CHEMISTRY
MODULE-II

PHYSICAL CHEMISTRY-II

for

JEE

(MAIN & ADVANCED)

Fully Solved

Ranveer Singh

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Education

CHEMISTRY
MODULE-II

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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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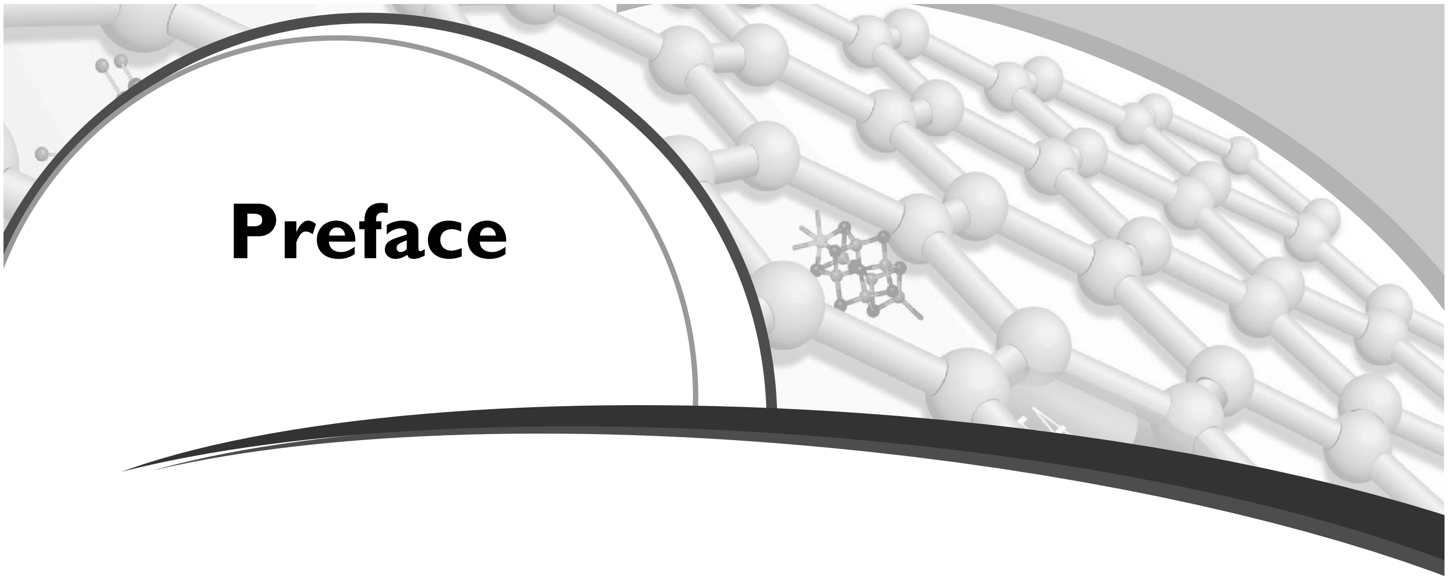
Dedicated
to
Shri Amar Chand Ji Maharaj

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.

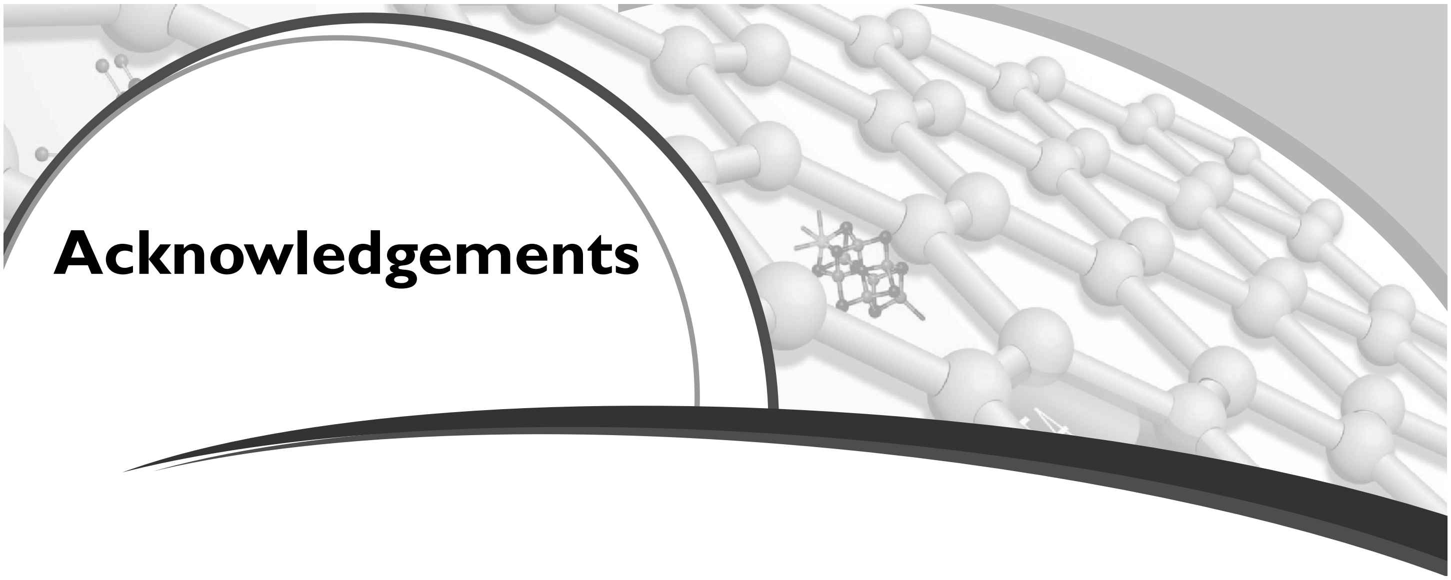
The exercises given at the end of every chapter is further categorised into three difficulty level of questions and their patterns asked in JEE along with the previous year questions with solutions.

- 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).

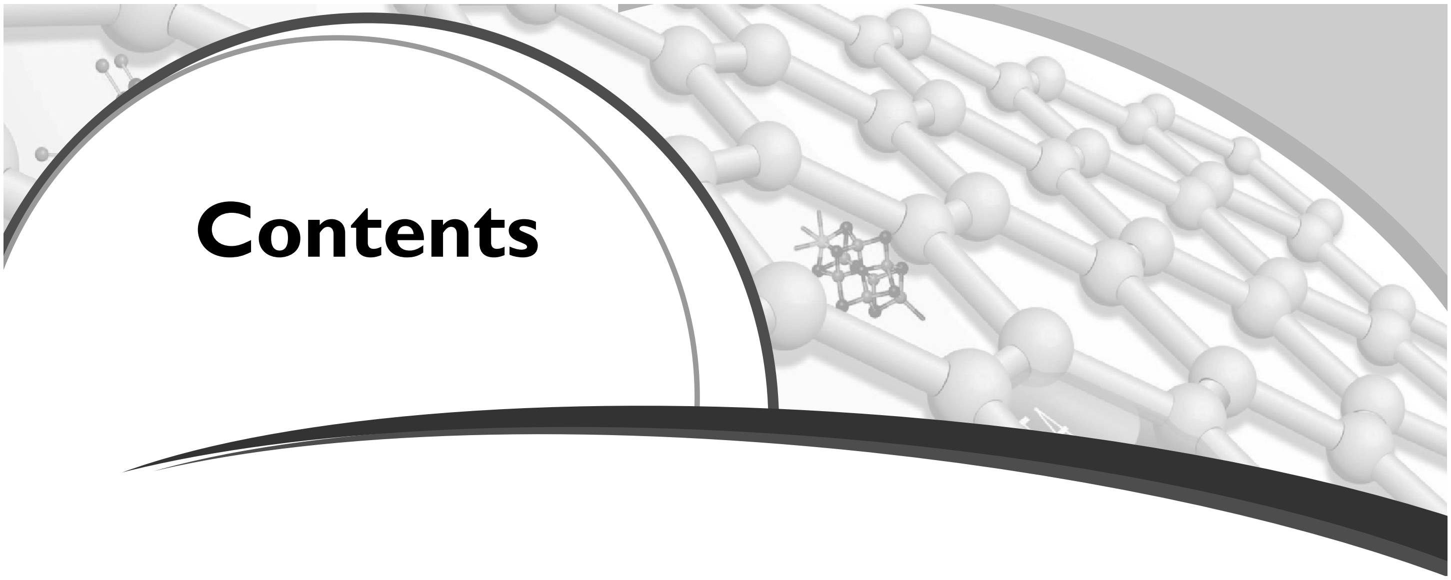
I hope this book will help in motivating and encouraging the students towards the preparation forthe Chemistry portion of the examinations. Every care has been taken to make the book error-free. However, some mistakes may have been crept in inadvertently. Constructive suggestions and comments from students 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

