_2\text{(g)}$$

The value of equilibrium constant (K_C) for the above reaction is

(a) 3.05×10^3 (b) 1.05×10^5
(c) 0.75×10^2 (d) 2.42×10^7

28. K_C for the reaction $\frac{1}{2}\text{N}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} + \frac{1}{2}\text{Br}_2\text{(g)} \rightleftharpoons$ NOBr(g) from the following information at 298 K:

$$2\text{NO}_{(g)} \rightleftharpoons \text{N}_{2(g)} + \text{O}_{2(g)} \qquad K_1 = 2.4 \times 10^{30}$$

$$\text{NO}_{(g)} + \frac{1}{2}\text{Br}_{2(g)} \rightleftharpoons \text{NOBr}_{(g)} \quad K_2 = 1.4$$

(a) 3.15×10^{-9} (b) $6.35 \times 5\ 10^{-18}$
(c) 9.03×10^{-16} (d) 17×10^{-17}

29. The equilibrium constant for the reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\ \text{SO}_3$ at 1000 K is 3.5. What will the partial pressure of oxygen gas have to be to give equal moles of SO_2 and SO_3?

(a) 0.29 atm (b) 3.5 atm
(c) 0.53 atm (d) 1.87 atm

30. For the reaction,

$$\text{NH}_2\text{COONH}_4\text{(s)} \rightleftharpoons 2\ \text{NH}_{3(g)} + \text{CO}_{2(g)}$$

The equilibrium constant $K_P = 2.9 \times 10^{-5}$ atm^3. The total pressure of gases at equilibrium when 1 mole of reactant was heated will be

(a) 0.0194 atm (b) 0.0388 atm
(c) 0.0580 atm (d) 0.0667 atm

Comprehension IV

A chemical reaction in the laboratory is carried out under the condition of constant temperature and pressure. The condition of spontaneity in terms of enthalpy and entropy are, respectively, $\Delta H < 0$ and $S > 0$ whereas condition of equilibrium are, respectively, $\Delta H = 0$ and $\Delta S = 0$. An endothermic reaction is driven by increase in entropy, i.e., increase in disorderness. The two criteria combined together, the condition of reversibility and irreversibility are as follows:

$\Delta G_{P,\,T} = \Delta H - T\Delta S \le 0$, where 'equal to' sign refers to reversibility and 'less than' sign refers to irreversibility. Reversibility is the condition of equilibrium whereas irreversibility is the condition of spontaneity. A reversible reaction is characterised by equilibrium constant (K), the magnitude of which measures the position of equilibrium, i.e., how far a chemical reaction will go to completion before attainment of equilibrium. The position of equilibrium constant of a reaction with temperature is given by Van Hoff equation of thermodynamics which is as follows:

This equation can be integrated assuming ΔH to be independent of temperature. Within the short interval of temperature.

For a gaseous equilibria k can be expressed K_c and K_p related as

where the symbols have their usual meanings. Δn_g of a reaction can be found out from the unit of equilibrium, though it is not customary to write unit of equilibrium constant. Another way of finding Δn_g of a reaction is to use the equation,

$$\Delta H = \Delta E + \Delta n_g RT$$

where the terms have their usual meanings.

Knowing K and reaction quotient, it is possible to calculate free energy change of a reaction using the equation:

$$\Delta G = \Delta G^0 + RT \ln Q$$

At equilibrium $Q = K$ and $\Delta G_{P,\,T} = 0$

So, $\Delta G^0 = -RT \ln K$ where ΔG^0 is the free energy change of the reaction in the standard state.

The standard state of a substance is defined as the state of unit activity at 25°C. In the case of solution of a substance, the activity is taken to be molar concentration while for a gas it is pressure in atm. The standard free energy of an element is taken to be zero.

31. At 27°C the heat of reaction at constant pressure is 600 cals more than that at constant volume. The ratio of K_p to K_c of the reaction is

(a) 24.63 (b) $(24.63)^2$
(c) 0.6 (d) 0.36

32. For the reaction,

$$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$$

K_p and K_c are interrelated as

(a) $K_p = K_cRT$ (b) $K_p = \dfrac{K_c}{(RT)^2}$

(c) $K_p = K_c(RT)^2$ (d) $K_p = K_c/RT$

33. The K_p of a reaction is 10 atm^{-2} at a temperature T on Kelvin scale. Hence,

(a) $K_p = K_c$ (b) $K_p < K_c$

(c) $K_p > K_c$ (d) Can't be predicted

34. The K_c of a reaction is 4.0 mol^2 L^{-2} at 27°C. Hence K_p of the reaction is

(a) $4\,(0.0821 \times 300)^2\ \text{atm}^2$

(b) $4\,(2 \times 300)^2\ \text{atm}^2$

(c) $\dfrac{4}{(0.0821 \times 300)^2\ \text{atm}^{-2}}$

(d) $\dfrac{4}{(2 \times 300)^2\ \text{atm}^2}$

Integer-Answer-Type Questions

35. For the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$

$$(G^0_{N_2O_4})_{298\,K} = 100\,\text{kJ mol}^{-1} \text{ and } (G^0_{NO_2})_{298\,K} = 50\ \text{kJ mol}^{-1}.$$

When 5 mole/L of each in taken, calculate the value of ΔG in KJ for the reaction at 298 K.

36. When NO and NO$_2$ are mixed, the following equilibria are readily obtained;

$2NO_2 \rightleftharpoons N_2O_4$ $K_p = 6.8$ atm^{-1}

and $NO + NO_2 \rightleftharpoons N_2O_3$

In an experiment when NO and NO$_2$ are mixed in the ratio of 1 : 2, the total pressure was 5.05 atm and the partial pressure of N_2O_4 was 1.7 atm. Calculate the equilibrium partial pressure of NO in atmospheres × 10.

37. At 25°C and 1 atmospheric pressure, for the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the partial pressures in equilibrium mixture of gaseous N_2O_4 and NO_2 are 0.7 and 0.3 atm respectively. Calculate the partial pressure of N_2O_4 in atm when they are in equilibrium at 25°C and the total pressure of 10 atm

38. For the reaction, $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$, K is 0.63 at 700°C and 1.66 at 1000°C. What is the average $H°$ in Kcal for the temperature range considered?

39. 16 moles of H$_2$ and 4 moles of N$_2$ are sealed in a 1 L vessel. The vessel is heated at a constant temperature until the equilibrium is established, it is found that the pressure in the vessel has fallen to 9/10 of its original value. Calculate newly concentration of N$_2$ in mol L^{-1}

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Subjective Questions

40. At 700 K, CO$_2$ and H$_2$ react to form CO and H$_2$O. For this process, K is 0.11. If a mixture of 0.45 mole of CO$_2$ and 0.45 mole of H$_2$ is heated to 700 K, then

(i) find out the amount of each gas at equilibrium.

(ii) After equilibrium is reached, another 0.34 mole of CO$_2$ and 0.34 mole of H$_2$ are added to the reaction mixture. Find the composition of the mixture at the new equilibrium state.

41. The equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$; is found to be 64 at 450°C. If 6 mole of hydrogen are mixed with 3 mole of iodine in a litre vessel at this temperature; what will be the concentration of each of the three components, when equilibrium is attained? If the volume of reaction vessel is reduced to half; then what will be the effect on equilibrium?

42. 5 gm of PCl$_5$ were completely vaporised at 250°C in a vessel of 1.9 L capacity. The mixture at equilibrium exerted a pressure of one atmosphere. Calculate the degree of dissociation and K_C.

43. If a mixture of N$_2$ and H$_2$ in the ratio 1 : 3 at 50 atmosphere and 650°C is allowed to react till equilibrium is reached. Ammonia present at equilibrium was at 25 atm pressure. Calculate the equilibrium constant for the reaction,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

44. A mixture of SO$_3$, SO$_2$ and O$_2$ gases is maintained in a 10.0 L flask at a temperature at which equilibrium constant K_c for the reaction

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 100.

(i) If the number of moles of SO$_2$ and SO$_3$ in the flask are equal, how many moles of O$_2$ are present?

(ii) If the number of moles of SO$_3$ in the flask is twice the number of mole of SO$_2$, how many moles of O$_2$ are present?

45. The equilibrium constant K_p of the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 900 atm^{-1} at 800 K. A mixture containing SO$_3$ and O$_2$ having initial partial pressures of 1 atm and 2 atm, respectively, is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K.

46. H$_2$S dissociates according to the equation $2H_2S\ (g) \rightleftharpoons 2H_2(g) + S_2(g)$. If a is the degree of dissociation of H$_2$S, show that K_p of the reaction is given as

$$K_p = \frac{\alpha^3 p}{2(1-\alpha)^2(1+\alpha/2)}$$

At 1125°C, the value of a is found to be 0.31 when the equilibrium pressure is 1 atm. Determine the values of K_p and K_c.

47. COCl$_2$ gas dissociates according to the equation $COCl_2 \rightleftharpoons CO + Cl_2$. When COCl$_2$ is heated to 724 K at 1atm, the density of gas mixture at equilibrium was found to be 1.162 g L^{-1}. Calculate (a) the degree of dissociation and (b) K_p of the reaction.

48. The density of an equilibrium mixture of N$_2$O and NO$_2$ at 1 atm and 348 K is 1.84 g dm^{-3}. Calculate the equilibrium constant of the reaction

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

49. For the reaction, $N_2O_5(g) \rightleftharpoons 2NO_2\ (g) + 0.5O_2\ (g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at constant volume and temperature, if the initial pressure is 600 mm-Hg and the pressure at any time is 960 mm Hg. Assuming ideal gas behaviour.

50. When 3.06 g of solid NH_4HS is introduced into a 2 L evacuated flask at 270°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (a) Calculate K_c and K_p for the reaction at 27°C. (b) What will happen to equilibrium when more solid NH_4HS is introduced into the flask?

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel, $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$. If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be **[AIEEE 2006]**

(a) $\left(\frac{x}{1-x}\right)P$ (b) $\left(\frac{x}{x+1}\right)P$

(c) $\left(\frac{2x}{1-x}\right)P$ (d) $\left(\frac{x}{x-1}\right)P$

2. The equilibrium constant for the reaction,

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$$

is $K_c = 4.9 \times 10^{-2}$. The value of K_c for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

will be **[AIEEE 2006]**

(a) 4.9×10^{-2} (b) 416

(c) 2.40×10^{-3} (d) 9.8×10^{-2}

3. The equilibrium constants K_{P1} and K_{P2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal, then the ratio of total pressures at these equilibria is **[AIEEE 2008]**

(a) 1 : 36 (b) 1 : 1 (c) 1 : 3 (d) 1 : 9

4. For the following three reactions 1, 2, and 3, equilibrium constants are given

(a) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}\ ;\ K_1$

(b) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}\ ;\ K_2$

(c) $CH_{4(g)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 4H_{2(g)}\ ;\ K_3$

Which of the following reactions is correct? **[AIEEE 2008]**

(a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$

(c) $K_3 = K_1K_2$ (d) $K_3 \cdot K_2^3 = K_1^2$

5. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_P is **[AIEEE 2011]**

(a) 1.8 atm (b) 3 atm

(c) 0.3 atm (d) 0.18 atm

6. The equilibrium constant (K_c) for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction

$NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is **[AIEEE 2012]**

(a) 0.02 (b) 2.5×10^2

(c) 4×10^{-4} (d) 50

7. For the reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g),$$

If $K_P = K_c(RT)^x$ where the symbols have usual meanings, then the value of x is (assuming ideality) **[AIEEE 2014]**

(a) –1 (b) –1/2 (c) 1/2 (d) 1

8. The standard Gibbs energy change at 300 K for the reaction $2A \rightarrow B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, $[B] = 2$ and $(C) = \frac{1}{2}$. The reaction proceeds in the $[R = 8.314$ J/K/mol, $e = 2.718]$ **[JEE Main 2015]**

(a) Forward direction because $Q > K_C$

(b) Reverse direction because $Q > K_C$

(c) Forward direction because $Q < K_C$

(d) Reverse direction because $Q < K_C$

JEE Advanced

Single-Correct-Answer Type

9. The Haber's process for the formation of NH_3 at 298 K is

$N_2 + 3H_2 \rightleftharpoons 2NH_3\ ;\ \Delta H = -46.0$ kJ. Which of the following is the correct statement? **[IIT JEE 2006]**

(a) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure.

(b) On adding N_2, the equilibrium will shift to forward direction because according to IIsecond law of thermodynamics the entropy must increase in the direction of spontaneous reaction.

(c) The catalyst will increase the rate of forward reaction by two times and that of backward reaction by 1.5 times.

(d) None of these.

Multiple-Correct-Answer Type

10. The equilibrium $2Cu^{I} \rightleftharpoons Cu^0 + Cu^{II}$ in aqueous medium at 25ºC shift towards the left in the presence of **[IIT JEE 2011]**

(a) $NO_3^{\ominus}$ (b) $Cl^{\ominus}$

(c) $SCN^{\ominus}$ (d) $CN^{\ominus}$

11. The thermal dissociation equilibrium of $CaCO_3$ is studied under different conditions
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. For this equilibrium, the correct statement(s) is (are)

[JEE Advanced 2014]

(a) ΔH is dependent on *T*.
(b) *K* is independent of the initial amount of $CaCO_3$.
(c) *K* is dependent on the pressure of CO_2 at a given *T*.
(d) ΔH is independent of the catalyst, if any.

Assertion-Reasoning Type

(A) Both Statements 1 and 2 are correct, but Statement 2 is not the correct explanation of Statement 1.
(B) Both Statements 1 and 2 are correct, but Statement 2 is not the correct explanation of Statement 1.
(C) Statement 1 is correct but Statement 2 is incorrect.
(D) Statement 1 is incorrect but Statement 2 is correct.

12. **Statement 1:** For every chemical reaction at temperature, standard Gibbs energy of reaction is zero.
Statement 2: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. **[IIT JEE 2008]**

Answer Key

LEVEL I

1. (a) 2. (c) 3. (b) 4. (b) 5. (d) 6. (b) 7. (b) 8. (b) 9. (d) 10. (d)
11. (c) 12. (b) 13. (b) 14. (d) 15. (d) 16. (b) 17. (b) 18. (c) 19. (b) 20. (b)
21. (b) 22. (a) 23. (a) 24. (c) 25. (a) 26. (c) 27. (c) 28. (b) 29. (a) 30. (d)
31. (d) 32. (b) 33. (a) 34. (a) 35. (b) 36. (a) 37. (b) 38. (a) 39. (c) 40. (b)
41. (a) 42. (d) 43. (c) 44. (a) 45. (d) 46. (b) 47. (d) 48. (d) 49. (c) 50. (a)
51. (a) 52. (d) 53. (b) 54. (b)

LEVEL II

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

LEVEL III

1. (A) → s; (B) → r; (C) → p; (D) → q 2. (A) → s, t; (B) → q, r; (C) → q; (D) → p
3. (A) → r; (B) → p, q; (C) → p; (D) → p, q 4. (A) → r; (B) → p; (C) → q; (D) → s
5. (A) → q; (B) → p, s; (C) → p, s; (D) → s
6. (a) 7. (c) 8. (b) 9. (d) 10. (c) 11. (a) 12. (a) 13. (b) 14. (b) 15. (c)
16. (d) 17. (c) 18. (d) 19. (d) 20. (c) 21. (b) 22. (b) 23. (a) 24. (c) 25. (d)
26. (d) 27. (b) 28. (c) 29. (a) 30. (c) 31. (a) 32. (c) 33. (b) 34. (a) 35. (4)
36. (18) 37. (9) 38. (8) 39. (3)
40. (i) $[CO_2] = [H_2] = 0.34$ mole, $[CO] = [H_2O] = 0.112$ mole (ii) $[CO_2] = [H_2] = 0.594$ mole, $[CO] = [H_2O] = 0.196$ mole
41. $[HI] = 5.68$ M, $[H_2] = [I_2] = 3.16$ M. 42. $\alpha = 0.84$, $K_C = 0.056$ 43. $K_P = 1.677 \times 10^{-3}$
44. (i) 0.1 mole (ii) 0.4 mole 45. $P\text{so}_2 = 0.23$ atm, $\text{Po}_2 = 2.0115$ atm, $\text{Pso}_3 = 0.977$ atm
46. $K_P = 2.71 \times 10^{-2}$ atm, $K_C = 2.39 \times 10^{-4}$ mole L^{-1} 47. $\alpha = 0.433$, $K_p = 0.231$ atm 48. $K_P = 5.206$ atm
49. $X_{N_2O_5} = 0.407$ 50. (i) $K_C = 8.1 \times 10^{-5}$ (mole $L^{-1})^2$, $K_p = 4.9 \times 10^{-2}$ atm^2 (ii) no effect

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (b) 2. (b) 3. (a) 4. (c) 5. (a) 6. (d) 7. (b) 8. (b) 9. (a) 10. (b, c, d)
11. (a, b, d) 12. (d)

Hints and Solutions

LEVEL I

1. (a) $K_c = 20\ k_f = 10\ k_b = ?$

$$K_c = \frac{k_f}{k_b} \quad 20 = \frac{10}{k_b}$$

$$\therefore \quad K_b = \frac{10}{20} = 0.5$$

2. (c) $NO(g) + \frac{1}{2} O_2(g) \rightleftharpoons NO_2(g)$

$$K_1 = \frac{[NO_2]}{[NO][O_2]^{1/2}} = 4 \times 10^{-3}$$

Now for reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$$K_2 = \frac{[NO]^2[O_2]}{[NO_2]^2} = \frac{1}{K_1^2}$$

$$= \frac{1}{(4 \times 10^{-3})^2} = 6.25 \times 10^4$$

3. (b) $K_C = \dfrac{[NOCl]^2}{[NO]^2[Cl_2]}$

4. (b) Number of moles of $O_2 = \dfrac{96}{32} = 3$ mol

Molar concentration $= \dfrac{\text{Number of moles}}{\text{Volume in litre}} = \dfrac{3}{2} = 1.5$ mol/ltr

5. Value of K_p is greater then K_c for those reaction in which $\Delta n > 0$.

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

Here for the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$; $\Delta n = 3 - 2 = 1 > 0$

Therefore $K_p > K_c$ for this reaction

6. (b) $K_p = 20R$ (given)

for the reaction $\Delta n = (2 - 1) = 1$

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

$$20R = K_c\ (RT)^1$$

$$\therefore \quad K_c = \frac{20R}{R \times 1000} = .02 \text{ mol L}^{-1}$$

7. (b) $N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$2NO_2$
Initially	1	0
Moles at equilibrium	$1 - \alpha$	2α

$\therefore$ total number of moles at equilibrium $= 1 - \alpha + 2\alpha$

$= 1 + \alpha$

8. (b)

	A	B	C	D
Initially	4	4	0	0
At equilibrium	$4 - x$	$4 - x$	x	x

$A + B \rightleftharpoons C + D$

Given at equilibrium mole of $C = 2$ ($\therefore x = 2$)

$\therefore \quad [A] = 4 - 2 = 2$ mole

$[B] = 4 - 2 = 2$ mole

$[D] = x = 2$ mole

$$K_c = \frac{[C][D]}{[A][B]} = \frac{2 \times 2}{2 \times 2} = 1$$

9. (d) $2HI \rightleftharpoons H_2 + I_2$

	$2HI$	H_2	I_2
Initially	1	0	0
Moles at equilibrium	$1 - \alpha$	$\alpha/2$	$\alpha/2$

50% of HI is dissociated therefore $\alpha = .5$

$[HI] = 1 - .5 = .5$

$[H_2] = .5/2$

$[I_2] = .5/2$

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{.5/2 \times .5/2}{[.5]^2} = \frac{1}{4} = 0.25$$

10. (d)

$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_35(l) + H_2O(l)$

	C_2H_5OH	CH_3COOH	$CH_3COOC_2H_5$	H_2O
Initially(l)	(1)		0	0
Moles of equilibrium	$1 - \alpha$	$1 - \alpha$	α	α

Given $\alpha = 2/3$

Therefore,

$C_2H_5OH = 1 - 2/3 = 1/3$

$CH_3COOH = 1–2/3 = 1/3$

$CH_3COOC_2H_5 = 2/3$

$H_2O = 2/3$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{2/3 \times 2/3}{1/3 \times 1/3} = 4$$

11. (c) $K_p = \dfrac{[p_{co}]^2}{[p_{co_2}]} = \dfrac{[4]^2}{[2]}$

$\therefore \quad K_p = 8$ atm

12. (b) D for $PCl_5 = \dfrac{\text{Molecular mass}}{2} = \dfrac{208.5}{2} = 104.25$

d for $PCl_5 = 100$

$$\alpha = \frac{D - d}{d} = \frac{104.25 - 100}{100} = 0.0425$$

13. (b) $H_2 + Cl_2 \rightleftharpoons 2HCl$

H_2	Cl_2	$2HCl$
3 mole	$\dfrac{9.023 \times 10^{23}}{6.023 \times 10^{23}}$	0 Initial mole
3 – 1.5 mole	1.5–1.5 mole	3.0 mole at equilibrium

Total mole at equilibrium = 1.5 + 3.0 = 4.5 mole

Partial pressure of HCl $= \dfrac{3.0}{4.5} \times 800 = \dfrac{1600}{3} = 533$ mm

14. (d) $N_2O_4 \rightleftharpoons 2NO_2$

$1 - x \quad 2x$

$P = 1$ atm. pressure. $x = 20\%$, i.e., 0.2 mole

$$K_p = \frac{4x^2P}{1 - x^2}$$

$$K_p = \frac{4 \times 0.2 \times 0.2 \times 1}{1 - (0.2)^2} = \frac{0.16}{0.96} = 0.17$$

15. **(d)** Equilibrium constant (K_c) will remain unchanged.

16. **(b)**

	$PCl_5 \rightleftharpoons$	$PCl_3 +$	Cl_2
Initial mole	1	0	0
Mole at equilibrium	$1 - 0.2$	0.2	0.2

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.2 \times 0.2}{0.8} = \frac{1}{20} = 0.5 \text{ atm}$$

17. **(b)** Volume of gases is increasing in the forward reaction. Therefore on increasing pressure, equilibrium will shift towards backward direction.

18. **(c)** On increasing pressure in the reaction, equilibrium will shift towards the direction where volume gets decreased, i.e., towards forward (right) direction.

19. The ratio $\dfrac{[\text{Product}]}{[\text{Reactant}]}$ is maximum when $K = 10^{10}$ and thus reaction goes farthest to completion when $K = 10^{10}$

20. For $A_{(g)} \rightleftharpoons B_{(g)}$; $K_c = \dfrac{[B]}{[A]} = 1.1 \Rightarrow [B] > [A]$.

If $[B] = 1$; $[A] = 0.91$

Case I	$0.91 < [A] \le 1$	Only $[B] > 1$
Case II	$[A] > 1$	Both $[A]$ and $[B] > 1$

21.

$$\begin{array}{cc} N_2O_4 \rightleftharpoons & 2NO_2 \\ 0.1 & 0 \\ (0.1 - \alpha) & 2\alpha \end{array}$$

$$K_p = \frac{(2\alpha)^2}{(0.1-\alpha)} \times \left[\frac{P}{0.1+\alpha}\right]^1 \text{ or } K_p = \frac{40\alpha^2}{(0.1-\alpha)}$$

$$\text{or } \frac{40\alpha^2}{(0.1-\alpha)} = 0.14$$

$\therefore \alpha = 0.017$ $\quad\therefore NO_2 = 0.017 \times 2 = 0.034$ mole

22. $K_c = \dfrac{[CO_2]}{[CO]}$

$$\therefore \quad 5 = \frac{[CO_2]}{2.5 \times 10^{-2}}$$

$\therefore$ $[CO_2]$ at equilibrium $= 2.5 \times 10^{-2} \times 5 = 12.5 \times 10^{-2}$ mol L^{-1}

23.

Reaction	$2H_2S \rightleftharpoons$	H_2 +	S_2
Mole before dissociation	1	0	0
Mole after dissociation	$(1 - \alpha)$	α	$\dfrac{\alpha}{2}$

where α is degree of dissociation of H_2S

Volume of container = 1.10 L

$$\therefore \quad K_C = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left[\frac{\alpha}{1.1}\right]^2\left[\frac{\alpha}{2\times 1.1}\right]}{\left[\frac{1-\alpha}{1.1}\right]^2} = 1 \times 10^{-6}$$

Assuming $1 - \alpha = 1$ since α is small because $K_c = 10^{-6}$

$$\therefore \quad \frac{\alpha^3}{2(1.1)} = 10^{-6} \quad \alpha = 1.3 \times 10^{-2} = 1.3\%$$

24.

	C(s) +	$CO_2(g) \rightleftharpoons$	2CO(g)
Gaseous mole before dissociation	–	1	0
Gaseous mole after dissociation	–	$\left(1 - \dfrac{50}{100}\right)$	$\dfrac{2 \times 50}{100}$
		0.5	1

$\therefore$ total mole = 1.5

Total pressure given at equilibrium = 12 atm

Partial pressure of CO = $\dfrac{1}{1.5} \times 12 = 8$

Partial pressure of CO_2 = $\dfrac{.5}{1.5} \times 12 = 4$

$$K_p = \frac{P_{CO}^2}{P_{CO_2}} = \frac{(8)^2}{4} = 16 \text{ atm}$$

25.

	$\alpha - D$ glucose $\rightleftharpoons$	$\beta - D$ glucose
At equilibrium	36.4	63.6

$$\therefore \quad K_C = \frac{63.6}{36.4} = 1.747$$

26. **(c)** Apply the formula, $K = \dfrac{k_f}{k_b} = \dfrac{1 \times 10^{-4}}{2.5 \times 10^{-2}} = 4 \times 10^{-3}$.

27. **(c)** $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

SO_2	NO_2	SO_3	NO	
1	1	1	1	Initial conc.
$1 - x$	$1 - x$	$1 + x$	$1 + x$	At equilibrium

$$K = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$16 = \frac{(1+x)^2}{(1-x)^2} \Rightarrow \frac{(1+x)}{(1-x)} = 4 \quad \text{or} \quad x = 0.6$$

$[NO_2] = 1 - x = 1 - 0.6 = 0.4$ mol L^{-1}.

28. **(b)** This is according to Le-Chatelier's principle.

29. **(a)** The degree of dissociation cannot be calculated from the vapour density data. Because here the number of moles remains unchanged before and after reaching equilibrium.

30. **(d)** Equilibrium constant depends only on temperature and stoichiometry of the reaction.

31. **(d)** $K_P = P_{CO_2}$ and active mass of solid is constant

32. **(b)** On adding reactant, (PCl_5) reaction proceed in forward direction $\therefore$ more Cl_2 formed.

33. **(a)** Keq $\propto$ Stability of Pdt

34. **(a)**

	$xy_{2(g)} \rightleftharpoons$	$xy_{(g)}$ +	$y_{(g)}$
Initial pressure	600 mm		
at equilibrium	$600 - p^1$	p^1	p^1

Total pressure at equilibrium $= 600 - p^1 + p^1 + p^1$
$= 600 + p^1$

$600 + p^1 = 800$

$p^1 = 800 - 600 = 200$ mm

35. **(b)** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[1.9]^2}{[0.6]^2 \times [0.82]} M^{-1} = 12.237 \text{ mol L}^{-1}$$

36. **(a)**

(i) $K_P = K_C(RT)^{\Delta n}$

$\because \quad \Delta n = 1$

$$\therefore \quad K_C = \frac{K_P}{RT} = \frac{1.8 \times 10^{-2}}{0.0821 \times 500} = 4.4 \times 10^{-4}$$

(ii) $\therefore \quad \Delta n = 1$

$$K_C = \frac{K_P}{RT} = \frac{167}{0.0821 \times 1073} = 1.90$$

37. **(b)** $K_{C(\text{reverse})} = \dfrac{1}{K_C} = \dfrac{1}{6.3 \times 10^{-14}} = 1.59 \times 10^{-15}$

38. **(a)** $K_P = K_C(RT)\ \Delta n$

$\Delta n = -1$

By putting the values and on solving

$K_C = 7.47 \times 10^{11}$ M^{-1}

39. **(c)**

Reaction	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
$t = 0$	0.2 atm		0		0
change	$-2x$		$+x$		$+x$
$t = t_{eq}$	$(0.2 - 2x)$		x		x

From question, $0.2 - 2x = 0.04$

$2x = 0.2 - 0.04 = 0.16$

$x = 0.08$

$$K_P = \frac{0.08 \times 0.08}{[0.04]^2} = 4$$

40. **(b)** $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3(g)$

$$Q = \frac{\left(\frac{8.13}{20}\right)^2}{\frac{1.57}{20} \times \left(\frac{1.92}{20}\right)^3} = \frac{[8.13]^2 \times [20]^2}{1.57 \times [1.92]^3}$$

$= 2.38 \times 10^3$ $Q > K_C$, so reaction proceeds in backward direction.

41. **(a)** $4NO(g) + 6H_2O\ (g) \rightleftharpoons 4NH_3(g) + 5O_2(g)$

42. **(d)**

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
$t = t_{eq}$	0.5×10^{-1} M		x		x

$$K_C = 8.3 \times 10^{-3} = \frac{x^2}{0.5 \times 10^{-1}}$$

$x^2 = 4.15$ m $\times 10^{-4}$

$x \simeq 0.02$ M

43. **(c)**

	$N_2(g)$	+	$3H_2\ (g)$	$\rightleftharpoons$	$2NH_3\ (g)$
$t = t_{eq}$	3M		2M		0.5M

$$Q = \frac{0.5 \times 0.5}{3 \times 2^3} = \frac{1}{3 \times 8 \times 4} = \frac{1}{96}$$

$\because Q < K$, system is not at equilibrium and equilibrium will be reached by shifting in forward direction

44. **(a)**

	$2BrCl\ (g)$	$\rightleftharpoons$	$Br_2\ (g)$	+	$Cl_2\ (g)$
$t = 0$	3.3×10^{-3} M		0		0
change	$-2x$		x		x
$t = t_{eq}$	$(3.3 \times 10^{-3} - 2x)$		x		x

$$K_C = \frac{x^2}{(3.3 \times 10^{-3} - 2x)^2} = 32$$

on solving, $x = 1.5 \times 10^{-3}$

$[BrCl] = 33 \times 10^{-4} - 2x = 33 \times 10^{-4} - 30 \times 10^{-4}$

$= 3 \times 10^{-4}$

45. **(d)** $\Delta G^0 = \Delta G^0_{NO_2} - \Delta G^0_{NO}$

$= (52 - 87)$ kJ mol^{-1} = -35 kJ mol^{-1}

$\because \quad \Delta G^0 = -2.303\ RT \log K$

$$\log K = \frac{-35 \text{ kJ mol}^{-1}}{-8.301 \text{ Jk}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times 2.303}$$

On solving, $K = 1.365 \times 10^6$

46. **(b)** $Q_p = \dfrac{(P_{NH_3})^2}{P_{N_2} \times (P_{H_2})^3} = \dfrac{(3)^2}{(1)(2)^3} = \dfrac{9}{8} \text{atm}^{-2}$

$= 1.125$ atm^{-2}.

Since value of Q_p is larger than K_p ($4.28\ 10^{-5}$ atm^{-2}), it indicates net reaction will proceed in backward direction.

47. **(d)** Moles of PCl_5 dissociated $= \dfrac{2 \times 35}{100} = 0.7$

Moles of PCl_5 left undissociated = 2 – 0.7 = 1.3 mol

$$[PCl_5] = \frac{1.3}{5} M, [PCl_3] = \frac{0.7}{5} M, [Cl_2] = \frac{0.7}{5} M$$

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{0.7}{5}\right)\left(\frac{0.7}{5}\right)}{\left(\frac{1.3}{5}\right)} = 0.75$$

48. **(d)** Suppose 1 mole of A and B each taken then 0.8 mole L^{-1} of C and D each formed remaining concentration of A and B will be (1 – 0.8) = 0.2 mole L^{-1} each.

$$K_c = \frac{[C][D]}{[A][B]} = \frac{0.8 \times 0.8}{0.2 \times 0.2} = 16.0$$

49. **(c)**

	A	+	B	$\rightleftharpoons$	C	+	D
Initial concentration	4,		4		0		0
After T time concentration	(4 – 2)		(4 – 2)		2		2

$$\text{Equilibrium constant} = \frac{[C][D]}{[A][B]} = \frac{2 \times 2}{2 \times 2} = 1$$

50. **(a)** $H_2 + I_2 \rightleftharpoons 2HI$; [HI] = 0.80, [$H_2$] = 0.10, [$I_2$] = 0.10

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.80 \times 0.80}{0.10 \times 0.10} = 64$$

51. **(a)** Those reactions which have more value of K proceed towards completion.

52. **(d)** K_c is a characteristic constant for the given reaction.

53. Equilibrium constant is independent of original concentration of reactant.

54. K_p is constant and does not change with pressure.

LEVEL II

1. **(b)** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{1.9^2}{0.6^2 \times 0.82} M^{-1} = 12.237 \text{ mol L}^{-1}$$

$$\therefore \quad K_C = SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3 (12.237)^{\frac{1}{2}}$$

2. **(a)**

$$\begin{array}{lccc} & CO\,(g) & +\ 2H_2\,(g) & \rightleftharpoons\ CH_3OH\,(g) \\ \text{Initial mole} & 0.2 & a & 0 \\ \text{Mole at equilibrium} & (0.2-0.1) & (a-0.2) & 0.1 \end{array}$$

Now total mole at equilibrium are $0.1 + a - 0.2 + 0.1 = a$

$$\text{Also Mole } (n) = \frac{PV}{RT} = \frac{4.92 \times 5}{0.0821 \times 600} = 0.499$$

$\therefore \quad a = 0.499$

$$\therefore \quad [CH_3OH] = \frac{0.1}{5}; [CO] = \frac{0.2-0.1}{5} = \frac{0.1}{5};$$

$$[H_2] = \frac{0.499 - 0.20}{5} = \frac{0.299}{5}$$

$$\because \quad K_C = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.1/5}{0.1/5 \times (0.299/5)^2}$$

$$= 279.64 \text{ L}^2\text{mol}^{-2}$$

$K_C = 279.64$ litre^2 mol^{-2}

$K_P = K_C\,(RT)^{\Delta n}$

$= 279.64 \times (0.0821 \times 600)^{-2}$

$K_P = 0.115$ atm^{-2}

3. **(c)**

$$\begin{array}{lccc} & 2N_2(g) & +\ O_2(g) & \rightleftharpoons\ 2N_2O(g) \\ t = 0 & 0.482 \text{ mol} & 0.933 \text{ mol} & 0 \\ \text{Change} & -2x \text{ M} & -x \text{ M} & +2x \text{ M} \\ \hline t = t_{eq} & (0.0482 - 2x) & (0.0933 - x) & 2x \end{array}$$

$K_c = 2 \times 10^{-37} =$

Since Kc has small value, x should be low

$0.0482 - 2x = 0.0482$ M

$0.0933 - x = 0.0933$ M

$$2 \times 10^{-37} = \frac{(2x)^2}{[0.0482]^2 \times [0.0933]}$$

On solving, $x = 3.3 \times 10^{-21}$ M

$[N_2O] = 2x = 6.6 \times 10^{-21}$ M

$[N_2] = 0.0482$ M ; $[O_2] = 0.0993$ M

4. **(d)**

$$\begin{array}{lccc} & 2NO\,(g) & +\ Br_2(g) & \rightleftharpoons\ 2NOBr\,(g) \\ t = 0 & 0.087 \text{ mol} & 0.043 \text{ mol} & 0 \\ & -2x & -x & 2x \\ \hline t = t_{eq} & 0.087 - 2x & 0.0437 - x & 2x \end{array}$$

From equation,

$2x = 0.0518$ mol

$x = 0.0259$ mol

Number of moles of NO = (0.087 – 0.0518) mol = 0.0352 mol

Number of moles of Br_2 = (0.043 – 0.0259) mol = 0.0178 mol

5. **(a)** $K_P = K_C(RT)\ \Delta n$

$\Delta n = -1$

By putting the values and on solving

$K_C = 7.47 \times 10^{11}$ M^{-1}

$\therefore \quad K_C$ for

$2SO_3 \rightleftharpoons 2SO_2 + O_2$

$$\frac{1}{7.47 \times 10^{11}}$$

6. **(c)**

$$\begin{array}{lccc} & 2HI(g) & \rightleftharpoons\ H_2(g) & +\ I_2(g) \\ t = 0 & 0.2 \text{ atm} & 0 & 0 \\ \text{change} & -2x & +x & +x \\ \hline t = t_{eq} & (0.2 - 2x) & x & x \end{array}$$

From question, $0.2 - 2x = 0.04$

$2x = 0.2 - 0.04 = 0.16$

$x = 0.08$

$$K_P = \frac{0.08 \times 0.08}{0.04^2} = 4$$

$K_P = K_C\,(RT)^{\Delta n}$

$\Delta n = 0$

$\therefore \quad K_P = K_C$

7. **(b)** The fraction of A decomposed at equilibrium is independent of initial concentration. In other words, the equilibrium constant expression is free from concentration term. The equilibrium reaction is

$$\begin{array}{lccc} & xA & \rightleftharpoons\ C & +\ D \\ \text{Initial conc.} & c & 0 & 0 \\ \text{Concentration at equilibrium} & c(1-\alpha) & \dfrac{c\alpha}{x} & \dfrac{c\alpha}{x} \end{array}$$

$$K_C = \frac{[C][D]}{[A]^x} = \frac{\left(\frac{c\alpha}{x}\right) \times \left(\frac{c\alpha}{x}\right)}{[c(1-\alpha)]^x} = \frac{(c\alpha)^2}{x^2[c(1-\alpha)]^x}$$

The expression of K_C will be free from concentration term only when value of x is 2. Putting $x = 2$, gives

$$K_C = \frac{c^2\alpha^2}{4[c(1-\alpha)]^2} = \frac{\alpha^2}{4(1-\alpha)^2}$$

8. **(c)**

$$\begin{array}{lcccc} & H_2O(g) + & CO(g) \rightleftharpoons & H_2(g) + & CO_2(g) \\ t = 0 & 1 \text{ mol} & 1 \text{ mol} & 0 & 0 \\ & -0.4 \text{ mol} & -0.4 \text{ mol} & 0.4 \text{ mol} & 0.4 \text{ mol} \\ \hline t = t_{eq} & 0.6 & 0.6 & 0.4 & 0.4 \end{array}$$

$$K_C = \frac{0.4 \times 0.4}{0.6 \times 0.6} = \frac{4}{9} = 0.44$$

9. **(d)**

$$\begin{array}{lccc} & PCl_5(g) & \rightleftharpoons\ PCl_3(g) & +\ Cl_2(g) \\ t = t_{eq} & 0.5 \times 10^{-1} \text{ M} & x & x \end{array}$$

$$K_C = 8.3 \times 10^{-3} = \frac{x^2}{0.5 \times 10^{-1}}$$

$x^2 = 4.15 \times 10^{-4}$

$x = 0.02$ M

10. (c)

$$\begin{array}{llll} & H_2(g) \quad + & Br_2(g) \rightleftharpoons & 2HBr(g) \\ t=0 & 0 & 0 & 10 \text{ bar} \\ & +x & +x & -2x \\ \hline t = t_{eq} & x & x & 10-2x \end{array}$$

$$K_C = 16 \times 10^{-6} = \frac{(10-2x)^2}{x^2}$$

$$4 \times 10^{-3} = \frac{10-2x}{x} \simeq \frac{10}{x};\ x = \frac{10}{4 \times 10^3} = 2.5 \times 10^{-3}$$

11. (a)

$$\begin{array}{llll} X_2 & + \quad X^- & \rightleftharpoons & X_3^- \\ 1 & 0.5 & & 0 \\ (1-x) & (0.5-x) & & x \end{array}$$

$(0.5 - x)$ = unreacted X^-

$X^- \equiv \text{Ag} + 0.25;\ x = 0.25$

$$K_c = \frac{[X_3^-]}{[X_2][X^-]} = \frac{0.25}{0.75 \times 0.25} = 1.33$$

12. (b)

$$\begin{array}{llll} & CO(g) \ + & 2H_2(g) \rightleftharpoons & CH_3OH(g) \\ \text{M before reaction} & 0.15 & a & 0 \\ \text{M after reaction} & (0.15-x) & (a-2x) & x \\ \text{and} & & & x = 0.08 \end{array}$$

Total mole at equilibrium $= 0.15 - x + a - 2x + x$
$= 0.15 + a - 2x$
$= 0.15 + a - 0.16$
$= a - 0.01$

Also total mole at equilibrium are obtained by $n = \dfrac{PV}{RT}$

$$n = \frac{8.5 \times 2.5}{0.0821 \times 750} \quad \because \left.\begin{array}{r} P = 8.5 \text{ atm} \\ V = 2.5 \text{ L} \\ T = 750 \text{ K} \end{array}\right\} \text{at equilibrium}$$

$\therefore \quad n = 0.345$
$\therefore \quad a - 0.01 = 0.345$
$\therefore \quad a = 0.355$

At equilibrium :

Mole of CO = 0.15 – 0.08 = 0.07
Mole of H_2 = 0.355 – 0.16 = 0.195
Mole of CH_3OH = 0.08

$$\therefore \quad K_C = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{0.08/2.5}{\left(\frac{0.07}{2.5}\right)\left(\frac{0.195}{2.5}\right)^2}$$

$= 187.85 \text{ mol}^{-2} \text{ L}$

Also $K_P = K_C\,(RT)^{\Delta n} = 187.85 \times (0.0821 \times 750)^{-2}$
$= 0.05$ atm

13. (b) 6.909 K cal/mol = –2.303 × R × 300 log K

$$\frac{1000}{200} = \log\left(\frac{1}{K}\right) \qquad 2A \rightleftharpoons A_2$$

$$5 = \log\left(\frac{1}{K}\right) \Rightarrow K = 10^{-5}\ K' = 10^5 \Rightarrow [A_2] = 0.4$$

14. (b) Case (i)

$$\begin{array}{lllll} & C_2H_5OH + & CH_3\ COOH \rightleftharpoons & CH_3COOC_2H_5 + & H_2O \\ \text{Mole before reaction} & 1 & 1 & 0 & 0 \\ \text{Mole at equilibrium} & 1-x & 1-x & x & x \end{array}$$

$\because \quad x = \dfrac{2}{3}$

$$\begin{array}{lllll} \therefore \text{ Mole at equilibrium} & \left(1-\frac{2}{3}\right) & \left(1-\frac{2}{3}\right) & \frac{2}{3} & \frac{2}{3} \end{array}$$

$$\therefore \quad K_C = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4$$

Note: Volume terms are eliminated as $\Delta n = 0$

Case (ii)

$$\begin{array}{lllll} & C_2H_5OH + & CH_3COOH \rightleftharpoons & CH_3COOC_2H_5 + & H_2O \\ \text{Mole before reaction} & 1 & 1 & 0 & 0 \\ \text{Mole at equilibrium} & 2-x & 2\text{-}x & x & x \end{array}$$

$$K_C = 4 = \frac{x^2}{(2-x)} \therefore \frac{x}{(2-x)} = 2$$

$x = 1.33$ g molecule

15. (c)

$$\begin{array}{llll} & S_{8(g)} & \rightleftharpoons & 4S_{2(g)} \\ \text{At start} & 1 & & 0 \\ \text{At eqbm} & 1 - 0.29 & & 4 \times 0.29 \\ & = 0.71 \text{ atm} & & = 1.16 \text{ atm} \end{array}$$

$$K_p = \frac{[pS_2]^4}{[pS_8]} = \frac{(1.16)^4}{(0.71)} = 2.55 \text{ atm}^3$$

16. $\underset{1-x}{A_{(s)}} \rightleftharpoons \underset{2x}{2B_{(g)}} + \underset{3x}{3C_{(g)}}$

$K_c = 4x^2 \times 27x^3$
$= 108x^5$

$A_{(s)} \rightleftharpoons \underset{2x \times c}{2B_{(g)}} + \underset{6x}{3C_{(g)}}$

$108x^5 = 4x^2 \times c^2 \times 216x^3$
$108 = c^2 \times 216 \times 4$

$$c^2 = \frac{108}{4 \times 216}$$

$$c = \frac{1}{2\sqrt{2}}$$

17. LiCl. $3NH_3$ (s) $\rightleftharpoons$ LiCl. NH_3 (s) + $2NH_3$ (g) [K_P = 9atm^2]

$\therefore \quad$ LiCl. NH_3 (s) + $2NH_3$(g) $\rightleftharpoons$ LiCl. $3NH_3$(s)

$$\left[K_{P_1} = \frac{1}{9}(\text{atm})^{-2}\right]$$

Inital mole	0.1	a	0
at equilibrium	0	(a – 0.2)	0.1

Let initial mole of NH_3 should be a to bring in completion of reaction.