Acknowledgements



I express my gratitude towards the publisher and the members of the editorial team. I would be failing in my duty if I don’t express my thankfulness to Mr. Sanjay Agrawal for encouraging me to start writing this book and helping me step by step while preparing the manuscript.



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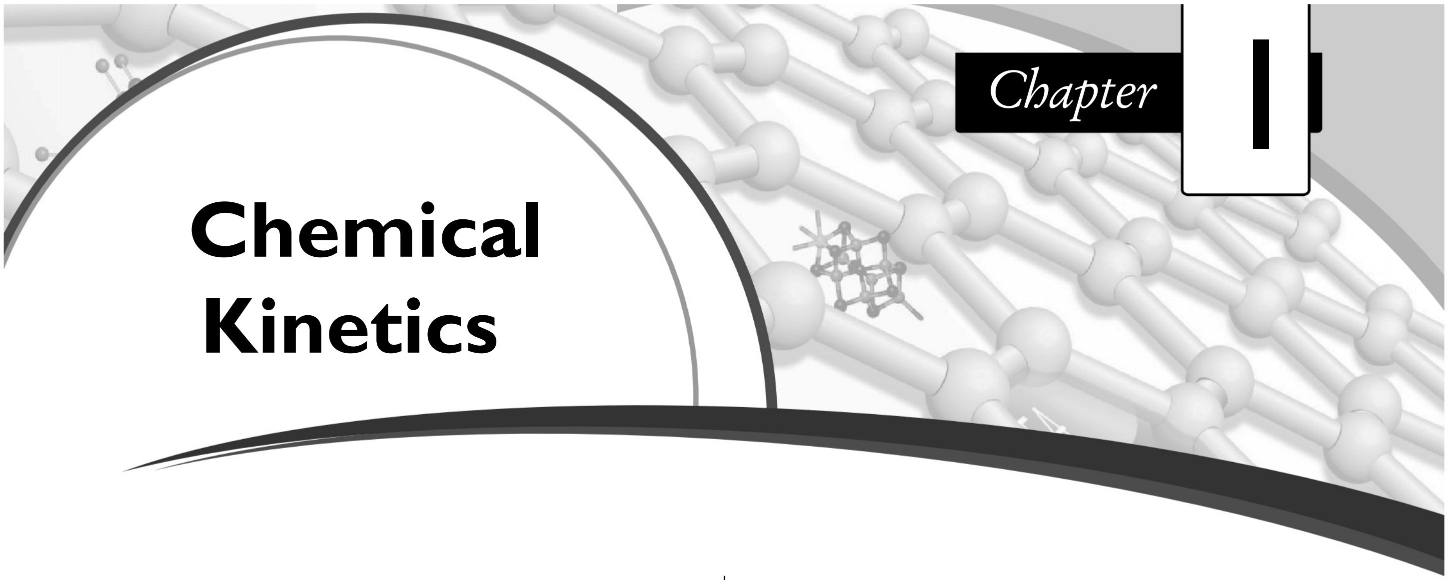


Chapter 1

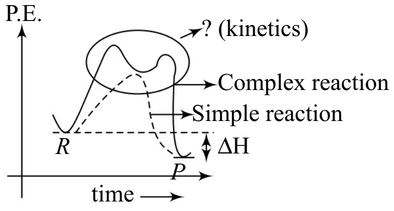
Chemical Kinetics

Key Concepts

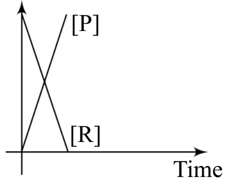
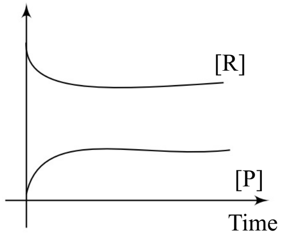
INTRODUCTION TO KINETICS

Thermodynamics deals with the feasibility of the reaction but kinetic deals with the rate of the reaction.

Thermodynamics deals with the initial and final state of the reactants and products but kinetics deal with the path by which reaction is taking place.

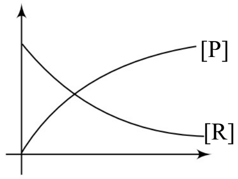


CLASSIFICATION OF CHEMICAL REACTION

Very fast	Very Slow
$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$ $HCl + NaOH \rightarrow NaCl + H_2O$	$Fe + \frac{1}{2}O_2 \xrightarrow{25°C} FeO$ $\text{Cellulose} \xrightarrow[25°C]{[O]} CO_2 + H_2O$
	

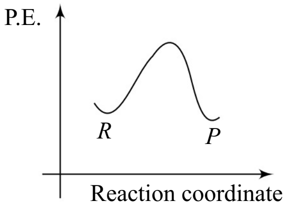
Moderate

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$



Simple reaction

Those chemical reactions which takes place in a single step are known as simple reaction.

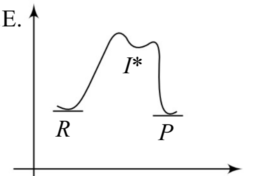


$$aA + bB \rightarrow P$$

$$r = K[A]^a[B]^b$$

Complex

Those chemical reactions which take in more than one step.



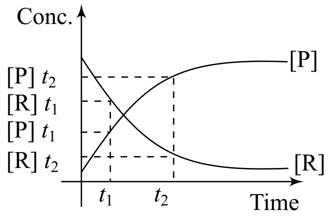
$$aA + bB \rightarrow P$$

$$r = k[A]^m\,[B]^n$$

$$(m, n) \neq (a, b)$$

Rate of reaction

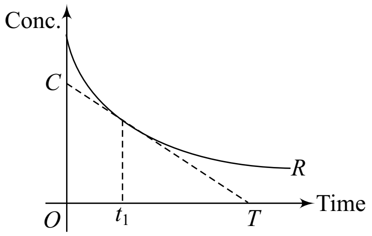
(1) Average Rate: $\left|\frac{\Delta C}{\Delta t}\right|$



$$\left|\frac{\Delta C}{\Delta t}\right| = -\left[\frac{[R]_{t_2}-[R]_{t_1}}{t_2-t_1}\right] = \frac{[P]_{t_2}-[P]_{t_1}}{t_2-t_1}$$

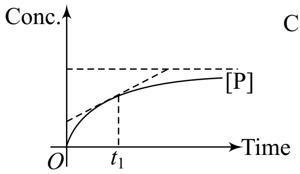
–Ve sign indicate decrease in concentration of reactant