At eq. $K_{P_1} = \frac{1}{(P'_{NH_3})^2}$

or $\frac{1}{9} = \frac{1}{(P'_{NH_3})^2}$

∴ $P'_{NH_3} = 3$ atm

∵ $PV = nRT$

$3 \times 5 = n \times 0.0821 \times 313$

∴ $n = 0.5837$

i.e., $(a - 0.2) = 0.5837$

∴ Initial mole of $NH_3 = a = 0.5837 + 0.2 = 0.7837$ mole

18. $2KCN + AgNO_3 \rightarrow Ag(CN)_2^- + KNO_3 + K^+$

$2KCN$	$AgNO_3$	$Ag(CN)_2^-$	KNO_3	K^+
0.1	0.03	0	0	0
(0.1-0.06)	0	0.03	0.03	0.03

$[Ag(CN)_2^-] = 0.03$ M

Now use $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$

$Ag(CN)_2^-$	Ag^+	$2CN^-$
0.03	0	0.04
$(0.03 - a)$	a	$0.04 + 2a = 0.04$

Since K_C is too small and dissociation of $Ag(CN)_2^-$ is very less and thus,

∴ $0.04 + 2a = 0.04$ and $0.03 - a = 0.03$

∴ $[Ag(CN)_2^-] = 0.03$; $[Ag^+] = a$, $[CN^-] = 0.04$

Now $K_C = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = \frac{a \times (0.04)^2}{0.3}$

$a = 0.75 \times 10^{-18}$

19. $\Delta G° = -2.303 \times RT \log_{10} K_C$

∴ $77.77 \times 10^3 = -2.303 \times 8.314 \times 1000 \log_{10} K_C$

$K_C = 8.67 \times 10^{-5}$

Reaction	$\frac{1}{2}N_2$	+ $\frac{1}{2}O_2$	$\rightleftharpoons$ NO
Initial pressure	0.8	0.2	0
Final pressure	$\left(0.8 - \frac{x}{2}\right)$	$\left(0.2 - \frac{x}{2}\right)$	x

$$\therefore \quad 8.67 \times 10^{-5} = \frac{x}{\left(0.8 - \frac{x}{2}\right)^{1/2}\left(0.2 - \frac{x}{2}\right)^{1/2}}$$

$x = 3.47 \times 10^{-5}$ atm

20. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$t = t_{eq}$ x x 0.5 M

$$K_C = 54.8 = \frac{0.5 \times 0.5}{x^2}$$

$$x^2 = \frac{0.5 \times 0.5}{54.8}$$

On solving, $x = 0.068$ M

21. $2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$; $K_C = 0.14$

	$2ICl(g)$	$I_2(g)$	$Cl_2(g)$
$t = 0$	0.78 M	0	0
	$-2x$	x	x
$t = t_{eq}$	$(0.78 - 2x)$	x	x

$$0.14 = \frac{x^2}{(0.78 - 2x)^2}$$

On solving, $x = 0.21$ M

22. $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

	$C_2H_6(g)$	$C_2H_4(g)$	$H_2(g)$
$t = 0$	4 atm	0	0
	$-x$	x	x
$t = t_{eq}$	$4 - x$	x	x

$$0.04 = \frac{x^2}{4 - x}$$

On solving, $x = 0.38$;

$P_{C_2H_6} = 3.62$ atm

23. $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

	$FeO(s)$	$CO(g)$	$Fe(s)$	$CO_2(g)$
$t = 0$	—	1.4 atm	—	0.8 atm
	—	$+x$	—	$-x$
At equilibrium		$(1.4 + x)$		$0.8 - x$

$$Q = \frac{0.8}{1.4} = \frac{4}{7} = 0.55$$

∵ $Q > K$, system is not at equilibrium and to attain equilibrium it will shift in backward direction

$$K_P = 0.265 = \frac{0.8 - x}{1.4 + x}$$

On solving, $x = 0.339$

∴ $[P_{CO}] = 1.739$ atm and $P_{CO_2} = 0.461$ atm

24. $H_2 + Br_2 \rightleftharpoons 2HBr$ $K_P = 25$

∴ KP for $2HBr \rightleftharpoons H_2 + Br_2$ $K'_P = \frac{1}{25}$

$10 - 2x$ x x

$$K'_P = \frac{1}{25} = \frac{x^2}{(10 - 2x)^2} \Rightarrow \frac{1}{5} = \frac{x}{10 - 2x} \therefore x = \frac{10}{7}\text{Bar}$$

25. **(a)** Given that $\Delta E - \Delta H = 1200$ cal

Where ΔE is heat of reaction at constant volume and ΔH is heat of reaction at constant pressure.

Also we have $\Delta H = \Delta E + \Delta nRT$

∴ $\Delta nRT = -1200$

or $\Delta n = \frac{-1200}{2 \times 300} = -2$ $(R = 2 \text{ cal})$

Now $K_P = K_C (RT)^{\Delta n}$

$$\therefore \quad \frac{K_P}{K_C} = (0.0821 \times 300)^{-2} = 1.648 \times 10^{-3}$$

26. **(d)** $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$–

$$\begin{array}{ccc} 1-\alpha & \frac{\alpha}{2} & \frac{\alpha}{2} \end{array}$$

$$K_p = \frac{\left(\frac{\alpha}{2}P_T\right)^2}{(1-\alpha)^2 P_T^2} \Rightarrow \frac{\alpha}{1-\alpha} = 2\sqrt{K_p}$$

$$\alpha = \frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$$

27. **(a)** For the given equilibrium, the equilibrium concentration are

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

Equilibrium

concentration $c(1-\alpha)$ $\quad c\alpha \quad \frac{c\alpha}{2}$

$$K_P = \frac{(P_{B_2})(P_{AB})^2}{(P_{AB_2})^2} = \frac{\frac{c\alpha}{2}\times(c\alpha)^2\times P_T}{[c(1-\alpha)]^2\left[c\left(1+\frac{\alpha}{2}\right)\right]};$$

$$K_P = \frac{\alpha^3\times P_T}{2(1-\alpha)^2\left(1+\frac{\alpha}{2}\right)}$$

Since, α is small compared to unity, so $1-\alpha = 1$ and $1+\frac{\alpha}{2}\simeq 1$ $K_P = \frac{\alpha^3\times P_T}{2}$

28. **(b)**

$$\begin{array}{lcccc} & 2NO & + & Cl_2 & \rightleftharpoons 2NOCl \\ \text{Pressure at} & t=0 & & 0.02 & \\ \text{at eq.} & \frac{0.02\times 99}{100} & & P & \frac{0.02\times 1}{100} \end{array}$$

$$\because \quad K_P = \frac{[P_{NOCl}]^2}{[P_{NO}]^2[P_{Cl_2}]} = \frac{(0.02\times 0.01)^2}{(0.99\times 0.02)^2\times P} = 1\times 10^{-3}$$

$\therefore$ $P = 0.102$ atm

For Cl_2 in vessel, using $PV = nRT$

$0.102\times V = n\times R\times T$ (i)

For a gas in vessel, $1\times V = 0.2\times R\times T$ (ii)

By Eqs. (i) and (ii)

$\therefore$ mole of Cl_2 (n) at equilibrium = 0.0204

2 atm of NO reacts with 1 atm of Cl_2 (If V, T are constant)

$\frac{0.02\times 1\text{ atm}}{100}$ NO react with $\frac{0.02\times 1}{2\times 100} = 0.0001$ atm Cl_2

Thus, $0.0001\times V = n_{Cl_{2\text{used}}}\times RT$ (iii)

By eqs. (ii) and (iii),

$\therefore$ which have reacted = 2×10^{-5}

$\therefore$ Total Cl_2 added = $0.0204 + 2\times 10^{-5} = 0.02042$

LEVEL III

Match the Columns

1. **(a – s); (b – r); (c – p); (d – q)**

$K_P = K_C\,(RT)^{\Delta n}$

(a) $\Delta n = 0$

(b) $\Delta n = 2 - 4 = -2$

(c) $\Delta n = 2 - 1 = 1$

(d) $\Delta n = 2 - 0 = 2$

2. **(a – s); (b – q, r); (c – q); (d – p)**

Q = ratio of active masses of product to the active masses of reactant.

$Q \neq K$ reaction is not at equilibrium

$Q = K$ Reaction at equilibrium ($R_f = R_b$)

$Q > K$ reaction proceed in back word direction

$Q < K$ Reaction proceed in forward direction.

3. **(a – r), (b – p, q), (c – p), (d – p, q)**

$$K_{\text{eq}} = \frac{K_f}{K_b} = Ae^{-\frac{\Delta H}{RT}}$$

If $K_F > K_b$ $K_{\text{eq}} > 1$

If $K_F < K_b$ $K_{\text{eq}} < 1$

4. **(a – r), (b – p), (c – q), (d – s)**

$$\text{degree of dissociation} \propto \left[\frac{1}{P}\right]^{\frac{\Delta n}{2}}$$

5. **(a – q), (b – p, s), (c – p, s), (d – r)**

$\Delta n_g = (\Sigma n_P)_g - (\Sigma n_R)_g$

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

$\Delta n_g > 0 \Rightarrow K_p > K_c$

Assertion and Reason

6. **(a)** Catalyst just helps to attain equilibrium fast.

7. **(c)** Catalyst does not alter the constant of components at equilibrium.

8. **(b)** No of moles ∝ Pressure

9. **(d)** The graph shows irreversible reaction whereas in reversible reaction, concentration of reactant and product become constant at equilibrium position.

10. **(c)** $K_p = \frac{n_{PCl_3}\times n_{Cl_2}}{n_{PCl_5}}\times\left(\frac{p}{\Sigma n}\right)^1$ with addition of more and more inert gas Σn will increase that leads to decrease in the value of $\frac{P}{\Sigma n}$ and hence to keep K_P constant moles of the product would increase, i.e., α increases.

11. **(a)** Effect of pressure Le chatlier Principle.

12. **(a)** Active mass of solid remain constant.

13. **(b)** A catalyst favours the forward and backward reaction equally by lowering the corresponding energy of activation by equal magnitude.

14. **(b)** $\log_{10} = \frac{k_2}{k_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

15 **(b)** $Q < K_c$ forward reaction
$Q = K_c$ equilibrium
$Q > K_c$ backward direction

16. **(d)** By the use of catalyst, the reaction rate increases. But equilibrium constant does not change until the temperature is varying.

17. **(c)** In exothermic reaction, equilibrium constant increases by decreasing the temperature.

18. **(d)** $K_p = \frac{p^3_{H_2} \times p_{N_2}}{p_{NH_3}} = \frac{\text{atm}^3\text{atm}}{(\text{atm})^2} = (\text{atm})^2$

or $\Delta n = 4 - 2 = 2$
Unit of $K_p = (\text{atm})^2$

19. **(d)** Reaction is exothermic, low temperature favours forward reaction. High press favours forward reaction as it is accompanied by decrease in the number of moles.

Comprehension I

20.

	$CaCO_{3(s)}$	$\Leftrightarrow$	$CaO_{(s)}$	+	$CO_{2(g)}$
Initial moles	0.1 –		–		–
Equilibrium moles at 1000 K	$0.1 - x_1$		x_1		x_1

$$K_{P_1} = P^1_{CO_2} = \frac{n^1_{CO_2} RT_1}{V}$$

$$= \frac{x \times 0.0821 \times 1000}{10} = 0.059$$

$$x = \frac{0.059}{8.21}$$

unreacted $CaCO_3 = \left(0.1 - \frac{0.059}{8.21}\right) \times 100 = 9.282$.

21.

	$CaCO_{3(s)}$	$\Leftrightarrow$	$CaO_{(s)}$	+	$CO_{2(g)}$
Initial moles	0.1 –		–		–
Equilibrium moles at 1000 K	$0.1 - x_1$		x_1		x_1

$$K_{P_1} = P^1_{CO_2} = \frac{n^1_{CO_2} RT_1}{V}$$

Degree of dissociation, $\alpha_1 = \frac{x_1}{0.1} = 10x_1$

Equilibrium moles 0.1- x_2 x_2 x_2

at 1100 K $K_{P_2} = P^{11}_{CO_2} = \frac{n^{11}_{CO_2} RT_2}{V}$

$$\alpha_2 = \frac{x_2}{0.1} = 10x_2$$

$$\frac{\alpha_2}{\alpha_1} = \frac{x_2}{x_1} = \frac{K_{P_2}}{K_{P_1}} \times \frac{T_1}{T_2} = \frac{0.08}{0.059} \times \frac{1000}{1100} = 1.356$$

22. **(b)** 913.2°C

23. $\log\frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

$\Delta H = 6699$ cal

Comprehension II

24. **(C*)** $\Delta G° = -2.303\, RT \log K$

25. $\Delta G^0 = -2.303RT \log K_P = -5.79$ k.cal

26. $\Delta G^0 = -2.303RT \log k$

$\log k = \bar{1}.665$

$K = \text{Antilog of } \bar{1}.665 = 0.4625$

	A	+	B	$\Leftrightarrow$	C	+	D
Initial concentration	2		2		0		0
Equilibrium concentration	$2 - x$		$2 - x$		x		x

$$K_C = \frac{x^2}{(2-x)^2} = 0.4625$$

$$\frac{[C]}{[A]} = \frac{x}{2-x} = 0.68$$

Comprehension III

27. **(b)** Since $\Delta n = 0$, so $K_c = K_p = K_x$

$$K_x = \frac{X^4_{H_2}}{X^4_{H_2O}} = \frac{(2/2)^4}{(1/18)^4} = 18^4 = 1.05 \times 10^5$$

28. **(c)** $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g) \quad K_c = \left(\frac{1}{2.4 \times 10^{30}}\right)^{1/2}$

$NO(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g) \qquad K_2 = 1.4$

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$$

$$K = K_C \times K_2 = 9.03 \times 10^{-16}$$

29. **(a)** $K_p = \frac{P^2_{SO_3}}{P^2_{SO_2} \cdot P_{O_2}}$

$\therefore \quad P_{O_2} = \frac{1}{K_P} = \frac{1}{3.5}\text{atm} = 0.29\text{ atm}$

30. **(c)** $K_p = (P_{NH_3})^2 \cdot P_{CO_2} = (2p)^2 \times P = 4p^3$

$$P = \left(\frac{K_P}{4}\right)^{1/3} = 1.95 \times 10^{-2}$$

$\therefore \quad P_T = 3P = 3 \times 1.96 \times 10^{-2} = 0.058$

Comprehension IV

31. From question,

$\Delta H - \Delta E = 600$ cals. $= \Delta n \times 2 \times 300$ cals.
$\therefore \quad \Delta n = 1$
$\therefore \quad K_P = K_C (RT)^{\Delta n}$
$\therefore \quad K_P/K_C = (RT)^{\Delta n} = (0.821 \times 300)^1 = 24.63$

32. $K_P = K_C(RT)^{\Delta n}$, where Δn = total number of gaseous product molecules – total number of gaseous reactant molecules

$\Delta n = (1 + 1 - 0) = 2$
$\therefore \quad K_P = K_C(RT)^2$

33. $K_P = 10\text{ atm}^{-2}$. from unit of K_P, we can calculate

$\Delta n = -2$

$$K_P = K_C(RT)^{\Delta n} = K_C(RT)^{-2} = \frac{K_C}{(RT)^2}$$

∴ $K_P < K_C$

34. The unit of K_C is mol^2 L^{-2}, hence $\Delta n = 2$.

∴ $K_P = K_C\,(RT)^2$

$4 \times [0.821 - 300]^2$ atm^2

Subjective Questions

Integer-Answer-Type Questions

35. $N_2O_4 \rightleftharpoons 2NO_2$; $\quad G^0_{N_2O_4} = 100$ kJ mol^{-1}

0 5 $\quad$ 5 $\quad G^0_{NO_2} = 50$ kJ mol^{-1}

ΔG^0 for reaction $= 2 \times G^0_{NO_2} - G^0_{N_2O_4} = 2 \times 50 - 100 = 0$

$$\Delta G = \Delta G^0 + 2.303RT \log Q$$

Now, $\Delta G = 0 + 2.303 \times 8.314 \times 10^{-3} \times 298 \log \frac{5^2}{5}$

$= +3.99$ kJ $\approx$ 4kJ

36. For I equilibrium $2NO_2 \rightleftharpoons N_2O_4$

$$K_P = \frac{P'_{N_2O_4}}{(P'_{NO_2})^2} = 6.8 \qquad \ldots(i)$$

$P'_{N_2O_4} = 1.7$ atm ∴ by eq. (i) $P'_{NO_2} = 0.5$ atm

The equilibria are maintained using NO and NO_2 in the ratio 1 : 2

For II equilibria	NO	+	NO_2	$\rightleftharpoons$	N_2O_3
Initial pressures	P		$2P$		0
Pressures at equi	$(p - x)$		$(2P - x - 3.4)$		x

3.4 atm of NO_2 are used for I equilibrium to have $P'_{N_2O_4} = 1.7$ atm.

At equilibrium	$(P - x)$	0.5	x

(∵ P'_{NO_2} is same for both the equilbria since both reactions are at equilibrium at a time)

Total pressure at equilibrium (Given 5.05 atm)

$= P'_{NO} + P'_{NO_2} + P'_{N_2O_3} + P'_{N_2O_4}$

$= P - x + 0.5 + x + 1.7$

$5.05 = P + 2.20$

$P = 2.85$ atm

$2P - x - 3.4 = 0.5$

$2 \times 2.85 - x - 3.4 = 0.5$

$x = 1.80$ atm $\approx$ 2 atm

37.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Pressure at equilibrium	0.7		0.3

$$\therefore \quad K_P = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{0.3 \times 0.3}{0.7} = 0.1286 \text{ atm}$$

Now assume decomposition at 10 atm pressure

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial mole	1		0
Mole at equilibrium	$(1 - x)$		$2x$

$$K_P = \frac{(n_{NO_2})^2}{n_{N_2O_4}} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n} = \frac{(2x)^2}{(1-x)} \times \left[\frac{10}{(1+x)}\right]^1$$

$x = 0.0565$

$P'_{NO_2} = 1.07$ atm ≈ 1

$P'_{N_2O_4} = 8.93$ atm ≈ 9 atm

38. $T_1 = 700 + 273 = 973$ K,

$T_2 = 1000 + 273 = 1273$ K

$K_1 = 0.63$, $K_2 = 1.66$

Using the Van't Hoff equation

$$\log \frac{K_2}{K_1} = \frac{\text{Ä}H°}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\Rightarrow \quad \log\left(\frac{1.66}{0.63}\right) = \frac{\Delta H°}{2.303(1.99)}\left(\frac{1273 - 973}{1273 \times 973}\right);$$

⇒ $\Delta H° = 8.0 \times 10^3$ cal $= 8.0$ kcal

Note: The units of R and ΔH must be same

39. The given equilibrium is

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
At $t = 0$	4		16		0
At equilibrium	$4 - x$		$16 - 3x$		$2x$

Total gaseous moles at equilibrium $= 4 - x + 16 - 3x + 2x = (20 - 2x)$.

Since, pressure has fallen to 9/10 of its original value, hence number of moles will also fall up to the same extent.

$$(20 - 2x) = \frac{9}{10} \times 20 = 18$$

$x = 1$

$$[N_2] = \frac{4 - x}{1} = \frac{4 - 1}{1} = 3 \text{ mole/L}^{-1}$$

$$[NH_3] = \frac{2x}{1} = 2 \text{ mole/L}^{-1}$$

40. (i) The given equilibrium is

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
At $t = 0$	0.45		0.45		0		0
At equilibrium	$(0.45 - x)$		$(0.45 - x)$		x		x

$$K_C = \frac{x^2}{(0.45 - x)^2}$$

$$0.11 = \frac{x^2}{(0.45 - x)^2}$$

$x = 0.112$

∴ $[CO_2] = [H_2] = (0.45 - x) = (0.45 - 0.112)$

$= 0.3379 \approx 0.34$ mole each

$[CO] = [H_2O] = x = 0.112$ mole each

(ii) When 0.34 mole of CO_2 and H_2 are added in above equilibrium then following case exists.

	$CO_{2(g)}$	+	$H_{2(g)}$	$\rightleftharpoons$	$CO_{(g)}$ +	$H_2O_{(v)}$
At $t = 0$						
	$(0.34 + 0.34)$		$(0.34 + 0.34)$		0.11	0.11

At eqbm

$$\begin{array}{cccc} (0.68 -) & (0.68 -) & (0.11 +) & (0.11 +) \end{array}$$

$$K_C = \frac{[CO][H_2O]}{[CO_2][H_2]}$$

$$0.11 = \frac{(0.11+\alpha)^2}{(0.68-\alpha)^2}$$

$$\alpha = 0.086$$

$[CO_2] = [H_2] = (0.68 - 0.086) = 0.594$ mole each

$[CO] = [H_2O] = 0.11 + = 0.11 + 0.086 = 0.196$ mole each

41. The given equilibrium reaction is

$$\begin{array}{lccccc} & H_2 & + & I_2 & \rightleftharpoons & 2HI \\ \text{At } t = 0 & 6 & & 3 & & 0 \\ \text{At equilibrium} & (6-x)/1 & & 3-x & & 2x \end{array}$$

Concentration at equilibrium

$$K_C = \frac{(2x)^2}{(6-x)(3-x)}$$

$$64 = \frac{4x^2}{x^2 + 18 - 9x}$$

On solving $x = 2.84$

$$[HI] = \frac{2x}{1} = \frac{2 \times 2.84}{1} = 5.68;$$

$$[H_2] = \frac{6-x}{1} = \frac{6-2.84}{1} = 3.16$$

$$[I_2] = \frac{6-x}{1} = \frac{6-2.84}{1} = 3.16$$

In the present reaction $\Delta n = 0$ hence, volume change will not affect the equilibrium.

42. Number of moles of PCl_5

$$= \frac{\text{Weight}}{\text{Molecular weight}} = \frac{5}{208.5} = 0.024$$

The equilibrium for dissociation of PCl_5 maybe represented as

$$\begin{array}{lccccc} & PCl_5 & \rightleftharpoons & PCl_3 & + & Cl_2 \\ \text{At } t = 0 & 0.024 & & 0 & & 0 \\ \text{At equilibrium} & (0.024 - x) & & x & & x \end{array}$$

Total moles of gas components $= 0.024 - x + x + x$
$= (0.024 + x)$

We know, $PV = nRT$

$$1 \times 1.9 = (0.024 + x)\, 0.0821 \times 523$$

$$(0.024 + x) = \frac{1.9}{0.0821 \times 523}$$

$$x = 0.0202$$

$$\text{Degree of dissociation} = \frac{0.0202}{0.024} = 0.843$$

$$[PCl_5] = \frac{0.024-\alpha}{1.9} = \frac{0.024-0.0202}{1.9} = \frac{0.0038}{1.9}$$

$$[PCl_3] = [Cl_2] = \frac{\alpha}{V} = \frac{0.0202}{1.9}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left[\dfrac{0.0202}{1.9}\right]^2}{\dfrac{0.0038}{1.9}} = \frac{4.08 \times 10^{-4}}{1.9 \times 0.0038}$$

$= 0.0565$ mole/L^{-1}

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

where $K_c = 0.0565$

$$\Delta n = 2 - 1 = 1$$

43. Equilibrium of formation of NH_3 may be given as,

$$\begin{array}{lccccc} & N_2 & + & 3H_2 & \rightleftharpoons & 2NH_3 \\ \text{At } t = 0 & 1 & & 3 & & 2 \\ \text{At equilibrium} & (1-x) & & 3(1-x) & & 2x \end{array}$$

Total moles at equilibrium $= 1 - x + 3\,(1 - x) + 2x = 4 - 2x$

$$\text{Mole fraction of } NH_3 = \frac{2x}{(4-2x)}$$

$$\text{Partial pressure of } NH_3 = \frac{2x}{(4-2x)} \times p = \frac{2x}{(4-2x)} \times 50$$

$$25 = \frac{2x \times 50}{(4-2x)} \quad \therefore \quad x = 0.666$$

$$K_p = \frac{16x^2(2-x)^2}{27p^2(1-x)^4} = \frac{16 \times (0.666)^2 (2-0.666)^2}{27 \times (50)^2 \times (0.334)^2}$$

$$= 1.677 \times 10^{-3}$$

44. The given equilibrium is

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \qquad \ldots(i)$$

(i) If $[SO_3] = [SO_2]$

$$\text{Then } K_C = \frac{1}{[O_2]}$$

$$[O_2] = \frac{1}{K_C} = \frac{1}{100} = 0.01 \text{ mole/L}^{-1}$$

Total moles of O_2 present $= 0.01 \times 10 = 0.1$ mole

Volume of vessel is 10 L^{-1}

(ii) When $[SO_3] = [SO_2] \times 2$

$$\text{Then } K_C = \frac{[SO_2]^2 \times [2]^2}{[SO_2]^2[O_2]} \text{ from Eq. (i)}$$

$$100 = \frac{4}{[O_2]}$$

$[O_2] = 4/100 = 0.04$ mole/L^{-1}

Total moles of O_2 in vessel at equilibrium $= 0.04 \times 10 = 0.4$ mole.

45. If $2x$ is the partial pressure of SO_3 that is decreased at equilibrium, we will have

$$\begin{array}{lccccc} & 2SO_2(g) & + & O_2(g) & \rightleftharpoons & 2SO_3(g) \\ t = 0 & 0 & & 2 \text{ atm} & & 1 \text{ atm} \\ t_{eq} & 2x & & 2 \text{ atm} + x & & 1 \text{ atm} - 2x \end{array}$$

Hence, $K_p = \dfrac{(p_{SO_3})^2}{(p_{SO_2})^2(pO_2)} = \dfrac{(1\text{ atm} - 2x)^2}{(2x)^2(2\text{ atm} + x)}$

$= 900\text{ atm}^{-1}$

Assuming $x << 2$ atm, we get

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2(pO_2)} = \frac{(1\text{ atm} - 2x)^2}{(2x)^2(2\text{ atm} + x)}$$

$= 900\text{ atm}^{-1}$

$$= \frac{1}{4x^2 \times 2} = 900, \frac{1}{x^2} = 7200\ x = \sqrt{\frac{1}{7200}}$$

$= 0.0115$

Hence, $p(SO_2) = 2x = 0.023$ atm; $p(O_2) = 2$ atm + $x = 2.0115$ atm
and $p(SO_3) = 1$ atm – $2x = 0.977$ atm

46. We have

$$\begin{array}{lll} 2H_2S\ (g) \rightleftharpoons & 2H_2\ (g)\ + & S_2(g) \\ n(1-a) & na & +\ n(a/2) \end{array}$$

Total amount of gases = $n(1 + a/2)$

Hence, $p_{H_2S} = \dfrac{1-\alpha}{1+\alpha/2}p$; $p_{H_2} = \dfrac{\alpha}{1+\alpha/2}p$;

$$p_{S_2} = \frac{\alpha/2}{1+\alpha/2}p$$

Thus, $K_p = \dfrac{(pH_2)^2(ps_2)}{(p_{H_2S})^2} = \dfrac{\left(\dfrac{\alpha}{1+\alpha/2}p\right)^2\left(\dfrac{\alpha/2}{1+\alpha/2}p\right)}{\left(\dfrac{1-\alpha}{1+\alpha/2}p\right)^2}$

$$= \frac{\alpha^3 p}{2(1-\alpha)^2(1+\alpha/2)}$$

Substituting the given value of a, we get

$$K_p = \frac{(0.31)^3(1\text{ atm})}{2(1-0.31)^2(1+0.31/2)} = 2.71 \times 10^{-2}\text{ atm}$$

For the given reaction, $\Delta n_g = +1$
Hence, $K_c = K_p(RT)^{-\Delta ng}$
$= (2.71 \times 10^{-2}\text{ atm})$
$\{(0.0821\text{ L atm K}^{-1}\text{ mol}^{-1})\ (1380\text{ K})\}^{-1}$
$= 2.39 \times 10^{-4}\text{ mol L}^{-1}$

47. **(a)** Let n be the initial amount of $COCl_2$ and α be its degree of dissociation. We will have

$$\begin{array}{llll} & COCl_2 \rightleftharpoons & CO\ + & Cl_2 \\ t = 0 & n & & \\ t_{eq} & n(1-\alpha) & n\alpha & n\alpha \end{array}$$

Total amount of gases = $n(1 - \alpha) + n\alpha + n\alpha = n(1 + \alpha)$
Now, the volume of the flask will be

$$V = \frac{n(1+\alpha)RT}{p}$$

The density of the mixture will be

or $\rho = \dfrac{nM_{COCl_2}}{V} = \dfrac{nM_{COCl_2}p}{n(1+\alpha)RT} = \dfrac{pM_{COCl_2}}{(1+\alpha)RT}$

$$\alpha = \frac{pM_{COCl_2}}{\rho RT} - 1$$

Substituting the given values, we get

$$\alpha = \frac{(1\text{ atm})(99\text{ g mol}^{-1})}{(1.162\text{ g L}^{-1})\ (0.0821\text{ L atm K}^{-1}\text{ mol}^{-1})\ (724\text{ K})} - 1$$

$= 1.433 - 1 = 0.433$

(b) The partial pressures of the species involved in the reactions are

$$p_{COCl_2} = \frac{1-\alpha}{1+\alpha}p;\ p_{CO} = \frac{\alpha}{1+\alpha}p;\ p_{Cl_2} = \frac{\alpha}{1+\alpha}p;$$

Hence, $K_p = \dfrac{p_{CO}p_{Cl_2}}{p_{COCl_2}} = \dfrac{\alpha^2}{1-\alpha^2}p$

Which gives $K_p = \dfrac{(0.433)^2}{1-(0.433)^2}(1\text{ atm}) = 0.231$

48. Let n be the amount of N_2O_4 at $t = 0$ and let α be the degree of dissociation of N_2O_4 at equilibrium. Then

$$\begin{array}{lll} & N_2O_4\ (g) \rightleftharpoons & 2NO_2\ (g) \\ t = 0 & n & 0 \\ t_{eq} & n(1-\alpha) & n(2\alpha) \end{array}$$

Total amount at equilibrium = $n(1 + \alpha)$
Using the ideal gas equation, we get

$$PV = n(1+\alpha)RT = \frac{\text{mass}}{M}(1+\alpha)RT$$

(or) $PM = r(1 + \alpha)RT$ (or) $\alpha = \dfrac{PM}{\rho RT} - 1$

Substituting the given data, we get

$$\alpha = \frac{(1\text{ atm})(92\text{ g mol}^{-1})}{(1.84\text{ g dm}^{-3})(0.082\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1})(348\text{ K})} - 1$$

$= 1.752 - 1 = 0.752$

Hence,

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{[2\alpha p/(1+\alpha)]^2}{(1-\alpha)p/(1+\alpha)} = \frac{4\alpha^2}{1-\alpha^2}p$$

$$= \frac{4(0.752)^2}{1-0.752^2} \times 1\text{ atm} = 5.206\text{ atm}$$

49. If p is the partial pressure of N_2O_5 that has decomposed,

$$\begin{array}{lll} N_2O_5\ (g) \rightleftharpoons & 2NO_2(g)\ + & \frac{1}{2}O_2 \\ 600\text{ mm-Hg} - p & 2p & p/2 \end{array}$$

Pressure at any time = (600 mm-Hg – p) + $2p$ + $p/2$ = 600 mm-Hg + $(3/2)p$

Equating this to 960 mm-Hg, we get

$$p = (2/3)\,(960 - 600)\text{ mm Hg} = 244\text{ mm-Hg}$$

The mole fraction of N_2O_5 decomposed would be $x = \dfrac{244\text{ mm-Hg}}{600\text{ mm-Hg}} = 0.407$

50. The reaction along with the given data is

	$NH_4HS(s)$	$\rightleftharpoons$ $NH_3(g)$	+ $H_2S(g)$
$t = 0$	3.06g (= 0.06 mol)	0	0
t_{eq}	0.7×0.06 mol	0.3×0.06 mol = 0.018 mol	0.3×0.06 mol = 0.018 mol

(i) The equilibrium constant K_c is

$$K_c = [NH_3][H_2S] = \left(\frac{0.018\text{ mol}}{2\text{L}}\right)\left(\frac{0.018\text{ mol}}{2\text{L}}\right)$$

$$= 8.1 \times 10^{-5}\ (\text{mol/L})^2$$

The equilibrium constant K_p is

$K_p = K_c\,(RT)^{\text{Dvg}} = (8.1 \times 10^{-5}\text{ mol}^2/\text{L}^2)[(0.082\text{ atm L mol}^{-1}\text{K}^{-1})(300\text{ K})]^2 = 4.90 \times 10^{-2}\text{ atm}^2$

(ii) There will not be any effect on the equilibrium by introducing more of solid NH_4HS as the equilibrium constant is independent of the quantity of solid.

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. **(b)** $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$$\begin{array}{ccc} 1 & 0 & 0 \\ 1-x & x & x \end{array}$$

Also $P'_{PCl_3} = \dfrac{P_{\text{eq.}} \cdot x}{(1+x)} = \left[\dfrac{x}{1+x}\right]P$

2. **(b)** $K'_C = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

$$K_C = 4.9 \times 10^{-2} = \frac{[SO_2][O_2]}{[SO_3]}$$

$$\therefore \quad K'_C = \left[\frac{1}{K_C}\right]^2 = \left[\frac{1}{4.9 \times 10^{-2}}\right]^2 = 416$$

3. **(a)** $X \rightleftharpoons 2Y$

$$\begin{array}{cc} 1 & 0 \\ (1-x) & 2x \end{array}$$

$$\Rightarrow \quad K_{P1} = \frac{(2x)^2}{(1-x)}\left(\frac{P_1}{1+x}\right)^1$$

$Z \rightleftharpoons P + Q$

$$\begin{array}{ccc} 1 & 0 & 0 \\ (1-x) & x & x \end{array}$$

$$\Rightarrow \quad K_{P2} = \frac{(2x)^2}{(1-x)}\left(\frac{P_1}{1+x}\right)^1$$

$$\frac{4 \times P_1}{P_2} = \frac{1}{9} = \frac{P_1}{P_2} = \frac{1}{36}$$

4. **(c)**

(a) $CO_{(g)} + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g);\ K_1$ (A)

(b) $CH_{4(g)} + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g);\ K_2$ (B)

(c) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g);\ K_3$ (C)

Equation (C) = Eq. (A) + Eq. (B)

Thus, $K_3 = K_1 \cdot K_2$

5. **(a)**

	$CO_2(g) + C(s)$	$\rightleftharpoons$	$2CO(g)$
Initial	0.5 atm		–
At equilibrium	$(0.5 - p)$		$2p$ atm

Total pressure of CO_2 and CO gases

$$P_{CO_2} + P_{CO} = P_{\text{total}}$$

$$0.5 - (p + 2p) = 0.8,\ p = 0.3\text{ atm}$$

$$\therefore \quad p_{CO_2} = 0.5 - 0.3 = 0.2\text{ atm}$$

$$P_{CO} = 2p = 0.6\text{ atm}$$

$$K_P = \frac{p^2_{CO}}{p_{CO_2}} = \frac{0.6 \times 0.6}{0.2} = 1.8\text{ atm}$$

6. **(d)** For the reaction

$N_2 + O_2 \rightarrow 2NO \qquad K_c = 4 \times 10^{-4}$

Hence for the reaction

$$NO \rightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2$$

$$K'_c = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = \frac{100}{2} = 50$$

7. **(b)** By using this formula, equilibrium constant,

$$K_P = K_c(\text{RT})^{\Delta ng}$$

where Δn_g = (number of moles of products) – (number of moles of reactants)

For the given reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$\Delta n_g = 1 - \left[\frac{1}{2} + 1\right] = 1 - \left[\frac{3}{2}\right] = -\frac{1}{2}$$

8. **(b)** $\Delta G = \Delta G^{\circ} + \text{RT ln Q}$

$$= 2494.2 + 8.1314 \times 300 \ln 4$$

$$= \text{Positive } \Delta G = \text{RT ln } \frac{Q}{K}$$

Since, ΔG is positive so, $Q > K$, so reaction shifts in reverse direction.

JEE Advanced

Single-Correct-Answer Type

9. **(a)**In a reversible reaction, a catalyst speeds up both forward and backward reactions to the same extent, so (C) is wrong. At equilibrium,

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} = 0$$

$$\Rightarrow \quad 2G_{NH_3} - (G_{N_2} + 3G_{H_2}) = 0 \text{ or } 2G_{NH_3} = G_{N_2} + 3G_{H_2}$$

Multiple-Correct-Answer Type

10. (b), (c), (d)

$$2Cu^{1} \rightleftharpoons Cu^{0} + Cu^{II}$$

$Cl^{\ominus}$ and $CN^{\ominus}$ both make precipitate with Cu^{1} and hence drive the reaction to the left.

Cupric thiocyanate $Cu(SCN)_2$, black powder, insoluble in water, readily turning into cuprous thiocyanate Cu(SCN) a whitish yellow powder, hence it also drives the equilibrium to the left.

11. (a), (b), (d)

(a) $\Delta H = C_{P(rxn)} \Delta T$

Hence enthalpy depends on temperature

(b) $CaCO_{3(g)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}\ K_P = P_{CO_2}$

(c) K_{eq} depends only on temperature and not on pressure.

(d) Enthalpy of reaction is independent of the catalyst. A catalyst generally lowers activation energy

Assertion-Reasoning Type

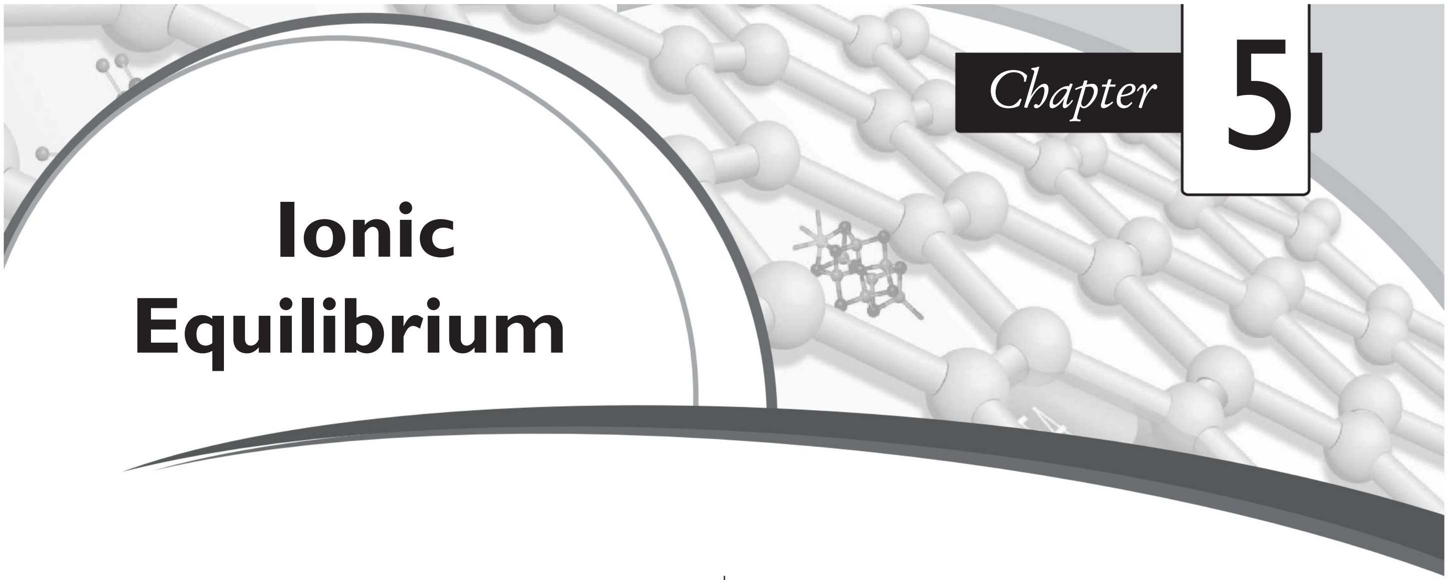
12. (d) We know that for every chemical reaction at equilibrium. Gibb's free energy ($\Delta G = 0$) is zero. However standard Gibb's free energy (ΔG^{o}) may or may not be zero. Thus Statement 1 is false.

For a spontaneous reaction, at constant temperature and pressure, the reaction proceed in the direction in which ΔG is < 0, i.e., in the direction of decreasing Gibb's energy (G) so Statement 2 is true.

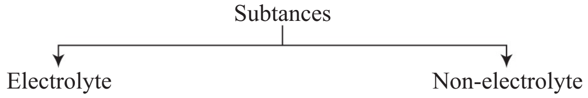
Thus, the only such option is (D) which is the correct answer.

Chapter 5

Ionic Equilibrium



Key Concepts



ELECTROLYTES

These are the species which can dissociate into the ions in their aqueous solution or in the molten state.

For example, NaCl, KCl

NON-ELECTROLYTE

These species cannot provide the ions in their molten state.

For example, sucrose, glucose.

Types of Electrolyte

1. **Strong electrolytes:** These electrolyte dissociate almost completely, i.e., $\alpha \simeq 1$ or 100%
   For example, Strong Acid, Strong Base and salts
   Strong Acid → $HClO_4$, HCl, HBr, HI, H_2SO_4, HNO_3
   Strong Base → group I and group II, hydroxide (except Li, Be)

   $$\begin{array}{lll} HCl(aq.) \rightarrow & H^+(aq.) + & Cl^-(aq.) \\ C & 0 & 0 \\ 0 & C & C \end{array}$$

2. **Weak electrolytes:** These electrolytes dissociate up to the small extent, i.e., not complete dissociation.
   For example, Weak Acid, Weak Base.

   $$CH_3COOH(aq.) \rightleftharpoons CH_3COO^-(aq.) + H^+(aq.)$$

Factors affecting degree of dissociation (α)

1. Nature of electrolyte: Strong or Weak
2. Nature of solvent: More is the polarity of solvent, more will be the α (degree of dissociation)
3. Temperature $T \propto \alpha$ (degree of dissociation)
4. Concentration: $\propto 1/\alpha$ (degree of dissociation)
   Dilution $\propto \alpha$
5. Common ion effect: Whenever common ion is added to the aqueous solution of weak electrolyte α decreases because of the increased concentration of common ion.

   $$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

   $$HCl \longrightarrow Cl^- + H^+$$

   Here the common ion is H^+. So dissociation of weak electrolyte $CH_3COOH \downarrow$ (decreases)

Ostwald's law of dilution

Applicable for weak electrolyte.

$'\alpha' \propto \frac{1}{\sqrt{C}}$ 'α' degree of dissociation of weak electrolyte

c = concentration

$'\alpha' \propto \sqrt{V}$ $V = \frac{1}{C}$ = dilution

Ostwald's law of dilution for monobasic acid

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial Molarity	C mole		–		–
at equilibrium	$C(1-\alpha)$		$C\alpha$		$C\alpha$

Dissociation constant of Weak Acid (K_a)

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{\alpha^2 C}{(1-\alpha)} = \alpha^2 C$$

If $\alpha << 1 \Rightarrow 1 - \alpha \simeq 1$

α will be neglected when less than equal to 0.05, i.e., 5% or

$10^{-3} > \frac{K_a}{C}$

$$\alpha = \sqrt{\frac{K_a}{C}} \quad \Rightarrow \quad \text{`}\alpha\text{'} \propto \frac{1}{\sqrt{C}}$$

$$[\mathrm{H^+}] = C \cdot \alpha = \sqrt{K_a \cdot C}$$

For Monoacidic Base

$$\begin{array}{lccc} \mathrm{BOH} & \rightleftharpoons & \mathrm{B^+} & + \quad \mathrm{OH^-} \\ C & & - & - \\ C(1-\alpha) & & C\alpha & C\alpha \end{array}$$

$$K_b = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{\alpha^2 C}{(1-\alpha)}$$

If $\alpha << 1 \quad \Rightarrow \quad 1 - \alpha \simeq 1$

α will be neglected when less than or equal to 0.05, i.e., 5%

$$K_b = \alpha^2 C \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_b}{C}}$$

$$[\mathrm{OH^-}] = C\alpha = \sqrt{K_b \cdot C}$$

Relative Strength of Weak Acid or Weak Base

For two Weak Acid

$$\text{Relative strength} = \frac{[\mathrm{H^+}]_1}{[\mathrm{H^+}]_2} = \frac{\sqrt{Ka_1 \cdot C}}{\sqrt{Ka_2 \cdot C}}$$

$$\text{Relative strength} = \sqrt{\frac{Ka_1}{Ka_2}}$$

For weak bases:

$$\text{Relative strength} = \sqrt{\frac{Kb_1}{Kb_2}}$$

$$K_a \uparrow \Rightarrow P^{K_a} \downarrow (P^{K_a} = -\log K_a) \Rightarrow \text{acidic strength} \uparrow$$

$$K_b \uparrow \Rightarrow P^{K_b} \downarrow \Rightarrow \text{basic nature} \uparrow$$

Dissociation of Polyproticacids

$$\mathrm{H_3PO_4} \rightleftharpoons \mathrm{H^+} + \mathrm{H_2PO_4^-};\ Ka_1$$

$$\mathrm{H_2PO_4^-} \rightleftharpoons \mathrm{H^+} + \mathrm{HPO_4^{2-}};\ Ka_2$$

$$\mathrm{HPO_4^{2-}} \rightleftharpoons \mathrm{H^+} + \mathrm{PO_4^{3-}};\ Ka_3$$

$$\mathrm{H_3PO_4} \rightleftharpoons 3\mathrm{H^+} + \mathrm{PO_4^{3-}}; \qquad Ka = Ka_1 \times Ka_2 \times Ka_3$$

For any polyprotic acid or any polyacidic base, successive dissociation constant will go on decreasing.

Ionic Product of Water (Kw)

Water is weak electrolyte and it self-ionises.

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}$$

Dissociation constant (Kd) of water

$$Kd = \frac{[\mathrm{H^+}][\mathrm{OH^-}]}{[\mathrm{H_2O}]}$$

then, ionic product of water or self-ionisation constant.

$$\mathrm{Kw} = k_d[\mathrm{H_2O}]$$
$$= [\mathrm{H^+}][\mathrm{OH^-}]$$

1. Kw is constant at a given temperature.
   Kw at 25°C is 10^{-14}
   P_{kw} at 25°C = 14
2. Variation of kw with temperature is given by:

$$\ln \frac{Kw_2}{Kw_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} = \frac{1}{T_2}\right]$$

$\Delta H \rightarrow$ heat of ionisation of water.

as ΔH is +ve $\Rightarrow Kw \uparrow \Rightarrow P_{\mathrm{kw}} \downarrow$

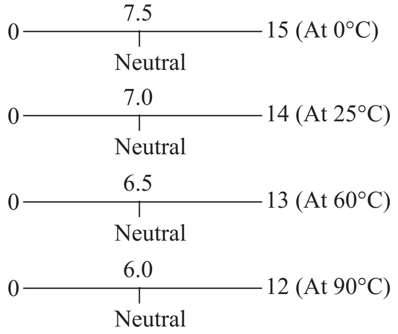
$$Kw = [\mathrm{H^+}]\,[\mathrm{OH^-}]$$

$$[\mathrm{H^+}] = [\mathrm{OH^-}] = \sqrt{Kw}$$

We know $Kw \propto$ temperature

Temperature	Kw	$[\mathrm{H^+}] = [\mathrm{OH^-}]$	$= \sqrt{Kw}$
0°C	10^{-15}	$\sqrt{10 \times 10^{-16}}$	$= 3.16 \times 10^{-8}$
25°C	10^{-14}	$\sqrt{10^{-14}}$	$= 10^{-7}$
60°C	10^{-13}	$\sqrt{10 \times 10^{-14}}$	$= 3.16 \times 10^{-7}$
90°C	10^{-12}	$\sqrt{10^{-12}}$	$= 10^{-6}$

Ph scale at different temperature



3. In neutral solution:

$$[\mathrm{H^+}] = [\mathrm{OH^-}] = \sqrt{Kw} = 10^{-7}\ \mathrm{mol/L}\,(\text{at } T = 25°\mathrm{C})$$

$[\mathrm{H^+}][\mathrm{OH^-}] = \mathrm{Kw}$ (for any solution)

at 25°C, neutral pH = 7

Relationship between *Ka* and *Kb* of conjugate acid base pair

$$\mathrm{HA(aq.)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq.)} + \mathrm{A^-(aq.)}$$

$$Ka = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \qquad \text{...(i)}$$

For conjugate base:

$$A^-(aq.) + H_2O(e) \rightleftharpoons HA(aq.) + OH^-(aq.)$$

$$Kb(A^-) = \frac{[HA][OH^-]}{[A^-]} \qquad ...(ii)$$

From Eqs (i) and (ii);

$$Ka(HA) \times Kb(A^-) = [H_3O^+][OH^-]$$

$$Ka(HA) \times Kb(A^-) = Kw$$

$$p^{Ka}(HA) + p^{Kb(A-)} = p^{Kw}$$

$$pH = -\log(a_{H^+}) \qquad a \rightarrow \text{activity}$$

$$= -\log[H^+]$$

$$[H^+] = 10^{-pH}$$

$$p^{OH} = -\log[OH^-]$$

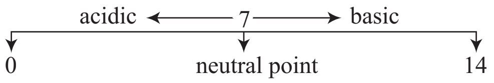
$$[OH^-] = 10^{-POH}$$

$$[H^+]\,[OH^-] = Kw$$

$$\Rightarrow \quad -\log[H^+] - \log[OH^-] = -\log Kw$$

$$\Rightarrow \quad pH + p^{OH} = p^{Kw} = 14 (\text{at } T = 25°C)$$

pH scale: (at 25°C)



$$pH \uparrow \quad \Rightarrow \quad p^{OH} \downarrow \quad \Rightarrow \quad \text{basic strength} \uparrow$$

Q. At 20°C, pH of a solution is 7, what will be its nature?

Ans. Since temperature 20°C and less than 25°C

$\therefore$ $[H^+]$ Neutral less than 10^{-7}. $\therefore$ Solution acidic in nature.

1. p^H calculation for strong acids:

$[H^+]$ = Normality of acid = N

= $M \times$ basicity = nf. M

2. p^H calculation for strong base:

$[OH^-]$ = Normality of base = N

= $M \times$ acidity. = nf. M

Ph = 14 – POH

Q. Find p_H of 10^{-7} MHCl.

Ans. $[H^+] = 10^{-7} + \{10^{-7}\}$ due to self-ionisation of H_2O.

$= 2 \times 10^{-7}$

pH = 7 – log 2 = 6.7

OR

Note:

For very diluted solution, i.e., when $[H^+]$ or $[OH^-]$ is < 10^{-6}M, while calculating the p^H H^+ or OH^- due to self-ionisation of water are taken.

If we consider, the common ion effect of water.

H_2O	$\rightleftharpoons$	H^+	+	OH^-
		$(x + 10^{-7})$		x
HCl	$\longrightarrow$	H^+	+	Cl^-
		$(x + 10^{-7})$		10^{-7}

$$K_W = [H^+][OH^-] = 10^{-14}$$

$$(x + 10^{-7})x = 10^{-14}$$

$$x^2 + 10^{-7}x - 10^{-14} = 0$$

$$x = 0.618 \times 10^{-7}$$

$$[H^+] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$$

$$pH = 6.79$$

3. pH calculation for weak acids

$[H^+] = C \cdot \alpha$: C = Normality

α = degree of dissociation

For monoprotic Weak Acide:-

$$[H^+] = C \cdot \alpha = \sqrt{K_a \cdot C}$$

$$pH = \frac{-1}{2}\log K_a - \frac{1}{2}\log C$$

$$pH = \frac{1}{2}[p^{Ka} - \log C]$$

4. pH calculation For weak base

$[OH^-] = C \cdot \alpha]$ C = Normality

α = degree of dissociation

For monoacidic base

$$[OH^-] = C\alpha = \sqrt{Kb \cdot C}$$

$$P^{OH} = \frac{1}{2}[P^{kb} - \log C]$$

5. pH calculation of mixing of Strong Acid and Strong Base

Resultant normality of solution (N_R)

$$N_R = \frac{|\Sigma(NV)acid - \Sigma(NV)base|}{V\ final}$$

(i) If $\Sigma(NV)acid > \Sigma(NV)base$ $\Rightarrow$ Acidic solution.

$\Rightarrow$ $[H+] = N_R$

(ii) If $\Sigma(NV)acid < \Sigma(NV)base$ $\Rightarrow$ Basic solution.

$\Rightarrow$ $[OH^-] = N_R$

(iii) If $\Sigma(NV)acid = \Sigma(NV)base$ $\Rightarrow$ Neutral solution

$= [H^+] = [OH^-] = 10^{-7}$

$\Rightarrow$ pH = 7

6. pH calculation of Mixture of Weak Acid and Strong Acid

	Weak acid					**Strong acid**				
	HA	$\rightleftharpoons$	H^+	+	A^-	HB	$\rightarrow$	H^+	+	B^-
Initial	C_1		–		–	C_2		–		–
Final	$C_1 - x$		$(x + C_2)$		x	–		C_2		C_2

$$K_a = \frac{(C_2 + x)x}{C_1 - x}$$

Due to common ion effect of Strong Acid for Weak Acid

$x << C_1$

$$\Rightarrow \quad C_1 - x \simeq C_1$$

$$K_a = \frac{(C_2 + x) \cdot x}{C_1}$$

If Strong Acid is highly concentrated

$$C_2 + x \simeq C_2$$

$$K_a = \frac{C_2 \cdot x}{C_1}$$

7. pH for mixing of weak acids

HA	$\rightleftharpoons$	H^+	+	A^-	HB	$\rightleftharpoons$	H^+	+	B^-
C_1		–		–	C_2		–		–
$C_1 - x$		$(x+y)$		x	$C_2 - y$		$(x+y)$		y

$$Ka_1 = \frac{(x+y)\cdot x}{C_1 - x} \qquad Ka_2 = \frac{(x+y)\cdot y}{C_2 - y}$$

Due to common ion effect, x, y will be negligible.

$$C_1 - x \simeq C_1 \qquad C_2 - y \simeq C_2$$

$$Ka_1 = \frac{(x+y)\cdot x}{C_1}; \; Ka_2 = \frac{(x+y)\cdot y}{C_2}$$

$$Ka_1C_1 = (x+y)\cdot x \qquad \text{...(i)}$$

$$Ka_2C_2 = (x+y)\cdot y \qquad \text{...(ii)}$$

(i) + (ii); ⇒ $(x+y)^2 = Ka_1C_1 + Ka_2C_2$

⇒ $[H^+] = \sqrt{Ka_1C_1 + Ka_2C_2}$

8. pH for mixing of weak bases

$$[OH^-] = \sqrt{Kb_1C_1 + Kb_2C_2 + \cdots}$$

9. p^H of polyprotic acids:

For H_2S if $Ka_1 = 10^{-7}$; $Ka_2 = 10^{-14}$

$$\begin{array}{lcccll}
H_2S & \rightleftharpoons & H^+ & + & HS^-; & Ka_1 \\
C & & – & & – & \\
C - x & & (x+y) & & x - y & \\
HS^- & \rightleftharpoons & H^+ & + & S^{2-}; & Ka_2 \\
(x - y) & & (x+y) & & y &
\end{array}$$

$$Ka_1 = \frac{(x+y)(x-y)}{(c-x)} = \frac{x^2}{(c-x)} = \frac{x^2}{c}$$

$$Ka_2 = \frac{(x+y)y}{(x-y)} = \frac{xy}{x} = y$$

$$Ka_1 >> Ka_2 \Rightarrow x >> y$$

$x + y = x,\; x - y \simeq x$

as Ka_1 is very low ⇒ $c - x \simeq c$.

> ***Note:*** $H_2S \rightleftharpoons 2H^+ + S^{2-}$; $Ka = Ka_1 \times Ka_2$
>
> The formula is used only when $[H^+]$ in the solution of H_2S is given and sulphide ion is asked or vice versa.
>
> $$Ka_1 \times Ka_2 = \frac{[H^+]^2 \times [S^{2-}]}{[H_2S]}$$

Example 1: H_3PO_4;

$$Ka_1 = 7 \times 10^{-3} \quad Ka_2 = 6 \times 10^{-8} \quad Ka_3 = 8 \times 10^{-13}$$

$$\begin{array}{lcccll}
H_3PO_4 & \rightleftharpoons & H^+ & + & H_2PO_4^-; & Ka_1 \\
c & & – & & – & \\
(c - x) & & (x+y+z) & & x - y & \\
H_3PO_4^- & \rightleftharpoons & H^+ & + & HPO_4^{2-}; & Ka_2 \\
(x - y) & & (x+y+z) & & y - z & \\
H_3PO_4^{2-} & \rightleftharpoons & H^+ & + & PO_4^{3-}; & Ka_3 \\
(y - z) & & (x+z+y) & & z &
\end{array}$$

$$Ka_1 = \frac{(x+y+z)(x-y)}{c-x} \qquad Ka_3 = \frac{(x+y+z)z}{(y-z)}$$

$$Ka_2 = \frac{(x+y+z)(y-z)}{x-y}$$

$Ka_1 >> Ka_2 >> Ka_3$

⇒ $x >> y >> z$

⇒ $x + y + z \simeq x$ and $x - y \simeq x$ and $y - z \simeq y$

$Ka_1 = \dfrac{x \cdot x}{c - x} = \dfrac{x^2}{c - x}$ as Ka_1 is significant x is not negligible

or $\dfrac{Ka}{c} > 10^{-3}$.

$$Ka_2 = y$$

$$Ka_3 = \frac{x \cdot z}{y}$$

TYPES OF SALT

(i) **Complete salts or normal salts**

These are the salts which cannot provide H^+ or OH^- ions in their aqueous solution.

K_2SO_4, Na_2HPO_3 (salt of H_3PO_3 (Basicity-2), NaH_2PO_2

(ii) **Incomplete salts**

Salts which can provide H^+ and OH^- in their aqueous solution.

(a) Acidic salts: provides H^+ in their aqueous solution.

For example, $NaHCO_3$, $KHSO_4$, NaH_2PO_3

(b) Basic salts: provide OH^- in their aqueous solution.

Ex. Ca(OH)Cl

Salt Hydrolysis

It is the reverse process of naturalisation in which ions of the salt react with water and form acid and base.

$$\text{Salt + Water} \rightleftharpoons \text{Acid + Base}$$

Types of salt hydrolysis

1. **Salt of Strong Acid and Strong Base.**

$NaCl + H_2O \rightleftharpoons NaOH + HCl$

$Na^+ + Cl^- + H_2O \rightleftharpoons Na^+ + OH^- + H^+ + Cl^-$

$H_2O \rightleftharpoons OH^- + H^+$

⇒ Salt of strong acid and Strong Base are not hydrolysed.

⇒ Their aqueous solution are neutral in nature.

2. **Salt of Strong Acid and Weak Base.**

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

⇒ Salt of Strong Acid and Weak Base show the cationic hydrolysis.

⇒ Their aqueous solution are acidic in nature.

Relation between hydrolysis constant (K_h), K_w and K_b

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad ...(i)$$

$$K_w = [H^+][OH^-] \quad ...(ii)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad ...(iii)$$

$$K_h = \frac{K_w}{K_b}$$

Degree of hydrolysis (h)

$$h = \frac{\text{Moles hydrolysed}}{\text{Moles taken initially}}$$

$$\begin{array}{llll} NH_4^+ + H_2O & \rightleftharpoons & NH_4OH & + H^+ \\ C & & - & - \\ C(1-h) & & Ch & Ch \end{array}$$

$$K_h = \frac{Ch \cdot Ch}{C(1-h)} = \frac{h^2C}{(1-h)}$$

As h is negligible $1 - h \simeq 1$.

$$K_h = h^2C$$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \times C}}$$

pH calculation

$$[H^+] = Ch = \sqrt{K_h \cdot C}$$

$$[H^+] = \sqrt{\frac{K_w}{K_b} \times C}$$

$$pH = \frac{-1}{2}\log K_w + \frac{1}{2}\log K_b - \frac{1}{2}\log C$$

$$= \frac{1}{2}P^{kw} - \frac{1}{2}P^{Kb} - \frac{1}{2}\log C$$

$$pH = 7 - \frac{1}{2}P^{kb} - \frac{1}{2}\log C$$

3. **Salt of Weak Acid and Strong Base:-**

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

⇒ Salt of W.A. and S.B. shows anionic hydrolysis.

⇒ Here, cation act as the spectator ion.

⇒ Aqueous solution of these salts are basic in nature.

Relation between K_h, K_w, Ka

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$Kw = [H^+][OH^-]$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K_h = \frac{Kw}{Ka}$$

Degree of hydrolysis(h)

$$\begin{array}{llll} CH_3COO^- + H_2O & \rightleftharpoons & CH_3COOH & + OH^- \\ C & & - & - \\ C(1-h) & & Ch & Ch \end{array}$$

$$Kh = \frac{Ch \cdot Ch}{C(1-h)} = \frac{h^2C}{1-h}$$

$1 - h = 1$

$$\Rightarrow \quad Kh = h^2C \Rightarrow h = \sqrt{\frac{K_h}{C}}$$

$$h = \sqrt{\frac{Kw}{Ka \times C}}$$

Calculation of Ph:

$$[OH^-] = Ch = \sqrt{Kh \cdot C}$$

$$= \sqrt{\frac{Kw \times C}{Ka}}$$

$$P^{OH} = \frac{-1}{2}\log Kw + \frac{1}{2}\log Ka - \frac{1}{2}\log C$$

$$P^{OH} = 7 - \frac{1}{2}P^{Ka} - \frac{1}{2}\log C$$

$$pH = 7 + \frac{1}{2}P^{Ka} + \frac{1}{2}\log C$$

4. **Salt of Weak Acid and Weak Base:**

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

Salt of weak acid and Weak Base shows both anion as well as cationic hydrolysis :

Their aqueous solution are neutral (slightly acidic or basic)

(i) If $Ka = Kb \Rightarrow P^{Ka} = P^{Kb}$ ⇒ neutral solution

(ii) If $Ka > Kb \Rightarrow P^{Ka} < P^{Kb}$ ⇒ acidic solution

(iii) If $Ka < Kb \Rightarrow P^{Ka} > P^{Kb}$ ⇒ basic solution

For example, NH_4CN ⇒ basic nature

Relation between *Kh*, *Kw*, *Ka* and *Kb*

$$Kh = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \quad (i)$$

$$Kw = [H^+][OH^-] \quad (ii)$$

$$Ka = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad (iii)$$

$$Kb = \frac{[\mathrm{NH_4^-}][\mathrm{OH^-}]}{[\mathrm{NH_4OH}]} \qquad \text{(iv)}$$

$$\text{eq.}\frac{\text{(ii)}}{\text{(iii)} \times \text{(iv)}} = \text{eq. (i)}$$

$$\therefore \quad K_h = \frac{Kw}{Ka \cdot Kb}$$

Degree of hydrolysis (h)

$$\begin{array}{cccc} \mathrm{CH_3COO^-} + & \mathrm{NH_4^+} + \mathrm{H_2O} \rightleftharpoons & \mathrm{CH_3COOH} + & \mathrm{NH_4OH} \\ C & C & - & - \\ C(1-h) & C(1-h) & Ch & Ch \end{array}$$

$$Kh = \frac{Ch \cdot Ch}{C(1-h) \cdot C(1-h)}$$

$$= \frac{h^2}{(1-h)^2}$$

$$\Rightarrow \quad \frac{h}{1-h} = \sqrt{Kh}$$

$$h \text{ is negligible} \quad \Rightarrow \quad h = \sqrt{Kh} = \sqrt{\frac{Kw}{Ka \times Kb}}$$

Hence, degree of hydrolysis '*h*' is independent of concentration or dilution for salt of Weak Acid and Weak Base

pH calculation:

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^-} + \mathrm{H^+}$$

$$Ka = \frac{[\mathrm{CH_3COO^-}][\mathrm{H^+}]}{[\mathrm{CH_3COOH}]}$$

$$[\mathrm{H^+}] = Ka \times \frac{[\mathrm{CH_3COOH}]}{[\mathrm{CH_3COO^-}]}$$

$$[\mathrm{H^+}] = Ka \times \frac{Ch}{C(1-h)} = Ka \times \frac{h}{1-h}$$

$$[\mathrm{H^+}] = Ka \times \sqrt{Kh} = \sqrt{\frac{Kw}{Kb} \times Ka}$$

$$\mathrm{pH} = \frac{-1}{2}\log Kw - \frac{1}{2}\log Ka + \frac{1}{2}\log Kb$$

$$\mathrm{pH} = 7 + \frac{P^{Ka}}{2} - \frac{P^{Kb}}{2}$$

⇒ pH of this solution is independent of dilution.

Hydrolysis of polyvalent anions

Example 2: $\mathrm{Na_2S} \longrightarrow \underset{\times}{2\mathrm{Na^+}} + \underset{\checkmark}{\mathrm{S^{2-}}}$ (hydrolyse)

$$\begin{array}{lcc} \mathrm{S^{2-}} + \mathrm{H_2O} \rightleftharpoons & \mathrm{HS^-} + & \mathrm{OH^-};\ Kh_1 \\ C & - & - \\ C - x & x - y & x + y \\ \mathrm{HS^-} + \mathrm{H_2O} \rightleftharpoons & \mathrm{H_2S} + & \mathrm{OH^-};\ \mathrm{Kh_2} \\ (x - y) & y & y + x \end{array}$$

$$Kh_1 = \frac{Kw}{Ka_2}$$

$$= \frac{(x-y)(x+y)}{c-x}$$

$$Kh_2 = \frac{Kw}{Ka_1} = \frac{y(x+y)}{x-y}$$

$$Ka_1 >> Ka_2 \Rightarrow Kh_1 >> Kh_2$$

$$\Rightarrow \quad x >> y$$

$$\frac{Kw}{Ka_2} = \frac{x^2}{C-x} \qquad \frac{Kw}{Ka_1} = y$$

$$[\mathrm{OH^-}] \simeq x \ \therefore \ \mathrm{POH} = -\log[x]$$

Example 3: $\mathrm{Na_3PO_4} \rightleftharpoons 3\mathrm{Na^+} + \mathrm{PO^{3-}_{4(Hydrolyse)}}$

$$\begin{array}{lcc} \mathrm{PO_4^{3-}} + \mathrm{H_2O} \rightleftharpoons & \mathrm{HPO_4^{2-}} + & \mathrm{OH^-};\ Kh_1 \\ C - x & (x-y) & (x+y+z) \\ \mathrm{HPO_4^{2-}} + \mathrm{H_2O} \rightleftharpoons & \mathrm{H_2PO_4^-} + & \mathrm{OH^-};\ Kh_2 \\ x - y & y - z & x + y + z \\ \mathrm{H_2PO_4^-} + \mathrm{H_2O} \rightleftharpoons & \mathrm{H_3PO_4} + & \mathrm{OH^-};\ Kh_3 \\ y - z & z & x + y + z \end{array}$$

$$Kh_1 = \frac{Kw}{Ka_3} = \frac{(x-y)(x+y+z)}{C-x} = \frac{x^2}{C-x}$$

$$\frac{Kw}{Ka_2} = Kh_2 = \frac{(y-z)(x+y+z)}{(x-y)} = y$$

$$Kh_3 = \frac{Kw}{Ka_1} = \frac{z(x+y+z)}{(y-z)} = \frac{x \cdot z}{y}$$

$$Ka_1 >> Ka_2 >> Ka_3 \Rightarrow Kh_1 >> Kh_2 >> Kh_3$$

$$\Rightarrow \quad x >> y >> z$$

Hydrolysis of polyvalent cations

$$\mathrm{Fe(NO_3)_2} \longrightarrow \mathrm{Fe^{+2}} + 2\mathrm{NO_3^-}$$

$$\begin{array}{lcc} \mathrm{Fe^{+2}} + \mathrm{H_2O} \rightleftharpoons & \mathrm{Fe(OH)^+} + & \mathrm{H^+};\ Kh_1 \\ (C - x) & x - y & x + y \\ \mathrm{Fe(OH)^+} + \mathrm{H_2O} \rightleftharpoons & \mathrm{Fe(OH)^2} + & \mathrm{H^+};\ \mathrm{Kh_2} \\ (x - y) & y & x + y \end{array}$$

$$Kh_1 = \frac{Kw}{Kb_2} = \frac{(x-y)(x+y)}{C-x}$$

$$Kh_2 = \frac{Kw}{Kb_1} = \frac{y \cdot (x+y)}{(x-y)}$$

$$Kb_1 >> Kb_2 \Rightarrow Kh_1 >> Kh_2 \Rightarrow x >> y$$

$$Kh_1 = \frac{x^2}{C-x} \qquad Kh_2 = y$$

Hydrolysis of salts containing amphiprotic anion

Amphiprotic anions can provide as well as accept $\mathrm{H^+}$ i.e., they can act as both acid as well as base.

For example, NaHS, $KHCO_3$, NaH_2PO_4, Na_2HPO_4

Acidic nature

$$HA^- + H_2O \rightleftharpoons H_3O^+ + A^{2-};\ Ka_2$$

$$Ka_2 = \frac{[H_3O^+][A^{2-}]}{[HA^-]} \quad ...(i)$$

Basic nature

$$HA^- + H_2O \rightleftharpoons H_2A + OH^-;$$

$$Kh = \frac{Kw}{Ka_1} \quad ...(ii)$$

$$(i)/(ii);\ \frac{Ka_1 \times Ka_2}{Kw} = \frac{[H_3O^+][A^{2-}]}{[H_2A][OH^-]}$$

$$\frac{Ka_1 \times Ka_2}{[H_3O^+][OH^-]} = \frac{[H_3O^+][A^{2-}]}{[H_2A][OH^-]}$$

$$[H_3O^+]^2 = Ka_1 \times Ka_2 \times \frac{[H_2A]}{[A^{2-}]}$$

Assuming $[H_2A] \simeq [A^{2-}]$ when $Ka_2 \simeq Kh$

$$[H^+] = \sqrt{Ka_1 \times Ka_2}$$

$$pH = \frac{P^{Ka_1} + P^{Ka_2}}{2}$$

Note:

$\Rightarrow$ If $Kh > Ka_2 \Rightarrow \frac{[H_2A]}{[A^{2-}]} > 1$

$\Rightarrow$ $[H^+]\uparrow$

$\therefore$ $p^H < \left(\frac{P^{Ka_1} + P^{Ka_2}}{2}\right)$

$\Rightarrow$ If $Kh < Ka_2 \Rightarrow \frac{[H_2A]}{[A^{2-}]} < 1$

$\Rightarrow$ $[H^+]\downarrow$

$p^H > \left(\frac{P^{Ka_1} + P^{Ka_2}}{2}\right)$

(i) $NaH_2PO_4 \Rightarrow H_2PO_4^- \longrightarrow Ka_2 \Rightarrow pH = \frac{P^{Ka_1} + P^{Ka_2}}{2}$

one –ve charge on –ve ion hence gives second H^+

(ii) $Na_2HPO_4 \Rightarrow HPO_4^{2-} \longrightarrow Ka_3 \Rightarrow pH = \frac{P^{Ka_2} + P^{Ka_3}}{2}$

(iii) $Na_3HA \Rightarrow HA^- \longrightarrow Ka_4 \Rightarrow pH = \frac{P^{Ka_3} + P^{Ka_4}}{2}$

(iv) $NaH_3A \Rightarrow H_3A^- \longrightarrow Ka_2 \Rightarrow pH = \frac{P^{Ka_1} + P^{Ka_2}}{2}$

Buffer solutions

These are the solution which resist pH change when small amount of acid or base is added.

These solutions can be kept for long time without changing the pH.

Due to dilution, there is no appreciable change in their pH value.

Types of buffer solutions

(a) Simple buffer solution:
Salt of Weak Acid and Strong Base
e.g. CH_3COONH_4

(b) Mixed buffer: Acidic Buffer / Basic Buffer

1. Acidic buffer

Weak Acid + its conjugate base or salt.

(i) $CH_3OOH + CH_3COONa$
(ii) HCN + KCN
(iii) $NaH_2PO_4 + Na_2HPO_4$
(iv) $H_2CO_3 + NaHCO_3$

It is found in human blood which keeps the pH 7.35.

2. Basic buffer

Weak Base + its conjugate acid or salt with strong acid.

(i) $NH_4OH + NH_4Cl$
(ii) $RNH_2 + RNH_3^+Cl^-$

Buffer action:

It is a mechanism by which buffer solution resist the pH change.

Buffer action for simple buffer solution:

$$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$$

On adding H^+

$$H^+ + CH_3COO^- \longrightarrow CH_3COOH$$

(Almost unionises)

On adding OH^-

$$OH^- + NH_4^+ \longrightarrow NH_4OH \text{ (almost unionised)}$$

Buffer action for acidic buffer:

$$CH_3COOH + CH_3COONa$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

On adding H^+ or HCl

$$H^+ + CH_3COO^- \longrightarrow CH_3COOH$$

(Almost unionised)

On adding OH^- or NaOH

$$OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$$

(No change in ph)

Buffer action for basic buffer:

$$NH_4OH + NH_4Cl$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

On adding H^+ or HCl

$$H^+ + NH_4OH \longrightarrow NH_4^+ + H_2O \quad \text{(No change in ph)}$$

On adding OH^-

$$OH^- + NH_4^+ \longrightarrow NH_4OH \quad \text{(Almost unionised)}$$

pH calculation for acidic buffer

$$CH_3COOH + CH_3COONa$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$$Ka = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[H^+] = Ka \times \frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$[H^+] = Ka \times \frac{[\text{Acid}]}{[\text{Salt of conjugate base}]}$$

$$\text{pH} = -\log Ka - \log\frac{[\text{acid}]}{[\text{salt}]}$$

$$\text{pH} = P^{Ka} + \log\frac{[\text{Salt}]}{[\text{acid}]}$$

Henderson equation or Henderson Hassel Baton equation,

pH calculation for basic buffer

$$[OH^-] = K_b \times \frac{[\text{Base}]}{[\text{Salt or conjugate acid}]}$$

$$P^{OH} = -\log k_b - \log\frac{[\text{Base}]}{[\text{Salt}]}$$

$$P^{OH} = P^{Kb} + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pH} = 14 - P^{kb} + \log\frac{[\text{Base}]}{[\text{Salt}]}$$

Calculate the concentration of NH_3 and NH_4Cl required to prepare 1 L solution of pH = 9. When total concentration of buffering reagent is 0.6 mL. P^{Kb} $(NH_3) = 4.7$

Ph = 9 means basic buffer

$$\therefore \quad P^{OH} = 5 = 4.7 + \log\frac{\text{Salt}}{\text{base}}$$

$$\log S/b = 0.3 = \log 2$$

$$\frac{S}{b} = 2$$

$$S + b = 0.6$$

$$S = [NH_4Cl] = 0.4\text{ M} \Rightarrow b = [NH_3] = 0.2\text{ M}$$

Buffer capacity (ϕ)

It is the measurement of capability of buffer solution to resist the pH change.

$$\phi = \frac{\begin{array}{c}\text{Number of moles of acid or bases added to}\\ \text{1 litre buffer solution}\end{array}}{\Delta\text{pH}}$$

$\phi \Rightarrow$ buffer action

Buffer capacity in terms of buffer index

$$\left(\frac{\Delta b}{\Delta\text{pH}}\right)$$

Let an acidic buffer

$$\text{pH}_1 = P^{Ka} + \log\frac{s}{a} \qquad \text{...(i)}$$

On adding Δb moles of base,

$$\begin{array}{ccccc} \text{acid} & + & \text{base} & \rightarrow & \text{salt} \\ a & & \Delta b & & s \\ a - \Delta b & & 0 & & s + \Delta b \end{array}$$

$$\text{pH}_2 = P^{Ka} + \log\frac{s + \Delta b}{a - \Delta b} \qquad \text{...(ii)}$$

$$\Delta\text{pH} = \text{pH}_2 - \text{pH}_1$$

$$= \log\frac{s + \Delta b}{a - \Delta b} - \log s/a$$

$$= \log\left(\frac{s + \Delta b}{a - \Delta b} \times \frac{a}{s}\right)$$

$$\log\left(\frac{1 + \Delta b/s}{1 - \Delta b/a}\right) = \frac{1}{2.303}\ln\left(\frac{1 + \Delta b/s}{1 - \Delta b/a}\right)$$

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4}\cdots$$

$$\ln(1 - x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4}\cdots$$

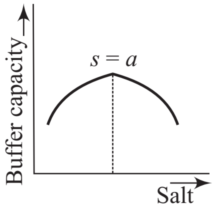
$$\simeq x \text{ (when } x \text{ is small)}$$

$$\Delta\text{pH} = \frac{1}{2.303}\left[\frac{\Delta b}{s} - \left(\frac{-\Delta b}{a}\right)\right]$$

$$= \frac{1}{2.303}\left[\frac{\Delta b}{s} + \frac{\Delta b}{a}\right]$$

$$= \frac{\Delta b}{2.303}\left(\frac{a + s}{a \cdot s}\right)$$

$$\text{Buffer index } \left(\frac{\Delta b}{\Delta\text{pH}}\right) = 2.303\left(\frac{a \cdot s}{a + s}\right)$$



We know,

$$a + s = \text{const.}(K)$$

$$\frac{\Delta b}{\Delta\text{pH}} = 2.303\frac{a \cdot (K - a)}{K}$$

For maximum buffer capacity:

$$\frac{d}{da}\left(\frac{\Delta b}{\Delta\text{pH}}\right) = 0$$

$$\Rightarrow \quad 0 = \frac{2.303}{K}(K - 2a) \Rightarrow a = \frac{K}{2} \Rightarrow s = \frac{K}{2}$$

For maximum buffer action

$$a = s$$

At maximum buffer action

For acidic buffer

[Salt] = [acid]

pH = P^{Ka}

For basic buffer

[Salt] = [base]

$P^{OH} = P^{Kb}$

pH range of buffer solution

It is the pH interval in which buffer solution works effectively and this pH range is $P^{Ka} + 1$ (for acidic buffer) any buffer solution works effectively only when $\frac{[\text{salt}]}{[\text{acid/base}]}$

$$\Rightarrow \quad \frac{1}{10} \text{ to } 10.$$

> ***Note:***
>
> More is the concentration of buffer solution, more will be its buffer action.

In Sol. (i) $a = s = 0.1$ M

If $\Delta b = 0.01$

$$\text{pH}_1 = P^{Ka};\ \text{pH}_2 = P^{Ka} + \log\frac{0.11}{0.09}$$

$$\Delta\text{pH} = \log\frac{11}{9}$$

In Sol. (ii) $a = s = 0.2$ M

If $\Delta b = 0.01$

$$\text{pH}_1 = P^{Ka};\ \text{pH}_2 = P^{Ka} + \log\frac{0.21}{0.13}$$

$$\Delta\text{pH} = \log\frac{21}{19}$$

Change in pH for solution I is more, so, buffer action is less.

INDICATORS

Indicators are the species which detect the end point in the titration by colour change.

Acid-base indicators are either weak organic acid or weak organic base.

Indicators show the colour change because of their ionisation.

Generally darker colour is associated with ionised part where as lighter colour is associated with unionised part.

Example 1: Phenophthalene (Hph)

$$\underset{\text{(colourless)}}{\text{Hph}} \rightleftharpoons \underset{\text{(pink)}}{\text{H}^+ + \text{Ph}^-\ \text{(Pink)}}$$

in, acidic medium $\longrightarrow$ colourless

in basic medium $\longrightarrow$ pink

Example 2: Methyl Orange (MeOH)

$$\underset{\text{(yellow)}}{\text{MeOH}} \rightleftharpoons \underset{\text{(red)}}{\text{Me}^+ + \text{OH}^-}$$

Red in acidic medium; yellow in basic medium

pH of indicators

$$\underset{\text{(colourless)}}{\text{HIn}} \rightleftharpoons \underset{\text{(coloured)}}{\text{H}^+ + \text{In}^-\ \text{(coloured)}}$$

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}^+] = K_{\text{In}} \times \frac{[\text{HIn}]}{[\text{In}^-]}$$

pH of indicator

$$\text{pH} = P^{K\text{In}} + \log\frac{[\text{In}^-]}{[\text{HIn}]} \qquad \text{Hendorson equation}$$

pH range of indicators

It is the pH interval for indicator in which it shows transition in colour (mixed colour).

pH range = $P^{K\text{In}} \pm 1$

In the pH range $\frac{[\text{In}^-]}{[\text{HIn}]}$ is $\frac{1}{10}$ to 10.

Example 1: Hph: pH range = 8.3 to 10

pH > 10 ⇒ dark pink

pH < 8.3 ⇒ colourless

8.3 to 10 ⇒ transition colour

Example 2: MeOH: pH range = 3.1 to 4.4

pH > 4.4 ⇒ yellow

pH < 3.1 ⇒ Red

3.1 to 4.4 ⇒ transition colour

Example 3: Bromothymol blue: (6 to 7.6)

pH < 6 ⇒ yellow

pH > 7.6 ⇒ blue

6 to 7.6 ⇒ transition colour

Example 4: Methyl Red (4.2 to 6.3)

pH < 4.2 ⇒ red

pH > 6.3 ⇒ yellow

In pH range

$$\%\ \text{ionised part} = \frac{[\text{In}^-]}{[\text{HIn}] + [\text{In}^-]} \times 100$$

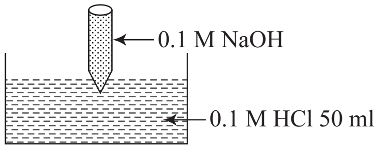
$$\%\ \text{unionised part} = \frac{[\text{HIn}]}{[\text{HIn}] + [\text{In}^-]} \times 100$$

SELECTION OF INDICATOR FOR ACID-BASE TITRATION

During the acid-base titration, there is a sudden change in pH nearby the equivalence point in certain limits called pH range of titration.

Those indicators will be suitable for the given titration whose pH lie in pH range of titration ideally. For best indicator, mid-point of the pH range is equal to the pH at equivalence point.

Titration of Strong Acid Vs Strong Base



$HCl \longrightarrow 0.1$ M, 50 mL

$NaOH \longrightarrow 0.1$ M

1. $V_{NaOH} = 0$ mL

   $[H^+] = 10^{-1} \Rightarrow pH = 1$
2. $V_{NaOH} = 20$ mL

   $$[H^+] = \frac{5-2}{50+20} = \frac{3}{70}$$

   $$pH = -\log\left(\frac{3}{70}\right) = 1.37$$
3. $V_{NaOH} = 40$ mL

   $$[H^+] = \frac{5-4}{90} = \frac{1}{90} = pH = 1.95$$
4. $V_{NaOH} = 49$ mL

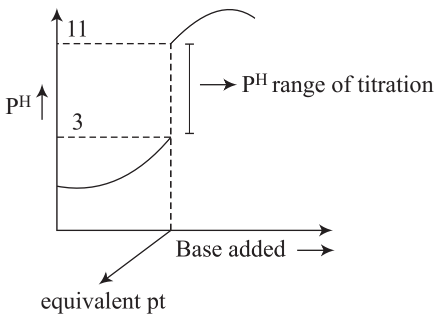
   $$[H^+] = \frac{5-4.9}{99} = \frac{0.1}{99} \Rightarrow pH = 3$$
5. $V_{NaOH} = 50$ mL

   $\Sigma NaVa = \Sigma NbVb$

   pH = 7 (equivalence point)
6. $V_{NaOH} = 51$ mL

   $$[OH^-] = \frac{5.1-5}{101} = \frac{0.1}{101}$$

   $P^{OH} = 3, pH = 11$



Indicator used

MeOH → 3.1 to 4.4

Boomothymol blue (6 to 7.6) Methylred

Titration of Weak Acid and Strong Base

$CH_3COOH \longrightarrow 0.1$ M, 50 ml

$NaOH \longrightarrow 0.1$ M

1. $V_{NaOH} = 0$ mL

   Since CH_3COOH is a weak acid

   $$pH = \frac{1}{2}[4.74 - \log 10^{-1}] = 2.87$$
2. $V_{NaOH} = 25$ mL

   $$\begin{array}{cccc} CH_3COOH + & NaOH \longrightarrow & CH_3COONa + & H_2O \\ 5 & 2.5 & - & - \\ 2.5 & - & 2.5 & - \end{array}$$

   After reaction both component present

   ∴ buffer solution

   $$pH = 4.74 \qquad \text{from } pH = PKa + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$
3. $V_{NaOH} = 40$ mL

   $$pH = 4.74 + \log\frac{4}{1} = 5.34$$
4. $V_{NaOH} = 49$ mL

   $$pH = 4.74 + \log\frac{4.9}{0.1} \Rightarrow 4.74 + 2 \times (0.85) = 6.44$$
5. $V_{NaOH} = 50$ mL; (equivalence point)

   $$\begin{array}{cccc} CH_3COOH + & NaOH \longrightarrow & CH_3COONa + & H_2O \\ 5 & 5 & - & \\ - & - & 5 & \end{array}$$

   After reaction only salt present ∴ salt hydrolysis

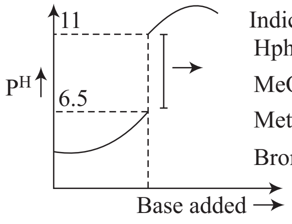
   $$pH = 7 + \frac{1}{2}pka + \frac{1}{2}\log C$$

   $$\therefore \quad pH = 7 + \frac{1}{2} \times 4.74 + \frac{1}{2}\log(5 \times 10^{-2}) = 8.7$$
6. $V_{NaOH} = 51$ mL

   $$\begin{array}{cccc} CH_3COOH + & NaOH \longrightarrow & CH_3COONa + & H_2O \\ 5 & 5.1 & - & \\ - & 0.1 & 5 & \end{array}$$

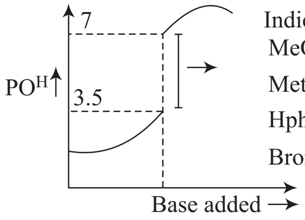
   $$[OH^-] = \frac{0.1}{101} \simeq 10^{-3}$$

   $P^{OH} = 3 \qquad pH = 11$



Indicator used	
Hph	✓
MeOH	✗
Methyl red	✗
Bromothymol blue	✓

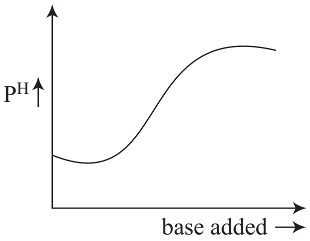
7. **Titration of Strong Acid and Weak Base:** as same as titration of Weak Acid and Strong Base



Indicator used	
MeOH	✓
Methyl red	✗
Hph	✗
Bromothymol blue	✓

Titration of Weak Acid and Weak Base

Such type of titration is generally not carried out because no sharp change in the pH is observed near equivalence point.



Titration of polyprotic acid with Strong Base

$$H_3PO_4 \longrightarrow 0.1\text{ M}, 50\text{ ml}$$

$$NaOH \longrightarrow 0.1\text{ M}$$

(i) $V_{NaOH} = 0$ mL

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

(ii) $V_{NaOH} = 25$ mL

$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$

after reaction both component

∴ buffer

5 2.5 –

2.5 – 2.5

$pH = P^{Ka_1}$

(iii) $V_{NaOH} = 40$ mL

$$pH = P^{Ka_1} + \log\frac{4}{1}$$

(iv) $V_{NaOH} = 50$ mL

$$\begin{array}{ccccccc} H_3PO_4 & + & NaOH & \longrightarrow & NaH_2PO_4 & + & H_2O \\ 5 & & 5 & & – & & – \\ – & & – & & 5 & & 5 \end{array}$$

After reaction, amphiprotic salt formed.

$$pH = \frac{P^{Ka_1} + P^{Ka_2}}{2} \quad \text{I equivalence Point}$$

(v) $V_{NaOH} = 75$ mL

$$pH = P^{Ka_2}$$

(vi) $V_{NaOH} = 100$ mL (second end point)

$$pH = \frac{P^{Ka_2} + P^{Ka_3}}{2}$$

(vii) $V_{NaOH} = 110$ mL

$$\begin{array}{ccccccc} Na_2HPO_4 & + & NaOH & \longrightarrow & Na_3PO_4 & + & H_2O \\ 5 & & 1 & & – & & – \\ 4 & & – & & 1 & & 1 \end{array}$$

$$pH = P^{Ka_3} + \log\frac{1}{4}$$

(viii) $V_{NaOH} = 125$ mL

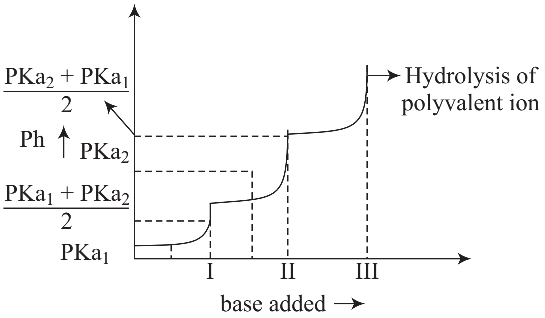
$$pH = P^{Ka_3}$$

(ix) $V_{NaOH} = 150$ mL

$$\begin{array}{ccccccc} Na_2HPO_4 & + & NaOH & \longrightarrow & Na_3PO_4 & + & H_2O \\ 5 & & 5 & & – & & \\ – & & – & & 5 & & \end{array}$$

$$C = \frac{5}{150+50} = \frac{5}{200} = 2.5 \times 10^{-2}$$

(hydrolysis of polyvalent ion)



Solubility (S)

It is the maximum amount of the solute that can be dissolved in one litre of the solution at saturation.