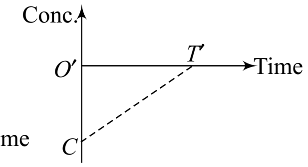
Units of reaction rate: $\frac{\text{moles}}{\ell - \text{sec}}$ or M/sec^{-1}



$$\left(\frac{dc}{dt}\right)_{t=t_1} = \frac{\text{OC}}{\text{OT}}$$

In general, rate of reaction changes with time





$$\left(\frac{dc}{dt}\right)_{t=t_1} = \frac{\text{CO}'}{\text{O}'\text{T}'}$$

Factors affecting rate of the reaction:

(1) Nature of reactants

$$C(\text{graphite}) + O_2 \xrightarrow[K_1]{700°\text{C}} CO_2 \quad \boxed{K_1 > K_2} \quad \therefore r_1 > r_2$$

$$C(\text{diamond}) + O_2 \xrightarrow[K_2]{700°\text{C}} CO_2$$

(2) Concentration or volume or pressure

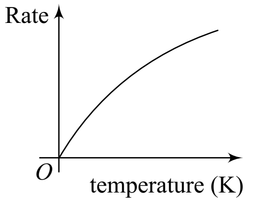
$$aA(g) + bB(g) \rightarrow P \qquad [A] = \frac{n_A}{V} = \frac{P_A}{RT}$$

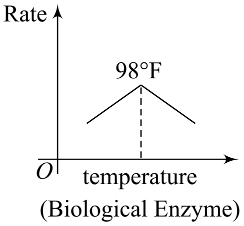
$$\text{Rate} = K[A]^m[B]^n$$

$$= \frac{K}{(RT)^{m+n}}(P_A)^m(P_B)^n$$

(3) Temperature

Rate of the reaction generally increases with the increases in temperature.

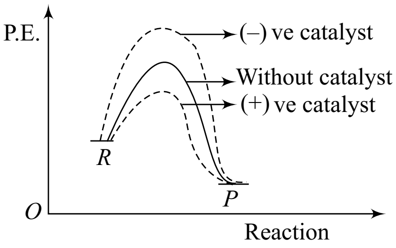




At $T \rightarrow \infty$; maximum rate

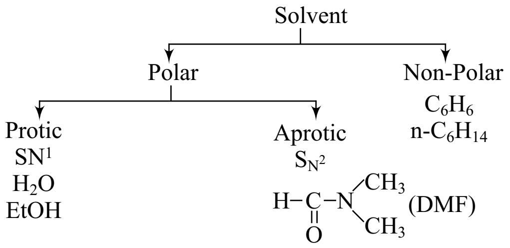
For majority of the reaction; on increasing temperature by 10°C rate of the reaction increases two to three times.

(4) Catalyst



Catalyst increases the rate of reaction

(5) Solvent



(6) Surface area

For reaction involving solid surface area,

rate ∝ surface Area

(7) Radiation

$$CH_4 + Cl_2 \xrightarrow[hv]{25°\text{C}} CH_3 - Cl + H - Cl$$

$$CH_4 + Cl_2 \xrightarrow[\text{Dark}]{25°\text{C}} \text{NO reaction}$$

Rate Constant (K)/Velocity constant/Specific reaction rate

Rate constant is defined as the rate of the reaction. When concentration of each reactant is unity.

$$aA + bB \longrightarrow \text{P}$$

$$\text{rate} = K[A]^m\,[B]^n$$

If $[A] = 1$ M

and $[B] = 1$ M

then rate = K

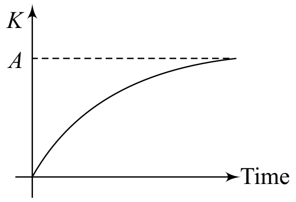
Characteristic of Rate constant (K)

Rate constant for any particular reaction is constant at constant temperature. It does not change with concentration volume, pressure, time, etc.

Catalyst increases rate constant 'k'.

K depends on temperature.

$$K = Ae^{-\frac{Ea}{RT}}$$



$$\text{Temperature Coefficient } (\mu) = \frac{K_{T+10}}{K_T} = 2 \text{ to } 3$$

Higher the value of rate constant; more will be the rate of the reaction

Higher value of rate constant; suggest reactant is kinetically unstable.

Graphite at 700°C is kinetically unstable than diamond

Units of rate const. (K)

$$R \longrightarrow P$$

Rate = $K[R]^m$ Order of reaction(m)

$$\frac{\text{Moles}}{\ell - \text{sec}} = K\left(\frac{\text{mole}}{\ell}\right)^m$$

$$K = \left(\frac{\text{moles}}{\ell}\right)^{1-m} \cdot \frac{1}{\text{sec}} = \frac{M^{1-m}}{\text{sec}}$$

Rate Law

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = \frac{1}{a}\left(-\frac{d[A]}{dt}\right) = \frac{1}{b}\left(-\frac{d[B]}{dt}\right) = \frac{1}{c}\left(+\frac{d[C]}{dt}\right)$$

$$= \frac{1}{d}\left(+\frac{d[B]}{dt}\right) = k[A]^m[B]^n$$

$-\dfrac{d[A]}{dt} \rightarrow$ rate of disappearance of A.

$+\dfrac{d[C]}{dt} \rightarrow$ rate of formation of C.

$m \rightarrow$ order w.r.t. A.

$n \rightarrow$ order w.r.t. B.

$m + n \rightarrow$ overall order of the reaction.

Relation between different rate constants

$$-\frac{d[A]}{dt} = K \cdot a[A]^m[B]^m = K_A[A]^m[B]^n$$

$$-\frac{d[B]}{dt} = K \cdot b[A]^m[B]^m = K_B[A]^m[B]^n$$

$$+\frac{d[C]}{dt} = K \cdot c[A]^m[B]^m = K_C[A]^m[B]^n$$

$$+\frac{d[D]}{dt} = K \cdot d[A]^m[B]^m = K_D[A]^m[B]^n$$

$$K = \frac{K_A}{a} = \frac{K_B}{b} = \frac{K_C}{c} = \frac{K_D}{d}$$

Molecularity

For a single step reaction: Molecularity is defined as number of reactant molecules participating in balanced chemical reaction. Molecularity of reaction is generally 1 or 2. For few reaction it is also observed to be 3.

Molecularity cannot be more than 3 because probability of more than 3 molecules colliding at the same instance is almost zero.

Molecularity cannot be –ve, zero, or fraction.

For complex reaction : each step has its own molecularity

$$R \longrightarrow P$$

If mechanism $R \longrightarrow P^* + Q^*$

$$P^* + Q^* \longrightarrow I^*$$

$$I^* \longrightarrow P$$

but overall molecularity has no significance.

For elementary reaction; molecularity and order are same.

Molecularity of a single step reaction can be obtained by reaction stoichiometry.

Example (1) $A \longrightarrow B$

or

$A \longrightarrow B + C$ **Molecularity = 1**

Example (2) $2A \longrightarrow P$

or

$A + B \longrightarrow P$

or

$A \longrightarrow 1/2\ P$ **Molecularity =2**

Example (3) $3A \longrightarrow P$

or

$A \longrightarrow 1/3\ P$

or

$2A + B \longrightarrow P$ **Molecularity = 3**

Unimolecular: $N_2O_5 \longrightarrow N_2O_3 + O_2$

Bimolecular: $H_2 + Cl_2 \longrightarrow 2HCl$

Tri/ter molecular: $2H_2 + O_2 \longrightarrow 2H_2O$

Order of the reaction

In the expression of rate law, order is defined as (coefficient) of active mass.

$$aA + bB \longrightarrow P$$

Rate = $K[A]^m\ [B]^n$

m = Order w.r.t. A

n = Order w.r.t. B

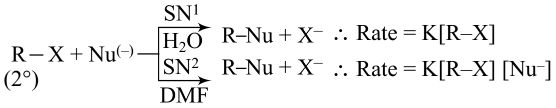
$(m + n)$ = overall order of reaction

Order of any reaction can be obtained only by experimental methods.