Solubility product (K_{SP})

$A^+B^-(s) \rightleftharpoons AB(aqueous)$

undissolved dissolved

$AB(s) \rightleftharpoons A^+(aqueous) + B^-(aqueous)$

$K_{eq} = K_{SP} = [A^+][B^-]$ (at saturation)

Solubility product is the product of ionic concentration of the solute in its saturated solution.

1. $AlCl_3(s) \rightleftharpoons Al^{+3} + 3Cl^-$

   $K_{SP} = [Al^{+3}][Cl^-]^3$

2. $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

   $K_{SP} = [Ag^+]^2[CrO_4^{2-}]$

3. $Sb_2S_3(s) \rightleftharpoons 2Sb^{+3} + 3S^{2-}$

   $K_{SP} = [Sb^{+3}]^2[S^{2-}]^3$

K_{SP} is constant at a given temperature variation of K_{SP} with temperature is given by

$$\ln\frac{K_{SP_2}}{K_{SP_1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

ΔH = heat of solution

Condition for precipitation

If $Q = K_{SP} \Rightarrow$ Saturated solution

Q = Reaction quotient as per K_{SP}

If $Q < K_{SP} \Rightarrow$ unsaturated solution more solute can be dissolved

If $Q > K_{SP} \Rightarrow$ Precipitate forms super saturated solution

Q. Equal volume of 2×10^{-8} M $BaCl_2$ and 2×10^{-2} M Na_2SO_4 are mixed. Will there be any precipitate? K_{SP} ($BaSO_4$) = 10^{-10}.

Ans. $Q = [Ba^{+2}][SO_4^{2-}]$

$= 10^{-8} \times 10^{-2}$

$= 10^{-10}$ K_{SP}. ∴ No Precipitate form

Note: Whenever two solutions having the concentration C_1 and C_2 respectively are mixed in the volume ratio $V_1 : V_2$ then, new concentration in the final solution is given by

$$C_1' = \frac{C_1V_1}{V_1+V_2} \quad C_2' = \frac{C_2V_2}{V_1+V_2}$$

Relationship between solubility product and solubility

$$AxBy(\text{s}) \rightleftharpoons xA^{+y} + yB^{-x}$$

Solubility: 'S' mol/L $\quad xS \quad yS$

$$K_{SP} = [A^{+y}]^x[B^{-x}]^y$$
$$= (xS)^x(yS)^y$$
$$K_{SP} = x^x \cdot y^y,\ s^{x+y}$$
$$\Rightarrow \quad Al_2(SO_4)_3;\ K_{SP} = 2^2 \cdot 3^3 \cdot S^5$$

Effect of common ion on solubility of sparingly soluble salts

On adding, common ion solubility decreases

$$AgCl(\text{s}) \rightleftharpoons Ag^+ + Cl^-;\ K_{SP} = S^2$$

Initials: 'S' mol/L $\quad$ S $\quad$ S

On adding NaCl, Conc. 'S' decreased to 'S′' mole/L.

$$\boxed{\begin{array}{ccccc} AgCl(\text{s}) & \rightleftharpoons & Ag^+ & + & Cl^- \\ \text{if } S' \text{ solubility} & & S' & & S' + C \\ NaCl & \longrightarrow & Na^+ & + & Cl^- \\ C \text{ gives} & & C & & C + S' \end{array}}$$

$$K_{SP} = [Ag^+][Cl^-]$$
$$K_{SP} = S'(S' + C)$$

$S' + C \simeq C$ due to common ion effect for sparingly soluble salt.

$$S' << C$$

$$S' = \frac{K_{SP}}{C} \quad C = \text{Concentration of common ion.}$$

Above formula is applicable, for AB type Salt.

If solubility of AgCl in

$$H_2O \to S_1,\ 0.1\text{ M } BaCl_2 \to S_2,\ 0.5\text{ M } AgNO_3 \to S_3$$

then order of solubility $S_1 > S_2 > S_3$ because

$$S' \times \frac{1}{C}$$

Eg. Solubility of PbI_2 = in

(i) 0.1 M KI

(ii) 0.1 M $Pb(NO_3)_2$

$K_{SP}(PbI_2) = 7.1 \times 10^{-9}$

Sol.

(i)
$$\begin{array}{ccccc} PbI_2 & \rightleftharpoons & Pb^{+2} & + & 2I^- \\ S' & & S' & & (2S' + 0.1) = 0.1 \end{array}$$

$$\begin{array}{ccccc} KI & \longrightarrow & K^+ & + & I^- \\ 0.1\text{ M} & & 0.1\text{ M} & & 0.1\text{ M} \end{array}$$

$$K_{SP} = 7.1 \times 10^{-9} = S' \times (0.1)^2$$
$$S' = 7.1 \times 10^{-7}\text{ M}$$

(ii)
$$\begin{array}{ccccc} PbI_2 & \rightleftharpoons & Pb^{+2} & + & 2I^- \\ & & (S' + 0.1) & & 2S' \end{array}$$

$$\begin{array}{ccccc} Pb(NO_3)_2 & \longrightarrow & Pb^{+2} & + & 2NO_3^- \\ 0.1 & & 0.1 & & 0.2 \end{array}$$

$$K_{SP} = 7.1 \times 10^{-9} = 0.1 \times (2S')^2$$

$$S' = \sqrt{\frac{7.1 \times 10^{-9}}{0.1 \times 4}}$$

$$S' = \sqrt{\frac{7.1}{4}} \times 10^{-4}$$

SIMULTANEOUS SOLUBILTY

If two sparingly soluble salt having common ions are present in a solution then, solubility of both the salts decreases because of common ion effects.

For example AgCl and AgBr

$$AgCl(\text{s}) \rightleftharpoons Ag^+ + Cl^-;$$
$$x\text{ mol/L} \quad (x + y) \quad x$$
$$AgBr(\text{s}) \rightleftharpoons Ag^+ + Br^-;$$
$$y\text{ mol/L} \quad (x + y) \quad y$$
$$K_{SP}(AgCl) = (x + y)x \qquad \text{...(i)}$$
$$K_{SP}(AgBr) = (x + y)y \qquad \text{...(ii)}$$
$$\text{(i)} + \text{(ii)} \Rightarrow$$

$$K_{SP}(AgCl) + K_{SP}(AgBr) = (x + y)^2$$

$$[Ag^+] = (x + y) = \sqrt{K_{SP}(AgCl) + K_{SP}(AgBr)}$$

$$\frac{K_{SP}(AgCl)}{K_{SP}(AgBr)} = \frac{x}{y}$$

COMPLEX FORMAITON

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

Formation constant or stability constant for complex.

$$K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \qquad \text{(i)}$$

Generally, K_f is the large value, so, reaction for the formation of complex proceeds almost completely.

Stability constant of complex

$$K_{inst} = \frac{1}{K_f}$$

$$K_f \uparrow \;\Rightarrow\; K_{inst} \downarrow \;\Rightarrow\; \text{Stability of complex} \uparrow$$

Complex formation in more than one-step process

$$Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+;\ K_{f_1}$$

$$K_{f_1} = \frac{[Ag(NH_3)]^+}{[Ag^+][NH_3]} \qquad \text{(ii)}$$

$$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+;\ K_{f_2}$$

$$K_{f_2} = \frac{[\mathrm{Ag(NH_3)_2}]^+}{[\mathrm{Ag(NH_3)}]^+[\mathrm{NH_3}]} \qquad \text{(iii)}$$

$$\therefore \quad K_f = K_{f_1} \times K_{f_2}$$

Effect of complex formation in solubility

Due to complex formation, solubility increases.

Solubility of AgCl in aqueous NH_3 solution:

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Cl^-};\ K_{SP} = x(x-y)$$

x mol/e $\quad x - y \quad x$

$$\mathrm{Ag^+} + 2\mathrm{NH_3} \rightleftharpoons [\mathrm{Ag(NH_3)_2}]^+;\ K_f = \frac{x}{(x-y)(C-2x)^2}$$

$x \quad C \quad -$

$x - y \quad C - 2y \quad y = x$

$\quad || $

$\quad C - 2x$

as K_f is high, so $x = y$

On adding both equations

$$\mathrm{AgCl(s)} + 2\mathrm{NH_3(aq.)} \rightleftharpoons [\mathrm{Ag(NH_3)_2}]^+ + \mathrm{Cl^-}$$

$c - 2x \qquad x \qquad x$

$$K_f \times K_{SP} = \frac{x^2}{(C-2x)^2}$$

Amphoterism

$Zn(OH)_2$, $Cr(OH)_3$, $Al(OH)_3$ shows amphoterism, show solubility increases because of acidic and basic behaviour.

For example, $Zn(OH)_2$

Solubility of $Zn(OH)_2$ is because of five forms in the aqueous solution.

(i) $\mathrm{Zn\,(OH)_2(s)} \rightleftharpoons \mathrm{Zn(OH)_2(aqueous)}$

$K_1 = [\mathrm{Zn(OH)_2}]\mathrm{(aqueous)}$

Basic nature

(ii) $\mathrm{Zn(OH)_2(aqueous)} \rightleftharpoons \mathrm{Zn(OH)^+} + \mathrm{OH^-}$;

$$Kb_1 = K_2 = \frac{[\mathrm{Zn(OH)^+}][\mathrm{OH^-}]}{[\mathrm{Zn(OH)_2}]}$$

(iii) $\mathrm{Zn(OH)^+} \rightleftharpoons \mathrm{Zn^{+2}} + \mathrm{OH^-}$

$$Kb_2 = K_3 = \frac{[\mathrm{Zn^{+2}}][\mathrm{OH^-}]}{[\mathrm{Zn(OH)^+}]}$$

Acidic nature

(iv) $\mathrm{Zn(OH)_2(aqueous)} + \mathrm{H_2O} \rightleftharpoons \mathrm{Zn(OH)_3^-} + \mathrm{H^+}$

$$K_4 = \frac{[\mathrm{Zn(OH)_3^-}][\mathrm{H^+}]}{[\mathrm{Zn(OH)_2}]}$$

(v) $\mathrm{Zn(OH)_3^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{Zn(OH)_4^{2-}} + \mathrm{H^+}$

$$K_5 = \frac{[\mathrm{Zn(OH)_4}]^{-2}[\mathrm{H^+}]}{[\mathrm{Zn(OH)_3^-}]}$$

$\therefore$ solubility of $Zn(OH)_2 = S$

$$= [\mathrm{Zn(OH)_2}]\mathrm{aq} + [\mathrm{Zn(OH)^+}] + [\mathrm{Zn^{+2}}] + [\mathrm{Zn(OH)_3^-}] + [\mathrm{Zn(OH)_4}]^{-2}$$

$$= K_1 + \frac{K_1K_2}{[\mathrm{OH^-}]} + \frac{K_1K_2K_3}{[\mathrm{OH^-}]^2} + \frac{K_1K_4}{[\mathrm{H^+}]} + \frac{K_1K_4K_5}{[\mathrm{H^+}]^2}$$

Solved Examples

1. Find the pH value:

(i) $\frac{M}{1000}\mathrm{H_2SO_4}$ **(ii)** $\frac{N}{100}\mathrm{Ba(OH)_2}$

(iii) $\frac{M}{10}\mathrm{Sr(OH)_2}$

Sol. **(i)** $[H^+] = 2 \times 10^{-3}$

$pH = 3 - \log 2 = 2.7$

(ii) $[OH^-] = 10^{-2}$

$P^{OH} = 2$

$pH = 14 - 2 = 12$

(iii) $[OH^-] = 2 \times 10^{-1}$

$P^{OH} = 1 - \log 2 = 1 - 0.3 = 0.7$

$\therefore \quad Ph = 14 - 0.7 = 13.3$

2. Find the pH of 10^{-7} MHCl.

Sol. $[H^+] = 10^{-7} + \{10^{-7}\}$ due to self-ionisation of H_2O.

$= 2 \times 10^{-7}$

$pH = 7 - \log 2 = 6.7$

OR

> ***Note:***
> For very diluted solution, i.e., when $[H^+]$ or $[OH^-]$ is $< 10^{-6}$M, while calculating the pH H^+ or OH^- due to self-ionisation of water are taken.

If we consider, the common ion effect of water.

$$\boxed{\begin{array}{llcccc} \mathrm{H_2O} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{OH^-} \\ & & x + 10^{-7} & & x \\ \mathrm{HCl} & \longrightarrow & \mathrm{H^+} & + & \mathrm{Cl^-} \\ & & x + 10^{-7} & & 10^{-7} \end{array}}$$

$K_W = [H^+][OH^-] = 10^{-14}$

$(x + 10^{-7})x = 10^{-14}$

$x^2 + 10^{-7}x - 10^{-14} = 0$

$x = 0.618 \times 10^{-7}$

$[H^+] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$

$pH = 6.79$

3. Find the pH of 10^{-8} M NaOH.

Sol. $[OH^-] = 10^{-8} + 10^{-7}$
$= 1.1 \times 10^{-7}$
$P^{OH} = 7 - \log 1.1$
$pH = 14 - 7 + \log(1.1)$
$7 + \log(1.1)$

4. Calculate the pH of

(i) 0.1 M CH_3COOH solution $K_a = 1.8 \times 10^{-5}$

(ii) 10^{-6} M CH_3COOH solution $pKa = 4.74$

Sol. (i) $\alpha = \sqrt{\dfrac{Ka}{C}}$

$$pH = \frac{1}{2}[4.74 - \log 10^{-1}]$$

$= 2.87$

(ii) $[H^+] = C \cdot \alpha$

$$Ka = \frac{\alpha^2 c}{1-\alpha}$$

$$\Rightarrow \quad 1.8 \times 10^{-5} = \frac{10^{-6} \times \alpha^2}{1-\alpha}$$

$\Rightarrow \quad \alpha = 0.95$
$[H^+] = 0.95 \times 10^{-6}$
$pH = 6.022$

5. If $\alpha = 0.01$ for centimolar solution of weak acid. Find the value of P^{Ka}.

Sol. $K_a = \alpha^2 C$
$= (10^{-2})^2 \times 10^{-2}$
$= 10^{-6}$
$P^{Ka} = 6$

6. Calculate the concentration of OH^- in 10^{-4} M solution if weak acid HA4% ionised.

Sol. $$[H^+] = 10^{-4} \times \frac{4}{100} = 4 \times 10^{-6}$$

$$[OH^-] = \frac{10^{-14}}{4 \times 10^{-6}} = 2.5 \times 10^{-9} \text{ M}$$

7. Calculate the molar concentration of NH_4OH solution that has pH = 12. Given $K_b = 1.8 \times 10^{-5}$.

Sol. $pH = 12 \Rightarrow pOH = 2 \Rightarrow [OH^-] = 10^{-2}$

$$[OH^-] = 10^{-2} = \sqrt{1.8 \times 10^{-5} \times C}$$

$C = 5.55$

8. What concentration of FCH_2COOH is needed so that $[H^+]$ is 4×10^{-4}. $K_a = 4 \times 10^{-4}$?

Sol. $$[H^+] = 4 \times 10^{-4} = \sqrt{4 \times 10^{-4} \times C}$$

$$C = 4 \times 10^{-4} \Rightarrow \alpha = \sqrt{\frac{Ka}{C}} = 1$$

$\Rightarrow \alpha$ is not negligible.
If $K_a/C > 10^{-3}$ or $\alpha > 5\%$

$$\begin{array}{lccc} FCH_2COOH \rightleftharpoons & FCH_2COO^- & + & H^+ \\ C & - & & - \\ C - x & x & & x = 4 \times 10^{-4} \end{array}$$

$$K_a = 4 \times 10^{-4} = \frac{(4 \times 10^{-4})^2}{C - 4 \times 10^{-4}}$$

$C = 8 \times 10^{-4}$ M

9. How much water must be added to 1 L of 0.2 M solution of HA, if α of acid is to be doubled, $K_a = 1.8 \times 10^{-4}$

Sol. 'α' $\propto \sqrt{V}$

$$V \propto (\alpha)^2 \;\therefore\; \frac{V_i}{V_f} = \left(\frac{\alpha}{2\alpha}\right)^2$$

$V_i = 1 \text{ L} \Rightarrow V_f = 4 \times 1 = 4\text{L}$
$\therefore$ water added = 3 L

10. Calculate the pH of the following solutions:

(i) 200 mL 0.1 M of H_2SO_4 + 300 mL 0.1 M NaOH

(ii) 400 mL 0.05 N H_2SO_4 + 200 mL 0.1 M KOH

(iii) 100 mL 0.1 N HCl + 100 mL 0.1 M $Ba(OH)_2$

Sol. **(i)** $$[H^+] = \frac{0.1 \times 2 \times 200 - 0.1 \times 1 \times 300}{500}$$

$$= \frac{10}{500} = 2 \times 10^{-2}$$

$pH = 2 - \log 2 = 1.7$

(ii) $pH = 7 \quad \because \Sigma N_a V_a = \Sigma N_b V_b$

(iii) $$[OH^-] = \frac{0.1 \times 100 - 0.1 \times 2 \times 100}{200}$$

$$= \frac{10}{200} = 5 \times 10^{-2}$$

$P^{OH} = 2 - \log 5 = 14 - (2 - \log 5) = 12 + \log 5 = 12.7$

11. Calculate the pH of the following solutions:

(i) 50 mL (pH = 1) + 50 mL (pH = 2)

(ii) 50 mL (pH = 2) + 50 mL (pH = 12)

Sol. **(i)** $[H^+]_1 = 10^{-1}$; 50 mL
$[H^+]_2 = 10^{-2}$; 50 mL

$$[H^+] = \frac{10^{-1} \times 50 + 10^{-2} \times 50}{100}$$

$= 5.5 \times 10^{-2}$
$pH = 2 - \log 5.5 = 1.26$

(ii) pH = 12 means basic solution
$\therefore \quad P_{OH} = 2$ So $[OH^-] = 10^{-2}$ M
and pH = 2 So $[H^+] = 10^{-2}$M
Since Σ(NV) acid = Σ(NV) base $\Rightarrow$ Neutral solution
$= [H^+] = [OH^-] = 10^{-7}$
$\Rightarrow \quad pH = 7$

12. K_a for acid HA is 2.5×10^{-8}. Calculate for its decimolar solution at 25°C.

(i) % dissociation

(ii) pH

(iii) OH^- ion concentration

Sol.
$$\begin{array}{llll} HA & \rightleftharpoons & H^+ & + \ A^- \\ C & & 0 & \ \ 0 \\ C(1-\alpha) & & C\alpha & \ \ C\alpha \end{array}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \approx C\alpha^2$$

(i) $\therefore \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.5\times10^{-8}}{1/10}}$ $\qquad (C = 1/10\text{ M})$

$= 5 \times 10^{-4} = 0.05\%$

(ii) $[H^+] = C\alpha = \frac{1}{10}\times5\times10^{-4} = 5\times10^{-5}$ mol/L

$\Rightarrow$ So pH = 5 – log 5 = 4.30

(iii) $[H^+]\,[OH^-] = 1\times10^{-14}$

$\therefore \quad [OH^-] = \frac{10^{-14}}{5\times10^{-5}} = 2\times10^{-10}$ mol/L.

13. Determine the degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 10.

Sol.
$$\begin{array}{llll} NH_4OH & \rightleftharpoons & NH_4^+ & + \ OH^- \\ C & & 0 & \ \ 0 \\ C - C\alpha & & C\alpha & \ \ C\alpha \end{array}$$

Given: pH = 10

$[H^+] = 10^{-10}$

$[H^+]\,[OH^-] = 1\times10^{-14}$

$\therefore \quad [OH^-] = \frac{1\times10^{-14}}{10^{-10}} = 10^{-4} = C\alpha$

$\therefore \quad \alpha = \frac{[OH^-]}{C} = \frac{10^{-4}}{0.05} = 2\times10^{-3}$ or 0.2 %

14. Two weak monobasic organic acids HA and HB have dissociation constants as 1.6×10^{-5} and 0.4×10^{-5} respectively at 25° C. If 500 mL of 1 M solution of each of these two acids are mixed to produce 1 L of mixed solution, what is the pH of the resulting solution ?

Sol. In such cases, we have to consider H^+ from both HA and HB simultaneously. The concentration of HA and HB in the mixture = 0.5 M [equal volumes are mixed] = say '*c*'

$HA \rightarrow H^+ + A^-$

$HB \rightarrow H^+ + B^-$

Let, $x = [H^+]$ from HA and $y = [H^+]$ from HB

$\Rightarrow \quad [H^+]_{final} = x + y$

$$K_{HA} = \frac{(x+y)x}{c} \text{ and } K_{HB} = \frac{(x+y)y}{c}$$

$$\frac{[H^+]_{HA}}{[H^+]_{HB}} = \frac{x}{y} = \sqrt{\frac{k_{HA}\times C}{k_{HB}\times C}}$$

$$\frac{x}{y} = \sqrt{\frac{1.6\times10^{-5}}{0.4\times10^{-5}}} = 2$$

$$x = 2y \Rightarrow y = \frac{x}{2}$$

Substitute for $y = \frac{x}{2}$ in $K_{HA} = \frac{x^2+xy}{c} =$

$$1.6\times10^{-5} = \frac{2x^2+x^2}{2\times0.5}$$

$3x^2 = 1.6\times10^{-5} \Rightarrow x^2 = 5.33\times10^{-6}$

$x = 2.30\times10^{-3}$ M, $y = 1.15\times10^{-3}$ M

$[H^+]_{Final} = x + y = 2.30\times10^{-3} + 1.15\times10^{-3}$

$= 3.45\times10^{-3}$ M

pH = $-\log_{10}(3.45\times10^{-3})$

pH = 2.462

15. Calculate pH of $[HS^-]$, $[S^{2-}]$, $[Cl^-]$ in a solution which is 0.1 M HCl and 0.1 M H_2S given that K_{a_1} (H_2S) = 10^{-7}, Ka_2 (H_2S) = 10^{-14}. Also calculate α_1 and α_2.

Sol. $HCl + H_2S$

0.1 $\quad$ 0.1

$C_1 = C_2 = 0.1$

$\therefore \quad$ pH = 1 $\quad$ (most of $[H^+]$ comes from HCl]

$$\begin{array}{llll} H_2S & \rightleftharpoons & H^+ & + \ HS^- \\ 0.1(1-\alpha_1) & & C\alpha_1 & \ \ C\alpha_1 = 0.1\,\alpha_1 \end{array}$$

$$Ka_1 = \frac{C\alpha_1\times10^{-1}}{C(1-\alpha_1)} = \frac{10^{-7}}{10^{-1}} = \alpha_1$$

$\Rightarrow \quad \alpha_1 = 10^{-6}$

$$\begin{array}{llll} HS^- & \rightleftharpoons & S^{2-} & + \ H^+ \\ C\alpha_1(1-\alpha_2) & & C\alpha_1\alpha_2 & \ \ 0.1 \end{array}$$

$10^{-14} = 0.1\times\alpha_2$

$\Rightarrow \quad \alpha_2 = 10^{-13}$

$[S^{2-}] = C\alpha_1\alpha_2$

$= 10^{-6}\times10^{-1}\times10^{-13} = 10^{-20}$ M

16. Find out K_h at 363 K (90°C) of a salt of [strong acid – weak base] if the value of K_b is 10^{-5} [At 90°C $K_w = 10^{-12}$].

Sol. $K_h = \frac{K_w}{K_b} = \frac{10^{-12}}{10^{-5}} = 10^{-7}$

17. How many grams of NH_4Cl should be dissolved per litre of solution to have a pH of 5.13 ? K_b for NH_3 is 1.8×10^{-5}?

Sol. NH_4Cl is a salt of strong acid and weak base for solutions of such salts.

$$pH = \frac{1}{2}\,[pK_W - \log C - pK_b]$$

$\Rightarrow \quad 10.26 = 14 - \log C - 4.74$

$\Rightarrow \quad \log C = 9.26 - 10.26 = -1.0$

$\therefore \quad C = 10^{-1}$ M

$[NH_4Cl] = 10^{-1}$ M

$W_{NH_4NO_3} = 10^{-1}\times53.5\text{ gL}^{-1} = 5.35\text{ gL}^{-1}$

18. What is the pH of 0.4 M aqueous NaCN solution? (Given: pK_b of CN^- = 4.70)

Sol. pK_a for HCN = 14 – 4.7 = 9.30

$$\begin{array}{llll} NaCN + H_2O & \rightleftharpoons & NaOH & + \ HCN \\ C & & 0 & \ \ 0 \\ C(1-h) & & Ch & \ \ Ch \end{array}$$

$$\therefore \quad [\mathrm{OH^-}] = Ch = C\sqrt{\frac{K_h}{C}} = \sqrt{K_h C} = \sqrt{\frac{K_w C}{K_a}}$$

$$\mathrm{pOH} = \frac{1}{2}[pK_w - pK_a - \log C]$$

$$= \frac{1}{2}[14 - 9.30 - \log (0.4)] = 2.548$$

$$\therefore \quad \mathrm{pH} = 14 - 2.5 = 11.45$$

19. The acid ionisation constant for
$Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$
is 1.0×10^{-9}. Calculate the pH of 0.10 M solution of $ZnCl_2$. Also calculate the basic dissociation constant of $Zn(OH)^+$.

Sol. $Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$

$$\therefore [\mathrm{H^+}] = C \cdot h = C\sqrt{\frac{K_h}{C}} = \sqrt{K_h C}$$

$$= \sqrt{\frac{K_w C}{K_b}} \quad \left[\begin{array}{l}\text{where } K_b \text{ is the basic dissociation of} \\ \mathrm{Zn(OH)^+} \\ \text{i.e., } \mathrm{Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^-}\end{array}\right]$$

We know Zn^{2+} and $Zn(OH)^+$ are conjugate acid and base.

$$\therefore \quad K_a \times K_b = 10^{-14}$$

$$\text{or} \quad K_b = \frac{10^{-14}}{10^{-9}} = 10^{-5}$$

$$\text{Now, } [\mathrm{H^+}] = \sqrt{\frac{10^{-14} \times 0.1}{10^{-9}}} = \sqrt{10^{-6}} = 10^{-3}$$

pH = 3

20. What is the pH of a mixture containing 0.2 M X^- (base) and 0.4 M HX with pK_b (X^-) = 4?

Sol. $HX \rightleftharpoons H^+ + X^-$, $K_a = \dfrac{10^{-14}}{K_b} = 10^{-10}$

$$[\mathrm{H^+}] = K_a\frac{[\mathrm{HX}]}{[\mathrm{X^-}]} = \frac{10^{-10} \times 0.4}{0.2}$$

$$\text{or} \quad \mathrm{pH} = 10 - \log 2$$

21. The pH of a mixture of 1 M benzoic acid (pK_a = 4.2) and 1 M sodium benzoate is 4.5, in 150 mL buffer, benzoic acid find volume of benzoic acid.

Sol. $\mathrm{pH} = pK_a + \log\dfrac{[\text{salt}]}{[\text{Acid}]}$

$4.5 = 4.2 + \log\left[\dfrac{(150 - x)}{x}\right]$ where x is the volume of benzoic acid

$$0.3 = \log\left[\frac{(150 - x)}{x}\right] \text{ or } 2.0 = \left[\frac{(150 - x)}{x}\right]$$

$$\text{or} \quad x = 50 \text{ mL}$$

22. What is the ratio of salt to acid when the buffering action of a mixture of CH_3COOH and CH_3COONa is maximum?

Sol. The buffer action of a buffer mixture is effective in the pH range $pK_a \pm 1$. It is maximum when pH = pK_a.

23. What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole of propanoic acid to obtain a buffer solution of pH 4.74? What will be the pH if 0.01 mol HCl is dissolved in the above buffer solution ? Compare the last pH value with the pH of 0.01 molar HCl solution. Dissociation constant of propanoic acid at 25°C is 1.34×10^{-5}.

Sol. Using Henderson's expression

$$\mathrm{pH} = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

We get $4.74 = -\log(1.34 \times 10^{-5}) + \log\dfrac{[\text{Salt}]}{0.02}$

which gives $4.74 = 4.87 + \log\dfrac{[\text{Salt}]}{0.02}$

$$\text{or} \quad \log\frac{[\text{Salt}]}{0.02} = -0.13 = \log 0.74$$

$$\text{or} \quad [\text{Salt}] = 1.48 \times 10^{-2}\ \mathrm{M}$$

Hence, amount of sodium propanoate to be added = $1.48 \times 10^{-2} \times 96$ g = 1.42 g.

The addition of 0.01 mol of HCl converts the equivalent amount of sodium propanoate into propanoic acid. Hence, we will have

$$\mathrm{pH} = 4.87 + \log\frac{(0.01482 - 0.01)\,\mathrm{mol\,L^{-1}}}{(0.02 + 0.01)\,\mathrm{mol\,L^{-1}}}$$

$$\mathrm{pH} = 4.87 + \log(0.160) = 4.87 - 0.79 = 4.08$$

(The pH of 0.01 molar HCl solution will be pH = – log (0.01) = 2)

24. Equal volumes of 0.04 M $CaCl_2$ and 0.0008 M Na_2SO_4 are mixed. Will we get a precipitate?
K_{sp} for $CaSO_4 = 2.4 \times 10^{-5}$

Sol.

$$\begin{array}{lcccccc} & CaCl_2 & + & Na_2SO_4 & \rightarrow & CaSO_4 & + \ 2NaCl \\ \text{Millimole added} & 0.04\text{ V} & & 0.0008 \times \text{V} & & 0 & 0 \end{array}$$

Suppose V mL of both are mixed

$$\therefore \quad [\mathrm{Ca^{2+}}] = \frac{0.04\text{ V}}{2\text{ V}}$$

$$[\mathrm{SO_4^{2-}}] = \frac{0.0008\text{ V}}{2\text{ V}}$$

$$\therefore \quad [\mathrm{Ca^{2+}}][\mathrm{SO_4^{2-}}] = \frac{0.04\text{ V}}{2\text{ V}} \times \frac{0.0008\text{ V}}{2\text{ V}} = 8 \times 10^{-6}$$

Thus, $[Ca^{2+}][SO_4^{2-}]$ in solution < K_{sp}

$8 \times 10^{-6} < 2.4 \times 10^{-5}$

∴ $CaSO_4$ will not precipitate.

25. Calculate the $[OH^-]$ of a solution after 50.0 mL of 0.2 M $MgCl_2$ is added to 50.0 mL of 0.4 M NaOH. K_{sp} of $Mg(OH)_2$ is 1.2×10^{-11}.

Sol.

$$\begin{array}{lcccc} & MgCl_2 + & 2NaOH \rightarrow & Mg(OH)_2 + & 2NaCl \\ \text{initially} & 10\text{ mm} & 20\text{ mm} & 0 & 0 \\ \text{final} & 0 & 0 & 10\text{ mm} & 20\text{ mm} \end{array}$$

Thus, 10 m mole of $Mg(OH)_2$ are formed. The product of $[Mg^{2+}][OH^-]^2$ is, therefore, $\left[\frac{10}{100}\right] \times \left[\frac{20}{100}\right]^2 = 4 \times 10^{-3}$ which is more than K_{sp} of $Mg(OH)_2$. Now solubility (S) of $Mg(OH)_2$ can be derived by

$K_{sp} = 4S^3$

$\therefore \quad S = \sqrt[3]{K_{sp}} = \sqrt[3]{1.2 \times 10^{-11}} = 1.4 \times 10^{-4}$ M

$\therefore \quad [OH^-] = 2S = 2.8 \times 10^{-4}$ M

26. Will a precipitate of $Mg(OH)_2$ be formed in a 0.002 M solution of $Mg(NO_3)_2$, if the pH of solution is adjusted to 9? K_{sp} of $Mg(OH)_2 = 8.9 \times 10^{-12}$.

Sol. pH = 9

$\therefore \quad [H^+] = 10^{-9}$ M

or $\quad [OH^-] = 10^{-5}$ M

Now if $Mg(NO_3)_2$ is present in a solution of $[OH^-] = 10^{-5}$ M, then,

Product of ionic conc.

$= [Mg^{+2}]\,[OH^-]^2 = [0.002]\,[[10^{-5}]^2$

$= 2 \times 10^{-13}$ lesser than K_{sp} of $Mg(OH)_2$, i.e., 8.9×10^{-12}

$\therefore \quad Mg(OH)_2$ will not precipitate.

27. You are given 10^{-5} M NaCl solution and 10^{-8} M $AgNO_3$ solution, they are mixed in 1:1 volume ratio. Predict whether AgCl will be precipitated or not, if solubility product of AgCl in 10^{-2} M $AgNO_3$ is $= 10^{-10}$ mole L^{-1}?

Sol. Ionic product $= \dfrac{10^{-5}}{2} \times \dfrac{10^{-8}}{2} = 25 \times 10^{-15} < k_{sp}$

Hence no precipitation will take place.

28. In the excess of NH_3(aqueous), Cu^{+2} ion form a deep blue complex ion $[Cu(NH_3)_4]^{2+}$ which has $K_f = 10^{11}$. If the concentration of Cu^{+2} ion in solution prepared by adding 5×10^{-3} mol. of $CuSO_4$ to 0.5 L of 0.4 M NH_3 (aqueous) is $\dfrac{A}{(36)^4}$. Then, what is the value of A?

Sol.

$$\begin{array}{llcl} & Cu^{+2} \quad + & 4NH_3 \quad \rightleftharpoons & [Cu(NH_3)_4]^{+2} \\ \text{Init.}: & 0.01 & 0.4 & - \\ \text{ion}: & [Cu^{+2}] & 0.4 - 4 \times 0.01 & 0.01 \\ & & = 0.36 & \end{array}$$

$$10^{11} = \frac{0.01}{[Cu^{+2}][0.36]^4} \Rightarrow [Cu^{+2}] = \frac{10^{-5}}{[36]^4}$$

29 Calculate the molar solubility of AgBr in 0.1 M $Na_2S_2O_3$ (aqueous) solution. K_{sp} of AgBr $= 5 \times 10^{-13}$ and $K_f[Ag(S_2O_3)_2^{3-}] = 5 \times 10^{13}$.

Sol.

$$\begin{array}{lcc} AgBr(s) \rightleftharpoons & Ag^+ + & Br^- \\ & x & x \end{array}$$

$$\begin{array}{lcc} Ag^+ + & 2S_2O_3^{2-} \rightleftharpoons & Ag(S_2O_3)_2^{3-} \\ x - y & 0.1 - 2x & x \end{array}$$

$$\begin{array}{lccc} AgBr(s) + & 2S_2O_3^{2-} \rightleftharpoons & Ag(S_2O_3)_2^{3-} + & Br^- \\ & (0.1 - 2x) & x & x \end{array}$$

$$K_f \times K_{SP} = 5 \times 10^{13} \times 5 \times 10^{-13} = \frac{x^2}{(0.1 - 2x)^2}$$

$$5 = \frac{x}{0.1 - 2x} \Rightarrow x = 0.045 \text{ M}$$

Selective Precipitation

30. In a solution of 10^{-3} M Cl^- and 10^{-2}M CrO_4^{2-}, if solid $AgNO_3$ is gradually added, which will precipitate first AgCl, Ag_2CrO_4. Assuming no change in volume, what % of Cl^- ion originally present remain in solution when Ag_2CrO_4 begin to precipitate? $K_{sp}(AgCl) = 10^{-10}$, $K_{sp}(Ag_2CrO_4) = 10^{-12}$.

Sol. $\dfrac{\text{For ppt. of AgCl}}{10^{-10} < [Ag^+][Cl^-]}$

$\therefore \quad [Ag^+] > 10^{-7}$M

For ppt. of Ag_2CrO_4

$10^{-12} < [Ag^+]^2[CrO_4^{2-}]$

$[Ag^+] > 10^{-5}$M

So AgCl Start Precipitate Before Ag_2CrO_4

To precipitate Ag_2CrO_4 before AgCl

$10^{-10} = [Ag^+][Cl^-]$

$= 10^{-5} \times [Cl^-]$

$[Cl^-] = 10^{-5}$ M

% of Cl^- ion originally present remain in solution when Ag_2CrO_4 begin to precipitate

$$\%[Cl^-] = \frac{10^{-5}}{10^{-3}} \times 100 = 1\%$$

31. What is the maximum volume of water required to dissolve 1 g of calcium sulphate at 25°C. For calcium sulphate, $K_{sp} = 9.0 \times 10^{-6}$.

Sol. $CaSO_4\,(aq) \rightleftharpoons Ca^{2+}\,(aq) + SO_4^{2-}\,(aq)$

If S is the solubility of $CaSO_4$ in moles L^{-1}

$K_{sp} = [Ca^{2+}] \times [SO_4^{2-}] = S^2$

$\therefore \quad S = \sqrt{K_{sp}} = \sqrt{9.0 \times 10^{-6}}$

$= 3 \times 10^{-3}$ mol L^{-1}

$= 3 \times 10^{-3} \times 136$ g $L^{-1} = 0.408$ g L^{-1}

For dissolving 0.408 g of $CaSO_4$ water required $\dfrac{1}{0.408}$L $= 1$ L

$\therefore$ for dissolving 1g $CaSO_4$ water required = 2.45 L.

32. Calculate simultaneous solubility of AgCNS and AgBr in a solution of water. K_{sp} of AgBr $= 25 \times 10^{-13}$ and K_{sp} of AgCNS $= 5 \times 10^{-12}$.

Sol. Let solubility of AgCNS and AgBr in a solution be a and b mol L^{-1} respectively.

$$\begin{array}{lcc} AgCNS\,(s) \rightleftharpoons & Ag^+ + & CNS^- \\ & a & a \end{array}$$

$$\text{AgBr (s)} \rightleftharpoons \underset{b}{\text{Ag}^+} + \underset{b}{\text{Br}^-}$$

$\therefore$ For AgCNS $K_{sp_{AgCNS}} = [Ag^+][CNS^-]$

$$5 \times 10^{-12} = (a + b)(a) \qquad ...(i)$$

For AgBr $K_{sp_{AgBr}} = [Ag^+][Br^-]$

$$25 \times 10^{-13} = (a + b)(b) \qquad ...(ii)$$

By Eqs (i) and (ii),

$$\therefore \quad \frac{a}{b} = \frac{5 \times 10^{-12}}{25 \times 10^{-13}} = 2 \quad \text{or} \quad a = 2b$$

$\therefore$ By Eq. (i), $(2b + b)(2b) = 1 \times 10^{-12}$

$6b^2 = 5 \times 10^{-12}$

$b = 0.912 \times 10^{-6}$ mol L^{-1} = 9.12×10^{-5} M

By Eq. (i), $(a + a/2)$ (a) = 5×10^{-12}

$a = 1.82 \times 10^{-6}$ mol L^{-1}

33. What [H$^+$] must be maintained in saturated H_2S(0.1 M) to precipitate CdS but not ZnS, if [Cd^{2+}] = [Zn^{2+}] = 0.1 initially ?

K_{sp} = (CdS) = 8×10^{-27}

K_{sp} = (ZnS) = 1×10^{-21}

K_a = (H_2S) = 1.1×10^{-21}

Sol. In order to prevent precipitation of ZnS

$[Zn^{2+}][S^{2-}] < K_{sp}(ZnS) = 1 \times 10^{-21}$

(ionic product)

or $(0.1)[S^{2-}] < 1 \times 10^{-21}$

or $[S^{2-}] < 1 \times 10^{-20}$

This is the maximum value of [S^{2-}] before ZnS will precipitate. Let [H$^+$] to maintain this [S^{2-}] be x. Thus for $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{x^2(1 \times 10^{-20})}{0.1}$$

$$= 1.1 \times 10^{-21}$$

or $x = [H^+] = 0.1$ M

$\therefore$ No ZnS will precipitate at a concentration of H$^+$ greater than 0.1 M.

Exercise

LEVEL I

1. If K_W for H_2O at 90ºC is 10^{-12} M^2, then what would be the dissociation constant of water at the same temperature? [Assume d_{H_2O} = 1 g/mL]

(a) 10^{-14} (b) 1.8×10^{-16}

(c) 1.8×10^{-14} (d) 10^{-12}

2. If 100 mL of 0.1 M CH_3COOH is titrated against 50 mL of 0.1 M NaOH. Calculate pH of resulting solution if p_{Ka} for CH_3COOH = 4.76.

(a) 4.76 (b) 4.46 (c) 5.06 (d) 2.76

3. What is the minimum pH required to prevent the precipitation of ZnS in a solution that is 0.01 M $ZnCl_2$ and saturated with 0.10 M H_2S ? [Given $K_{sp} = 10^{-21}$, $K_{a_1} \times K_{a_2} = 10^{-20}$]

(a) 0 (b) 1 (c) 2 (d) 4

4. 4 mL of HCl solution of pH = 2 is mixed with 6 mL of NaOH solution of pH = 12. What will be the final pH of solution? log 2 = 0.3

(a) 10.3 (b) 11.3 (c) 11 (d) 4.3

5. A solution of $CuSO_4$ is

(a) acidic in nature (b) alkaline in nature

(c) neutral in nature (d) amphoteric in nature

6. The pH of 0.5 (M) $Ba(CN)_2$ solution is [Given: pK_b of CN$^-$ = 9.3]

(a) 8.35 (b) 3.35 (c) 9.35 (d) 9.5

7. On diluting a buffer solution, its pH

(a) is increased

(b) is decreased

(c) remain constant

(d) changes which cannot be predicted unless dissociation constant of weak acid or weak base is provided.

8. 100 mL solution (I) of buffer containing 0.1(M) HA and 0.2 (M) A$^-$, is mixed with another solution (II) of 100 mL containing 0.2(M) HA and 0.3(M) A$^-$.
After mixing, what is the pH of resulting solution? [Given: pK_a of HA = 5]

(a) 5 – log 5/3 (b) 5 + log 5/3

(c) 5 + log 2/5 (d) 5 – log 5/2

9. K_b of an acid-base indicator H In is 10^{-9}. The pH at which its 10^{-3} (M) solution shows the colour change?

(a) 9 (b) 7 (c) 5 (d) 3

10. K_{sp} of SrF_2 (s) in water is 3.2×10^{-14}. The solubility of SrF_2 (s) in 0.1 (M) NaCl solution is

(a) 3.2×10^{-9} (M)

(b) 2×10^{-5} (M)

(c) 4×10^{-4} (M)

(d) Slightly higher than 2×10^{-5} (M)

11. What will be the value of K_w at 90ºC, if [H$^+$] in pure water is 10^{-6} gram ion per litre?

(a) 10^{-10} (b) 10^{-16}

(c) 1×10^{-12} (d) 2×10^{-6}

12. Concentration of [H$^+$] will decrease on mixing which of the following salts with the solution of acetic acid?

(a) KCN (b) NaCl

(c) NH_4Cl (d) $Al_2(SO_4)_3$

13. Aqueous solution of $FeCl_3$
(a) turns blue litmus solution red.
(b) turns red litmus solution blue.
(c) decolourises litmus solution.
(d) does not affect litmus solution.

14. When HCl gas is passed in saturated solution of common salt, then pure NaCl is precipitated, because
(a) Ionic product of Na^+ and Cl^- exceeds the solubility product of NaCl.
(b) HCl is highly soluble in water.
(c) ionisation of NaCl is decreased due to chloride ions of HCl.
(d) HCl absorbs impurities.

15. Which of the following has maximum value of solubility product?
(a) $Fe(OH)_3$ (b) $Al(OH)_3$
(c) $Cr(OH)_3$ (d) $Zn(OH)_2$

16. Which of the following is true for aqueous solution of CH_3NH_2 of 0.1 M concentration?
(a) $[OH^-] = 0.1M$ (b) $pH = 0$
(c) $pH < 7$ (d) $pH > 7$

17. If pH of 0.1M acetic acid is 3.0, then dissociation constant of this acid will be
(a) 1×10^{-4} (b) 1×10^{-5}
(c) 1×10^{-3} (d) 1×10^{-8}

18. Solution of which of the following will have maximum pH value?
(a) NaCl (b) Na_2CO_3
(c) NH_4Cl (d) $NaHCO_3$

19. A precipitate will be obtained on mixing equal volume of which of the following solutions, if $K_{sp} = 1.8 \times 10^{-10}$?
(a) 10^{-4} M $[Ag^+]$ and 10^{-4}M $[Cl^-]$
(b) 10^{-5} M $[Ag^+]$ and 10^{-5}M $[Cl^-]$
(c) 10^{-6} M $[Ag^+]$ and 10^{-6}M $[Cl^-]$
(d) 10^{-10} M $[Ag^+]$ and 10^{-4}M $[Cl^-]$

20. Which of the following is present in an aqueous solution of Na_2CO_3?
(a) H_2CO_3, Na^+, OH^- (b) H_2CO_3, OH^-
(c) CO_3^{-2} ion (d) Na^+ and OH^- ion

21. Why is NH_4Cl added before NH_4OH in qualitative analysis of third group ions?
(a) To increase concentration of OH^-.
(b) To decrease concentration of OH^-.
(c) To make solution dilute.
(d) For pure precipitation.

22. What is the volume of water needed to make normality of the solution 3N, prepared by mixing 250 mL 6 M HCl and 350 mL 8M HNO_3?
(a) 833.3 mL (b) 933.3 mL
(c) 1000 mL (d) 500 mL

23. On dilution of a solution formed from CH_3COONH_4
(a) pH decreases
(b) pH increases
(c) pH remains unchanged
(d) None of the above

24. Which of the following indicators is appropriate in the titration of NH_4OH and strong acid?
(a) Phenolphthalein (b) Methyl orange
(c) Phenol red (d) Litmus

25. What will be the mole fraction of acetone in the solution formed by 1.8 gram of water and 2.9 gram of acetone?
(a) $\frac{2}{3}$ (b) 2.9 (c) $\frac{1}{3}$ (d) $\frac{2.9}{4.7}$

26. Value of pK_a for acetic acid at 25ºC is 4.75, then what will be the pH value of the solution in which ratio of concentration of sodium acetate and acetic acid is 10?
(a) 3.75 (b) 4.75 (c) 5.75 (d) 10.0

27. Phenophthalein gives which of the following colours in acidic medium?
(a) Pink (b) Red
(c) No colour (d) Violet

28. If pKa of acetic acid at 25ºC is 4.75, then determine the pH of that solution in which 0.02 M sodium acetate and acetic acid are present.
(a) 4.75 (b) 3.75 (c) 5.75 (d) 2.75

29. Which of the following ions are present in the solution of the monosodium salt of orthophosphoric acid?
(a) Na^+, PO_4^{-3}, $H_2PO_4^{-2}$, HPO_4^{-1}
(b) Na^+, HPO_4^{-2}
(c) Na^+, $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}
(d) Na^+, HPO_4^{-2}, PO_4^{-3}

30. What is the concentration of Ag^+ ion in a 1L solution containing 0.02 mol of $AgNO_3$ and 0.14 mol of NH_3. For $Ag(NH_3)_2^+$, $K_{stab} = 10^8$.
(a) 2×10^{-7}(M) (b) 10^{-8}(M)
(c) 2×10^{-8}(M) (d) 2×10^{-9}(M)

31. A 50 mL solution of pH = 1 is mixed with a 50 mL solution of pH = 2. then pH of the mixture will be nearly
(a) 0.76 (b) 1.26 (c) 1.76 (d) 2.26

32. The pH of a solution is 7.00. To this solution, sufficient base is added to increase the pH to 12.0. The increase in OH– ion concentration is-
(a) 5 times (b) 1000 times
(c) 10^5 times (d) 4 times

33. The dissociation constants of two acids HA_1 and HA_2 are 3.0×10^{-4} and 1.8×10^{-5} respectively. The relative strengths of the acids will be approximately
(a) 1 : 4 (b) 4 : 1 (c) 1 : 16 (d) 16 : 1

34. If 50 mL of 0.2 (M) KOH is added to 40 mL of 0.5(M) HCOOH. The pH of the resulting solution is ($K = 1.8 \times 10^{-4}$)
(a) 3.75 (b) 5.6 (c) 7.5 (d) 3.4

35. The sodium salt of a certain weak monobasic organic acid is hydrolysed to an extent of 3% in its 0.1 M solu-

tion at 25°C. Given that the ionic product of water is 10^{-14} at this temperature, what is the dissociation constant of the acid ?
(a) $\approx 1 \times 10^{-10}$ (b) $\approx 1 \times 10^{-9}$
(c) 3.33×10^{-9} (d) 3.33×10^{-10}

36. When 100 mL of 0.4 M CH_3COOH are mixed with 100 mL of 0.2 M NaOH, the $[H_3O^+]$ in the solution is approximately : $[Ka(CH_3COOH) = 1.8 \times 10^{-5}]$
(a) 1.8×10^{-6} (b) 1.8×10^{-5}
(c) 9×10^{-6} (d) 9×10^{-5}

37. What will be the pH at the equivalence point during the titration of a 100 mL 0.2 M solution of CH_3COONa with 0.2 M solution of HCl ? $Ka = 2 \times 10^{-5}$
(a) $3 - \log\sqrt{2}$ (b) $3 + \log\sqrt{2}$
(c) $3 - \log 2$ (d) $3 + \log 2$

38. What % of the carbon in the H_2CO_3, HCO_3^-. Buffer should be in the form of HCO_3^- so as to have a neutral solution ? ($Ka = 4 \times 10^{-7}$)
(a) 20 % (b) 40 % (c) 60 % (d) 80 %

39. 50 mL of 0.1 M NaOH is added to 60 mL of 0.15 M H_3PO_4 solution (K_1, K_2 and K_3 may be taken as 10^{-3}, 10^{-8} and 10^{-13} respectively). The pH of the mixture would be about
(a) 3.1 (b) 5.5 (c) 4.1 (d) 6.5

40. The concentration of Mg^{2+} in the solution made by mixing 10 mL of 0.25 M $Mg(NO_3)_2$ and 25 mL of 0.2 M NaF will be ($K_{sp}(MgF_2 = 8 \times 10^{-8}$)
(a) 0.0027 M (b) 0.0714 M
(c) 0.0030 M (d) 0.0060 M

41. The precipitate of $CaF_2(K_{sp} = 1.7 \times 10^{-10})$ is obtained when equal volumes of which of the following are mixed?
(a) 10^{-4} M Ca^{2+} + 10^{-4} M F^-
(b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-
(c) 10^{-5} M Ca^{2+} + 10^{-3} M F^-
(d) 10^{-3} M Ca^{2+} + 10^{-5} M F^-

42. 1 CC of 0.1 N HCl is added to 99 CC solution of NaCl. The pH of the resulting solution will be
(a) 7 (b) 3 (c) 4 (d) 1

43. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is
(a) 1.74×10^{-5} (b) 3.52×10^{-3}
(c) 6.75×10^{-4} (d) 5.38×10^{-2}

44. The pH of 2.0×10^{-4} M H_3X solution assuming first dissociation to be 100%, second to be 50% and third to be negligible is
(a) 3.7 (b) 2.4 (c) 3.0 (d) 3.52

45. What is the pH of 10% dissociated $\frac{M}{200}$ H_2CO_3 solution ?
(a) 3 (b) 4 (c) 5 (d) 6

46. pH of 0.01 M solution of potassium propionate is 8. What is the pK_a of propionic acid?
(a) 4 (b) 2
(c) 0 (d) None of these

LEVEL II

1. 100 mL of 0.02 M benzoic acid ($pK_a = 4.2$) is titrated using 0.02 M NaOH. pH after 50 mL and 100 mL of NaOH have been added are
(a) 3.50,7 (b) 4.2, 7
(c) 4.2, 8.1 (d) 4.2, 8.25

2. What is the difference in pH for 1/3 and 2/3 stages of neutralisation of 0.1 M CH_3COOH with 0.1 M NaOH?
(a) – 2 log 3 (b) 2 log (1/4)
(c) 2 log (2/3) (d) –2 log 2

3. The pH of 1.0 M $NaHSO_4$ solution will be (given that K_1 and K_2 for H_2SO_4 equal to ∞ and 10^{-2} respectively)-
(a) nearly 1.0 (b) between 2 and 3
(c) between 1.2 and 1.8 (d) between 3 and 4

4. At 25 °C, the dissociation constant of HCN and HF are 4×10^{-10} and 6.7×10^{-4}. The pH of a mixture of 0.1 M HF and 0.1 M HCN.
(a) 2.087 (b) 3.0 (c) 5.5 (d) 6.0

5. The pH of a solution prepared by mixing 50.0 mL of 0.200 M CH_3CO_2H and 50.0 mL of 0.100 M NaOH. $K_a = 1.8 \times 10^{-5}$.
(a) 5 (b) 4.74 (c) 10.3 (d) 7

6. What fraction of an indicator Hln is in the basic form at a pH of 6 if pK_a of the indicator is 5 ?
(a) $\frac{1}{2}$ (b) $\frac{1}{11}$ (c) $\frac{10}{11}$ (d) $\frac{1}{10}$

7. An acid-base indicator which is a weak acid has a pK_a value = 5.5. At what concentration ratio of sodium acetate to acetic acid will the indicator show a colour half-way between those of its acid and conjugate base forms ? pK_a of acetic acid = 4.75.
(a) 4.93 : 1 (b) 6.3 : 1 (c) 5.62 : 1 (d) 2.37 : 1

8. What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$.
(a) 2.48 (b) 5.26 (c) 8.2 (d) 9.6

9. The OH^- concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for the acid = 1.9×10^{-5}.
(a) 7×10^{-7} (b) 5.2×10^{-7}
(c) 5.2×10^{-6} (d) 7.2×10^{-7}

10. A solution contains HCl, $Cl_2HCCOOH$ and CH_3COOH at concentrations 0.09 M in HCl, 0.09 M in $Cl_2HCCOOH$ and 0.1 M in CH_3COOH, pH for the solution is 1. K_a $CH_3COOH = 10^{-5}$. What is the Ka for dichloroacetic acid?
(a) 1.25×10^{-4} (b) 1.25×10^{-3}
(c) 1.25×10^{-6} (d) 1.25×10^{-2}

11. A solution of ammonia bought for cleaning the windows was found to be 10% ammonia by mass, having a density of 0.935 $g.mL^{-1}$. What is the pH of the solution. Take K_b for protonation of ammonia = 5.5×10^{-6}.
(a) 10.7 (b) 2.3 (c) 11.7 (d) 6.7

12. The k_w of water at two different temperature is:-

T	25°C	50°C
k_w	1.08×10^{-14}	5.474×10^{-14}

Assuming that ΔH of any reaction is independent of temperature. The enthalpy of neutralization of a strong acid and strong base.

(a) 51.95 J/mole (b) 51.95 kJ/mole
(c) 5.195 kJ/mole (d) 519.5 kJ/mole

13. Calculate the pH of the following solution 40 mL of 0.050 M Na_2CO_3 + 50 mL of 0.040 M HCl Use H_2CO_3; For $H_2CO_3 \rightarrow k_1 = 4.2 \times 10^{-7}$, $k_2 = 4.8 \times 10^{-11}$

(a) 8.35 (b) 8.0 (c) 6.65 (d) 7.0

14. Calculate the pH of the following solution given for $H_3PO_4 \rightarrow k_1 = 7.5\times 10^{-3}$, $k_2 = 6.2\times 10^{-8}$, $k_3 = 10^{-12}$
40 mL of 0.020 M Na_3PO_4 + 40 mL of 0.040 M HCl:

(a) 4.66 (b) 12.66 (c) 8.64 (d) 2.66

15. How many moles of HCl can be added to 1.00 L of a solution 0.1 M in NH_3 and 0.1 M in NH_4Cl without changing the pOH by more than 1.00 unit ? Assume no change in volume. $K_b(NH_3) = 1.8 \times 10^{-5}$.

(a) 0.82 moles (b) 0.05 moles
(c) 0.082 moles (d) 0.03 moles

16. Calculate the OH^- concentration of a solution prepared by dissolving 0.1 mol of Na_3PO_4 in sufficient water to make 1 L of solution $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

(a) 3.73×10^{-2} M (b) 3.73×10^{-4} M
(c) 3.73×10^{-6} M (d) 3.73×10^{-10} M

17. Calculate the H_3PO_4 concentration of a solution prepared by dissolving 0.1 mol of Na_3PO_4 in sufficient water to make 1 L of solution $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

(a) 3.93×10^{-12} M (b) 5.93×10^{-18} M
(c) 4.5×10^{-13} M (d) 6.3×10^{-8} M

18. A solution of weak acid HA was titrated with base NaOH. The equivalence point was reached when 36.12 mL of 0.1 M NaOH was added. Now 18.06 mL of 0.1 M HCl were added to titrated solution, the pH was found to be 4.92. What will be the pH of the solution obtained by mixing 10 mL of 0.2 M NaOH and 10 mL of 0.2 M HA?

(a) 5 (b) 9 (c) 10 (d) 8

19. A weak base BOH was titrated against a strong acid. The pH at 1/4th equivalence point was 9.24. Enough strong base was now added (6 m. eq.) to completely convert the salt. The total volume was 50 mL. Find the pH at this point.

(a) 11.2 (b) 2.8 (c) 10 (d) 6.8

20. Calculate pH of 1M $NaHCO_3$ is given

$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$, $pK_1 = 6.38$
$HCO_3^- + H_2O \rightleftharpoons CO_3^{-2} + H_3O^+$, $pK_2 = 10.26$

(a) 8.32 (b) 6.38 (c) 5.32 (d) 10.26

21. At 25 °C, the solubility product values of AgCl and AgCNS are 1.7×10^{-10} and 1.0×10^{-12} respectively. When water is saturated with both solids, calculate the ratio $[Cl^-]/[CNS^-]$ and also $[Ag^+]$ in the solution.

(a) 1.3×10^2, 1.7×10^{-5} M
(b) 1.7×10^2, 1.308×10^{-5} M
(c) 1.3×10^4, 1.308×10^{-4} M
(d) 1.7×10^3, 1.67×10^{-6} M

22. If K_{sp} for $HgSO_4$ is 6.4×10^{-5}, then solubility of this substance in mole per m^3 is

(a) 8×10^{-3} (b) 6.4×10^{-5}
(c) 8×10^{-6} (d) None of these

23. How many moles NH_3 must be added to 2.0 L of 0.80 M $AgNO_3$ in order to reduce the Ag^+ concentration to 5×10^{-8} M. K_f of $[Ag(NH_3)_2{}^+] = 10^8$

(a) 0.4 (b) 2 (c) 3.52 (d) 4

24. Solubility of solid zinc hydroxide at a pH of 5

$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq)$ $k_1 = 10^{-6}$ M (i)
$Zn(OH)_2(aq) \rightleftharpoons Zn(OH)^+ + OH^-$ $k_2 = 10^{-7}$ M (ii)
$Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^-$ $k_3 = 10^{-4}$ M (iii)
$Zn(OH)_2(aq) + OH^- \rightleftharpoons Zn(OH)_3^-$ $k_4 = 10^3\ M^{-1}$ (iv)
$Zn(OH)_3^- + OH^- \rightleftharpoons Zn(OH)_4^{2-}$ $k_5 = 10\ M^{-1}$ (v)

(a) 0.1 M (b) 2×10^{-2}M
(c) 2×10^{-6}M (d) 10M

25. Calculate the solubility of solid zinc hydroxide at a pH of 13. Given:

$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq)$ $k_1 = 10^{-6}$ M (i)
$Zn(OH)_2(aq) \rightleftharpoons Zn(OH)^+ + OH^-$ $k_2 = 10^{-7}$ M (ii)
$Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^-$ $k_3 = 10^{-4}$ M (iii)
$Zn(OH)_2(aq) + OH^- \rightleftharpoons Zn(OH)_3{}^-$ $k_4 = 10^3\ M^{-1}$ (iv)
$Zn(OH)_3^- + OH^- \rightleftharpoons Zn(OH)_4^{2-}$ $k_5 = 10\ M^{-1}$ (v)

(a) 0.1 M (b) 2×10^{-2} M
(c) 2×10^{-4} M (d) 1.0 M

26. Salt mixture containing $Cu_3(AsO_4)_2$ ($K_{sp} = 8 \times 10^{-36}$) and $Pb_3(AsO_4)_2$ ($K_{sp} = 4.096 \times 10^{-36}$) is shaken with water. Find the concentration of Pb^{+2} cations in the solution at equilibrium. Neglect any hydrolysis of the dissolved ions.

(a) 7.1×10^{-8} M (b) 2.875×10^{-8} M
(c) 8.825×10^{-8} M (d) 2.3×10^{-8} M

27. At what minimum pH will 1.0×10^{-3} mol of $Al(OH)_3$ go into 1 L solution as $[Al(OH)_4]^-$?
Given : $K_{sp}\,[Al(OH)_3] = 5.0 \times 10^{-33}$ and for $[Al(OH)_4^-] \Leftrightarrow Al^{3+} + 4OH^-$.$K = 1.3 \times 10^{-34}$.

(a) 6.4 (b) 9.4 (c) 4.4 (D) 7.0

28. What is the solubility of AgCl in 0.20 M NH_3 ?
Given: $K_{sp}(AgCl) = 1.7 \times 10^{-10}\ M^2$, $K_1 = [Ag(NH_3)^+]/[Ag^+][NH_3] = 2.33 \times 10^3\ M^{-1}$ and $K_2 = [Ag(NH_3)_2{}^+]/[Ag(NH_3)^+][NH_3] = 7.14 \times 10^3\ M^{-1}$.

(a) 9.6×10^{-5} M (b) 9.6×10^{-6} M
(c) 9.6×10^{-1} M (d) 9.6×10^{-3} M

29. Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in $KAg(CN)_2$. Given $K_{inst}(Ag(CN)_2^-) = 4.0 \times 10^{-19}\ M^2$ and K_{sp} (AgCl) $= 2.8 \times 10^{-10}\ M^2$.

(a) Data insufficient
(b) AgCl will precipitate

(c) AgCl will not precipitate
(d) None of these

30. Equal volumes of 0.02 M $AgNO_3$ and 0.02 M HCN were mixed. Calculate $[Ag^+]$ at equilibrium. Take $K_a(HCN) = 9 \times 10^{-10}$, $K_{sp}(AgCN) = 4 \times 10^{-16}$.
(a) 6.67×10^{-4} M (b) 6.00×10^{-3} M
(c) 6.7×10^{-5} M (d) 4.5×10^{-8} M

LEVEL III

Match the Columns

1. Match the Columns:

Column I		Column II	
(A)	Buffer capacity is maximum for an acid buffer is	(P)	$pH = pKa + \log \frac{1}{3}$
(B)	At the $\frac{1}{4}$ th of the equivalence point for the titration of weak acid HA	(Q)	$\frac{1}{2}(pKa + \log 3)$
(C)	At the $\frac{3}{4}$ th of the equivalence point for the titration of weak acid HA	(R)	$pH = pKa - \log \frac{1}{3}$
(D)	The pH of $\frac{1}{3}$ (M) solution of weak acid HA	(S)	$pH = pKa$

2. Match the columns:

Column I		Column II	
(A)	CH_3COOH ($pKa = 4.74$;0.1 M) + CH_3COONa (0.1 M)	(P)	Acidic buffer at its maximum capacity
(B)	CH_3COOH (0.1 M) + HCl (0.1 M)	(Q)	Buffer solution
(C)	CH_3COOH ($pKa = 4.74$, (0.1 M) + NH_4OH ($pKa = 4.74$, 0.1 M)	(R)	pH < 7 at 25° C
(D)	CH_3COONa (300 mL of 0.1 M) + HCl (100 mL of 0.1 M)	(S)	pH = 7 at 25° C

3. K_a and K_b are the dissociation constant of weak acid and weak base and K_w is the ionic product of water.

Column I		Column II	
(A)	0.1(M) KCN solution	(P)	$pH \simeq 7$
(B)	0.1(M) $C_6H_5NH_3Cl$ solution	(Q)	$pH = 6.5 + \frac{1}{2}pK_a$
(C)	0.1(M) KCl solution	(R)	$pH = 7.5 - \frac{1}{2}pK_b$
(D)	0.1(M) CH_3COONH_4 solution	(S)	$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

4. Match the columns:

Column I		Column II	
(A)	$NaHCO_3$ solution	(P)	Cationic hydrolysis
(B)	$CuSO_4$ solution	(Q)	Anionic hydrolysis
(C)	Potash alum solution	(R)	Acidic
(D)	NaCN solution	(S)	Alkaline

5. Match the columns:

Column I		Column II	
(A)	pH of 0.1M HA ($pK_a = 5$) and 0.01 M NaA	(P)	4
(B)	pH of 0.1 M BOH ($pK_b = 6$) and 0.1 M BCl	(Q)	7
(C)	pH of 0.1 M salt of HA ($pK_a = 5$) and BOH ($pK_b = 7$)	(R)	6
(D)	pH of 500 L of 0.2 M HNO_3 and 500 L 0.2M NaOH	(S)	8

6. Match the columns:

Column I		Column II	
(A)	Salt of weak acid and weak base ($pK_a = pK_b$)	(P)	pH of solution at 25ºC is less than 7
(B)	Salt of weak acid and strong base	(Q)	pH of solution at 25ºC greater than 7
(C)	Salt of strong acid and strong base	(R)	pH of solution at 25ºC equal to 7
(D)	Salt of strong acid and weak base	(S)	pH can not be find until the value of K_a/K_b is given

7. Match the columns:

Column I		**Column II**	
(A)	pK_b of X^- (K_a of HX = 10^{-6})	(P)	6.9
(B)	pH of 10^{-8} M HCl	(Q)	8
(C)	pH of 10^{-2} M acetic acid solution (Take K_a of acetic acid = 1.6×10^{-5})	(R)	10.7
(D)	pOH of a solution obtained by Mixing equal volumes of solution with pH 3 and 5.	(S)	3.4

8. Match the columns:

Column I		**Column II**	
(A)	The relation between K_{sp} and the solubility of Ag_2CrO_4	(P)	$\dfrac{[H^+][OH^-]}{[H_2O]}$
(B)	Ionisation constant of water	(Q)	$K_{sp} = s^2$
(C)	The relation between K_{sp} and solubility of $BaCrO_4$	(R)	pH > 7
(D)	pH of aqueous solution of potassium carbonate	(S)	$K_{sp} = 4s^3$

Comprehension

Comprehension 1

The pH of blood stream (7.4) is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentration.

9. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3 in order to maintain its pH? : If PKa_1 6.11 and PKa_2 10.2
(a) 40 mL (b) 38 mL (c) 50 mL (d) 78 mL

10. Following reaction occurs in the body :
$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
If CO_2 escapes from the system :
(a) pH will decrease
(b) pH will increase
(c) $[H_2CO_3]$ remains unchanged
(d) forward reaction is promoted

Comprehension 2

To the 100 mL of 10^{-2} (M) aqueous solution of HCl 0.1 (M) HA ($K_a = 10^{-2}$) is added in such a way so that the final pH of the solution become 1.7.
Given log 2 = 0.3

11. What volume of 0.1 (M) HA was required to add in aqueous HCl to reduced the final pH equal to 1.7?
(a) 175 mL (b) 100 mL (c) 10^4 mL (d) 75 mL

12. Which of the following solution is isohydric with 0.1(M) aqueous solution of HA?
(a) 0.01(M) aqueous solution of HB ($K_a = 10^{-2}$)
(b) 0.01(M) aqueous solution of HC ($K_a = 10^{-5}$)
(c) 0.01(M) aqueous solution of HNO_3
(d) 1(M) aqueous solution of HD ($K_a = 10^{-3}$)

13. 100 mL of 0.1 (M) HA and 100 mL of 1(M) HD ($K_a = 10^{-3}$) solutions are mixed. What is the final approximate pH of the solution neglecting the degree of dissociation of HA and HD?
(a) 2.5
(b) 2.0
(c) 1.5
(d) Final pH cannot be determined

Comprehension 3

50 mL of 0.1(M) Na_2CO_3 solution is titrated with 0.1(M) HCl solution

Given: $CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$ $\quad K_1 = 2.1 \times 10^{10}$

$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$ $\quad K_2 = 2.2 \times 10^6$

Given: log 3 = 0.48

14. The pH of solution at the start of titration is
(a) 6.4 (b) 7.5 (c) 8.3 (d) 11.5

15. The pH of solution at the half-neutralisation point is
(a) 6.4 (b) 7.5 (c) 8.3 (d) 11.50

16. The pH of solution at the complete neutralisation point is about
(a) 4.0 (b) 6.0 (c) 7.0 (d) 8.0

Comprehension 4

A solution of paranitrophenol indicator of concentration 6×10^{-4} (M) was prepared and indicator solution was used in the spectrophotometric measurement. The experimental results are tabulated as below.

Condition	Form of Indicator	Absorbance
Strongly Acidic	H In	0.142
Strongly Alkaline	In^-	0.943
pH = 8	H In + In^-	0.527

Given: log 2 = 0.3; log 3 = 0.48; log 5 = 0.7; log 7 = 0.85

17. What is the molar concentration of In^- at pH = 8?
(a) 3.11×10^{-4} (M) (b) 2.88×10^{-4} (M)
(c) 6×10^{-4} (M) (d) None of these

18. What is the K_{in} of the indicator ?
(a) 3.117×10^{-4} (b) 6.12×10^{-9}
(c) 9.25×10^{-10} (d) 9.25×10^{-9}

19. What will be the pH of the solution if the total absorbance is equal to 0.625 ?
(a) 8.00 (b) 10.22 (c) 11.23 (d) 8.215

Subjective

20. Calculate
(i) K_a for H_2O ($K_w = 10^{-14}$)
(ii) K_b for $B(OH)_4^-$, $K_a(B(OH)_3) = 6 \times 10^{-10}$
(iii) K_a for HCN, $K_b(CN^-) = 2.5 \times 10^{-5}$

21. Calculate the ratio of degree of dissociation (α_2/α_1) when 1 M acetic acid solution is diluted to $\dfrac{1}{100}$ times. (Given: $K_a = 1.8 \times 10^{-5}$)

22. Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids (Given: $K_a = 1.8 \times 10^{-5;} = 6.2 \times 10^{-10}$]

23. Calculate: K_a for a monobasic acid whose 0.10 M solution has pH of 4.50.

24. Calculate pH of the following solution:
 (i) 0.1 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
 (ii) 10^{-8} M HCl
 (iii) 10^{-10} M NaOH

25. The value of K_w at the physiological temperature (37° c) is 2.56×10^{-14}. What is the pH at the neutral point of water at this temperature, where there are equal number of H^+ and OH^- ?

26. The pH of aqueous solution of ammonia is 11.5. Find molarity of solution. $K_b(NH_4OH) = 1.8 \times 10^{-5}$.

27. The solution of weak monoprotic acid which is 0.01 M has pH = 3. Calculate K_a of weak acid.

28. Calculate $[H^+]$ and $[CHCl_2COO^-]$ in a solution that is 0.01 M in HCl and 0.01 M in $CHCl_2COOH$. Take ($K_a = 2.55 \times 10^{-2}$).

29. Calculate $[H^+]$, $[CH_3COO^-]$ and $[C_7H_5O_2^-]$ in a solution that is 0.02 M in acetic acid and 0.01 M in benzoic acid. K_a(acetic) = 1.8×10^{-5}, K_a(benzoic) = 6.4×10^{-5}.

30. Determine the $[S^{2-}]$ in a saturated (0.1 M) H_2S solution to which enough HCl has been added to produce a $[H^+]$ of 2×10^{-4}. $K_1 = 10^{-7}$, $K_2 = 10^{-14}$

31. Calculate $[H^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ in a 0.01 M solution of H_3PO_4.
Take $K_1 = 7.225 \times 10^{-3}$, $K_2 = 6.8 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

32. Determine $[OH^-]$ of a 0.050 M solution of ammonia to which has been added sufficient NH_4Cl to make the total $[NH_4^+]$ equal to 0.100. [= 1.8×10^{-5}].

33. A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x.

34. What is the OH^- concentration of a 0.08 M solution of CH_3COONa? [$K_a(CH_3COOH) = 1.8 \times 10^{-5}$]

35. 0.25 M solution of pyridinium chloride $C_5H_6N^+Cl^-$ was found to have a pH of 2.699. What is K_b for pyridine, C_5H_5N?

36. What is the pH of 0.1 M $NaHCO_3$? $K_1 = 4.5 \times 10^{-7}$, $K_2 = 4.5 \times 10^{-11}$ for carbonic acids.

37. A solution of volume V contains n_1 moles of QCl and n_2 moles of RCl where QOH and ROH are two weak bases of dissociation constants k_1 and k_2 respectively. Show that the pH of the solution is given by

$$\mathrm{pH} = \frac{1}{2}\log\left[\left(\frac{k_1k_2}{k_W}\right)\frac{V}{(n_1k_2 + k_1n_2)}\right]$$

State assumptions, if any.

38. EDTA, often abbreviated as H_4Y, forms very stable complexes with almost all metal ions. Calculate the fraction of EDTA in the fully protonated form, H_4Y in a solution obtained by dissolving 0.1 mol Na_4Y in 1 L. The acid dissociation constants of H_4Y :
$k_1 = 1.02 \times 10^{-2}$, $k_2 = 2.13 \times 10^{-3}$, $k_3 = 6.92 \times 10^{-7}$, $k_4 = 5.50 \times 10^{-11}$:

39. Calculate the solubility of solid zinc hydroxide at a pH of 9. Given:

$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq) \quad k_1 = 10^{-6}\,M$ (i)
$Zn(OH)_2(aq) \rightleftharpoons Zn(OH)^+ + OH^- \quad k_2 = 10^{-7}\,M$ (ii)
$Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^- \quad k_3 = 10^{-4}\,M$ (iii)
$Zn(OH)_2(aq) + OH^- \rightleftharpoons Zn(OH)_3^- \quad k_4 = 10^3\,M^{-1}$ (iv)
$Zn(OH)_3^- + OH^- \rightleftharpoons Zn(OH)_4^{2-} \quad k_5 = 10\,M^{-1}$ (v)

40. The standard free energy of formation for AgCl at 298 K is –109.7 kJ mole^{-1} .
$\Delta G°\ (Ag^+) = 77.2$ kJ/mole, $\Delta G°\ (Cl^-) = -131.2$ kJ/mole. Find the solubility of AgCl in 0.05 M KCl. Neglect any complication due to complexation.

41. At what minimum pH will 1.0×10^{-3} mol of $Al(OH)_3$ go into 1 L solution as Al^{3+} ?
Given: $K_{sp}\,[Al(OH)_3] = 5.0 \times 10^{-33}$ and for
$[Al(OH)_4^-] \Leftrightarrow Al^{3+} + 4OH^-$. $K = 1.3 \times 10^{-34}$.

42. What is the pH of a 1.0 M solution of acetic acid ? To what volume must 1 L of the solution be diluted so that the pH of the resulting solution will be twice the original value. Given $K_a = 1.8 \times 10^{-5}$.

43. A handbook states that the solubility of methylamine CH_3NH_2 (g) in water at 1 atm pressure at 25°C is 959 volumes of CH_3NH_2 (g) per volume of water ($pk_b = 3.39$):
 (a) Estimate the maximum pH that can be attained by dissolving methylamine in water.
 (b) What molarity NaOH (aqueous) would be required to yield the same pH?

44. Mixture of solutions. Calculate the pH of the following solutions:
For H_3PO_4, $k_1 = 7.5 \times 10^{-3}$, $k_2 = 6.2 \times 10^{-8}$, $k_3 = 10^{-12}$,
 (a) 50 mL of 0.12 M H_3PO_4 + 20 mL of 0.15 M NaOH;
 (b) 50 mL of 0.12 M H_3PO_4 + 40 mL of 0.15 M NaOH;
 (c) 40 mL of 0.12 M H_3PO_4 + 40 mL of 0.18 M NaOH;
 (d) 40 mL of 0.10 M H_3PO_4 + 40 mL of 0.25 M NaOH.

45. Mixture of solutions. Calculate the pH of the following solution:
Use data of above question for H_3PO_4
 (i) 50 mL of 0.10 M Na_3PO_4 + 50 mL of 0.10 M NaH_2PO_4;
 (ii) 40 mL of 0.10 M H_3PO_4 + 40 mL of 0.10 M Na_3PO_4.

46. When a 40 mL of a 0.1 M weak base is titrated with 0.16 M HCl, the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution :-

47. A buffer solution was prepared by dissolving 0.05 mol formic acid and 0.06 mol sodium formate in enough water to make 1.0 L of solution. K_a for formic acid is 1.80×10^{-4}.

(a) Calculate the pH of the solution.
(b) If this solution was diluted to 10 times its volume, what will be the pH?
(c) If the solution in (b) was diluted to 10 times its volume, what will be the pH?

48. If 0.00050 mol $NaHCO_3$ is added to 1 L of a buffered solution at pH 8.00. How much material will exist in each of the three forms H_2CO_3, HCO_3^- and CO_3^{2-}? For H_2CO_3, $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-13}$.

49. Equilibrium constant for the acid ionisation of Fe^{3+} to $Fe(OH)^{+2}$ and H^+ is 6.5×10^{-3}. What is the maximum pH, which can be used so that at least 95% of the total Fe^{3+} in a dilute solution. exists as Fe^{3+}.

50. How much Na_2HPO_4 must be added to one litre of 0.005 M solution of NaH_2PO_4 in order to make a 1 L of the solution of pH = 6.7? $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$ for H_3PO_4.

51. The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50% of the new indicator is in ionic form.

52. A buffer solution, 0.080 M in Na_2HPO_4 and 0.020 M in Na_3PO_4, is prepared. The electrolytic oxidation of 1.0 m mol of the organic compound RNHOH is carried out in 100 mL of the buffer. The reaction is

$$RNHOH + H_2O \longrightarrow RNO_2 + 4H^+ + 4e$$

Calculate the approximate pH of the solution after the oxidation is complete ?

53. SO_2 dissolves in water to form an acidic solution. Explain.

54. Explain the following:
CaC_2O_4 is insoluble in CH_3COOH but soluble in dilute HCl.

55. A solution of HCl has a pH = 5. If one mL of it is diluted to 1 L, what will be the pH of resulting solution?

56. Calculate the pH of a solution of given mixtures :

(a) (2g CH_3COOH + 3g CH_3COONa) in 100 mL of mixture; $K_a = 1.8 \times 10^{-5}$
(b) 5 mL of 0.1 M NH_4OH + 250 mL of 0.1 M NH_4Cl; $K_b = 1.8 \times 10^{-5}$
(c) (0.25 mole of acid + 0.35 mole of salt) in 500 mL mixture; $K_a = 3.6 \times 10^{-4}$

57. Out of the following :

$H_2PO_4^-$, SO_3^{2-}, ClO^-, Fe^{3+}, BCl_3, NH_4^+,

select

(a) Bronsted Lowry acid
(b) Bronsted Lowry base
(c) Lewis acid
(d) Lewis base

58. What will be the resultant pH of the solution when 200 mL of an aqueous solution of HCl (pH = 2) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0) ?

59. Calculate the pH value at the equilibrium point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for acetic acid is 1.9×10^{-5}.

60. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with 10 mL of blood which is 2 M in H_2CO_3 in order to maintain pH of 7.4. K_a for H_2CO_3 in blood is 7.8×10^{-7}?

61. What will be the pH of a solution obtained by mixing 800 mL of 0.05 N sodium hydroxide and 200 mL of 0.1 N HCl, assuming complete ionisation of the acid and the base ?

62. What is the pH of the solution when 0.2 mol of hydrochloric acid is added to 1 ltr of a solution containing 1 M acetic acid and acetate ion ? Assume that the total volume is 1 ltr. K_a for $CH_3COOH = 1.8 \times 10^{-5}$.

63. Calculate the change in pH of one litre buffer solution containing 0.10 mol each of NH_3 and NH_4Cl upon addition of (i) 0.02 mol of dissolved gaseous HCl, (ii) 0.02 mol of dissolved NaOH. Assume no change in volume (K_b for $NH_3 = 1.8 \times 10^{-5}$).

64. Calculate the composition of an acidic buffer solution (HA + NaA) of total molarity 0.29 having pH = 4.4 and $K_a = 1.8 \times 10^{-5}$.

65. Find the pH of a 2 L solution which is 0.1 M each with respect to CH_3COOH and $(CH_3COO)_2Ba$.

66. A solution is found to contain 0.63 g of nitric acid per 100 mL of the solution. What is the pH of the solution if the acid is completely dissociated ?

67. 4.0 g of NaOH are dissolved per litre. Find (i) molarity of the solution, (ii) OH^- ion concentration, and (iii) pH value of the solution (Atomic weight: Na = 23, O = 16, H = 1).

68. If $\frac{N}{10}$, 200 mL HNO_3 and $\frac{N}{20}$, 100 mL HCl and $\frac{N}{20}$, 100 mL H_2SO_4 were mixed in 1 L vessel. Calculate the pH of resulting solution.

69. Determine the pH of a solution by mixing 2000 mL, $\frac{N}{10}$ HCl and 1000 mL, $\frac{N}{10}$ NaOH.

70. The pOH of basic buffer [e.g., NH_4OH/NH_4Cl] is 5. If the concentration of the salt is tripled whereas that of base remains same, what is the value of new pOH? (Given log 3 = 0.48)

71. Calculate the pH of a solution obtained by mixing 50 mL of 0.01 M $Ba(OH)_2$ solution with 50 mL water.

72. How much water must be added to 300 mL of 0.2 M solution of CH_3COOH for the degree of dissociation of the acid to double ?

73. Find the concentration of H^+, HCO_3^- and CO_3^{-2} in a 0.01 M solution of carbonic acid if the pH of this is 4.18 Ka_1 $(H_2CO_3) = 4.45 \times 10^{-7}$, Ka_2 $(HCO_3^-) = 4.69 \times 10^{-11}$.

74. The self-ionisation constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} at room temperature. What percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is 1.22 gcm^{-3}.

75. Calculate the concentration of H_3O^+ ion in a mixture of 0.02 M of acetic acid and 0.2 M sodium acetate. Given: K_a for acetic acid is 1.8×10^{-5}.

76. The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenate ion in 0.05 M solution of phenol?

77. Write the correctly balanced net ionic equation for the reaction whose equilibrium constant at 298 K is
  (i) $K_a(C_6H_5COOH) = 6.3 \times 10^{-5}$
  (ii) $K_a(HSO_3^-) = 2.8 \times 10^{-7}$
  (iii) $K_b(CH_3NH_2) = 4.4 \times 10^{-5}$
  (iv) $Ka_1(H_2S) = 1.0 \times 10^{-7}$

78. The ionisation constant of dimethyl amine is 5.40×10^{-4} .Calculate the ionisation constant of its conjugate acid.

79. How many grams of NaOH must be dissolved in 1 ltr of the solution to have a solution of pH = 12?

80. What should be the ratio of concentrations of formate ion and formic acid in a buffer solution so that its pH should be 4? Around what pH will this buffer have maximum buffer capacity? K_a for formic acid is 1.8×10^{-4}.

81. Calculate the pH of a solution obtained by mixing of 100.0 mL of 0.1 M HCl with 100 mL of 0.2 M NH_3 . K_b for NH_3 is 1.8×10^{-5}.

82. An organic monoprotic acid [0.1 M] is titrated against 0.1 M NaOH. By how much does the pH change between 1/4 and 3/4 stages of neutralisation? If at one third stage of neutralisation, the pH is 4.45 what is the dissociation constant of the acid ? Between what stages of neutralisation may the pH change by two units?

Integer Answer Type Question

83. The salt $Zn(OH)_2$ is involved in the following two equilibria:
$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq); K_{sp} = 1.2 \times 10^{-17}$
$Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq); K_c = 0.13$
Calculate the pH of solution at which solubility is minimum.

84. Show that solubility of a sparingly soluble salt $M^{2+}A^{2-}$ in which A^{2-} ions undergoes hydrolysis is given by

$$S = \sqrt{K_{sp}\left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}\right)}$$

where K_1 and K_2 are the dissociation constant of acid H_2A.K_{sp} is solubility product of MA.

85. The pH of a saturated aqueous solution of CO_2 is 5; For H_2CO_3 , $Ka_1 = 10^{-7}$ and $Ka_2 = 10^{-11}$. At the given pressure the solubility of CO_2 in water is 10^{-2} (M). What is the value of –log $[CO_3^{2-}]$ in the nearest posssible integers ?

86. 200 mL of a saturated solution of $CaC_2O_4(s)$ requires 8 mL of 5×10^{-3} (N) $KMnO_4$ solution for complete oxidation in the presence of acid. Determine the –log Ksp value of a saturated solution of $CaC_2O_4(s)$ in nearest possible integers.

87. How much water in mL must be added to 300 mL of 0.2 M solution of CH_3COOH ($K_a = 1.8 \times 10^{-5}$) for the degree of ionisation (α) of the acid to Triple.

88. You have given 100 mL of buffer solution containing weak acid HA ($K_a = 10^{-5}$) and its salt with strong base NaA at the concentration of 0.1(M) each.
If 5×10^{-3} moles of HCOOH ($K_a = 10^{-4}$) is added to this solution what will be value in the change in pH $\times 10^3$ in nearest possible integers.
Given: $\sqrt{76} = 8.71$; log 2.34 = 0.369

89. What is the ratio of moles of $Mg(OH)_2$ and $Al(OH)_3$ in 1 L of their saturated solution. K_{sp} of $Mg(OH)_2 = 4 \times 10^{-12}$ and K_{sp} of $Al(OH)_3 = 1 \times 10^{-33}$ (give your answer by multiplying the ratio with 10^{-17}).

90. A given solution is saturated with both Ag_2CrO_4 and $Ag_2C_2O_4$. The K_{sp} of
$Ag_2CrO_4 = 9 \times 10^{-12}$ and K_{sp} of $Ag_2C_2O_4 = 6 \times 10^{-12}$
In the resulting solution determine $[Ag^+] \times 10^5$ in the nearest possible integers.
Given: $(240)^{1/3} = 6.214$

Multiple Answer Type Question

91. An acid-base indicator has a K_a of 3.0×10^{-5}. The acid form of the indicator is red and the basic form is blue. Then
  (a) pH is 4.05 when indicator is 75% red.
  (b) pH is 5.00 when indicator is 75% blue.
  (c) pH is 5.00 when indicator is 75% red.
  (d) pH is 4.05 when indicator is 75% blue.

92. pH of the following solution is not affected by dilution:
  (a) 0.01 M CH_3COONa
  (b) 0.01 M $NaHCO_3$
  (c) Buffer of 0.01 M CH_3COONa and 0.01 M CH_3COOH
  (d) 0.01 M CH_3COONH_4

93. Which of the following expression(s) is/are true?
  (a) $[H^+] = [OH^-] = \sqrt{K_W}$ for a neutral solution
  (b) $[OH^-] < \sqrt{K_W}$ for an acidic solution
  (c) pH + pOH = 14 at all temperature
  (d) $[OH^-] = 10^{-7}$ M at 25°C for water

94. In the given question K_a values of five weak acids are given. K_a for HA = 10^{-8}, HB = 10^{-6}, HC = 2×10^{-8}, HD = 10^{-10}, HE = 10^{-7}.
Select the correct statement (s) as per the information. Given: log 2 = 0.3

(a) Among NaA, NaB, NaC, NaD and NaE, the NaD is most extensively hydrolysed.
(b) Among NaA, NaB, NaC, NaD and NaE, NaB is most extensively hydrolysed.
(c) pH of 0.1 (M) aqueous solution of NaB is approximately 9.5.
(d) 0.1(M) solution of HE and 0.01(M) solution of HB are isohydric to each other approximately.

95. The solubility of AgCl in water, 0.01 M $CaCl_2$, 0.02 M NaCl and 0.05 M $AgNO_3$ are S_1, S_2, S_3 and S_4 respectively. Which of the following is true? (Neglect any complex formation).

(a) $S_2 > S_1$
(b) $S_2 > S_3$
(c) $S_3 > S_4$
(d) $S_1 > S_4$

96. Solubility of MnS($K_{sp} = 8 \times 10^{-37}$) is S_1, of ZnS($K_{sp} = 7 \times 10^{-16}$) is S_2, of Bi_2S_3($K_{sp} = 10^{-72}$) is S_3, of Ag_3PO_4 ($K_{sp} = 1.8 \times 10^{-18}$) is S_4 in water. Which of the following is correct?