Order of reaction may have –ve, +ve, zero or fractional value.

Order of reaction is related with reaction mechanism.

∵ reaction mechanism may change with experiment condition order may also change with reaction condition:



Zero order reaction

$$\begin{array}{lcc} & A & \rightarrow P \\ t=0 & a & — \\ t & (a-x) & x \end{array}$$

$$\text{Rate} = \frac{-d[A]}{dt} = \frac{+d[P]}{dt} = K[A]^{\circ} \qquad \text{(i)}$$

$$\frac{-d[A]}{dt} = K \qquad \text{[or]} \qquad \frac{+d[P]}{dt} = K$$

$$\int_0^{a-x} -d[A] = K\int_0^{f} dt \qquad \Bigg| \qquad \int_0^{x} dx = K\int_0^{t} dt$$

$$(a-x) - a = -Kt \qquad \Big| \qquad x = Kt \qquad \text{(ii)}$$

$$(a-x) = -Kt + a$$

$$[A]_t = -Kt + [A]_0 \qquad \text{(iii)}$$

Half-life of zero order reaction

$x = Kt$

at $t = t½ = t_{50\%}$ = when $x = a/2$

$$t_{1/2} = \frac{a}{2K} \qquad \text{(iv)}$$

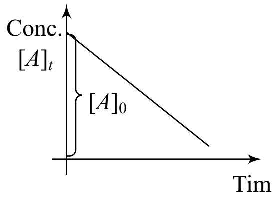
$$\ln t_{1/2} = \ln a + \ln\left(\frac{1}{2K}\right) \qquad \text{(v)}$$

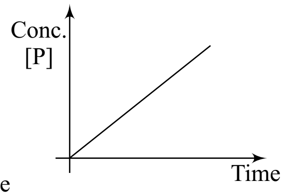
Time of completion for zero order reaction.

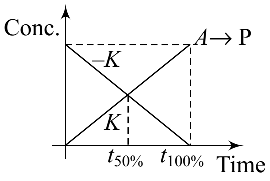
$x = Kt$

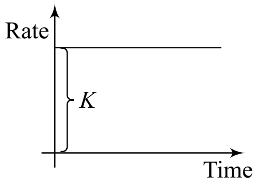
$$t_{100\%} = \frac{a}{K} = 2 \times t_{1/2} \text{ or } 2 \times t_{50\%}$$

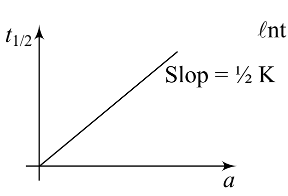
Few graphs related to zero order reaction

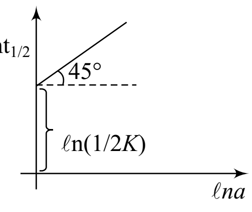












Characteristics of zero order reaction

(1) Rate is independent of concentration and does not changes as the reaction progress.

$$\text{Rate} = \frac{K[A]}{[A]+K'}$$

If $[A] >> K'$ then, Rate $= \dfrac{K[A]}{[A]}$

(2) Half-life of zero order reaction

	A	$\rightarrow$ P
$t = 0$	100	–
$t = 10$ min	50	50
$t = 15$ min	25	75
$t = 17.5$ min	12.5	87.5

Form the above information, reaction is zero order reaction.

We know $t_{1/2} \propto \dfrac{1}{a^{n-1}}$

$$\frac{(t_{1/2})_{\text{I}}}{(t_{1/2})_{\text{II}}} = \left(\frac{a_{\text{II}}}{a_{\text{I}}}\right)^{n-1}$$

$$\Rightarrow \quad \frac{10}{5} = \left(\frac{50}{100}\right)^{n-1} = 2 = 2^{1-n}$$

$\Rightarrow \quad n = 0.$

(3) Zero order reaction is 100% completed.

(4) For zero order reaction in the same time interval, equal amount of reactants are consumed and concentration of reactants at the same time intervals are in A.P. with C.D. –Kt.

$$\begin{array}{ll} & A \longrightarrow P \\ t=0 & a \\ t & a-Kt \\ 2t & a-K(2t) \\ 3t & a-K(3t) \\ & x = Kt \end{array}$$

Examples:

(1) Photochemical reaction

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

(2) Reaction taking place at the solid catalyst surface.

$$C_2H_2 + H_2 \xrightarrow{\text{Ni}} C_2H_6$$

First order reaction

$$\begin{array}{lcc} & A & \longrightarrow \quad P \\ t=0 & \text{a M} & — \\ t & (a-x) & x \end{array}$$

$$\text{Rate} = \frac{-d[A]}{dt} = \frac{+d[P]}{dt} = K[A]^1 \qquad \text{(i)}$$

$$\int_a^{a-x} \frac{-d[A]}{[A]} = K\int_0^{t} dt$$

$$\Rightarrow \quad \ln(a-x) - \ln a = -Kt$$

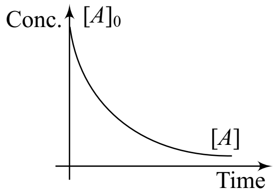
$$\Rightarrow \quad \ln(a-x) = -Kt + \ln a \qquad \text{(ii)}$$

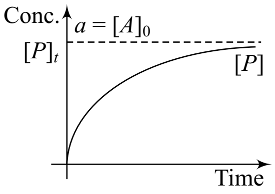
$$\ln\frac{a-x}{a} = -Kt \Rightarrow a - x = ae^{-Kt}$$

$$\ln\frac{a}{a-x} = Kt \qquad \text{(iii)}$$

$$\boldsymbol{K = \frac{2.303}{t}\log_{10}\frac{a}{a-x}} \qquad \text{(iv)}$$

Few graph related to first order reaction





$(a - x) = ae^{-kt}$

$x = a(1 - e^{-kt})$

Degree of dissociation of first order reaction

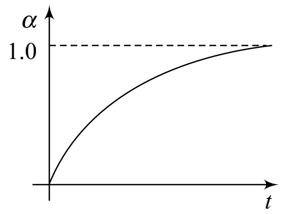
$A \longrightarrow P$

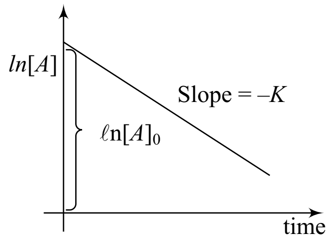
$a \quad —$

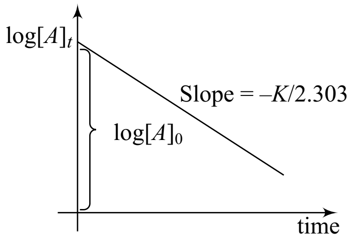
$a - x$

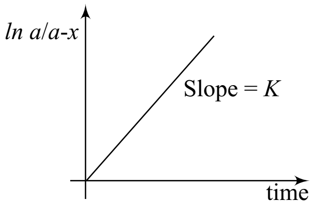
$a(1 - x/a)$

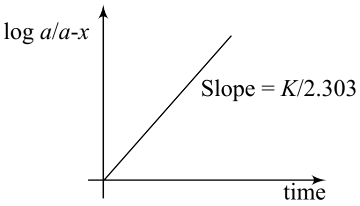
$$\alpha = \frac{x}{a} = 1 - e^{-kt}$$

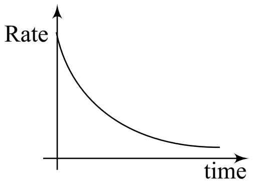












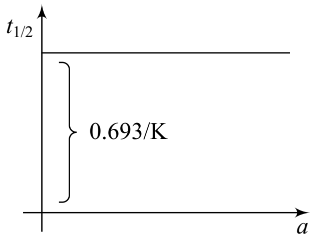
$\text{Rate} = K[A]_t = K[A]_0\, e^{-[Kt]}$