(a) $S_4 > S_2$
(b) $S_4 > S_3$
(c) $S_4 < S_1$
(d) $S_2 > S_1$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

JEE Main

1. How many litres of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **[AIEEE 2006]**

(a) 0.1 L (b) 0.9 L (c) 2.0 L (d) 9.0 L

2. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionisation constant, K_a of the acid is **[AIEEE 2006]**

(a) 3×10^{-1}
(b) 1×10^{-3}
(c) 1×10^{-5}
(d) 1×10^{-7}

3. The first and second dissociation constant of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be **[AIEEE 2007]**

(a) 5.0×10^{-5}
(b) 5.0×10^{15}
(c) 5.0×10^{-15}
(d) 0.2×10^{5}

4. The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is **[AIEEE 2008]**

(a) $\sqrt[2]{1.6 \times 10^{-30}}$
(b) $\sqrt[4]{1.6 \times 10^{-30}}$
(c) $\sqrt[4]{1.6 \times 10^{-30}/27}$
(d) $1.6 \times 10^{-30}/27$

5. An acid HA ionises as $HA \rightleftharpoons H^+ + A^-$. The pH of 1.0 M solution is 5. Its dissociation constant will be **[AIEEE 2009]**

(a) 1×10^{-10}
(b) 5
(c) 5×10^{-8}
(d) 1×10^{-5}

6. Three reactions involving $H_2PO_4^-$ are given below. **[AIEEE 2010]**

I. $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$

II. $H_2PO_4^- + H_2O \rightarrow H_2PO_4^{-2} + H_3O^+$

III. $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2+}$

In which of the above does $H_2PO_4^-$ act as an acid ?

(a) II only
(b) I and II
(c) III only
(d) I only

7. In aqueous solution, the ionisation constants for carbonic acid are
$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$ **[AIEEE 2010]**
Select the correct statement for a saturated 0.034 M solution of the carbonic acid.

(a) The concentration of CO_3^{2-} is 0.034 M.
(b) The concentration of CO_3^{2-} is greater than that of HCO_3^-.
(c) The concentration of H^+ and HCO_3^- are approximately equal.
(d) The concentration of H^+ is double that of CO_3^{2-}.

8. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 gm mol^{-1}) to be added to 1 L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **[AIEEE 2011]**

(a) 1.2×10^{-10} g
(b) 1.2×10^{-9} g
(c) 6.2×10^{-5} g
(d) 5.0×10^{-8} g

9. At 25ºC, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ? **[AIEEE 2012]**

(a) 9 (b) 10 (c) 11 (d) 8

10. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+}, will it begin to precipitate ? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) **[AIEEE 2012]**

(a) 4.1×10^{-5} M
(b) 5.1×10^{-5} M
(c) 8.1×10^{-5} M
(d) 8.1×10^{-7} M

11. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **[AIEEE–2010]**

(a) 5.0×10^{-8} g
(b) 1.2×10^{-10} g
(c) 1.2×10^{-9} g
(d) 6.2×10^{-5} g

12. In aqueous solution the ionisation constants for carbonic acid are **[AIEEE–2010]**

$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid:

(a) The concentration of H^+ is double that of CO_3^{2-}.

(b) The concentration of CO_3^{2-} is 4.8×10^{-11} M.

(c) The concentration of CO_3^{2-} is greater than that of HCO_3^-.

(d) The concentrations of H^+ less than HCO_3^- are approximately equal.

13. At 25° C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ? **[AIEEE–2010]**

(a) 8 (b) 9 (c) 10 (d) 11

14. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will it begin to precipitate?

(K_{SP} for Ba $CO_3 = 5.1 \times 10^{-9}$) **[AIEEE-2009]**

(a) 8.1×10^{-8} M (b) 8.1×10^{-7} M

(c) 4.1×10^{-5} M (d) 5.1×10^{-5} M

15. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt. BA, will be **[AIEEE-2008]**

(a) 9.58 (b) 4.79 (c) 7.01 (d) 9.22

16. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is **[AIEEE-2007]**

$$AgIO_3 \rightleftharpoons Ag^+_{(aq)} + IO^-_{3(aq)}$$

If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution ?

(a) 28.3×10^{-2} g (b) 2.83×10^{-3} g

(c) 1.0×10^{-7} g (d) 1.0×10^{-4} g

17. The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **[AIEEE-2005]**

(a) 1.0×10^{-4} M (b) 2.0×10^{-6} M

(c) 4.0×10^{-10} M (d) 1.6×10^{-4} M

18. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be **[AIEEE-2005]**

(a) 3.88×10^{6} (b) 3.98×10^{8}

(c) 3.98×10^{-6} (d) 3.68×10^{-6}

19. The molar solubility in mol L^{-1} of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{sp}. 's' is given in terms of K_{sp} by which relation? **[AIEEE-2004]**

(a) $s = (K_{sp}/128)^{1/4}$ (b) $s = (128\ K_{sp})^{1/4}$

(c) $s = (256\ K_{sp})^{1/5}$ (d) $s = (K_{sp}/256)^{1/5}$

20. The solubility of $Mg(OH)_2$ is x mole/lit. Then its solubility product is **[AIEEE-2002]**

(a) x^3 (b) $5x^3$ (c) $4x^3$ (d) $2x^2$

21. The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol L^{-1}. Its solubility product will be **[AIEEE-2003]**

(a) 1×10^{-15} (b) 1×10^{-10}

(c) 4×10^{-15} (d) 4×10^{-10}

JEE Advanced

Single Correct Answer Type

22. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $k_1 = 3.5 \times 10^{-3}$

$[Ag^+(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $k_2 = 1.7 \times 10^{-3}$

Then the formation constant of $[Ag(NH_3)_2]^+$ is **[IIT JEE 2006]**

(a) 6.08×10^{-6} (b) 6.08×10^{6}

(c) 6.08×10^{-9} (d) None of these

23. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and MX_3 at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order **[IIT JEE 2008]**

(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$

(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

24. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates. **[IIT JEE 2011]**

(a) CuS and HgS (b) MnS and CuS

(c) MnS and NiS (d) NiS and HgS

25. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1 M) is 1/100th of that of a strong acid (HX, 1M), at 25ºC. The K_a of HA is **[JEE Advanced 2013]**

(a) 1×10^{-4} (b) 1×10^{-5}

(c) 1×10^{-6} (d) 1×10^{-3}

26. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is **[JEE Advanced 2013]**

(a) 1.1×10^{-11} (b) 1.1×10^{-10}

(c) 1.1×10^{-12} (d) 1.1×10^{-9}

Multiple Correct Answer Type

27. Aqueous solutions of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentration are provided. The pair(s) of solutions which form a buffer upon mixing is (are) **[IIT JEE 2010]**

(a) HNO_3 and CH_3COOH

(b) KOH and CH_3COONa

(c) HNO_3 and CH_3COONa

(d) CH_3COOH and CH_3COONa

Linked Comprehension Type

When 100 mL of 1.0 M HCl was mixed 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7ºC was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralisation of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment can be used to measure the calorimeter constant. In a second experiment (Expt 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M

NaOH (under identical conditions to Expt.1) where a temperature rise of 5.6ºC was measured.(Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1}) **[JEE Advanced 2015]**

28. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from Excerpt 2 is
(a) 1.0 (b) 10.0 (c) 24.5 (d) 51.4

29. The pH of the solution after Excerpt 2 is
(a) 2.8 (b) 4.7 (c) 5.0 (d) 7.0

Integer Answer Type

30. The dissociation constant of a substituted benzoic acid at 25ºC is 1.0×10^{-4}. The pH of a 0.01 M solution of its sodium salt is **[IIT JEE 2009]**

31. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is
KCN, K_2SO_4, $(NH_4)_2C_2O_4$, NaCl, $Zn(NO_3)_2$, $FeCl_3$, K_2CO_3, NH_4NO_3, LiCN **[IIT JEE 2010]**

32. The total number of diprotic acids among the following is
H_3PO_4 H_2SO_4 H_3PO_3 H_2CO_3 $H_2S_2O_7$
H_3BO_3 H_3PO_2 H_2CrO_4 H_2SO_3

33. In 1 L saturated solution of AgCl [K_{sp}(AgCl) = 1.6×10^{-10}], 0.1 mol of CuCl[K_{sp}(CuCl) = 1.0×10^{-6}] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of ‘x’ is **[IIT JEE 2011]**

Answer Key

LEVEL I

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

LEVEL II

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

LEVEL III

1. (A) → s; (B) → p; (C) → r; (D) → q 2. (A) → p, q, r; (B) → r; (C) → q, s; (D) → q, r
3. (A) → q; (B) → r; (C) → q, s; (D) → p, s 4. (A) → q, s; (B) → p, r; (C) → p, r; (D) → q, s
5. (A) → p; (B) → s; (C) → r; (D) → q 6. (A) → r; (B) → q, s; (C) → r; (D) → p, s
7. (A) → q; (B) → p; (C) → s; (D) → r 8. (A) → s; (B) → p; (C) → q; (D) → r
9. (d) 10. (b) 11. (d) 12. (d) 13. (c) 14. (d) 15. (c) 16. (a) 17. (b) 18. (d)
19. (d) 20. (i) [1.8×10^{-16}], (ii) [1.67×10^{-5}], (iii) [4×10^{-10}] 21. (10) 22. (170 : 1)
23. ($Ka = 10^{-8}$) 24. (i) [2.38], (ii) [6.95], (iii) [7.0004] 25. (6.795) 26. (0.556M)
27. (1.1×10^{-4}) 28. (0.07, 6.126×10^{-2}) 29. (10^{-3}, 3.6×10^{-4}, 6.4×10^{-4}) 30. (2.5×10^{-15})
31. $[H^+] \geq [H_2\,PO_4^-] = 5.6 \times 10^{-3}$ M, $[HPO_4^{-2}] = 6.8 \times 10^{-8}$ M $[PO_4^{-3}] = 5.46 \times 10^{-18}$ M
32. (9×10^{-6} M) 33. (0.05 mole) 34. (6.6×10^{-6} M) 35. ($10^{-9.8}$) 36. (8.34)
37. (Solve by salt hydrolysis) 38. (3.82×10^{-26}) 39. (1.12×10^{-6} M) 40. (3.4×10^{-9} M)
41. [4.23] 42. (2.77×10^4 L) 43. (i) [13.1] (b) [0.125 M] 44. (a) [2.12] (b) [4.66] (c) [7.2] (d) [12]
45. (i) [9.6] (ii) 7.2 46. (9.16) 47. (3.823, 3.846, 3.98)
48. $(H_2CO_3) = 9.8 \times 10^{-6}$ M, $(HCO_3^-) = 4.9 \times 10^{-4}$ M, $(CO_3^{--}) = 2.45 \times 10^{-8}$ M 49. (0.908)
50. (1.58×10^{-3} mole) 51. [7.898, 7.3 and 7.3] 52. (7.8) 53. (Conceptual)
54. (SA+ SB $\rightleftharpoons$ WA+ WB ∴ feasible) 55. (6.978) 56. (a) [4.78] (b) [7.55] (c) [3.58] 57. (Conceptual)
58. (11.3) 59. (8.71) 60. (78.36ml) 61. [12.3] 62. (4.5) 63. (0.176↓, 0.176↑)

64. (salt = 0.087 M acid = 0.203 M) 65. (5.046) 66. (1) 67. (i) [0.1M] (ii) [0.1 M] (iii) [13]
68. (1.12) 69. (1.47) 70. (5.48) 71. [12] 72. (900 ml)
73. $[H^+] = 6.61 \times 10^{-5}$ M, $[HCO_3^-] = 6.73 \times 10^{-5}$ M, $[CO_3^{--}] = 4.8 \times 10^{-11}$ M 74. (0.004%)
75. $(1.8 \times 10^{-6}$ M) 76. $(2.2 \times 10^{-6}$ M) 77. (SA + SB $\rightleftharpoons$ WA + WB then feasible) 78. (1.23×10^{-11})
79. (0.4 g) 80. (1.8:1 & 3.74) 81. [9.26] 82. $\left(0.9542, 4.751, \frac{10}{11}\text{th stage to }\frac{1}{11}\text{th stage}\right)$ 83. (10)
84. (conceptual) 85. (10) 86. (8) 87. (2400) 88. (369) 89. (8) 90. (31) 91. (a, b) 92. (b, c, d)
93. (a, b, d) 94. (a, c, d) 95. (c, d) 96. (a, b, d)

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (d) 2. (c) 3. (c) 4. (c) 5. (a) 6. (a) 7. (c) 8. (b) 9. (b) 10. (b)
11. (c) 12. (b) 13. (c) 14. (d) 15. (c) 16. (b) 17. (a) 18. (a) 19. (c) 20. (c)
21. (c) 22. (a) 23. (d) 24. (a) 25. (a) 26. (b) 27. (c, d) 28. (a) 29. (b) 30. (8)
31. (3) 32. (6) 33. (7)

Hints and Solutions

LEVEL I

1. (c) $K_{H_2O} = \dfrac{[H^+][OH^-]}{[H_2O]} = \dfrac{10^{-12}}{55.55}$

$\therefore \quad K_{H_2O} = 1.8 \times 10^{-14}$

2. (a) $\text{pH} = pK_a + \log \dfrac{[\text{salt}]}{[\text{weak acid}]}$

$\therefore \quad \text{pH} = pK_a$

3. (b) $K_{sp} = [Zn^{2+}]\,[S^{2-}]$

$$[S^{2-}] = \frac{10^{-21}}{0.01} = 10^{-19}$$

for $\quad K_{a_1} \cdot K_{a_2} = \dfrac{[H^+]^2[S^{2-}]}{[H_2S]}$

$$10^{-20} = \frac{[H^+]^2 \times 10^{-19}}{0.1} \Rightarrow [H^+] = 0.1$$

or $\quad$ pH = 1

4. (b) pH = 2, $[HCl] = 10^{-2}$ (M) and pOH = 2

or $\quad [NaOH] = 10^{-2}$ (M)

4 mL of 10^{-2} (M) HCl $\equiv 4 \times 10^{-5}$ moles HCl.

6 mL of 10^{-2} (M) NaOH $\equiv 6 \times 10^{-5}$ moles NaOH

After mixing excess moles of $OH^- = 2 \times 10^{-5}$

$$[OH^-] = \frac{2 \times 10^{-5}}{10} \times 10^3 = 2 \times 10^{-3}$$

or $\quad$ pOH = 3 – log 2 = 3 – 0.3 = 2.7

or $\quad$ pH = 11.3

5. (a) A solution of $CuSO_4$ is acidic due to hydrolysis of strong conjugate acid Cu^{2+} ions,

$$Cu^{2+} + H_2O \rightleftharpoons Cu(OH)^+ + H^+$$

6. (c) Ba^{2+} is not hydrolysed , $CN^- = 1$ (M)

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$\text{pH} = \frac{1}{2}(pK_w + pK_a + \log c)$$

$$\text{pH} = \frac{1}{2}(pK_w + pK_a) \text{ since } c = 1(\text{M})$$

$$\text{pH} = \frac{1}{2}(2pK_w - pK_b) = \frac{1}{2}(28 - 9.3)$$

$$\text{pH} = \frac{1}{2}(28 - 9.3) = 9.35$$

7. (c) On diluting a buffer solution, the ratio of salt to acid (or base) does not change. Hence, its pH remains constant.

8. (b) After mixing total moles of A^-

$= 100 \times 0.2 \times 10^{-3} + 100 \times 0.3 \times 10^{-3}$

$= 100 \times 10^{-3} \times 0.5$ moles

After mixing total moles of HA

$= 100 \times 0.1 \times 10^{-3} + 100 \times 0.2 \times 10^{-3}$

$= 100 \times 0.3 \times 10^{-3}$ moles

After mixing resulting pH $= 5 + \log \dfrac{5}{3}$

9. (c) $K_aK_b = 10^{-14}$

or $\quad K_a = K_{in} = 10^{-5}$

$\therefore \quad [H^+] = 10^{-5}$

or $\quad$ pH = 5

10. (d)

$$SrF_2\,(s) \rightleftharpoons \underset{s}{Sr^{2+}} + \underset{2s}{2F^-}$$

where s is the solubility

$\therefore \quad 4s^3 = 32 \times 10^{-15}$

or $\quad s = 2 \times 10^{-5}$ (M)

But practically the solubility of SrF_2 (s) in NaCl solution is slightly greater than 2×10^{-5} because NaCl increases ionic strength of the solution.

11. **(c)** $K_w = [H^+][OH^-]$

$[H^+]$ in pure water $= 10^{-6}$

$[OH^-] = 10^{-6}$

Therefore, $K_w = 10^{-12}$

12. **(a)** Solution of KCN is basic. Therefore, concentration of $[H^+]$ will decrease on mixing it with CH_3COOH and thus pH will increase.

13. **(a)** On dissolving $FeCl_3$ in water, it will give $Fe(OH)_3$, H^+ and Cl^-. Ionisation of $Fe(OH)_3$ will be low. Therefore, concentration of $[H^+]$ will be more than $[OH^-]$ in the solution, so the solution will be acidic and blue litmus solution will turn red.

14. **(a)** Ionic product of Na^+ and Cl^- becomes more than the solubility product of NaCl.

15. **(d)** Fe Al and Cr are third group elements. Therefore, their solubility product is low, whereas Zn is of fourth group and therefore its solubility product is high.

16. **(d)** CH_3NH_2 (an amine) is basic, therefore its pH will be greater than 7.

17. **(b)** $\because$ pH = 3, $[H^+] = 10^{-3}$ $C = 10^{-1}$

$[H^+] = C \cdot \alpha$

$10^{-3} = 10^{-1}\alpha$

$$\alpha = \frac{10^{-3}}{10^{-1}} = 10^{-2}, K_a = C\alpha^2$$

$K_a = C\alpha^2 = 10^{-1} \times 10^{-2} \times 10^{-2} = 10^{-5}$

18. **(b)** among all Na_2CO_3 is most basic, therefore its pH value will be highest.

19. **(a)** Volume is increasing twice, therefore concentration will become half.

$K_{sp} = [Ag^+][Cl^-]$

Ionic product $= 0.5 \times 10^{-4} \cdot 10^{-4} \times 0.5 = 10^{-8} \times 0.25$

Solubility product $= 1.8 \times 10^{-10}$

Ionic product > Solubility product, therefore precipitation will take place.

20. **(a)** $Na_2^+ CO_3^- + 2H_2O \rightleftharpoons 2Na^+ + 2OH^- + H_2CO_3$

$CO_3^{-2} + 2H_2O \rightleftharpoons 2OH^- + H_2CO_3$

21. **(b)** To precipitate only the metal hydroxides of third group, NH_4Cl is added before NH_4OH in qualitative analysis, because the concentration of OH^- decreases due to common ion effect.

22. **(a)** $N_1V_1 + N_2V_2 = N_3V_3$

$250 \times 6M + 350 \times 8 = 3N \times V_3$

$1500 + 280 = 3N \times V_3$

$V_3 = 1433.3$ mL

Volume $1433.3 - (250 + 350) = 833.3$ mL

Therefore, 833.3 mL water has to be mixed.

23. **(c)** CH_3COONH_4 salt is made up of weak acid and weak base. Therefore, pH remains unchanged on diluting it, because it acts as an amphiresistant solution.

24. **(b)** In the titration of weak base and a strong acid, the resulting solution will be acidic. Therefore, methyl orange is an appropriate indicator.

25. **(c)** 1.8 g water = 0.1 g mole

$$2.9 \text{ g acetone} = \frac{2.9}{58} = 0.05 \text{ g mole}$$

Total mole = 0.15 gram mole

$$\text{Mole fraction of acetone} = \frac{0.05}{0.15} = \frac{1}{3}$$

26. **(c)** $\text{pH} = pK_a + \log \dfrac{[\text{Salt}]}{[\text{Acid}]} = 4.75 + \log 10$

pH = 5.75

27. **(c)** Henolphthalein is colourless in acid medium because concentration of Ph range 8.3 to 10.

28. **(a)** [Salt] = [Acid]

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

$$\text{pH} = 4.75 + \log \frac{0.02}{0.02}$$

pH = 4.75

29. **(b)** Na^+ and undissociated $H_2PO_4^-$, $HPO_4^{2,}$ PO_4^{-3} ions will be there, because H_3PO_4 dissociates in three steps.

30. **(c)**

$$\begin{array}{llcl} Ag^+ & + \quad 2NH_3 & \overset{K=10^8}{\rightleftharpoons} & Ag(NH_3)_2^+ \\ 0.02 \text{ mol} & 0.14 \text{ mol} & & \\ — & 0.1 \text{ mol} & & 0.02 \text{ mol} \end{array}$$

$$10^8 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{0.02}{[Ag^+] \times 0.01}$$

or $[Ag^+] = 2 \times 10^{-8}$ (M)

31. **(b)**

pH = 1 pH = 2

$[H^+] = 0.1$ $[H^+] = 0.01$

$V = 50$ $V = 50$

$$[H^+] \text{ of mixture is } [H^+] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} \Rightarrow \frac{50(0.1 + 0.01)}{100}$$

$$[H^+] \Rightarrow \frac{0.11}{2} \Rightarrow 0.055$$

pH = 1.26

32. **(c)** pH = 7 $\therefore$ $[H^+] = 10^{-7}$, $[OH^-] = 10^{-7}$

New pH after addition of base

pH = 12 $\therefore$ $[H^+] = 10^{-12}$

and $[OH^-] = 10^{-2}$

$[OH^-]$ concentration increase 10^5 times.

33. **(b)** $\text{Relative strength} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}} = \sqrt{\dfrac{3 \times 10^{-4}}{1.8 \times 10^{-5}}} \Rightarrow 4 : 1$

34. **(a)** $HCOOH + KOH \rightarrow HCOOK + H_2O$

after reaction it forms Buffer solution

$[HCOOH] = \dfrac{10}{90}$ $[HCOOK] = \dfrac{10}{90}$

$\text{pH} = pK_a + \log \dfrac{[\text{salt}]}{[\text{acid}]}$ $\text{pH} = pK_a$

pH = 4 – log (1.8) pH = 3.75

35. **(a)** Let weak acid be HA and its sodium salt be NaA.

$$K_a = \frac{K_w}{K_h} \qquad K_h = C\alpha^2 \Rightarrow 0.1 \times (0.03)^2$$

$$K_a = \frac{10^{-14}}{9\times10^{-5}} \quad K_a = \approx 1\times10^{-10}$$

36. **(b)** $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

40 20 0 0

After reaction

$[CH_3COOH] = \frac{20}{200}$, $[CH_3COONa] = \frac{20}{200}$

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$pH = pK_a$ $[H^+] = K_a = 1.8\times10^{-5}$

37. **(a)** $CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$

at equivalence the $[CH_3COOH] = \frac{20}{200} \Rightarrow 0.1$

$$pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$$

$$pH = \frac{1}{2}[5 + \log 2 - \log 10^{-1}]$$

$$pH = \frac{1}{2}[6 - \log 2] \Rightarrow pH = 3 - \log\sqrt{2}$$

38. **(d)** $pH = pK_a + \log\frac{HCO_3^-}{H_2CO_3}$

$$7 = 7 - \log 4 + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$4 = \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$[\%\ HCO_3^-] = \frac{4}{5}\times100 \quad\Rightarrow\quad 80\ \%$$

39. **(a)**

$NaOH + H_3PO_4 \rightleftharpoons NaH_3PO_3 + H_2O$

5 mm 9 mm 0 0

form buffer

$$\therefore \quad Ph = Pka_1 + \log\frac{5}{4}$$

$$= 3 + 0.7 - 0.6 = 3.1$$

40. $Mg(NO_3)_2 + 2NaF \longrightarrow MgF_2 + 2NaNO_3$

2.5 5

0 0 2.5

$$(Mg^{+2})\frac{2.5}{35} = 0.0714\ M$$

$MgF_2 \longrightarrow Mg^{+2} + 2\ F$

Ionic product

41. $IP > K_{sp}$ $I.P. = [Ca^{+2}][F^-]^2$

$$I.P. \Rightarrow \left[\frac{10^{-2}}{2}\right]\left[\frac{10^{-3}}{2}\right]^2 \Rightarrow \left[\frac{10^{-8}}{4}\right]$$

$IP > K_{sp}\ (1.7\times10^{-10})$

42. **(b)**

HCl + NaCl

1 mL, 0.1 99 mL

$$[H^+] = \frac{0.1}{100} \Rightarrow 0.001 \qquad pH = 3$$

43. **(c)** $HF + H_2O \rightleftharpoons F^- + H_3O^+$

$K_a \times K_b = K_w$ $pK_a + pK_b = pK_w$

$pK_a = 14 - 10.83$ $\therefore pK_a = 3.17$

and $K_a = 6.75\times10^{-4}$

44. **(d)**

First dissociation : $H_3X \longrightarrow H_2X^- + H^+$

$\therefore$ H^+ ion concentration $= 2\times10^{-4}$ M

Second dissociation : $H_2X^- \rightleftharpoons HX^- + H^+$

$\therefore$ H^+ ion concentration $= C\alpha = 2\times10^{-4}\times0.5 = 10^{-4}$

$\because$ Third dissociation is negligible

$\therefore$ $[H^+] = 2\times10^{-4} + 10^{-4} = 3\times10^{-4}$

$pH = 4 - \log 3 = 3.52$

45. **(a)** $[H^+] = 2C\alpha = 2\times\frac{1}{200}\times\frac{10}{100} = 10^{-3}$ M

$\therefore$ $pH = 3$

46. **(a)**

Formula of pH is $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$

$$8 = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log(10^{-2})$$

$$8 = 7 + \frac{1}{2}pK_a - 1$$

$$4 = pK_a \text{ or } pK_a = 4$$

LEVEL II

1. $C_6H_5COOH + NaOH \longrightarrow C_6H_5COONa + H_2O$

2 1

1 0 1

$pH = pK_a\ \log\frac{[salt]}{[acid]} +$ $pH = 4.2 + \log\frac{1}{1}$

$pH = 4.2$

$C_6H_5COOH + NaOH \longrightarrow C_6H_5COONa + H_2O$

2 2

0 0 2

$$pH = 7 + \frac{1}{2}pKa + \frac{1}{2}\log C$$

$$pH = 7 + 2.1 + \frac{1}{2}\log\frac{2}{200}$$

$pH = 9.1 - 1$ $pH = 8.1$

2. **(d)**

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

0.1 0.1 0 0

At 1/3 neutralisation

2/3 1/3 1/3 1/3

$$pH = pKa + \log\frac{(salt)}{(acid)}$$

$$pH_1 = pKa + \log\frac{1/3}{2/3} = pKa + \log\frac{1}{2} \qquad ...(1)$$

at 2/3 neutralization

$$\text{pH}_2 = pKa + \log \frac{2/3}{1/3} = PKa + \log 2 \qquad ...(2)$$

$$\text{pH}_1 - \text{pH}_2 = \log \frac{1}{2} - \log 2$$

$$= \log \frac{1}{4} = -2 \log 2$$

3. $HSO_4^- \longrightarrow H^+ + SO_4^{2-}$

1

$(1-\alpha)$ $\quad\alpha\quad\alpha$

$$10^{-2} = \frac{\alpha^2}{1-\alpha} \therefore \alpha \Rightarrow 0.09 \text{ pH} = 1.02$$

4. **(a)** HCN is a weak acid so H^+ due to it can neglect. As comparison to HF.

$$[H^+] = \sqrt{KaC} = \sqrt{6.7 \times 10^{-4} \times 0.1} = \sqrt{67 \times 10^{-6}}$$

$$= 8.18 \times 10^{-3}$$

$\text{pH} = -\log [8.18 \times 10^{-3}] = 3 - \log [8.18]$

$\text{pH} = 2.087$

5. **(b)**

$CH_3CO_2H + NaOH \longrightarrow CH_3COONa + H_2O$

10m mol $\quad$ 5m mol

$\text{pH} = pK_a = 5 - \log 1.8 \qquad \text{pH} = 4.74$

6. **(b)** $\text{pH} = \text{pk}_{\text{in}} + \log \dfrac{[\text{In}^-]}{[\text{HIn}]} \qquad 6 = 5 + \log \dfrac{[\text{In}^-]}{[\text{HIn}]}$

$$\frac{\text{In}^-}{\text{HIn}} = 10 \quad \therefore \quad \frac{[\text{HIn}]}{[\text{HIn}] + [\text{In}^-]} = \frac{1}{11}$$

7. **(c)** At half way $[\text{HIn}] = \text{In}^-$

$$\text{pH} = 5.5 + \log \frac{[\text{salt}]}{[\text{acid}]} \qquad 5.5 = pKa + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\log \frac{[\text{salt}]}{[\text{acid}]} = 0.75 \Rightarrow \frac{[\text{salt}]}{[\text{acid}]} = 5.62$$

8. **(a)** $h = \sqrt{\dfrac{K_h}{C}} \qquad h = \sqrt{\dfrac{K_w}{K_a \times C}}$

$$h = \sqrt{\frac{10^{-14} \times 80}{1.3 \times 10^{-9} \times 1}} \qquad h = 2.48\%$$

9. **(c)** $CH_3COOH + NaOH \rightarrow CH_3COO^- + H_2O$

(WASB)

$$\text{pH} = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[14 + 5 - \log 1.9 + \log \frac{1}{20}]$$

$$= \frac{1}{2}[19 - \log 1.9 - \log 20]$$

$$\text{pH} = \frac{1}{2}[19 - \log 20 \times 1.9] = 8.78$$

$\text{pOH} = 5.28 \qquad [OH^{\ominus}] = 5.24 \times 10^{-6}$

10. **(d)**

$HCl \rightarrow 0.09$ M

$CH_3COOH \rightarrow C_1 = 0.1$ M, α_1 $K_{a_1} = 10^{-5}$,

$Cl_2CHCOOH \rightarrow C_2 = 0.09$ M, α_2, $K_{a_2} = ?$

$\text{pH} = 1, [H^+] = 0.1$

$0.1 = 0.09 + C_1\alpha_1 + C_2\alpha_2$

$C_1\alpha_1 + C_2\alpha_2 = 0.01 \qquad ...(i)$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

C_1

$C_1 - C_1\alpha_1 \qquad C_1\alpha_1 \qquad 0.1$

$Cl_2HCCOOH \rightleftharpoons Cl_2HCCOO^- + H^+$

C_2

$C_2 - C_2\alpha_2 \qquad C_2\alpha_2 \qquad 0.1$

$$K_{a_1} = \frac{(C_1\alpha_1)(0.1)}{C_1(1-\alpha_1)} \simeq \alpha_1 \times 0.1 = 10^{-5}$$

$\alpha_1 = 10^{-4}$

Putting this in equation (i)

$10^{-4} \times 0.1 + 0.09\alpha_2 = 0.01$

$\alpha_2 = 0.111$

$$K_{a_2} = \frac{(C_2\alpha_2)(0.1)}{C_2(1-\alpha_2)} = \frac{(0.111)(0.1)}{1 - 0.111} = 1.25 \times 10^{-2}$$

11. **(c)** $M = \dfrac{w}{w}\% \dfrac{10d}{\text{Molar Mass}} = C$

$$\frac{10 \times 10 \times 0.935}{17} = 5.5$$

$K_b = C\alpha^2 \Rightarrow 5.5 \times 10^{-6} = 5.5\alpha^2$

$\alpha = 10^{-3}$

$[OH^-] = C\alpha = 5.5 \times 10^{-3}$

$\text{pOH} = 2.26$, $\text{pH} = 11.7$

12. **(b)**

$$\ln \frac{k_{w_2}}{k_{w_1}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{5.474 \times 10^{-14}}{1.08 \times 10^{-14}} = \frac{\Delta H}{8.314}\left(\frac{1}{298} - \frac{1}{323}\right)$$

$\Delta H = 51952.6 \text{ J} = 51.95$ kJ/mole

13. **(a)**

$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

$2 \qquad 2$

$- \qquad - \qquad 2$

$$\text{pH} = \frac{pk_1 + pk_2}{2} = 8.35$$

14. **(a)**

$Na_3PO_4 + HCl \longrightarrow Na_2HPO_4 + NaCl$

$0.8 \qquad 1.6$

$- \qquad 0.8 \qquad 0.8$

$Na_2HPO_4 + HCl \longrightarrow NaH_2PO_4 + NaCl$

$0.8 \qquad 0.8$

$- \qquad - \qquad 0.8$

$$\text{pH} = \frac{pk_1 + pk_2}{2} = 4.66$$

15. (c) Initial pOH = pK_b = 4.744

Let x mole of HCl has been added so

$[NH_4^+] = 0.1 + x$, $[NH_3] = 0.1 - x$

pOH = 5.744

$$5.744 = 4.744 + \log\frac{0.1+x}{0.1-x}$$

$$1 = \log\frac{0.1+x}{0.1-x}$$

$$\frac{0.1+x}{0.1-x} = 10 \Rightarrow x = \frac{0.9}{11} = 0.082 \text{ moles}$$

16. (a) $Na_3PO_4 + H_2O \longrightarrow Na_2HPO_4 + NaOH$

$$K = \frac{K_w}{Ka_3} = 0.0222$$

$Na_2HPO_4 + H_2O \longrightarrow NaH_2PO_4 + NaOH$

$$K = \frac{K_w}{Ka_2} = 1.58 \times 10^{-7}$$

$NaH_2PO_4 + H_2O \longrightarrow H_3PO_4 + NaOH$

$$K = \frac{K_w}{Ka_3} = 1.4 \times 10^{-12}$$

Since equilibrium constant of second and third reaction is very less, $[OH^-]$ will mainly come from first reaction.

$Na_3PO_4 + H_2O \longrightarrow Na_2HPO_4 + NaOH$

0.1

$0.1 - x$ $\quad x \quad x$

$$\frac{x^2}{0.1-x} = 0.0222 \Rightarrow 45x^2 + x - 0.1 = 0$$

$x = 3.73 \times 10^{-2}$

$[OH^-] = x = 3.73 \times 10^{-2}$ M

17. (b) $Na_3PO_4 + H_2O \longrightarrow Na_2HPO_4 + NaOH$

$$K = \frac{K_w}{K_3} = 0.0222$$

$Na_2HPO_4 + H_2O \longrightarrow NaH_2PO_4 + NaOH$

$$K = \frac{K_w}{K_2} = 1.58 \times 10^{-7}$$

$NaH_2PO_4 + H_2O \longrightarrow H_3PO_4 + NaOH$

$$K = \frac{K_w}{K_3} = 1.4 \times 10^{-12}$$

Since equilibrium constant of second and third reaction is very less, $[OH^-]$ will mainly come from first reaction.

$Na_3PO_4 + H_2O \longrightarrow Na_2HPO_4 + NaOH$

0.1

$0.1 - x$ $\quad x \quad x$

$$\frac{x^2}{0.1-x} = 0.0222 \Rightarrow 45x^2 + x - 0.1 = 0$$

$x = 3.73 \times 10^{-2}$

$[OH^-] = x = 3.73 \times 10^{-2}$ M

$Na_2HPO_4 + NaOH \longrightarrow NaH_2PO_4 + NaOH$

x

$x - y$ $\quad$ — $\quad y \quad y + x$

$x - y \simeq x$, $\quad y + x \simeq x$, so

$$1.58 \times 10^{-7} = \frac{(y+x)}{(x-y)}y;\ y$$

$NaH_2PO_4 + H_2O \longrightarrow H_3PO_4 + NaOH$

y

$y - z$ $\quad$ — $\quad z \quad z + x$

$y - z \simeq y$, $\quad z + x \simeq x$

$$1.4 \times 10^{-12} = \frac{z(x+z)}{(y-z)} = \frac{z \times x}{y} = \frac{z \times 3.73 \times 10^{-2}}{1.58 \times 10^{-7}}$$

$z = 5.93 \times 10^{-18}$

$[H_3PO_4] = z = 5.93 \times 10^{-18}$ M

18. (b) At equivalence point

meq. of HA = meq. of NaOH = 3.612

$NaA \quad + \quad HCl \longrightarrow HA \quad + \quad HCl \quad + \quad NaCl$

$3.612 \quad 1.806$

$1.806 \quad - \quad 1.806$

$$pH = pK_a + \log\frac{[S]}{[A]}$$

$$4.92 = pK_a + \log\frac{1.806}{1.806}$$

$pK_a = 4.92$

Now $NaOH + HA \longrightarrow NaA$

$2 \quad 2$

$- \quad - \quad 2$

$$[NaA] = \frac{2}{20} = 0.1$$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C = 7 + \frac{4.92}{2} + \frac{1}{2}\log 0.1$$

pH = 9

19. (a) In the beginning, let x m mole of BOH are present.

$BOH + HCl \longrightarrow BCl + H_2O$

$x \quad \frac{x}{4} \quad - \quad -$

$\frac{3x}{4} \quad 0 \quad \frac{x}{4}$

$$pOH = pk_b + \log\frac{1}{3}$$

$14 - 9.24 = pk_b - \log 3$

$pk_b = 5.237$

$k_b = 5.8 \times 10^{-6}$

now $BCl + NaOH \longrightarrow BOH$

$\frac{x}{4} \quad 6$

$- \quad - \quad x$

$$\frac{x}{4} = 6, \Rightarrow x = 24$$

$$[BOH] = \frac{24}{50} = 0.48$$

$$[OH^-] = \sqrt{k_b \times C} = 1.668 \times 10^{-3}$$

pOH = 2.77

pH = 11.22

20. **(a)** HCO_3^- is proton acceptor (a base) as well as proton donor (an acid) and it is amphiprotic. For such a case $[H^+] = \sqrt{K_1K_2}$

or $$pH = \left(\frac{pK_1 + pK_2}{2}\right)$$

HCO_3^- is an amphiprotic ion. It can undergo hydrolysis forming alkaline solution.

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

HCO_3^- can also ionise to form acidic solution,

pH of this type of salt is –

$$HCO_3^- + H_2O \quad H_3O^+ + CO_3^{-2}$$

$$pH = \left(\frac{pK_1 + pK_2}{2}\right) = \frac{6.38 + 10.26}{2} = 8.32$$

21.

$$\begin{array}{lcccc} & AgCNS & \rightleftharpoons & Ag^+ \quad + & CNS^- \\ \text{solubility} & (1 - S_1) & & (S_1 + S_2) & S_1 \\ & AgCl & \rightleftharpoons & Ag^+ \quad + & Cl^- \\ \text{solubility} & (1 - S_2) & & (S_1 + S_2) & S_2 \end{array}$$

$$(K_{sp})_{AgCNS} = (S_1)(S_1 + S_2) \qquad ...(i)$$

$$(K_{sp})_{AgCl} = (S_2)(S_1 + S_2) \qquad ...(ii)$$

Adding Eqs (i) and (ii)

$$(S_1 + S_2)^2 = (K_{sp})_{AgCNS} + (K_{sp})_{AgCl}$$

$$(S_1 + S_2) = \sqrt{(K_{sp})_{AgCNS} + (K_{sp})_{AgCl}}$$

$$= \sqrt{1.0 \times 10^{-12} + 1.7 \times 10^{-10}}$$

$$[Ag^+] = (S_1 + S_2) = 1.3 \times 10^{-5}$$

Divide Eq. (ii) from Eq. (i)

$$\frac{[Cl^-]}{[CNS^-]} = \frac{S_2}{S_1} = \frac{1.7 \times 10^{-10}}{1.0 \times 10^{-12}} \Rightarrow 1.7 \times 10^2$$

22. $K_{sp} = s^2$ $\qquad s = \sqrt{K_{sp}} = \sqrt{6.4 \times 10^{-5}}$

$s = 8 \times 10^{-3}$ $\qquad s = 8$ mol/m^3

23.

$$\begin{array}{lcccc} AgNO_3 & + & 2NH_3 & \longrightarrow & [Ag(NH_3)_2{}^+] \\ 1.6 & & x & & \\ 5 \times 10^{-8} & & (x - 3.2) & & 0.8 \end{array}$$

$$K_s = \frac{[Ag(NH_3)_2]^+}{(AgNO_3)(NH_3)}$$

$$10^8 = \frac{0.8/2}{(5 \times 10^{-8})\left(\frac{x - 3.2}{2}\right)^2} \therefore \left(\frac{x - 3.2}{2}\right)^2 = 0.16$$

$x = 2$ M $\qquad$ mole of $NH_3 = 4.0$

24. **(d)** $s = [Zn(OH)_2(aq)] + Zn(OH)^+ + Zn^{+2} + Zn(OH)_3^- + Zn(OH)_4^{-2}$

$$s = k_1 + \frac{k_1k_2}{[OH^-]} + \frac{k_1k_2k_3}{[OH^-]^2} + k_1k_4[OH^-] + k_1k_4k_5[OH^-]^2$$

$$s = 10^{-6} + \frac{10^{-13}}{[OH^-]} + \frac{10^{-17}}{[OH^-]^2} + 10^{-3}[OH^-] + 10^{-2}[OH^-]^2$$

pH = 5, pOH = 9, $[OH^-] = 10^{-9}$

$s = 10^{-6} + 10^{-4} + 10 + 10^{-12} + 10^{-20} = 10$ M

25. **(c)** $s = [Zn(OH)_2(aq)] + Zn(OH)^+ + Zn^{+2} + Zn(OH)_3^- + Zn(OH)_4^{-2}$

$$s = k_1 + \frac{k_1k_2}{[OH^-]} + \frac{k_1k_2k_3}{[OH^-]^2} + k_1k_4[OH^-] + k_1k_4k_5[OH^-]^2$$

$$s = 10^{-6} + \frac{10^{-13}}{[OH^-]} + \frac{10^{-17}}{[OH^-]^2} + 10^{-3}[OH^-] + 10^{-2}[OH^-]^2$$

pH = 13, pOH = 1, $[OH^-] = 10^{-1}$

$s = 10^{-6} + 10^{-12} + 10^{-15} + 10^{-4} + 10^{-4} = 2 \times 10^{-4}$ M

26. **(a)** Let solubility of $Cu_3(AsO_4)_2$ and $Pb_3(AsO_4)_2$ is x and y respectively.

$$\begin{array}{lcll} Cu_3(AsO_4)_2 \rightleftharpoons & 3Cu^{+2} & + \; 2AsO_4^{-3} & K_{sp} = 8 \times 10^{-36} \\ & 3x & \;\; 2x + 2y & \\ Pb_3(AsO_4)_2 \rightleftharpoons & 3Pb^{+2} & + \; 2AsO_4^{-3} & K_{sp} = 4.096 \times 10^{-36} \\ & 3y & \;\; 2y + 2x & \end{array}$$

$$108\, x^3(x + y)^2 = 8 \times 10^{-36} \qquad ...(i)$$

$$108\, y^3(x + y)^2 = 4.096 \times 10^{-36} \qquad ...(ii)$$

$$\frac{(i)}{(ii)} \Rightarrow \frac{x^3}{y^3} = \frac{8}{4.096} \Rightarrow x = 1.25y$$

Putting this in Eq. (ii)

$108y^3\,(2.25y)^2 = 4.096 \times 10^{-36}$

$y = 2.3 \times 10^{-8}$ $\quad x = 1.25y = 2.875 \times 10^{-8}$

$[Cu^{+2}] = 3x = 8.825 \times 10^{-8}$

$[Pb^{+2}] = 3y = 7.1 \times 10^{-8}$

27. **(b)** $Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^- \qquad K_{sp}$

$Al(OH)_4^- \rightleftharpoons Al^{+3} + 4OH^- \qquad K$

$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-$

$$\frac{K_{sp}}{K} = 38.46$$

$$38.46 = \left[\frac{Al(OH^-)_4}{[OH^-]}\right] = \frac{10^{-3}}{[OH^-]}$$

$[OH^-] = 2.6 \times 10^{-5}$

pOH = 4.585

pH = 9.415

28. **(d)** $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^- \qquad K_{sp}$

$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2{}^+ \qquad K_1 \times K_2$

$AgCl_{(s)} + 2NH_3 \rightleftharpoons Ag(NH_3)_2{}^+ + Cl^-, \; K = K_{sp}K_1K_2$

$$\begin{array}{ccc} 0.2 & & \\ 0.2 - 2x & x & x \end{array}$$

$$K = K_{sp}K_1K_2 = \frac{x^2}{(0.2 - 2x)^2} = 0.002828$$

$$\frac{x}{0.2 - 2x} = 0.05318$$

$x = 0.009613$

Solubility = 9.6×10^{-3} M

29. (b)

$[Cl^-] = 0.02$ M

$$\begin{array}{llll} Ag(CN)_2^- \rightleftharpoons & Ag^+ + & 2CN^- & K_{inst} = 4 \times 10^{-19} \\ 0.05 & & & \\ 0.05 - x \simeq 0.05 & x & 2x & \end{array}$$

$$4 \times 10^{-19} = \frac{x \cdot (2x)^2}{0.05}$$

$$\frac{4x^3}{0.05} = 4 \times 10^{-19} \Rightarrow x = 1.7 \times 10^{-7}$$

$[Ag^+][Cl^-] = 1.7 \times 10^{-7} \times 0.02 = 3.4 \times 10^{-9} > K_{sp}$

so AgCl will precipitate.

30. (c) After mixing with equal volume

$[Ag^+] = 0.01$ M, $HCN = 0.01$ M

$HCN \rightleftharpoons H^+ + CN^- \quad K_a$

$$Ag^+ + CN^- \rightleftharpoons AgCN_{(s)} \quad \frac{1}{K_{sp}}$$

$HCN + Ag^+ \rightleftharpoons H^+ + AgCN(s)$,

$$K = \frac{K_a}{K_{sp}} = 2.25 \times 10^6$$

$$\begin{array}{llll} HCN + & Ag^+ \rightleftharpoons & H^+ + & AgCN(s), \\ 0.01 & 0.01 & 0 & 0 \\ x & x & 0.01 & - \end{array}$$

since K value is very high, almost all of reactants will convert into product.

$$\frac{0.01}{x^2} = 2.25 \times 10^6 \qquad x = 6.6 \times 10^{-5}$$

$[Ag^+] = 6.7 \times 10^{-5}$ M

LEVEL III

Match the Column

1. [A → S; B → P; C → R; D → Q]

At maximum buffer capacity, [salt] = [acid] hence $pH = pK_a$

∴ (A) → (S)

At the $\frac{1}{4}$th equivalence point of titration of weak acid HA, $pH = pK_a + \log \frac{1}{3}$

(B) → P

At the $\frac{3}{4}$th equivalence point of titration of weak acid HA, $pH = pK_a + \log 3 = pK_a - \log \frac{1}{3}$

(C) → R

For C(M) solution of weak acid HA, $pH = \frac{1}{2}(pK_a - \log c) = \frac{1}{2}\left(pK_a - \log\frac{1}{3}\right)$

(D) → $Q = \frac{1}{2}(pK_a + \log 3)$

2. [A → P,Q,R; B → R; C → Q,S; D → Q,R]

(A) $CH_3COOH + CH_3COONa \Rightarrow$ Buffer Solution

[S] = [A] ∴ acidic buffer at its maximum capacity

$pH = pK_a = 4.74$ ∴ **[P, Q, R]**

(B) Mixture of S.A. and W.A.

$pH = -\log [H^+]_{SA}$ ∴ $pH < 7$

(C)
$$\begin{array}{lll} CH_3COOH + & NH_4OH \rightarrow & CH_3COONH_4 \\ 0.1 & 0.1 & 0 \\ 0 & 0 & 0.1 \end{array}$$

∴ salt of WA and WB formed

$$\therefore \quad pH = 7 + \frac{1}{2}Pka - \frac{1}{2}Pkb = 7$$

$Pka = Pkb$

(CH_3COONH_4) also acts as simple buffer.

(D)
$$\begin{array}{llll} CH_3\,COONa + & HCl & \rightarrow CH_3COOH + & NaCl \\ 300 \times 0.1 & 100 \times 0.1 & & \\ 30 & 10 & & \\ 20 & 0 & 10 & 10 \end{array}$$

means buffer

$$\therefore \quad pH = 4.74 + \log\frac{1}{2}$$

$pH < 7$

3. [A → Q; B → R; C → P; D → P, S]

(A) 0.1 M KCN Salt of S.B. and W.A.

$$pH = 7 + \frac{1}{2}Pka + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2}Pka + \frac{1}{2}\log[10^{-1}] = 6.5 + \frac{1}{2}Pka$$

(B) 0.1 M $C_6H_5\,NH_3Cl$ Salt of WB and SA

$$pH = 7 - \frac{1}{2}Pkb - \frac{1}{2}\log C$$

$$= 7 - \frac{1}{2}Pkb - \frac{1}{2}\log[10^{-1}]$$

$$= 7.5 - \frac{1}{2}Pkb$$

(C) 0.1 MKCl salt of SA and SB ∴ pH = 7

(D) 0.1 MCH_3COONH_4

Salt of W.A. and W.B.

$$pH = 7 + \frac{1}{2}Pka - \frac{1}{2}Pkb$$

if $ka = kb$

∴ pH = 7

4. [A → Q, S; B → P, R; C → P, R; D → Q, S]

Only ion of W.A. or W.B. hydrolysis.

(A) $NaHCO_3 \rightarrow Na^+ + \underset{\substack{\downarrow \\ \text{Anionic hydrolysis}}}{HCO_3^-}$

∴ solution basic

(B) $CuSO_4 \rightarrow Cu^{+2} + SO_4^{--}$

$$\underset{\text{Cationic hydrolysis}}{\downarrow}$$

$\therefore$ solution acidic in nature

(C) $K_2SO_4.\ Al_2\ (SO_4)_3.\ 24H_2O$

$\therefore$ Al^{+3} hydrolysis

cationic hydrolysis

$\therefore$ acidic solution.

(D) NaCN Salt of SB and WA

$NaCN \rightarrow Na^+ + CN^-$

$$\underset{\text{Aniomic Hydrolysis}}{\downarrow}$$

$\therefore$ anionic hydrolysis and solution basic in nature.

5. [A $\rightarrow$ P; B $\rightarrow$ S; C $\rightarrow$ R; D $\rightarrow$ Q]

(A) If H.A. and NaA both present means buffer solution

$$Ph = Pka + \log\frac{0.01}{0.1} \Rightarrow 5 - 1 = 4$$

(B) BOH and BCl form basic buffer solution

$$POH = PKb + \log\frac{0.1}{0.1} \Rightarrow 6 - 0 = 6$$

$\therefore$ Ph = 8

(C) $HA + BOH \rightleftharpoons \underset{\text{Salt of W.A. and W.B.}}{\underset{\downarrow}{BA}} + H_2O$

$$\therefore \quad Ph = 7 + \frac{1}{2}pka - \frac{1}{2}pkb$$

$$= 7 + \frac{1}{2}(5) - \frac{1}{2}(7) = 6$$

(D) $HNO_3 + NaOH \longrightarrow NaO_3 + H_2O$

500×0.2 $\quad 500 \times 0.2$

– $\quad$ – $\quad$ 100 $\quad$ 100

Salt of S.A. and S.B. formed $\therefore$ Ph = 7

6. [A $\rightarrow$ R; B $\rightarrow$ Q,S; C $\rightarrow$ R; D $\rightarrow$ P,S]

(A) $pH = 7 + \frac{1}{2}Pka - \frac{1}{2}Pkb$

If $Pka = Pkb$

pH = 7

(B) $pH = 7 + \frac{1}{2}Pka + \frac{1}{2}\log C$

$\therefore$ Ph > 7

(C) No hydrolysis $\therefore$ Ph = 7

(D) $pH = 7 - \frac{1}{2}pkb - \frac{1}{2}\log C$ $\quad$ pH < 7

7. **[A $\rightarrow$ Q; B $\rightarrow$ P; C $\rightarrow$ S; D $\rightarrow$ R]**

(A) $PKa + Pkb = 14$

$\therefore$ $Pkb = 8$

(B) $[H^+] = 10^{-8} + x$

use $x \approx 10^{-7}$

(C) $Ph = \frac{1}{7}[Pka - \log C]$

(B) $Ph = -\log [H^+] = -\log [5 \times 10^{-4}]$

And $[H^+] = \dfrac{10^{-3}V + 10^{-5}V}{2V} = 5 \times 10^{-4}$

$\therefore$ POH = 14 – 4.4 = 10.7

8. [A $\rightarrow$ S; B $\rightarrow$ P; C $\rightarrow$ Q; D $\rightarrow$ R]

(A) $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^-$

$KsP = (2S)^2(S) = 4s^3$

(B) $H_2O \rightleftharpoons H^+ + OH^-$

$$Kd = \frac{[H^+][OH^-]}{[H_2O]}$$

(C) $BaCrO_4 \rightleftharpoons Ba^{+2} + CrO_4^-$

$Ksp = S \times S$

(d) $K_2CO_3 \longrightarrow 2K^+ + CO_3^-$

CO_3^{-2} anionic hydrolysis

$\therefore$ Basic in nature Ph > 7

Comprehension

Comprehension 1

9. (d)

Suppose volume of $HCO_3^- = V$ mL

Millimoles of $HCO_3^- = 5$ V

Millimoles of $H_2CO_3 = 20$

$$pH = pK_a + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$7.40 = 6.11 + \log,\ \frac{V}{4} \qquad V = 78 \text{ mL}$$

10. (b) If CO_2 escapes, $[H^+]$ decreases, hence pH increases.

Comprehension 2

11. (d)

Final pH = 1.7

or $\quad -\log [H^+] = 1.7$

or $\quad \log [H^+] = -2 + 0.3$

or $\quad [H^+] = 2 \times 10^{-2}$

Let V mL of 0.1 (M) HA solution is mixed with 100 mL of 10^{-2} (M) HCl. In the mixed solution, [HA] $= \dfrac{V \times 10^{-4}}{(100 + V)} \times 10^3$

$$= \frac{0.1V}{(100+V)}(M) \text{ and } [HCl] = \frac{10^{-3} \times 10^3}{(100+V)}$$

$$= \frac{1}{(100+V)}$$

$$\begin{array}{cccc} HA & \rightleftarrows & H^+ & + \quad A^- \\ \dfrac{0.1V}{(100+V)}(1-\alpha) & & \dfrac{0.1V\alpha}{(100+V)} & \dfrac{0.1V\alpha}{(100+V)} + \dfrac{1}{(100+V)} \end{array}$$

$$\therefore \quad [H^+] = \frac{(0.1V\alpha + 1)}{(100+V)} = 2 \times 10^{-2}$$

or $0.1V\alpha + 1 = 2 + 2\times10^{-2}\times V$

$$K_a = \frac{\dfrac{(0.1V\alpha+1)}{(100+V)}\times\dfrac{0.1V\alpha}{(1.00+V)}}{\dfrac{0.1V(1-\alpha)}{(100+V)}} = \frac{\alpha}{(1-\alpha)}\times 2\times10^{-2}$$

$\therefore$ $\dfrac{\alpha}{(1-\alpha)}\times 2\times10^{-2} = 10^{-2}$

or $\dfrac{\alpha}{1-\alpha} = \dfrac{1}{2}$

or $2\alpha = 1 - \alpha$

or $\alpha = \dfrac{1}{3}$

$\therefore$ $0.1V\times\dfrac{1}{3} + 1 = 2 + 2\times10^{-2}\times V$

or $\dfrac{V}{30} - \dfrac{V}{50} = 1$

or $\dfrac{20V}{30\times50} = 1$

or $V = \dfrac{150}{2} = 75$ ml

12. **(d)** For isohydric solution, $Ka_1C_1 = Ka_2C_2$

13. **(c)**

$$\begin{array}{cccccccc}
HA & \rightleftharpoons & H^+ & + & A^- & HD & \rightleftharpoons & H^+ + D^- \\
\frac{0.1}{2}(1-\alpha_1) & & \frac{0.1}{2}\alpha_1 & & \frac{0.1}{2}\alpha_1 & \frac{1}{2}(1-\alpha_2) & \frac{\alpha_2}{2} & \frac{\alpha_2}{2} \\
 & & +\frac{\alpha_2}{2} & & & & +\frac{0.1}{2}\alpha_1 &
\end{array}$$

$\therefore$ Total H^+ in solution $0.1/2\alpha_1 + \alpha_2/2$ for HA

$\therefore$ Total H^+ in solution $0.1/2\alpha_1 + \alpha_2/2$ for HB

$$10^{-2} = \frac{\alpha_1}{(1-\alpha_1)}\times\frac{(0.1\alpha_1+\alpha_2)}{2} \quad \text{and}$$

$$10^{-3} = \frac{\alpha_2}{(1-\alpha_2)}\times\frac{(0.1\alpha_1+\alpha_2)}{2}$$

Neglecting α_1 and α_2 with respect to 1

$$\frac{\alpha_1}{\alpha_2} = 10$$

or $10^{-2} \simeq \alpha_1\times\dfrac{2\alpha_2}{2} = \alpha_1\alpha_2 = \dfrac{\alpha_1^2}{10}$

or $\alpha_1^2 = 0.1$

or $\alpha_1 = 0.316$

$\alpha_2 = 0.0316$

$\therefore$ final $[H^+] = \dfrac{(0.0316+0.0316)}{2} = 0.0316$

or final pH = 1.5

It is the approximate pH since practically α_1 cannot be neglected with respect to 1

Comprehension 3

14. **(d)**

$$K_{a_2} \text{ of } HCO_3^- = \frac{10^{-10}}{2.1}$$

or $pK_{a_2} = 10 + \log 2.1$

$\therefore$ pH $= 7 + \dfrac{1}{2}(10 + \log 2.1) - 1 = 11.161$

15. **(c)**

$$K_{a_1} \text{ of } H_2CO_3 = \frac{10^{-6}}{2.2}$$

$pK_{a_1} = 6 + \log 2.2$

$\therefore$ at the half neutralisation point, pH $= \dfrac{1}{2}(pK_{a_1} + pK_{a_2})$

$= \dfrac{1}{2}[10 + \log 2.1 + 6 + \log 2.2]$

$= \dfrac{1}{2}[16 + \log((2.1\times2.2)]$

$= \dfrac{1}{2}[16 + 0.665] = 8.33$

16. **(a)**

At complete equivalence point, an aqueous solution of H_2CO_3 is produced.

$[H_2CO_3] = \dfrac{0.1}{2}$ (M)

$\therefore$ $[H^+] = \sqrt{K_{a_1}C}$

or $\log[H^+] = \dfrac{1}{2}[\log K_{a_1} + \log C]$

or $\text{pH} = \dfrac{1}{2}[pK_{a_1} - \log C]$

or $\text{pH} = \dfrac{1}{2}\left[6 + \log 2.2 - \log\dfrac{0.1}{3}\right]$

or $\text{pH} = \dfrac{1}{2}[6 + 0.3424 + 1.48] = 3.91 \simeq 4$

Comprehension 4

17. **(b)**

Let molar absorbance of H In $= \alpha_{\text{H In}}$ and molar absorbance of $In^- = \alpha_{In^-}$

$\therefore$ $6\times10^{-4}\times\alpha_{\text{H In}} = 0.142$

or $\alpha_{\text{H In}} = \dfrac{0.142}{6\times10^{-4}}$

and $6\times10^{-4}\times\alpha_{In^-} = 0.943$

or $\alpha_{In^-} = \dfrac{0.943}{6\times10^{-4}}$

At pH = 8, $[In^-] + [\text{H In}] = 6\times10^{-4}$

and $\dfrac{0.142}{6\times10^{-4}}\times[\text{H In}]+\dfrac{0.943}{6\times10^{-4}}[\text{In}^-]=0.527$

or $0.142[\text{H In}] + 0.943[\text{In}^-] = 0.527 \times 6 \times 10^{-4}$

and $0.142[\text{H In}] + 0.142[\text{In}^-] = 6 \times 10^{-4} \times 0.142$

$\therefore$ $0.801[\text{In}^-] = 0.385 \times 6 \times 10^{-4}$

or $[\text{In}^-] = \dfrac{0.385}{0.801} \times 6 \times 10^{-4}$

$= 0.48 \times 6 \times 10^{-4} = 2.88 \times 10^{-4}$ (M)

18. (d)

$[\text{H In}] = (6 - 2.88) \times 10^{-4} = 3.12 \times 10^{-4}$

$\text{H In} \xrightleftharpoons{K_{in}} \text{H}^+ + \text{In}^-$

$$K_{in}=\frac{[\text{H}^+][\text{In}^-]}{[\text{H In}]}=\frac{10^{-8}\times2.88\times10^{-4}}{3.12\times10^{-4}}$$

$$=\frac{2.88}{3.12}\times10^{-8}=9.25\times10^{-9}$$

19. (d)

$$0.625=[\text{H In}]\times\frac{0.142}{6\times10^{-4}}+[\text{In}^-]\times\frac{0.943}{6\times10^{-4}}$$

$\therefore$ $0.625 \times 6 \times 10^{-4} = [\text{H In}] \times 0.142 + 0.943 \times [\text{In}^-]$

$[\text{H In}] + [\text{In}^-] = 6 \times 10^{-4}$

$\therefore$ $0.142 \times 6 \times 10^{-4} = [\text{H In}] \times 0.142 + 0.142[\text{In}^-]$

or $0.801\ [\text{In}^-] = 0.483 \times 6 \times 10^{-4}$

or $[\text{In}^-] = \dfrac{0.483}{0.801} \times 6 \times 10^{-4} = 3.618 \times 10^{-4}$ (M)

$\therefore$ $[\text{H In}] = (6 - 3.618) \times 10^{-4} = 2.382 \times 10^{-4}$

$$K_{in}=\frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

or $9.5\times10^{-9}=\dfrac{[\text{H}^+]\times3.618\times10^{-4}}{2.382\times10^{-4}}$

or $[\text{H}^+] = \dfrac{2.382}{3.618} \times 9.25 \times 10^{-9} = 6.09 \times 10^{-9}$

or pH = 9 – log 6.09 = 8.215

Subjective

20. (i) $\text{H}_2\text{O} \xrightleftharpoons{Ka} \text{H}^+ + \text{OH}^-$

10^{-7} 10^{-7}

$$K_a=\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}=\frac{10^{-7}\times10^{-7}}{1000/8}$$

$$=\frac{10^{-14}}{55.5}=1.8\times10^{-16}$$

(ii) $K_a=\dfrac{10\times10^{-15}}{6\times10^{-10}}=1.67\times10^{-5}$

(iii) $K_a=\dfrac{10\times10^{-15}}{2.5\times10^{-5}}=4\times10^{-10}$

21. $Ka=C\alpha^2 \Rightarrow \dfrac{\alpha_2}{\alpha_1}=\sqrt{\dfrac{C_1}{C_2}}=\sqrt{\dfrac{1}{1/100}}=10$

22. $K_a = C\alpha^2$

$$\frac{\alpha_1}{\alpha_2}=\sqrt{\frac{Ka_1}{Ka_2}}=\sqrt{\frac{1.8\times10^{-5}}{6.2\times10^{-10}}}=\sqrt{\frac{18}{6.2}\times10^4}=170:1$$

23. **(a)** $\text{pH}=\dfrac{1}{2}pK_a-\dfrac{1}{2}\log C$

$4.50 \times 2 = pK_a - \log(0.1)$

$9 - 1 = pK_a$ $pK_a = 8$ $K_a = 10^{-8}$

24. (i) $[\text{H}^+] = \sqrt{Ka\,C}=\sqrt{18\times10^{-6}}$

$\therefore$ pH = 3 – log $[18]^{\frac{1}{2}}$

= 3 – 0.62 = 2.38

(ii) $[\text{H}^+] = 10^{-8} + 10^{-7} = 10^{-7}[0.1 + 1]$

pH = 7 – log 1.1 = 6.95

(iii) $[\text{OH}^-] = 10^{-10} + 10^{-7} = 10^{-7}[1.001]$

POH = 7 – log 1.001 = 6.99

pH = 7.0004

25. $pK_w = 14 - \log 2.56 = 13.59 \approx 13.6$

$$\text{pH}=\frac{pK_w}{2}=6.795$$

26. pH = 11.5 $[\text{H}^+] = 10^{-11.5}$

$[\text{OH}^-] = 10^{-2.5}$

$\text{NH}_4\text{OH} \xrightleftharpoons{K_b} \text{NH}_4^+ + \text{OH}^-$

$10^{-2.5}$ $10^{-2.5}$

$\dfrac{10^{-5}}{C} = 1.8 \times 10^{-5}$ $C=\dfrac{1}{1.8}$ =0.556 M

27. $C = 10^{-2}$, $[\text{H}^+] = 10^{-3}$

$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$10^{-2} - 10^{-3}$ 10^{-3} 10^{-3}

$$K_a=\frac{10^{-3}\times10^{-3}}{10^{-2}-10^{-3}}=\frac{10^{-3}}{9}=1.1\times10^{-4}$$

28. $\text{CHCl}_2\text{COOH} \longrightarrow \text{H}^+ + \text{CHCl}_2\text{COO}^-$

0.01

$0.01 - x$ $(0.01 + x)$ x

$$\frac{x(0.01+x)}{0.01-x}=2.55\times10^{-2}$$

$0.01\,x + x^2 = 2.55 \times 10^{-4} - 2.55 \times 10^{-2}\,x$

$x^2 + 0.0355x - 0.000255 = 0$

$\text{CHCl}_2\text{COO}^- = 6.126 \times 10^{-2} = x$

29. For weak acid

$$[\text{H}^+]=\sqrt{K_1C_1+K_2C_2\ldots+K_w}$$

$$=\sqrt{1.8\times10^{-5}\times0.02+6.4\times10^{-5}\times.01+10^{-14}}$$

$$=\sqrt{100\times10^{-8}}$$

$$[H^+] = 10^{-3} \qquad K_a = \frac{[H^+][ACO^-]}{[ACOH]_2}$$

$[ACO^-] = 3.6 \times 10^{-4}$

same $[C_7H_5O_2^-] = 6.4 \times 10^{-4}$

30. $H_2S \longrightarrow 2H^+ + S^{-2}$

$[H^+] = 2 \times 10^{-4}$, $[H_2S] = 0.1$ M

$K = K_1 \times K_2 \qquad K = 10^{-7} \times 10^{-14}$

$K = 10^{-21}$

$$\Rightarrow \quad 10^{-21} = \frac{[2\times10^{-4}]^2[S^{-2}]}{[0.1]} \quad 10^{-21} = \frac{4\times10^{-8}}{0.1}[S^{-2}]$$

$$\frac{1}{4}\times10^{-14} = [S^{-2}] \qquad 2.5 \times 10^{-15} = [S^{-2}]$$

31. (i) $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad K_1 = 7.225 \times 10^{-3}$

$C(1-\alpha) \quad C\alpha_1 \quad C\alpha_1$

(ii) $H_2PO_4^- \rightleftharpoons HPO_4^{-2} + H^+ \quad K_2 = 6.8 \times 10^{-8}$

$C\alpha_1(1-\alpha_2) \quad C\alpha_1\alpha_2 \quad [C\alpha_1]$

(iii) $HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3} \quad K_3 = 6.8 \times 10^{-8}$

$\alpha_1\alpha_2C_1(1-\alpha_3) \quad [C\alpha_1] \quad C(\alpha_1\alpha_2\alpha_3)$

$$7.225\times10^{-3} = \frac{C\alpha_1^2}{(1-\alpha_1)} = \frac{0.01\times\alpha_1^2}{1-\alpha}$$

RxN. …(i)

$(1-\alpha) \times 0.7225 = \alpha_1^2$

$\alpha_1^2 + 0.7225\,\alpha - 0.7225 = 0$

$\alpha_1 = 0.562$

$\Rightarrow \quad [H^+] = 0.01 \times 0.562 \quad [H^+] = 5.6 \times 10^{-3}$

$[H_2PO_4^{\ominus}] \approx 5.6 \times 10^{-3}$ RxN. …(ii)

$$6.8 \times 10^{-8} = \frac{[HPO_4^{-2}][H^+]}{[H_2PO_4^-]}$$ from [i] reaction.

$\Rightarrow \quad [HPO_4^{-2}] = 6.8 \times 10^{-8}$ M RxN. …(iii)

$$4.5\times10^{-13} = \frac{[PO_4^{-3}][H^+]}{[HPO_4^{-2}]}$$

$$\frac{4.5\times10^{-13}\times6.8\times10^{-8}}{5.6\times10^{-3}} = [PO_4^{-3}]$$

$5.464 \times 10^{-18} = [PO_4^{-3}]$

32. $NH_4Cl \longrightarrow NH_4^+ + Cl^-$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$[NH_4^+]$ = is due to salt because NH_4OH ionises in less amount due to common ions effect.

$$1.8\times10^{-5} = \frac{0.1\times[OH^-]}{0.05} \quad 9\times10^{-6} = [OH^-]$$

33. POH = 14 – 9.26 = 4.74

$$4.74 = 4.74 + \log\frac{[NH_4^+]}{[NH_4OH]}$$

$$\log 1 = \log\frac{[NH_4^+]}{[NH_4OH]}$$

$[NH_4OH] = [NH_4^+]$

$\therefore$ number of moles of $(NH_4)_2SO_4 = \dfrac{n_{NH_4OH}}{2}$

$= \dfrac{0.1}{2} = 0.05$ moles, $x = 0.05$ mole

34. $CH_3COO^{\ominus} + H_2O \rightleftharpoons CH_3COOH + OH^{\ominus}$

$0.08 - x \qquad x \qquad x$

$$K_h = \frac{10^{-14}}{1.8\times10^{-5}}$$

$$Kh = \frac{x^2}{0.08} = \frac{10}{1.8}\times10^{-10} \qquad x^2 = \frac{0.8}{1.8}\times10^{-10}$$

$x^2 = 0.44 \times 10^{-10} \qquad x = 0.66 \times 10^{-5}$

35. $C_5H_6N^+ + H_2O \rightleftharpoons C_5H_5NOH + H^+$

$$pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

$$2.699 = \frac{1}{2}[14 - pK_b + 0.6]$$

$5.398 = 14.6 - pK_b$

$pK_b = 14.6 - 5.398 = 9.802$

$K_b = 10^{-9.802}$

36. $pH = \dfrac{pK_1 + pK_2}{2}$

$$pH = \frac{11 + 7 - 2\log 4.5}{2} = 9 - \log 4.5 = 8.34$$

37. $Q^+ + H_2O \rightleftharpoons QOH + H^+ \quad k_w/k_1 \quad \dfrac{n_1}{V} = n_1'$

$n_1' - x \qquad x \qquad x + y$

$R^+ + H_2O \rightleftharpoons ROH + \quad H^+ \quad \dfrac{n_2}{V} = n_2'$

$n_2' - y \qquad y \qquad y + x$

$$\frac{k_w}{k_1} = \frac{x(x+y)}{n_1' - x} \simeq \frac{x(x+y)}{n_1'} \qquad \text{...(i)}$$

$$\frac{k_w}{k_2} = \frac{y(x+y)}{n_2' - y} \simeq \frac{y(x+y)}{n_2'} \qquad \text{...(ii)}$$

Assuming $x << n_1'$ and $y << n_2'$

from Eqs (i) and (ii)

$$x(x+y) = \frac{k_w}{k_1}n_1' \text{ and } y(x+y) = \frac{k_w}{k_2}n_2'$$

Adding both

$$(x+y)^2 = k_w\left[\frac{n_1'}{k_1} + \frac{n_2'}{k_2}\right] = \frac{k_w(k_2n_1' + k_1n_2')}{k_1k_2}$$

$$[H^+] = (x+y) = \sqrt{\frac{k_w}{k_1k_2V}(k_2n_1 + k_1n_2)}$$

$$pH = -\log[H^+]$$

$$pH = \frac{1}{2}\log\left[\left(\frac{k_1k_2}{k_w}\right)\frac{V}{(k_2n_1 + k_1n_2)}\right]$$

38. $Na_4Y + H_2O \rightleftharpoons Na_3HY + NaOH \quad \frac{k_w}{k_4} = 1.818 \times 10^{-4}$

0.1

$0.1 - x \qquad\qquad x \qquad\qquad x$

$\frac{x^2}{0.1 - x} = 1.818 \times 10^{-4} \Rightarrow 5500.55x^2 + x - 0.1 = 0$

$x = 4.17 \times 10^{-3}$

$Na_3HY + H_2O \rightleftharpoons Na_2H_2Y + NaOH \quad \frac{k_w}{k_3} = 1.445 \times 10^{-8}$

x

$x - y \qquad\qquad y \qquad\qquad y + x$

since $y << x$ $x - y \simeq x, x + y \simeq x$

$1.445 \times 10^{-8} = \frac{y \cdot x}{x} = y$

$Na_2H_2Y + H_2O \rightleftharpoons NaH_3Y + NaOH \frac{k_w}{k_2} = 4.7 \times 10^{-12}$

y

$y - z \qquad\qquad z \qquad\qquad z + x$

$y - z \simeq y, \quad z + x \simeq x$

$4.7 \times 10^{-12} = \frac{z \cdot x}{y} \quad z = 1.628 \times 10^{-17}$

$NaH_3Y + H_2O \rightleftharpoons H_4Y + NaOH \frac{k_w}{k_1} = 9.8 \times 10^{-13}$

z

$z - t \qquad\qquad t \qquad\qquad t + x$

$z - t \simeq z, \quad t + x \simeq x$

$9.8 \times 10^{-13} = \frac{t \cdot x}{z} \quad t = 3.82 \times 10^{-27}$

Fraction $= \frac{t}{0.1} = 3.82 \times 10^{-26}$

39. $s = [Zn(OH)_2(aq.)] + Zn(OH)^+ + Zn^{+2} + Zn(OH)_3^-$
$+ Zn(OH)_4^{-2}$

$$s = k_1 + \frac{k_1k_2}{[OH^-]} + \frac{k_1k_2k_3}{[OH^-]^2} + k_1k_4[OH^-] + k_1k_4k_5[OH^-]^2$$

$$s = 10^{-6} + \frac{10^{-13}}{[OH^-]} + \frac{10^{-17}}{[OH^-]^2} + 10^{-3}[OH^-] + 10^{-2}[OH^-]^2$$

(b) pH = 9, pOH = 5, $[OH^-] = 10^{-5}$
$s = 10^{-6} + 10^{-8} + 10^{-7} + 10^{-8} + 10^{-12} = 1.12 \times 10^{-6}$ M

40. Given:

$Ag + \frac{1}{2}Cl_2 \rightleftharpoons AgCl \quad \Delta G°_1 = –109.7 kJ/mole^{-1}$

$Ag \longrightarrow Ag^+ + e^- \quad \Delta G°_2 = 77.2$ kJ/mole^{-1}

$e^- + \frac{1}{2}Cl_2 \longrightarrow Cl^- \quad \Delta G°_3 = -131.2$ kJ/mole^{-1}

so for reaction

$AgCl \rightleftharpoons Ag^+ + Cl^- \quad \Delta G° = -\Delta G°_1 + \Delta G°_2 + \Delta G°_3$

$\Delta G° = 55.7$ kJ/mole

$\Delta G° = -$ RT ln K_{sp}

$55.7 \times 10^{-3} = -8.314 \times 298 \ln K_{sp}$

$K_{sp} = 1.723 \times 10^{-10}$

$1.723 \times 10^{-10} = [Ag^+][Cl^-] = s \times 0.05$

$s = 3.446 \times 10^{-9}$ M

41. $K_{sp} = [Al^{+3}][OH^-]^3$

$5 \times 10^{-33} = [1 \times 10^{-3}][OH^-]^3$

$[OH^-] = 1.7 \times 10^{-10}$

pOH = 9.767

pH = **4.23**

42. In beginning $[H^+] = \sqrt{K_aC}$

$[H^+] = \sqrt{1.8 \times 10^{-5}} = 0.004242$

pH = 2.372

On doubling pH, new pH= 4.744

$[H^+] = 1.8 \times 10^{-5}$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

C

$C - C\alpha \qquad\qquad C\alpha \qquad\qquad C\alpha$

$K_a = \frac{(C\alpha)^2}{C(1-\alpha)}, \; C\alpha = [H^+] = 1.8 \times 10^{-5}$

$1.8 \times 10^{-5} = \frac{(1.8 \times 10^{-5})^2}{C - C\alpha}$

$C - C\alpha = 1.8 \times 10^{-5}$

$C = 3.6 \times 10^{-5}$

$V = \frac{1}{C} = 2.77 \times 10^4$ L

43. (a) $PV = nRT$

$1 \times 0.959 = n \times 0.0821 \times 298$

$n = 0.03919$

959 ml in 1 ml H_2O

Volume of H_2O = 1 mL (per volume of H_2O)

$C = \frac{n}{V} = \frac{0.03919}{10^{-3}} = 39.19$ M

$pk_b = 3.39 \Rightarrow k_b = 4 \times 10^{-4}$

$[OH^-] = \sqrt{K_bC} = 0.1252$ M

pOH = 0.9023 pH = 13.097

(b) $M = 0.1252$ for NaOH

44. (a) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

$6 \qquad 3$

$3 \quad - \qquad\qquad 3$

pH = pk_1 = 2.12

(b) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

$6 \qquad 6$

$- \qquad - \qquad\qquad 6$

pH $= \frac{pk_1 + pk_2}{2} = \mathbf{4.66}$

(c) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

$4.8 \qquad 7.2$

$- \qquad 2.4 \qquad\qquad 4.8$

$NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

$4.8 \qquad 2.4$

$2.4 \qquad - \qquad\qquad 2.4$

pH = pk_2 = **7.2**

(d) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$
4 10
– 6 4
$NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$
4 6
– 2 4
$Na_2HPO_4 + NaOH \longrightarrow Na_3PO_4 + H_2O$
4 2
2 – 2
$pH = pk_3 = \mathbf{12}$

45. $H_3PO_4 \rightarrow k_1 = 7.5 \times 10^{-3}, k_2 = 6.2 \times 10^{-8}, k_3 = 10^{-12}$
(i) $Na_3PO_4 + NaH_2PO_4 \longrightarrow 2Na_2HPO_4$
5 5
– – 10

$$pH = \frac{pk_2 + pk_3}{2} = \mathbf{9.6}$$

(ii) $H_3PO_4 + Na_3PO_4 \longrightarrow Na_2HPO_4 + NaH_2PO_4$
4 4
– – 4 4
$pH = pk_2 = \mathbf{7.2}$

46. $BOH + HCl \longrightarrow BCl + H_2O$
4 4
– – 4
At end point, m moles of BOH = m moles of HCl
$0.16 \times V = 4$ $V = 25$ mL
Total volume = 40 + 25 = 65 mL

$$[BCl] = \frac{4}{65}$$

Since BCl is salt of SAWB.

$$pH = 7 - \frac{1}{2}pk_b - \frac{1}{2}\log C$$

$$5.23 = 7 - \frac{1}{2}pk_b - \frac{1}{2}\log\frac{4}{65}$$

$pk_b = 4.75$
Now on further adding NaOH
$BCl + NaOH \longrightarrow BOH + NaCl$
4 1.8
2.2 – 1.8

$$pOH = pk_b + \log\frac{2.2}{1.8} = 4.837 \Rightarrow pH = \mathbf{9.1628}$$

47. (a) $pH = pK_a + \log\dfrac{0.06}{0.05}$
$pH = 3.744 + \log 1.2 = \mathbf{3.823}$
(b) On diluting solution 10 times
$[HCOOH] = 0.005, [HCOONa] = 0.006$
$HCOOH \rightleftharpoons H^+ + HCOO^-$
0.005
$0.005\,(1 - \alpha)$ 0.005α $0.005\alpha + 0.006$

$$K_a = 1.8 \times 10^{-4} = \frac{(0.005\alpha + 0.006)(0.005\alpha)}{0.005(1-\alpha)}$$

$$\frac{0.005\alpha^2 + 0.006\alpha}{1-\alpha} = 1.8 \times 10^{-4}$$

$\Rightarrow 27.77\alpha^2 + 34.33\alpha - 1 = 0\alpha = 0.0285$
$[H^+] = 0.005\alpha = 1.425 \times 10^{-4}$ $pH = \mathbf{3.846}$
(c) On further diluting solution by 10 times
$[HCOOH] = 0.0005, [HCOONa] = 0.0006$
$HCOOH \rightleftharpoons H^+ + HCOO^-$
0.0005
$0.0005(1-\alpha)$ 0.0005α $0.0005\alpha + 0.0006$

$$K_a = 1.8 \times 10^{-4} = \frac{(0.0005\alpha + 0.0006)(0.0005\alpha)}{0.0005(1-\alpha)}$$

$$= \frac{0.0005\alpha^2 + 0.0006\alpha}{1-\alpha} = 1.8 \times 10^{-4}$$

$2.77\alpha^2 + 4.33\alpha - 1 = 0 \Rightarrow \alpha = 0.2047$
$[H^+] = 0.0005\alpha = 1.0235 \times 10^{-4}$
$pH = \mathbf{3.9899}$

48. $pH = 8, [H^+] = 10^{-8}, [OH^-] = 10^{-6}$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$ $K = 5 \times 10^{-13}$
0.0005
$0.0005 - y - z$ 10^{-8} y
$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ $K = \dfrac{K_w}{K_1} = 2 \times 10^{-8}$
0.0005
$0.0005 - y - z$ z 10^{-6}
since equilibrium constant for first reaction is very less
$y << z$

$$2 \times 10^{-8} = \frac{z(10^{-6})}{0.0005 - z}$$

$51\,z = 0.0005 \Rightarrow z = \mathbf{9.8 \times 10^{-6}}$
$[H_2CO_3] = 9.8 \times 10^{-6}$ M
$[HCO_3^-] = 0.0005 - 9.8 \times 10^{-6} = \mathbf{4.9 \times 10^{-4}\ M}$

$$5 \times 10^{-3} = \frac{10^{-8} \times y}{4.9 \times 10^{-4}}$$

$[CO_3^{-2}] = y = \mathbf{2.45 \times 10^{-8}\ M}$

49. $Fe^{+3} + H_2O \longrightarrow Fe(OH)^{+2} + H^+$ $k = 6.5 \times 10^{-3}$
x
$0.95x$ $0.05x$ $0.05x$

$$6.5 \times 10^{-3} = \frac{(0.05)^2 x}{0.95} \qquad x = 2.47$$

$[H^+] = 0.05x = 0.1235$ $pH = 0.908$

50. $pH = pK_2 + \log\dfrac{\text{salt}}{\text{acid}}$

$$6.7 = 7.2 + \log\frac{y}{0.005}$$

$y = 1.58 \times 10^{-3}$ mole

51. When indicator is half in ionic form $pH = pK_a = 7.2$
$pH = 7.2 + \log 5 = 7.898$
Now with this pH
$7.898 = pK_{a1} + \log 4 = pK_{a1} = 7.2959$
Again when 50% of new indicator is in ionic form
$pH = pK_{a1} = 7.2959$

52. 4 m mole of H^+ ion will produce

$$[H^+] = \frac{4\times10^{-3}}{0.1} = 0.04$$

$$PO_4^{-3} + H^+ \longrightarrow HPO_4^{-2} \quad \frac{1}{k_3}$$

0.02 0.04 0.08

0.02 0.10

$$HPO_4^{-2} + H^+ \longrightarrow H_2PO_4^- \quad \frac{1}{k_2}$$

0.10 0.02

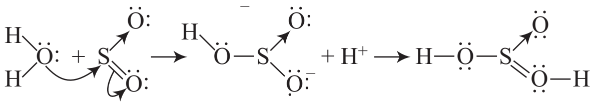
0.08 – 0.02

So now they form a buffer solution of HPO_4^{-2} and $H_2PO_4^-$

$$pH = pk_2 + \log\frac{0.08}{0.02} \qquad (k_2 = 6.3\times10^{-8})$$

$pH = 7.2 + \log 4$ **= 7.8**

53. In terms of Lewis acid-base theory, the reaction of SO_2 with water is very similar to the reaction of SO_2 with pyridine. SO_2 acts as an electron pair acceptor (Lewis acid) and water acts as the electron pair donor (Lewis base).



54. CH_3COOH being weaker acid than oxallic acid, does not decompose CaC_2O_4. On the other hand, HCl being stronger acid forms Ca^{2+} and oxalate ion to pass CaC_2O_4 in solution state.

$$CaC_2O_4 + 2HCl \rightarrow CaCl_2 + H_2C_2O_4$$

55. Meq. of HCl_I in 1 mL = $10^{-5}\times1$

Meq. of HCl_{II} in 1000 mL = N × 1000

i.e., Meq. of HCl (conc.) = Meq. of HCl (dil.)

∴ $10^{-5}\times1 = N\times1000$

∴ $N_{HCl_{II}} = 10^{-8}$

pH = 6.9788

56. (a) $pH = -\log K_a + \log\frac{[salt]}{[acid]}$

$$\because\ [salt] = \frac{3\times1000}{82\times100}M \text{ and } [acid] = \frac{2\times1000}{60\times100}M$$

$$\therefore\ pH = -\log 1.8\times10^{-5} + \log\frac{\frac{3\times1000}{82\times100}}{\frac{2\times1000}{60\times100}}$$

pH = 4.7851

(b) $pOH = -\log K_b + \log\frac{[salt]}{[base]}$

∵ total volume after mixing = 250 + 5 = 255 mL

Meq. of salt = 250 × 0.1 = 25

Meq. of base = 5 × 0.1 = 0.5

$$\therefore\quad [salt] = \frac{25}{255} M \text{ and } [base] = \frac{0.5}{255} M$$

$$\therefore\quad pOH = -\log 1.8\times10^{-5} + \log\frac{\frac{25}{255}}{\frac{0.5}{255}}$$

pOH = 6.4437

pH = 14 – pOH = 7.5563

(c) $pH = -\log K_a + \log\frac{[salt]}{[acid]}$

$$= -\log 3.6\times10^{-4} + \log\frac{\frac{0.35}{500}}{\frac{0.25}{500}}$$

pH = 3.5898

57. (a) Bronsted Lowry acid : $H_2PO_4^-$, NH_4^+

(b) Bronsted Lowry base: SO_3^{2-}, ClO^-, $H_2PO_4^-$

(c) Lewis acid : Fe^{3+}, BCl_3

(d) Lewis base : $H_2PO_4^-$, SO_3^{2-}, ClO^-

58. pH of HCl solution = 2; $[H_3O^+]$ in solution = 10^{-2} M

Meq. of HCl solution $(N_1V_1) = 10^{-2}\times200 = 2$

pH of NaOH solution = 12; $[OH^-]$ in solution = 10^{-2} M

Meq. of NaOH solution $(N_2V_2) = 10^{-2}\times300 = 3$

Total volume V_{net} of the solution after mixing = (200 + 300) = 500 mL

For heterogeneous mixtures

$N_1V_1 \sim N_2V_2 = NV_{net}$

$2 \sim 3 = N(500)$

$N[OH^-] = 1/500 = 2\times10^{-3}$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{(10^{-14}\,M^2)}{(2.0\times10^{-3}\,M)} = 5\times10^{-12}\,M$$

$pH = -\log[H_3O^+] = -\log(5.0\times10^{-12})$

$= (12 - \log 5) = (12 - 0.69897) = 11.30103$

59. The reaction between an acid and base is

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

The concentration of CH_3COONa at the equilibrium point $= \frac{0.1}{2} = 0.05$ M

The formula for finding the pH of the salt solution is

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log C]$$

$$= -\frac{1}{2}[\log 10^{-14} + \log(1.9\times10^{-5}) - \log(5.0\times10^{-2})]$$

$$= -\frac{1}{2}[-14 + (-5 + 0.2788) - (-2 + 0.6990)]$$

$$= -\frac{1}{2}[-14 - 4.7217 + 1.301]$$

$$= -\frac{1}{2}[-17.420] = 8.71$$

60. Let the volume of $NaHCO_3$ solution mixed = x mL

Number of moles of $NaHCO_3$ in x mL of 5M $NaHCO_3$ solution $= \frac{5 \times x}{1000} = 0.005x$ mol

Number of moles of H_2CO_3 in 10 mL of 2M H_2CO_3 solution $= \frac{2 \times 10}{1000} = 0.02$ mol

pH of the solution = 7.4, K_a for $H_2CO_3 = 7.8 \times 10^{-7}$

According to Henderson's equation,

$$\text{pH} = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$7.4 = -\log (7.8 \times 10^{-7}) + \log \left(\frac{0.005x}{0.02}\right)$$

or $$\text{pH} = -\log K_a + \log \frac{M_1V_1}{M_2V_2}$$

$$7.4 = (7 - \log 7.8) + \log \frac{0.005x}{0.02}$$

$$\text{pH} = -\log K_a + \log \frac{5 \times x}{2 \times 10}$$

$7.4 = (7 - 0.892) + \log (0.25x)$

$7.4 = 6.108 + \log (0.25\, x)$

$\log (0.25x) = 7.4 - 6.108 = 1.292$

$0.25x = \text{Antilog } 1.292 = 19.59$

$$\therefore \quad x = \frac{19.59}{0.25} = 78.36$$

Thus, the volume of 5M $NaHCO_3$ solution to be mixed = 78.36 mL

61. Number of milli-equivalents of NaOH = 800 × 0.05 = 40

Number of milli-equivalents of HCl = 200 × 0.1 = 20

Number of milli-equivalents of NaOH left after the addition of HCl = 40 – 20 = 20

Total volume = (200 + 800) mL = 1000 mL = 1 L

20 milli-equivalents or 0.02 equivalent of NaOH are present in 1 L, i.e.,

0.02 N NaOH = 0.02 M NaOH and the base is completely ionised.

$[OH^-] = 0.02 \text{ M} = 2 \times 10^{-2}$ M

$\text{pOH} = -\log (2 \times 10^{-2}) = 1.7$

$\text{pH} = 14 - 1.7 = 12.3$

62. On adding HCl, the free hydrogen ions will combine with CH_3COO^- ions to form CH_3COOH. Thus, the concentration of acetic acid increases while that of CH_3COO^- ions decreases.