Half-life of first order reaction

$$K = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$K = \frac{2.303}{t_{1/2}}\log\frac{a}{a-a/2} \Rightarrow K = \frac{2.303}{t_{1/2}}\log 2$$

$$\Rightarrow \quad t_{1/2} = \frac{0.693}{K} = \frac{\ln 2}{K} \quad \text{or} \quad t_{1/2} \propto \frac{1}{a^{1-1}}$$



	A	⟶	P
$t = 0$	100		—
$t = 10$ min	50		50
$t = 20$ min	25		75
$t = 30$ min	12.5		87.5

Characteristic of first order reaction

(1) In first order reaction, in equal time interval, same fraction of reactants are consumed and concentration of reactants at same time interval are in GP with a common ratio e^{-Kt}.

	A	⟶	P
$t = 0$	a		
t	ae^{-Kt}		
$2t$	$ae^{-K(2t)}$		
$3t$	$ae^{-K(3t)}$		

Since $[A]_t = [A]_0\, e^{-Kt}$

(2) Rate $\propto [A]_t$

(3) $t_{1/2} \propto \frac{1}{a^{1-1}}$ and $t_{1/2} = \frac{0.693}{K}$

Examples of first order reaction

(1) $CH_3COOEt + H_2O \xrightarrow{H^+} CH_3COOH + EtOH$

(2) $2H_2O_2 \longrightarrow 2H_2O + O_2$

(3) All nuclear reaction

(4) Decomposition of N_2O_5

Second order reaction

Case I: When concentration of both reactants are same

	A	⟶	P
$t = 0$	a		–
$t = 1$	$a - x$		x

or $$\frac{dx}{dt}\int_0^x (a-x)^{-n} = \frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

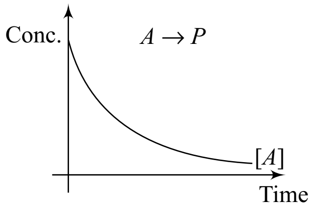
$$\frac{dx}{dt} = K(a-x)^2 \quad \text{So} \quad \int_0^x (a-x)^{-2}\,dx = \int_0^t K\,dt$$

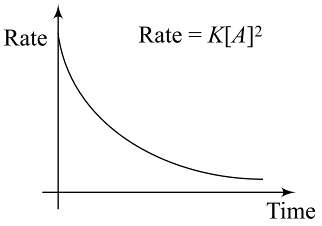
$$\Rightarrow \quad Kt = \frac{1}{a-x} - \frac{1}{a} = \frac{1}{[A]_t} - \frac{1}{[A]_0}$$

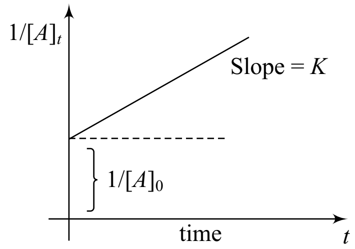
Half-life of second order reaction

$$t_{1/2} = \frac{1}{K \cdot a}$$

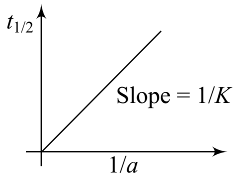
Graphical representation of second order reaction



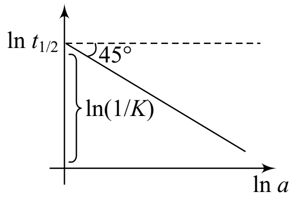




$$\text{since}\ \frac{1}{a-x} = Kt + \frac{1}{a}$$



$$\text{Since}\ t_{1/2} = \frac{1}{K} \times \frac{1}{a}$$



$$\ln t_{1/2} = \ln(1/K) + \ln(1/a)$$
$$\ln t_{1/2} = \ln(1/K) - \ln a$$

Characteristics of second order reaction:

$$A \longrightarrow P$$

(1) Rate = $K[A]^2$

(2) $t_{1/2} \propto \dfrac{1}{a^{2-1}}$

	A $\longrightarrow$	P
$t = 0$	100	–
$t = 10$	50	50
$t = 30$	25	75
$t = 70$	12.5	87.5

(3) At equal time interval, concentration of reactants are in H.P.

$$K(t) = \frac{1}{[A]_t} - \frac{1}{[A]_0} \qquad (2)$$

$$K(2t) = \frac{1}{[A]_{2t}} - \frac{1}{[A]_0} \qquad (1)$$

$$K(3t) = \frac{1}{[A]_{3t}} - \frac{1}{[A]_0} \qquad (3)$$

Eq. (2) – (1) = Eq. (3) – (2)

$$= Kt = \frac{1}{[A]_{2t}} - \frac{1}{[A]_t}$$

Examples of second order reaction

(1) Hydrolysis of ester in basic medium

(2) Decomposition of actatdehyde

$$CH_3CHO \longrightarrow CH_4 + CO$$

Case II: When concentration of both reactants are different

	A	+	B	$\rightarrow$	P
$t = 0$	a		b		–
$t = t$	$a - x$		$b - x$		x

$$\frac{dx}{dt} = K(a-x)(b-x)$$

$$\int_0^x \frac{dx}{(a-x)(b-x)} = K\int_0^t dt$$

$$\Rightarrow \quad \frac{1}{(a-b)}\int_0^x \left[\frac{(a-x)-(b-x)}{(a-x)(b-x)}\right]dx = K(t-0)$$

$$\Rightarrow \quad \frac{1}{(a-b)}\left[\int_0^x \frac{1}{(b-x)}dx - \int_0^x \frac{1}{(a-x)}dx\right] = Kt$$

$$\Rightarrow \quad \frac{1}{(a-b)}\left[\ln\frac{b}{b-x} - \ln\frac{a}{a-x}\right] = Kt$$

$$\Rightarrow \quad \frac{1}{(a-b)}\ln\left[\frac{b}{(b-x)} \cdot \frac{(a-x)}{a}\right] = Kt$$

Special case

If concentration of A is too greater than B.

$[A] >> [B]$

$a - x \simeq a$

$K' = \dfrac{1}{t}\ln\dfrac{b}{b-x}$ 1st order w.r.t. $[B]$

Rate = $K[A]^0[B]^1$

$$H_2O + CH_3COOC_2H_5 \xrightarrow{H^+} EtOH + CH_3COOH$$

(excess) Rate = $K'[\text{ester}]^1$ (Pseudo unimolecular)

Nth order

	A	$\longrightarrow$	P
$t = 0$	a		–
$t = t$	$a - x$		x

$$\frac{dx}{dt} = K(a-x)^n$$

$$\int_0^x \frac{dx}{(a-x)^n} = K\int_0^t dt$$

$$Kt = \frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

Half-life of n^{th} order reaction

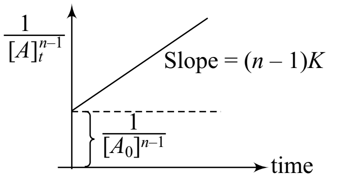
$$Kt_{1/2} = \frac{1}{(n-1)}\left[\frac{1}{(a-a/2)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

$$t_{1/2} = \frac{1}{K(n-1)}\frac{2^{n-1}-1}{a^{n-1}} = \frac{C}{a^{n-1}}$$

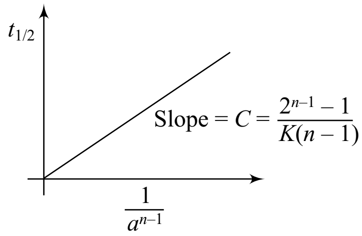
$$C = \frac{2^{n-1}}{K(n-1)} \text{ for } n \neq 1 \therefore t_{1/2} \propto \frac{1}{a^{n-1}}$$