$[CH_3COOH] = (0.2 + 1) = 1.2 \text{ mol L}^{-1}$

$[\text{Salt}] = (1 - 0.2) = 0.8 \text{ mol L}^{-1}$

Applying Henderson's equation,

$$\text{Ph} = PKa + \log \frac{[\text{salt}]}{[\text{Acid}]}$$

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$= \log \frac{0.8}{1.2} - \log 1.8 \times 10^{-5}$$

$= \log 2 - \log 3 - \log 1.8 \times 10^{-5}$

$= 4.5687$

63. pOH of NH_3 and NH_4Cl buffer

$$= -\log K_b + \log \frac{[S]}{[B]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1} = 4.75$$

$\text{pH} = (14 - 4.75) = 9.25$

First case

$NH_3 + HCl \longrightarrow NH_4Cl$

$[S] = (0.1 + 0.02) = 0.12$ M

$[B] = (0.1 - 0.02) = 0.08$ M

$$\text{pOH} = -\log K_b + \log \frac{0.12}{0.08}$$

$= 4.75 + 0.176 = 4.926$

$\text{pH} = 14 - 4.926 = 9.074$

$\Delta \text{pH} = (9.25 - 9.074) = 0.176$ pH unit

Second case:

$NH_4Cl + NaOH \rightleftharpoons NH_4OH + NaCl$

$[S] = (0.1 - 0.02) = 0.08$ M

$[B] = (0.1 + 0.02) = 0.12$ M

$$\text{pOH} = -\log K_b + \log \frac{0.08}{0.12}$$

$= (4.75 - 0.176) = 4.576$

$\text{pH} = (14 - 4.574) = 9.426$

$\Delta \text{pH} = (9.426 - 9.25) = 0.176$ pH unit

64. $$\text{pH} = pK_a + \log \frac{[S]}{[A]} = pK_a + \log \frac{a}{(0.29 - a)}$$

$$4.4 = 4.76 + \log \frac{a}{(0.29 - a)}$$

$$-0.36 = \log \frac{a}{(0.29 - a)}$$

$$\log \frac{0.29 - a}{a} = 0.36 = \log 2.3$$

$2.3a = 0.29 - a$

$3.3a = 0.29$

$a = 0.087 \text{ M} = \text{salt}$

$\text{acid} = 0.29 - 0.087 = 0.203$ M

65. $$\text{pH} = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$pK_a = -\log (1.8 \times 10^{-5}) = 4.7447$

$[CH_3COO^-] = 2 \times [(CH_3COO)_2Ba] = 0.2$ M

$[CH_3COOH] = 0.1$ M

$$\text{pH} = 4.7447 + \log \frac{0.2}{0.1} = 5.046$$

66. Concentration of HNO_3 solution = 0.63 g per 100 mL (Given)

$$= 6.3\ \text{g L}^{-1} = \frac{6.3}{63}\ \text{mol L}^{-1} = 0.1\ \text{M}$$

($\because$ Mol. wt. of $HNO_3 = 63$)

Now, HNO_3 completely ionizes as

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

$\because$ $[H_3O^+] = [HNO_3] = 10^{-1}$M

$\therefore$ pH = –log $[H_3O^+]$ = – log 10^{-1} = 1

67. (i) Calculation of molarity:

Weight of NaOH dissolved = 4.0 g L^{-1}

Molecular weight of NaOH = 40

$\therefore$ molarity of the solution

$$= \frac{\text{Strength in gL}^{-1}}{\text{Molecular weight}} = \frac{4.0}{40} = 0.1\,\text{M}$$

(ii) Calculation of the OH^- ion concentrated NaOH completely ionises as

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$\therefore$ $[OH^-] = [NaOH] = 0.1\ \text{M} = 10^{-1}$ M

(iii) Calculation of pH

We know that

$$[H_3O^+][OH^-] = K_W = 1.0 \times 10^{-14}$$

$$\because \quad [H_3O^+] = \frac{K_W}{[OH^-]} = \frac{1.0\times10^{-14}}{10^{-1}} = 10^{-13}\ \text{M}$$

$\therefore$ pH = –log $[H_3O^+]$ = –log 10^{-13} = 13

68. $N_1V_1 + N_2V_2 + N_3V_3 = NV$

$$\frac{N}{10}\times 200 + \frac{N}{20}\times 100 + \frac{N}{20}\times 100 = N(400)$$

$$20 + 5 + 5 = N(400)$$

$$N = \frac{30}{400} = \frac{3}{4}\times 10^{-1}$$

This is the normality of $[H^+]$

$\because$ final solution is acidic

$\therefore$ pH = 1 + log 4 – log 3 = 1.12

69. $N_1V_1 \sim N_2V_2 = NV$

$$\frac{N}{10}\times 2000 \sim \frac{N}{10}\times 1000 = N\,(2000 + 1000)$$

$$200 - 100 = N\,(3000)$$

$$N = \frac{100}{3000} = \frac{1}{30}$$

Hence, the resulting solution is $\frac{N}{30}$ HCl

$$[H^+] = \frac{1}{30} = 0.033\ \text{mol L}^{-1}$$

$$\text{pH} = -\log\,[H^+]$$

$$= -\log\frac{1}{30} = -\log 1 + \log 30$$

$$= 0 + 1.4771 = 1.4771$$

70. $\text{pOH} = pK_b + \log\dfrac{[\text{Salt}]}{[\text{Base}]}$ or $5 = pK_b + \log\dfrac{[\text{Salt}]}{[\text{Base}]}$

If the concentration of salt is increased three times, then p'OH = 5 + log 3 = 5 + 0.48 = 5.48

71. Applying $N_1V_1 = N_2V_2$

$Ba(OH)_2$ Mixture

(Normality of solution of $Ba(OH)_2$ = 2 × its molarity)

We have, $0.01 \times 2 \times 50 = N_2 \times (50 + 50)$ because it is assumed as 100% ionised)

$$N_2 = \frac{0.01\times100}{100} = 0.01\ \text{N} = [OH^-]$$

pOH = –log $[OH^-]$ = –log 10^{-2} = 2 log 10 = 2

pH + pOH = 14 or pH + 2 = 14 or pH = 12

72. For acetic acid (weak acid)

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{v_1}{v_2}}$$

$$\left(\frac{1}{2}\right)^2 = \frac{300}{V_2}$$

or $V_2 = 1200$ mL

So, 1200 – 300 = 900 mL water should be added.

73. We have,

pH = –log $[H^+]$

4.18 = –log $[H^+]$

or log $[H^+]$ = –4.18

Taking antilog,

$[H^+] = 6.61 \times 10^{-5}$ mol L^{-1}

Now, for equilibrium

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$$K_{a_1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

$$\text{or} \quad 4.45\times10^{-7} = \frac{[HCO_3^-](6.61\times10^{-5})}{0.01}$$

$$\therefore \quad [HCO_3^-] = \frac{4.45\times10^{-7}\times0.01}{6.61\times10^{-5}}$$

$$= 6.73 \times 10^{-5}\ \text{mol L}^{-1}$$

Again for the dissociation of HCO_3^-, we have

$$HCO_3^- \rightleftharpoons CO_3^{-2} + H^+$$

$$K_{a_2} = \frac{[CO_3^{-2}][H^+]}{[HCO_3^-]}$$

$$\therefore \quad [CO_3^{-2}] = \frac{K_{a_2}\times[HCO_3^-]}{[H^+]}$$

$$= \frac{4.69\times10^{-11}\times6.73\times10^{-5}}{6.61\times10^{-5}}$$

$$= 4.8\times10^{-11}\ \text{mol L}^{-1}$$

74. Given density of formic acid = 1.22 g cm^{-3}

$\therefore$ weight of formic acid in 1 L solution

= 1.22×10^3 g

Thus,

$$[HCOOH] = \frac{1.22\times10^3}{46} = 26.5\ \text{M}$$

Since in case of auto-ionisation

$$[HCOOH_2^+]\times[HCOO^-] = 10^{-6}.$$

$$\therefore \quad [HCOO^-] = 10^{-3}$$

Now % dissociation of HCOOH

$$\frac{[HCOO^-]\times 100}{[HCOOH]} = \frac{C\alpha}{C(1-\alpha)} = \frac{10^{-3}}{26.5}\times 100 = 0.004\%$$

75. Acetic acid ionises partially while sodium acetate ionises strongly in solution. Let x be the number of moles of acetic acid ionised. The concentration can be formulated as follows :

$$\underset{(0.02-x)}{CH_3COOH(aq)} + H_2O \rightleftharpoons \underset{x}{H_3O^+(aq)} + \underset{x}{CH_3COO^-(aq)}$$

$$\underset{0.2\text{ gives}}{CH_3COONa} \longrightarrow \underset{0.2}{Na^+(aq)} + \underset{0.2}{CH_3COO^-(aq)}$$

Because x is small as compared to 0.2, the total concentration of CH_3COO^- is approximately 0.2 mol L^{-1}. Thus,

$$[CH_3COO^-] = 0.2 + x \simeq 0.2 \text{ mol } L^{-1}$$

and $[CH_3COOH] = 0.2 - x \simeq 0.2 \text{ mol } L^{-1}$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$1.8\times10^{-5} = \frac{[H_3O^+]\times 0.2}{0.02}$$

$$[H_3O^+] = \frac{1.8\times10^{-5}\times0.02}{0.2} = 1.8\times10^{-6} \text{ mol } L^{-1}.$$

76. $\underset{(0.05-x)}{C_6H_5OH} + H_2O \rightleftharpoons \underset{x}{C_6H_5O^-} + \underset{x}{H_3O^+}$

$$[H_3O^+] = \sqrt{K_a\times C} = \sqrt{1\times10^{-10}\times0.05} = \sqrt{5\times10^{-12}}$$

$$= 2.2\times10^{-6} \text{ M}$$

$$[\text{Phenate}] = [H_3O^+] = 2.2\times10^{-6} \text{ M}$$

77. (i) $C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

(ii) $HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$

(iii) $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$

(iv) $H_2S + H_2O \rightleftharpoons HS^- + H_3O^+$

78. Given: $K_b = 5.4\times10^{-4}$

$$K_a\times K_b = K_w$$

$$\Rightarrow \quad K_a = \frac{K_w}{K_b} = \frac{1\times10^{-14}}{5.40\times10^{-4}} = 1.23\times10^{-11}$$

79. $pH = -\log[H_3O^+] = 12$

$$\log[H_3O^+] = -12$$

$$\therefore \quad [H_3O^+] = 1\times10^{-12} \text{ mol } L^{-1}$$

We know that $K_w = [H_3O^+][OH^-] \quad \therefore [OH^-] = \dfrac{K_w}{[H_3O^+]}$

Since NaOH is a strong base, it is completely ionised.

$\therefore \quad [NaOH] = [OH^-] = 1\times10^{-2} \text{ mol } L^{-1}$

Molecular mass of NaOH = 40

$\therefore$ amount of NaOH in grams per litre

$$= 1\times10^{-2}\times40 = 0.4 \text{ g}$$

80. We know, $pH = pK_a + \log\dfrac{[\text{Salt}]}{[\text{Acid}]}$

$$4 = -\log(1.8\times10^{-4}) + \log\frac{[\text{Formate}]}{[\text{Formic acid}]}$$

$$4 = 3.74 + \log\frac{[\text{Formate}]}{[\text{Formic acid}]}$$

$$\log\frac{[\text{Formate}]}{[\text{Formic acid}]} = 4 - 3.74 = 0.26$$

$$\frac{[\text{Formate}]}{[\text{Formic acid}]} = 1.8$$

The buffer capacity of this solution would be maximum near the pK_a of the acid.

$\therefore$ for maximum buffer capacity

$$pH = pK_a = -\log K_a = -\log(1.8\times10^{-4}) = 3.74.$$

81. 100 mL of 0.1 M HCl = 10 m mol of HCl, 100 mL of 0.2 M NH_3 = 20 m mol of NH_3

$$NH_3 + HCl \longrightarrow NH_4Cl$$

NH_4Cl formed = 10 m mol, NH_3 left unreacted = 10 m mol, Volume of solution = 200 mL

$$[NH_3] = \frac{10}{200}\text{ M} = 0.05 \text{ M};\ [NH_4^+] = \frac{10}{200}\text{ M} = 0.05 \text{ M}$$

$$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log(1.8\times10^{-5}) + \log\frac{0.05}{0.05} = 4.74$$

$$pH = 14 - pOH = 14 - 4.74 = 9.26$$

82. (a) pH at 1/4 neutralisation

$$(pH)_1 = pk_a + \log\frac{x/4}{3x/4} = pk_a + \log\frac{1}{3}$$

pH at 3/4 neutralisation

$(pH)_2 = pk_a + \log = pk_a + \log 3$

$\Delta pH = (pH)_2 - (pH)_1 = 2\log 3 = \mathbf{0.9542}$

(b) $4.45 = pk_a + \log\dfrac{x/3}{2x/3} = pk_a - \log 2$

$pk_a = \mathbf{4.751}$

(c) $\Delta pH = 2$, i.e.,

$(pH)_1 = pk_a + 1$, $(pH)_2 = pk_a - 1$

For $pk_a + 1 \Rightarrow \dfrac{[S]}{[A]} = 10$

$$\frac{x}{a-x} = 10 \quad \Rightarrow \quad x = 10a - 10x$$

$$x = \frac{10a}{11}$$

i.e., $\dfrac{10^{th}}{11}$ **stage**

For $pk_a - 1 \quad \Rightarrow \quad \dfrac{[S]}{[A]} = \dfrac{1}{10}$

$$\frac{x}{a-x} = \frac{1}{10}$$

$$x = \frac{a}{11}$$

i.e., $\frac{1}{11}$ th **stage**

83. $Zn(OH)_2(s) \rightleftharpoons Zn^{+2}(aq) + 2OH^-(aq)\ K_{sp}$

$Zn(OH)_2(s) + 2OH^- \rightleftharpoons [Zn(OH)_4]^{-2}(aq)\ K_C$

dissolved $Zn(OH)_2$ is present in form of Zn^{+2} and $[Zn(OH)_4^{-2}]$

so solubility $S = [Zn^{+2}] + [Zn(OH)_4]^{-2}$

$$S = \frac{K_{sp}}{[OH^-]^2} + K_C[OH^-]^2$$

For minimum solubility

$$\frac{ds}{d[OH^-]} = 0 \Rightarrow \frac{-2K_{sp}}{[OH^-]^3} + 2K_C[OH^-] = 0$$

$$[OH^-] = \left(\frac{K_{sp}}{K_C}\right)^{1/4}$$

$[OH^-] = 9.8 \times 10^{-5}$

pOH = 4.00869

pH = **9.9913**

84. $$\begin{array}{ccccc} MA & \longrightarrow & M^{+2} & + & A^{-2} \\ & & S & & S \end{array}$$

Let solubility of MA is S mole L^{-1}.

But some amount of A^{-2} will undergo hydrolysis. Let x is the amount of A^{-2} left in solution.

$$A^{-2} + H_2O \rightleftharpoons HA^- + OH^- \quad \frac{k_w}{k_2}$$

$$HA^- + H_2O \rightleftharpoons H_2A + OH^- \quad \frac{k_w}{k_1}$$

$$\frac{k_w}{k_2} = \frac{[HA^-][OH^-]}{[A^{-2}]} \Rightarrow [HA^-] = \frac{k_w[A^{-2}]}{k_2[OH^-]}$$

$$\frac{k_w}{k_1} = \frac{[H_2A][OH^-]}{[HA^-]} \Rightarrow [H_2A] = \frac{k_w[HA^-]}{k_1[OH^-]}$$

$$[H_2A] = \frac{k_w^2}{k_1k_2}\frac{[A^{-2}]}{[OH^-]^2}$$

From mass balance

$$S = x + \frac{k_w}{k_2}\frac{[A^{-2}]}{[OH^-]} + \frac{k_w^2[A^{-2}]}{k_1k_2[OH^-]^2}$$

$$S = x + \frac{[H^+]x}{k_2} + \frac{[H^+]^2x}{k_1k_2}$$

$$x = \frac{S}{1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2}}$$

$$k_{sp} = [M^{+2}][A^{-2}] = s \cdot x = \frac{s^2}{1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2}}$$

$$S = \sqrt{k_{sp}\left(1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2}\right)}$$

85. $Ka_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}; Ka_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

$$Ka_1 \times Ka_2 = \frac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]} = 10^{-18}$$

$$\therefore \quad \frac{10^{-10} \times [CO_3^{2-}]}{10^{-2}} = 10^{-18}$$

$[CO_3^{2-}] = 10^{-10}$

$\therefore$ $-\log[CO_3^{2-}] = 10$

86. 8 mL of 5×10^{-3} (N) $KMnO_4 \equiv 40 \times 10^{-6}$ equiv $KMnO_4 \equiv 40 \times 10^{-6}$ equivalent $C_2O_4^{2-} \equiv 20 \times 10^{-6}$ mole $C_2O_4^{2-}$

$\therefore$ in the saturated solution of $CaC_2O_4(s)$,

$$[C_2O_4^{2-}] = s = \frac{20 \times 10^{-6}}{200} \times 10^3 = 10^{-4}(M)$$

$\therefore$ for CaC_2O_4, $Ksp = s^2 = 10^{-8}$

$\therefore$ $pKsp = 8$

87. $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{V_1}{V_2}}$

$$\therefore \quad \left(\frac{1}{3}\right)^2 = \frac{300}{V_2}$$

$V_2 = 2700$ mL

$V_{H_2O} = 2700 - 300 = 2400$ ml

88. The initial pH of solution = 5

$$\begin{array}{ccccc} A^- & + HCOOH & \xrightleftharpoons{K_{eq}} & HA & + \quad HCOO^- \\ 10^{-2} & 5 \times 10^{-3} & & 10 \times 10^{-3} & - \\ (10 \times 10^{-3} - x) & (5 \times 10^{-3} - x) & & (10 \times 10^{-3} + x) & x \end{array}$$

$$K_{eq} = \frac{[HA][HCOO^-]}{[A^-][HCOOH]} = \frac{(KA)\ HCOOH}{(Ka)\ HA}$$

$$\therefore \quad \frac{x(10^{-2} + x)}{(10^{-2} - x)(5 \times 10^{-3} - x)} = 10$$

or $x^2 + 10^{-2} \times x$

$= 10(5 \times 10^{-5} - 5 \times 10^{-3} \times x - 10 \times 10^{-3} \times x + x^2)$

or $x^2 + 10 \times 10^{-3} \times x$

$= 10(x^2 - 15 \times 10^{-3} \times x + 5 \times 10^{-5})$

or $x^2 + 10 \times 10^{-3} \times x$

$= 10x^2 - 150 \times 10^{-3} \times x + 5 \times 10^{-4}$

or $9x^2 - 160 \times 10^{-3} \times x + 5 \times 10^{-4} = 0$

or $x = \dfrac{+160 \times 10^{-3} \pm \sqrt{(16)^2 \times 10^{-4} - 4 \times 9 \times 5 \times 10^{-4}}}{2 \times 9}$

or $x = \dfrac{+16 \times 10^{-2} \pm \sqrt{(256 - 180) \times 10^{-4}}}{2 \times 9}$

$= \dfrac{+16 \times 10^{-2} \pm 8.71 \times 10^{-2}}{2 \times 9}$

or $x = 4.05 \times 10^{-3}$

$\therefore$ in the final solution moles of $HCOO^- = 4.05 \times 10^{-3}$
and moles of $HCOOH = 0.95 \times 10^{-3}$

$\therefore \quad HCOOH \xrightleftharpoons{10^{-4}} H^+ + HCOO^-$

$\therefore \quad 10^{-4} = \dfrac{[H^+][HCOO^-]}{[HCOOH]}$

or $\quad [H^+] = \dfrac{10^{-4} \times [HCOOH]}{[HCOO^-]} = \dfrac{10^{-4} \times 0.95 \times 10^{-3}}{4.05 \times 10^{-3}}$

or $\quad [H^+] = \dfrac{0.95}{4.05} \times 10^{-4} = 0.234 \times 10^{-4}$

$= 2.34 \times 10^{-5}$ (M)

$\therefore \quad pH = 5 - \log 2.34 = 5 - 0.369 = 4.631$

$\therefore \quad \Delta pH = 5 - 4.631 = 0.369$

$\therefore \quad \Delta(pH) \times 10^3 = 369$

89. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$
$\qquad x \qquad 2x + 3y$

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$
$\qquad y \qquad 2x + 3y$

Now $x >> y$ because K_{sp} of $Mg(OH)_2 >> K_{sp}$ of $Al(OH)_3$

$\Rightarrow \quad x \times (2x)^2 = 4 \times 10^{-12} \Rightarrow x = 10^{-4}$ ...(1)

and $\quad y \times (2x)^3 = 1 \times 10^{-33}$

$$y = \frac{10^{-33}}{8x^3} = \frac{10^{-33}}{8 \times 10^{-12}} = \frac{10^{-21}}{8}$$

$\Rightarrow \quad \dfrac{x}{y} = \dfrac{10^{-4}}{10^{-21}} \times 8 = 8 \times 10^{17}$ ...(2)

So answer $8 \times 10^{+17} \times 10^{-17} = 8$

90. $Ag_2CrO_4(s) \rightleftarrows 2Ag^+ + CrO_4^{2-}$
$\qquad 2s_1 + 2s_2 \qquad s_1$

$Ag_2C_2O_4(s) \rightleftarrows 2Ag^+ + C_2O_4^{2-}$
$\qquad 2s_2 + 2s_1 \qquad s_2$

$\therefore \quad 4(s_1 + s_2)^2 \times s_1 = 9 \times 10^{-12}$
$\quad 4(s_1 + s_2)^2 \times s_2 = 6 \times 10^{-12}$

or $\quad \dfrac{s_1}{s_2} = 3/2$

or $\quad s_1 = 3/2 s_2$

$\therefore \quad 4 \times \left(\dfrac{5}{2}\right)^2 \times s_2^3 = 6 \times 10^{-12}$

or $\quad s_2^3 = \dfrac{6 \times 10^{-12}}{25} = 24 \times 10^{-14} = 240 \times 10^{-15}$

or $\quad s_2 = (240)^{1/3} \times 10^{-5} = 6.214 \times 10^{-5}$ (M)

$s_1 = 6.214 \times 10^{-5} \times \dfrac{3}{2} = 9.321 \times 10^{-5}$ (M)

$\therefore \quad [Ag^+] = 2(6.214 + 9.321) \times 10^{-5}$
$= 31.07 \times 10^{-5}$

or $\quad [Ag^+] \times 10^5 = 31.07 \simeq 31$

91. **(a, b)** HIn (Red) $\rightleftharpoons H^+ + In^-$ (Blue)

$pH = p^{K}_{In} + \log \dfrac{[In^-]}{[HIn]}$

(a) $pH = (5 - \log 3) + \log\left(\dfrac{25}{75}\right) = 4.05$

(b) $pH = p^{K}_{In} + \log\left(\dfrac{75}{25}\right) = 5 - \log 3 + \log 3 = 5$

92. **(b, c, d)**

pH of

[I] Salts of weak acid and weak base as $RCOONH_4$.

[II] Amphiprotic ions as HCO_3^-, HS^-.

[III] Buffer solutions are not affected by dilution.

Thus (b), (c), (d) are the correct options.

93. **(a, b, d)** At 25°C $K_w = [H^+][OH^-] = 10^{-14}$ for water

94. **(a, c, d)**

For NaA, $K_h = \dfrac{K_W}{K_a} = \dfrac{10^{-14}}{10^{-8}} = 10^{-6}$

For NaB, $K_h = \dfrac{K_W}{K_a} = \dfrac{10^{-14}}{10^{-6}} = 10^{-8}$

For NaC, $K_h = \dfrac{K_W}{K_a} = \dfrac{10^{-14}}{2 \times 10^{-8}} = \dfrac{10^{-6}}{2}$

For NaD, $K_h = \dfrac{K_W}{K_a} = \dfrac{10^{-14}}{10^{-10}} = 10^{-4}$

For NaE, $K_h = \dfrac{K_W}{K_a} = \dfrac{10^{-14}}{10^{-7}} = 10^{-7}$

Since K_h of NaD is the highest, therefore, NaD is most extensively hydrolysed

For NaB pH = $\dfrac{1}{2}(pK_w + pK_a + \log C)$

or $\quad pH = \dfrac{1}{2}\left(14 + 6 + \log\dfrac{1}{10}\right) = \dfrac{1}{2}(20 - 1) = \dfrac{1}{2} \times 19$

or $\quad pH = 9.5$

For isohydric solution, $Ka_1C_1 = Ka_2C_2$

$\because \quad 10^{-7} \times 0.1 = 10^{-6} \times 0.01 = 10^{-8}$

Hence, 0.1(M) HE is isohydric to 0.01(M) HB solution

95. **(c, d)** Solubility of sparing soluble salt decreases due to presence to common ion effect.

$Ksp = S^2$ in water

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$NaCl \rightarrow Na^+ \quad Cl^-$

$\qquad C \qquad C + S'$

KsP = $S'(S' + C)$

$$S' = \frac{\text{KsP}}{C}$$

$\therefore \quad S_1 > S_2 = S_3 > S_4$

96. **(a, b, d)**

$$S_1 = \sqrt{8 \times 10^{-37}}$$

$$S_2 = \sqrt{7 \times 10^{-16}}$$

$$S_3 = \sqrt[5]{10^{-72} \times 108}$$

$$S_4 = \sqrt[4]{1.8 \times 10^{-18} \times 27}$$

$\therefore \quad S_4 > S_2 = S_3 > S_1$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. **(d)** pH = 1

$\therefore \quad [H^+] = 10^{-1} = 0.1$ M

pH = 2

$\therefore \quad [H^+] = 10^{-2} = 0.01$ M

For dilution of HCl,

$M_1V_1 = M_2V_2$

$0.1 \times 1 = 0.01 \times V_2$

$V_2 = 10$ L

Volume of water to be added to 10 – 1 = 9 L

2. **(c)** $HQ \rightleftharpoons H^+ + Q^-$

$[H^+] = \sqrt{K_aC}$ by Ostawald's dilution law

$[H^+] = 10^{-pH} = 10^{-3}$ M

$C = 0.1$ M

Thus, $10^{-3} = \sqrt{K_a \times 0.1}$

$10^{-6} = K_a \times 0.1$

$\therefore \quad K_a = 10^{-5}$

Alternate method

$$HQ \rightleftharpoons H^+ + Q^-$$

Initial concentration 0.1 M 0 0

Given, pH = 3. This suggests $[H^+] = 10^{-3}$ M at equilibrium so $[Q] = 10^{-3}$ m

Hence, $[HQ] = 0.1\text{ M} - 10^{-3}$ M

≈ 0.1 M [10^{-3} M <<< 0.1 M]

K_a for the above reaction is given by

$$K_a = \frac{[H^+][Q^-]}{[HQ]} = \frac{[10^{-3}][10^{-3}]}{[0.1]}$$

$K_a = 1 \times 10^{-5}$

3. **(c)** $H_2A \rightleftharpoons HA^- + H^+$

$$\therefore \quad K_1 = 1.0 \times 10^{-5} = \frac{[H^+][HA^-]}{[H_2A]} \text{ (given)}$$

$$HA^- \rightleftharpoons H^+ + A^{2-}$$

$$\therefore \quad K_2 = 5.0 \times 10^{-10} = \frac{[H^+][A^2]}{[HA^-]} \text{ (given)}$$

$$K = \frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_1 \times K_2$$

$$= (1.0 \times 10^{-5}) \times (5 \times 10^{-10}) = 5 \times 10^{-15}$$

4. **(c)** Let molar solubility of $Cr(OH)_3$ = S mol L^{-1}

$$Cr(OH)_3\,(S) \rightleftharpoons \underset{S}{Cr^{3+}}(aq) + \underset{3S}{3OH^-}(aq) \lim_{x\to\infty}$$

$K_{sp} = 1.6 \times 10^{-30}$

$= [Cr^{3+}][OH^-]^3 = (S)(3S)^3 = 27\,S^4$

$$\therefore \quad S^4 = \frac{1.6 \times 10^{-30}}{27}$$

$$\therefore \quad S = \sqrt[4]{\frac{1.6 \times 10^{-30}}{27}}$$

5. **(a)** pH of a solution = 5

$\therefore \quad [H^+] = 10^{-pH} = 10^{-5}$

HA (a weak acid) ionises as

$HA \rightleftharpoons$	H^+	+ A^-
1.0	0	0
$(1–10^{-5})$	10^{-5}	10^{-5}

$$K_a = \frac{[H^-][A^-]}{[HA]} = \frac{10^{-5} \times 10^{-5}}{(1 - 10^{-5})} = \frac{10^{-10}}{1} \quad [1 >>> 10^{-5}]$$

6. **(a)** Only in reaction (II), $H_2PO_4^-$, gives H^+ to H_2O. Thus, behaves as an acid.

7. **(c)** $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-;\ K_1 = 4.2 \times 10^{-7}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-};\ K_2 = 4.8 \times 10^{-11}$

$K_1 >> K_2$

$\therefore \quad [H^+] = [HCO_3^-]$

$$K_2 = \frac{[H^+][CO_3^{-2}]}{[HCO_3^-]}$$

So, $[CO_3^{2-}] = K_2 = 4.8 \times 10^{-11}$

8. **(b)** $[AgNO_3] = [Ag^+] = 0.05$ M

$K_{sp}[AgBr] = [Ag^+][Br^-]$

$$\Rightarrow \quad [Br^-] = \frac{K_{sp}(AgBr)}{[Ag^+]}$$

$$= \frac{5.0 \times 10^{-13}}{0.05} = 10^{-11}\,[\text{mol L}^{-1}]$$

Moles of KBr needed to precipitate AgBr

$= [Br^-] \times V = 10^{-11}$ mol $L^{-1} \times 1\,L = 10^{-11}$ mol

Therefore, amount of KBr needed to precipitate AgBr

$= 10^{-11}$ mol × 120 g mol^{-1} × 1 L = 1.2×10^{-9} g

9. **(b)** $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$K_{sp} = [Mg^{2+}]\,[OH^-]^2$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1 \times 10^{-11}}{0.001}} = 10^{-4}$$

pOH = –log[OH^-] = –log[10^{-4}]

pOH = 4

$\therefore \quad$ pH = 14 – pOH = 14 – 4 = 10

10. **(b)** $Na_2CO_3 \rightleftharpoons Na^+ + CO_3^{2-}$

$$[Na_2CO_3] = [CO_3^{2-}] = 1 \times 10^{-4}\ M$$

$$BaCO_3 \rightleftharpoons Ba^{2+} + CO_3^{2-}$$

$$K_{sp(BaCO_3)} = [Ba^{2+}][CO_3^{2-}]$$

$$[Ba^{2+}] = \frac{K_{sp}[BaCO_3]}{[CO_3^{2-}]}$$

$$[Ba^{2+}] = \frac{5.1 \times 10^{-9}}{1 \times 10^{-4}}$$

$$[Ba^{2+}] = 5.1 \times 10^{-5}\ M$$

Hence, at 5.1×10^{-5} concentration of Ba^{2+}, a precipitate will begin to form.

11. $AgBr \rightleftharpoons Ag^+ + Br^-$

$$K_{sp} = [Ag^+][Br^-]$$

For precipitation to occur

Ionic product > Solubility product

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5 \times 10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to 1 l $AgNO_3$ solution

∴ number of moles of Br^- needed from KBr $= 10^{-11}$

∴ mass of KBr $= 10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

12. **(b)**

$$\underset{0.034-x}{H_2CO_3(aq)} + H_2O(l) \rightleftharpoons \underset{x}{HCO_3^-(aq)} + \underset{x}{H_3O^+(aq)}$$

$$K_1 = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = \frac{x \times x}{0.034 - x}$$

$$\Rightarrow \quad 4.2 \times 10^{-7}\ \frac{x^2}{0.034} \quad \Rightarrow \quad x = 1.195 \times 10^{-4}$$

As H_2CO_3 is a weak acid so the concentration of H_2CO_3 will remain 0.034 as $0.034 >> x$.

$$x = [H^+] = [HCO_3^-] = 1.195 \times 10^{-4}$$

Now, $\underset{x-y}{HCO_3^-\ (aq)} + H_2O(l) \rightleftharpoons \underset{y}{CO_3^{2-}(aq)} + \underset{y}{H_3O^+(aq)}$

As $HCO^-{}_3$ is again a weak acid (weaker than H_2CO_3) with $x >> y$.

$$K_2 = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = \frac{y \times (x + y)}{(x - y)}$$

Note: $[H_3O^+] = H^+$ from first step (x) and from second step (y) $= (x + y)$

[As $x >> y$ so $x + yx$ and $x - yx$]

So, $\quad K_2 \simeq \dfrac{y \times x}{x} = y$

$$\Rightarrow \quad K_2 = 4.8 \times 10^{-11} = y = [CO_3^{2-}]$$

So the concentration of $[H^+] \simeq [HCO_3^-]$ = concentrations obtained from the first step. As the first step. As the dissociation will be very low in the second step so there will be no change in these concentrations.

$[H^+] = [HCO_3^-] = 1.195 \times 10^{-4}$ and $[CO_3^{2-}] = 4.8 \times 10^{-11}$

13. **(c)** $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$[OH^-] = \frac{K_{sp}}{[Mg^{2+}]} = \sqrt{\frac{1 \times 10^{-11}}{0.001}} = 10^{-4}$$

$$pOH = -\log[OH^-] = -\log[10^{-4}]$$

$$pOH = 4$$

$$\therefore \quad pH = 14 - pOH = 14 - 4 = 10$$

14. **(d)** $Na_2CO_3 \longrightarrow 2Na^+ + CO_3{}^{2-}$

1×10^{-4} M Na_2CO_3 gives 1×10^{-4}M Na^+ and 1×10^{-4}M CO_3^{--}

$$K_{SP}(BaCO_3) = [Ba^{2+}][CO_3{}^{2-}]$$

$$[Ba^{2+}] = \frac{5.1 \times 10^{-9}}{1 \times 10^{-4}} = 5.1 \times 10^{-5}\ M$$

15. **(c)** It corresponds to choice (c) which is the correct answer.

$$BA + H_2O \rightleftharpoons \underset{Base}{BOH} + \underset{Acid}{HA}$$

Now pH is given by

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

Substituting given values, we get

$$pH = \frac{1}{2}(14 + 4.80 - 4.78) = 7.01$$

16. **(b)** Let s = solubility

$$AgIO_3 \rightleftharpoons \underset{S}{Ag^+} + \underset{S}{IO_3^-}$$

$$K_{sp} = [Ag^+][IO_3{}^-] = S \times S = S^2$$

Given: $K_{sp} = 1 \times 10^{-8}$

$$\therefore \quad S = \sqrt{K_{sp}} = \sqrt{1 \times 10^{-8}}$$

$= 1.0 \times 10^{-4}$ mol/lit

$= 1.0 \times 10^{-4} \times 283$ g/lit

(∵ molecular mass of $AgIO_3 = 283$)

$$= \frac{1.0 \times 10^{-4} \times 283 \times 100}{1000}\ \text{gm/100 ml}$$

$= 2.83 \times 10^{-3}$ gm/100 mL

17. **(a)** $MX_2 \rightleftharpoons \underset{S}{M^{+2}} + \underset{2S}{2X^-}$

where s is the solubility of MX_2

then $K_{sp} = 4 \times 10^{-12} = 4S^3$; $S = 1 \times 10^{-4}$

$\therefore \quad [M^{+2}] = S = 1\ [M^{+2}] = 1 \times 10^{-4}$

18. **(c)** $pH = -\log[H^+] = \log\dfrac{1}{[H^+]}$

$$5.4 = \log\frac{1}{[H^+]}$$

On solving, $[H^+] = 3.98 \times 10^{-6}$

19. **(c)** $MX_4 \rightleftharpoons \underset{S}{M^{4+}} + \underset{4S}{4X^-}$

$$K_{SP} = [S][4S]^4 = 256\ S^5$$

$$\therefore \quad S = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

20. **(c)** $Mg(OH)_2 \longrightarrow [Mg^{2+}] + 2[OH^-]$

$$\qquad\qquad x \qquad\quad 2x$$

$K_{sp} = [Mg][OH]^2 = [x][2x]^2 = x.4x^2 = 4x^3.$

21. **(c)** $AB_2 \rightleftharpoons A^{+2} + 2B^-$

$[A] = 1.0 \times 10^{-5}$, $[B] = [2.0 \times 10^{-5}]$,

$K_{sp} = [B]^2[A] = [2 \times 10^{-5}]^2[1.0 \times 10^{-5}]$

$= 4 \times 10^{-15}$

JEE Advanced

Single Correct-Answer Type

22. **(a)**

i. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $k_1 = 3.5 \times 10^{-3}$

ii. $[Ag^+(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$;

$k_2 = 1.7 \times 10^{-3}$

On the basis of above reaction

$$k_1 = \frac{[Ag(NH_3)]^+}{[Ag^+][NH_3]} \qquad \text{....(i)}$$

$$k_2 = \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)]^+[NH_3]} \qquad \text{...(ii)}$$

For the formation of $[Ag(NH_3)_2]^+$

$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$

$$\text{Formation constant (K)} = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \qquad \text{...(iii)}$$

When two equations are added their equilibrium constants are multiplied.

From Eqs (i) and (ii), we get

$k = k_1 \times k_2$

$= 3.5 \times 10^{-3} \times 1.7 \times 10^{-3}$

$= 5.95 \times 10^{-6} = 6.08 \times 10^{-6}$

23. **(d)** $MX \rightarrow M^+ + X^-$ (where s is the solubility)

$$\qquad S \quad S$$

Then $K_{sp} = S^2$ or $S = \sqrt{K_{sp}}$

Similarly for $MX_2 \rightarrow M^{2+} + 2X^-$

$$K_{sp} = S \times (2S)^2 = 4S^3 \text{ or } S = \left[\frac{K_{sp}}{4}\right]^{1/3}$$

and for $M_3X \rightarrow 3M^+ + X^{-3}$

$$\qquad S \quad S$$

Then $K_{sp} = S^2$ or $S = \sqrt{K_{sp}}$

$$K_{sp} = (3S)^3 \times S = 27S^4 \text{ or } S = \left[\frac{K_{sp}}{27}\right]^{1/4}$$

From the given values of K_{sp} for MX, MX_2 and M_3X, we can find the solubilities of those salts at temperature, T

$$\text{Solubility of MX} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$$

$$\text{Solubility of } MX_2 = \left[\frac{3.2 \times 10^{-14}}{4}\right]^{1/3} \text{ or } \left[\frac{32}{4} \times 10^{-15}\right]^{1/3}$$

$$= [8 \times 10^{-15}]^{1/3} \text{ or } 2 \times 10^{-5}$$

$$\text{Solubility of } M_3X = \left[\frac{2.7 \times 10^{-15}}{27}\right]^{1/4}$$

$$= [10^{-16}]^{1/4} \text{ or } 10^{-4}$$

24. **(a)** In acidic solution $[S^{2-}]$ is low. So CuS and HgS (second group cations) will be precipitated more easily due to low K_{sp} value. NiS and MnS (IV group cation) will precipitate if H_2S is passed in basic medium.

25. **(a)** Rate in weak acid $= \frac{1}{100}$ (rate of strong acid)

$$\therefore \quad [H^+]_{\text{weak acid}} = \frac{1}{100}[H^+]_{\text{strong acid}}$$

$$\therefore \quad [H^+]_{\text{weak acid}} = \frac{1}{100}\,M = 10^{-2}\,M$$

$\therefore \quad C\alpha = 10^{-2}$

$\therefore \quad K_a = 10^{-4}$

Hence (a) is correct.

26. **(b)** $K_{sp} = 1.1 \times 10^{-12} = [Ag^+]^2[CrO_4^{-2}]$

$1.1 \times 10^{-12} = [0.1]^2[S]$

$S = 1.1 \times 10^{-10}$

Multiple Correct-Answer Type

27. **(c), (d)**

1. Not buffer since it is a mixture of strong acid and weak acid.
2. Not buffer since it is a mixture of strong base and salt of weak acid/strong base.
3. It is an acidic buffer since some of HNO_3 will react with CH_3COONa to produce weak acid and some CH_3COONa will be left. So buffer is formed

$$\begin{array}{lcccc} & HNO_3 & + \; CH_3COONa & \rightarrow NaNO_3 & + \; CH_3COOH \\ \text{Initial} & x & y & 0 & 0 \\ \text{Final} & — & (y-x) & (y-x) & (y-x) \end{array}$$

4. It is acidic buffer (mixture of weak acid and salt of weak acid/strong base).

Linked Comprehension Type

28. **[A]** Let the heat capacity of insulated beaker be C.

Mass of aqueous content in experiment

$1 = (100 + 100) \times 1 = 200$ g

$\Rightarrow \quad \therefore$ Total heat capacity $= (C + 200 \times 4.2)$ J/K

Mole of acid, base neutralized in Experiment 1

$= 0.1 \times 1 = 0.1$

$\Rightarrow$ Heat released in Expt. $1 = 0.1 \times 5.7 = 5.7$ KJ

$= 5.7 \times 1000$ J

$\Rightarrow \quad 5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta T$

$5.7 \times 1000 = (C + 200 \times 4.2) \times 5.7$

$\Rightarrow \quad (C + 200 \times 4.2) = 1000$

In second experiment

$$N_{CH_3COOH} = 0.2, N_{NaOH} = -0.1$$

Total mass of aqueous content = 200 g

$\Rightarrow$ Total heat capacity = $(C + 200 \times 4.2) = 1000$

$\Rightarrow$ Heat released = $1000 \times 5.6 = 5600$ J

Overall, only 0.1 mol of CH_3COOH undergo neutralisation.

$$\Rightarrow \Delta H_{\text{neutralisation}} \text{ of } CH_3COOH = \frac{-5600}{0.1}$$

$$\Rightarrow \Delta H_{\text{dissociation}} \text{ of } CH_3COOH = 57 - 56 = 1 \text{ kJ/mol.}$$

29. **[B]** Final solution contains 0.1 mole of CH_3COOH and CH_3COONa each.

Hence it is a buffer solution

$$pH = pK_a + \log\left[\frac{CH_3COO^-}{CH_3COOH}\right]$$

$$= 5 - \log 2 + \log\frac{0.1}{0.1} = 4.7$$

Integer Answer Type

30. **(8)** $K_a(C_6H_5COOH) = 1 \times 10^{-4}$

pH of 0.01 M C_6H_5COONa

$$\underset{0.01(1-h)}{C_6H_5COO^-} + H_2O \rightleftharpoons \underset{0.01h}{C_6H_5COO^-} + \underset{0.01h}{OH^{-1}}$$

$$K_h = \frac{K_w}{K_a} = \frac{0.01h^2}{1-h}$$

$$\frac{10^{-14}}{10^{-4}} = \frac{10^{-2}h^2}{1-h} \quad (1 - h \approx 1)$$

$[OH^-] = 0.01\,h = 0.01 \times 10^{-4} = 10^{-6}$

$[H^+] = 10^{-8}$

pH = 8

31. **(c)** KCN, K_2CO_3 and LiCN are the salts of weak acid and strong base. So, their aqueous solution turns red litmus paper blue.

32. **(6)** Diprotic acids are H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_2CrO_4 and H_2SO_3.

33. **(3)** Let the solubility of AgCl is x mol L^{-1}

$$AgCl \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{Cl^-}$$

and that of CuCl is y mol L^{-1} $CuCl \rightleftharpoons \underset{y}{Cu^+} + \underset{y}{Cl^-}$

$\therefore$ K_{sp} of AgCl = $[Ag^+][Cl^-]$

$1.6 \times 10^{-10} = x(x + y)$ …(i)

Similarly K_{sp} of CuCl = $[Cu^+][Cl^-]$

$1.6 \times 10^{-6} = y(x + y)$ …(ii)

On solving Eqs (i) and (ii)

$[Ag^+] = 1.6 \times 10^{-7}$

$\therefore$ $x = 7$