Graph related to n^{th} order reaction

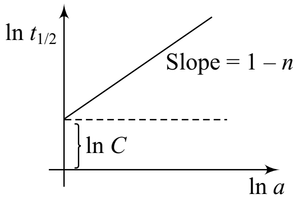
(i) $\dfrac{1}{[A]_t^{n-1}} = (n-1)Kt + \dfrac{1}{[A]_0^{n-1}}$



(ii) $t_{1/2} = C \cdot \dfrac{1}{a^{n-1}}$



(iii) $\ln t_{1/2} = \ln C - (n-1) \ln a$



Prediction of order of the reaction

(1) Initial rate method or different method

$$A + B \longrightarrow P$$

$$\text{Rate} = \frac{dx}{dt} = K[A]^m[B]^n$$

Exp. No.	$[A]_0$	$[B]_0$	Initial Rate (M sec^{-1})
1.	x	y	z
2.	$2x$	y	$4z$
3.	$2x$	$2y$	$8z$
4.	p	q	x

$z = K(x)^m (y)^n$ (i)

$4z = K(2x)^m (y)^n$ (ii)

$8z = K(2x)^m (2y)^n$ (iii)

$m = 2, n = 1$

Rate = $K[A^2][B]$

(2) Using integrated rate equation (Hit and Trial)

	A	$\rightarrow$	P
$t = 0$	a		–
t_1	$a - x_1$		x_1
t_2	$a - x_2$		x_2
⋮	⋮		
⋮	⋮		

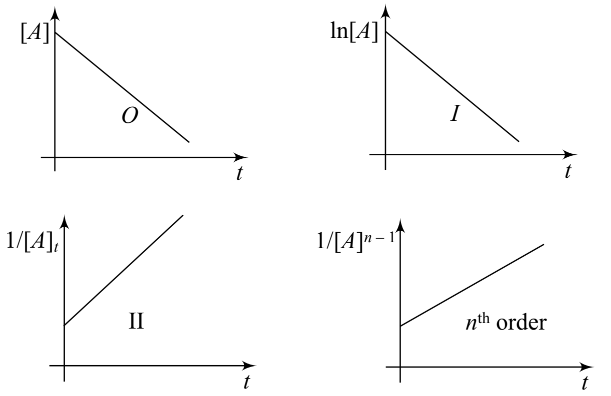
Zero order reaction

$$K = \frac{x}{t} \Rightarrow K = \frac{x_1}{t_1} = \frac{x_2}{t_2} = \frac{x_3}{t_3}$$

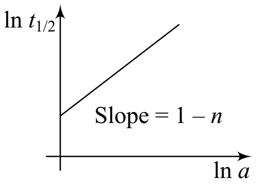
$$K = \frac{2.303}{t}\log\frac{a}{a-x} \quad \text{if } K_1 = K_2 = K_3 \ldots \text{ first order}$$

$$K = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right] \quad \text{if } K_1 = K_2 = K_3 \ldots \text{ second order}$$

(3) Graphical method using concentration



(4) Graphical method using half-life



(5) Half-life method
For n^{th} order reaction:

$$t_{1/2} = \frac{C}{a^{n-1}}$$

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\frac{\ln\frac{t_1}{t_2}}{\ln\frac{a_2}{a_1}} = n-1 \Rightarrow n = 1 + \frac{\ln t_1 - \ln t_2}{\ln a_2 - \ln a_1}$$

Concentration terms replaced by other terms in first order integrated equation.

	$A \xrightarrow{\text{Ist order}} P$	
$t = 0$	aM	–
$t = t$	$a - x$	x

$$\frac{a}{a-x} = \frac{[A]_0}{[A]_t} = \frac{(n_A)_0}{(n_A)_t} = \frac{(W_A)_0}{(W_A)_t} = \frac{(\text{No. of } A)\ at\ t=0}{(\text{No. of } A) at\ t=t}$$

$$= \frac{(P_A)_0}{(P_A)_t} \text{ for gas since } P \propto n \text{ (If } V \text{ and } T \text{ const.)}$$

(1) Concentration term replaced by partial pressure

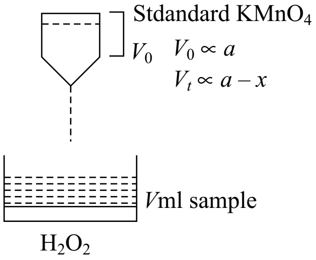
$$\begin{array}{llll} & A(g) \rightarrow & B(g) + & C(g) \\ t=0 & P_0 & - & - \\ t=t & P_0 - p & p & p \end{array}$$

$$P_T = (P_0 - p) + p + p$$
$$P_T = P_0 + p$$
$$p = P_T - P_0$$
$$\therefore \quad P^\circ - p = P_0 - (P_T - P_0) = 2P_0 - P_T$$
$$P_0 \propto a \text{ and } P_0 - P \propto (a - x)$$

$$K = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_T}$$

$$\frac{a}{a-x} = \frac{P_0}{P_0 - p} = \frac{P_0}{2P_0 - P_T}$$

(2) Concentration term replaced by volume of reagent used in titration



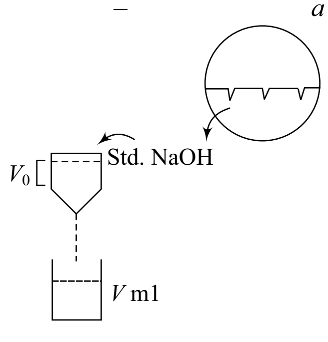
$$\begin{array}{lll} & 2H_2O_2 \xrightarrow{\text{1st order}} & 2H_2O + O_2 \\ t=0 & a & - \\ t=t & a-x & x \end{array}$$

$$K = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

V_0 → Vol. of $KMnO_4$ used in titration against V ml sample of Solution of H_2O_2 at $t = 0$.

(3) Hydrolysis of ester in acidic medium

$$\begin{array}{llll} CH_3COOC_2H_5 + & H_2O \xrightarrow{H^+} & CH_3COOH + & EtOH \\ a & - & - & - \\ a-x & - & x & x \\ - & - & a & a \end{array}$$



$$V_0 \propto H^+ \qquad \text{(i)}$$
$$V_t \propto H^+ + x \qquad \text{(ii)}$$
$$V_\infty \propto H^+ + a \qquad \text{(iii)}$$
$$V_\infty - V_0 \propto a \qquad \text{(iv)}$$
$$V\infty - V_t \propto a - x \qquad \text{(v)}$$

$$K = \frac{2.303}{t}\log\left[\frac{a}{a-x} = \frac{V_\infty - V_0}{V_\infty - V_t}\right]$$

(4) Inversion of cone sugar

$$\begin{array}{lllll} \text{optical rot. } (+r_1^0) & & & +r_2^0 & -r_3^0 \\ C_{12}H_{22}O_{11} + & H_2O & \longrightarrow & C_6H_{12}O_6 + & C_6H_{12}O_6 \\ & & & (G) & (F) \\ t=0 & a & - & - & - \\ t=t & a-x & - & x & x \\ t\rightarrow\infty & - & - & a & a \end{array}$$

$$|r_2^0| < |r_3^0|$$

$$r^0 = ar_1^0 \qquad \text{(i)}$$
$$r^t = (a-x)r_1^0 + xr_2^0 - xr_3^0 \qquad \text{(ii)}$$
$$r^\infty = ar_2^0 - ar_3^0 \qquad \text{(iii)}$$

From (i) and (ii); (i) and (iii)

$$\frac{-r^t t + r^0}{r_1^0 - r_2^0 + r_3^0} = x \quad \text{and} \quad \frac{r^0 - r^\infty}{r_1^0 - r_2^0 + r_3^0} = a$$

$$a - x = \frac{r^t - r^\infty}{r_1^0 - r_2^0 + r_3^0}$$

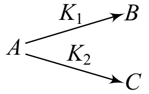
$$\frac{a}{a-x} = \frac{r^0 - r^\infty}{r^t - r^\infty}$$

$$\boldsymbol{k = \frac{2.303}{t}\log\frac{r^0 - r^\infty}{r^t - r^\infty}}$$

Parallel Reaction

$$A \xrightarrow{K_1} B$$
$$A \xrightarrow{K_2} C$$

OR



Rate of decomposition of 'A', $\frac{-d[A]}{dt} = K_1[A] + K_2[A]$
$= [K_1 + K_2][A]$

$$K_1 + K_2 = \frac{1}{t}\ln\frac{[A]_0}{[A]_t}$$

$$[A]_t = [A]_o \cdot e^{-[K_1+K_2]\times t}$$

Rate of formation of 'B'$= \frac{d[B]}{dt} = K_1[A]$

Rate of formation of 'C'$= \frac{d[C]}{dt} = K_2[A]$

$$= \frac{d[B]}{d[C]} = \frac{K_1}{K_2} \Rightarrow \frac{[B]}{[C]} = \frac{K_1}{K_2}$$

$$\% \text{ yield of } B = \frac{K_1}{K_1 + K_2} \times 100$$

$$\% \text{ yield of } C = \frac{K_2}{K_1 + K_2} \times 100$$

$$[A]_0 = [A]_\text{t} + [B]_t + [C]_t$$

eg:

$$A \begin{array}{l} \xrightarrow{K_1} 2B \\ \xrightarrow[K_2]{} 3C \end{array} \qquad \text{or} \qquad \begin{array}{l} A \xrightarrow{K_1} 2B \\ A \xrightarrow{K_2} 3C \end{array}$$

K_1 and K_2 are dissociation constants of A

$$-\frac{d[A]}{dt} = [K_1 + K_2][A]$$

$$[A_0] = [A]_t + \frac{[B]_t}{2} + \frac{[C]_t}{3}$$

$$\frac{d[B]}{dt} = 2K_1[A] = K_B[A]$$

$$\frac{dC}{dt} = 3K_2[A]$$

$$\frac{[B]}{[C]} = \frac{2K_1}{3K_2} \text{ and } \% B = \frac{2K_1}{2K_1 + 3K_2} \times 100$$

$$\% C = \frac{3K_2}{2K_1 + 3K_2} \times 100$$

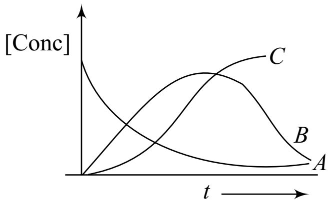
Reaction in series

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

Rate of decomposition of $A = \dfrac{-d[A]}{dt} = K_1[A]$

Rate of formation of $B = K_1[A] - K_2[B]$

Rate of formation of $C = K_2[B]$



$$\frac{dB}{dt} = K_1[A] - K_2[B] \Rightarrow \frac{dB}{dt} + K_2[B] = K_1[A]_0 e^{-K_1 t}$$

On multiplying by $e^{K_2 t}$ on both sides

$$e^{K_2 t} \cdot \frac{d[B]}{dt} + K_2 e^{K_2 t}[B] = K_1[A]_0 e^{(K_2 - K_1)t}$$

$$\frac{d[e^{K_2 t}[B]]}{dt} = K_1[A]_0 e^{(K_2 - K_1)} t$$

$$d[e^{K_2 t}[B]] = K_1[A]_0 e^{(K_2 - K_1)t} \cdot dt$$

On integration

$$e^{K_2 t}[B] = \frac{K_1 \cdot [A]_0}{K_2 - K_1} e^{(K_2 - K_1)t} + C$$

at $t = 0$, $[B] = 0 \Rightarrow C = \dfrac{-K_1[A]_0}{K_2 - K_1}$

Concentration of $[B]$ at any time

$$e^{K_2 t}[B] = \frac{K_1[A]_0 e^{(K_2 - K_1)t}}{K_2 - K_1} - \frac{K_1[A]_0}{K_2 - K_1}$$

$$[B] = \frac{K_1[A_0]}{K_2 - K_1}[e^{-K_1 t} - e^{-K_2 t}]$$

$$\frac{d[B]}{dt} = \frac{K_1[A]_0}{K_2 - K_1}[-K_1 e^{-K_1 t} + K_2 e^{-K_2 t}] = 0$$

$$\Rightarrow \qquad K_1 e^{-K_1 t} = K_2 e^{-K_2 t}$$

$$e^{(K_2 - K_1)t} = \frac{K_2}{K_1}$$

$$\Rightarrow \qquad t_\text{max} = \frac{1}{K_2 - K_1} \ln \frac{K_2}{K_1}$$

If $K_2 >> K_1$, then concentration of $[B]$ is very small and practically becomes constant.

$$\frac{d[B]}{dt} = 0 \Rightarrow K_1[A] - K_2[B] = 0$$

$$\Rightarrow \qquad [B] = \frac{K_1}{K_2}[A]$$

Reversible reaction

$$\text{H}_2 + \text{I}_2 \underset{K_b}{\overset{K_f}{\rightleftharpoons}} 2\text{HI}$$

$$r = K_f[\text{H}_2][\text{I}_2] - K_b[\text{HI}]^2$$

$$r = \frac{1}{2}\frac{d[\text{HI}]}{dt}$$

$$\frac{d[\text{HI}]}{dt} = 2[K_f[\text{H}_2][\text{I}_2] - K_b[\text{HI}]^2]$$

$$r = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt} = \frac{d[\text{HI}]}{2dt}$$

Kinetics for reversible reaction

When I order opposed by I order

	A	$\underset{K_b}{\overset{K_f}{\rightleftharpoons}}$	B
$t = 0$	a		–
$t = t$	$a - x$		x
at equilibrium	$a - xe$		xe

$$-\frac{d[A]}{dt} = \frac{-d[a - x]}{dt} = \frac{dx}{dt}$$

$$\frac{dx}{dt} = K_f(a - x) - K_b(x)$$

at equilibrium $\dfrac{dx}{dt} = 0$

$$K_f(a - x_e) = K_b x_e$$

$$K_b = \frac{K_f(a - x_e)}{x_e} \qquad \text{(i)}$$

$$K_b x_e = K_f a - K_f x_e$$

$$(K_f + K_b)x_e = K_f a$$

$$K_f + K_b = \frac{K_f \cdot a}{x_e} \qquad \text{(ii)}$$

From Eq. (i),

$$\frac{dx}{dt} = K_f(a-x) - \frac{K_f(a-x_e)\cdot x}{x_e}$$

$$\frac{dx}{dt} = \frac{K_f}{x_e}[ax_e - xx_e - ax + xx_e]$$

$$\frac{dx}{dt} = \left[\frac{K_f}{x_e}a\right](x_e - x)$$

$$\frac{dx}{dt} = (K_f + K_b)(x_e - x)$$

On integration,

$$\int \frac{dx}{(x_e - x)} = (K_f + K_b)\int dt$$

$$-\ln(x_e - x) = (K_f + k_b)t + C$$

$$\text{at} \qquad t = 0; \quad C = -\ln x_e$$

$$-\ln(x_e - x) = (K_f + K_b)\,t - \ln x_e$$

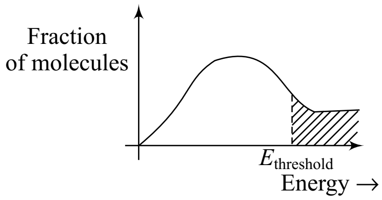
$$\boldsymbol{(K_f + K_b) = \frac{1}{t}\ln\frac{x_e}{(x_e - x)}}$$

Arrhenius collision theory

1. This theory is mainly applied to bimolecular collision.
2. When reactant molecules collide among themselves then, only they can convert themselves into product if Effective collision occur.
3. Collision frequency is generally very high but number of effective collision or active molecules are comparatively low.
4. For any collision to be effective, there are two barriers.

(a) Energy barriers

In order to have effective collisions, reactant molecules must possess some minimum amount of energy known as threshold energy.



Shaded area represents the fraction of active molecule which are having energy ≥ $E_{\text{threshold}}$

$f = e^{-Ea/RT}$ [fraction of active molecules]

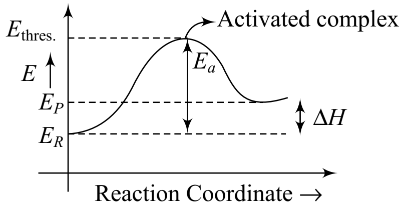
Ea → activation energy

R → Gas constant

T → temperature

Activation energy (Ea)

It is the extra amount of energy required by reactant molecules to reach up to the threshold energy.



$$E_a = E_{\text{threshold}} - E_R$$

$$= E_{\text{activated complex}} - E_R$$

(b) Orientation Barrier

In order to have effective collisions, the reactant molecules must collide in the proper direction.

Factor affecting rate of reaction

(i) Physical state

Solid < Liquid < gas

(ii) Particle size

Smaller is the size if particle, more will be the rate of reaction because effective surface area increases.

(iii) Temperature

For both endo- and exo-thermic reactions, rate of reaction increased on increasing the temperature.

On increasing the temperature by 10°C generally rate of reaction becomes 2 to 3 times.

$$\text{Rate} = z \times e^{-Ea/RT}$$

$$z \propto \sqrt{T}$$

On increasing the temperature by 10°C, rate of reaction changes mainly because of fraction of effective collisions, i.e., $e^{-Ea/RT}$ which becomes almost 2 to 3 times.

Temperature coefficient (μ)

It is the ratio of two rates when temperature is increased by 10°C.

$$\mu = \frac{R_{t+10°\text{C}}}{R_{t°\text{C}}} = \frac{K_{t+10°\text{C}}}{K_{t°\text{C}}} = 2 \text{ to } 3.$$

$$\frac{R_2}{R_1} = \frac{K_2}{K_1} = (\mu)^{\frac{\Delta T}{10}}$$

Effect of temperature on rate constant (K)

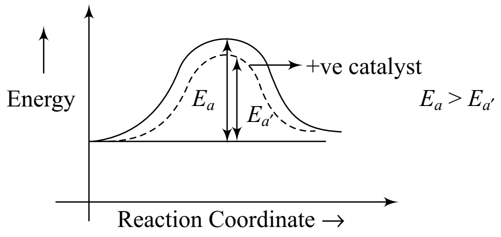
A/C to Arrhenius equation;

$$K = Ae^{-Ea/RT}$$

A → Arrhenius constant or pre-exponential factor or frequency factor.

$$\ln K = \ln A - \frac{Ea}{RT}$$

$$\log K = \log A - \frac{E_a}{2.303\,RT}$$



$$\log K_2 = \log A - \frac{E_a}{2.303RT_2}$$

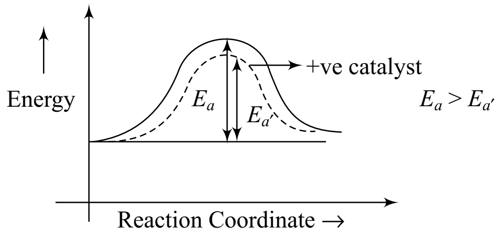
$$\log K_1 = \log A - \frac{E_a}{2.303RT_1}$$

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

> ***Note:***
> 1. As the activation energy of reaction increases, rate of reaction decreases.
> 2. For two different reactions:
>
> $Ea_1 > Ea_2$
>
> $\Delta T \Rightarrow$ identical ($T_1 = T_2$)
>
> $$\Rightarrow \quad \left(\frac{K_2}{K_1}\right)_1 > \left(\frac{K_2}{K_1}\right)_2$$

Catalyst

Positive catalyst speed up the reaction by providing alternating path of both for the reaction. In which energy of activated complex is lesser, so activation energy is lesser. Hence, rate of reaction increases.



Negative catalyst or inhibitor decrease the rate of reaction by providing an alternating path in which activation energy increases.

Types of catalysis

(1) Homogenous catalysis:

When reactants and catalysts are present in the same phase.

For example by lead chamber process

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(2) Heterogeneous catalysis:

When reactants and catalyst are present in different phase.

For example → manufacture of H_2SO_4 by contact process

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$$

For example manufacture of NH_3 by Haber's process:

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(S)} 2NH_3(g)$$

(3) Auto Catalysts:

In these reactions, one of the products formed act as a catalyst during the reaction.

$$CH_3COOC_2H_5(aq.) + H_2O \xrightarrow{H^+(aq)} CH_3COOH(aq.) + C_2H_5OH(aq.)$$

(autocatalyst)

Photochemical reactions

These are reactions which occur in presence of light and radiation.

For example $H_2 + Cl_2 \xrightarrow{hv} 2HCl$

These reactions follow zero order kinetics.

$r \propto I \quad I =$ intensity of light

$r = \phi \cdot I$

$\phi =$ quantum efficiency or quantum yield.

$$\phi = \frac{\text{Number of moles of reactant reacted}}{\text{Number of moles of photon absorbed}}$$

Reaction mechanism

In order to find the rate expression from the given reaction mechanism, there are two methods:

(1) R.D.S. method (Rate determining step method)

(a) Select the R.D.S. from reaction mechanism which is slowest step.

(b) Write the rate expression from the R.D.S. taking it as elementary.

(c) If there is any intermediate then, remove it.

For example,

Ex (1) Reaction: $2NO_2 + F_2 \longrightarrow 2NO_2F$

Mechanism:

$NO_2 + F_2 \xrightarrow{K_1} NO_2F + F$; (slow)

$F + NO_2 \xrightarrow{K_2} NO_2F$; (fast)

$r = K_1[NO_2][F_2]$

(2) Reaction: $2O_3 \longrightarrow 3O_2$

Mechanism:

$O_3 \underset{}{\overset{K_C}{\rightleftharpoons}} O_2 + O$; (fast)

$O_3 + O \xrightarrow{K} 2O_2$; (slow)

$r = K[O_3][O]$ (i)

$$K_C = \frac{[O_2][O]}{[O_3]}$$

here (O) is intermediate.

$$\therefore \quad [O] = \frac{K_C[O_3]}{[O_2]}$$

From (i)

$$r = K \cdot K_C \frac{[O_3]^2}{[O_2]}$$

$$r = K \cdot K_C[O_3]^2[O_2]^{-1}$$

(2) Steady state approximation method

This method is based on the fact that net rate of formation of intermediate is zero.

$$r = \frac{1}{2} \times \frac{-d[\mathrm{NO_2}]}{dt}$$

$$\frac{-d[\mathrm{NO_2}]}{dt} = K_1[\mathrm{NO_2}][\mathrm{F_2}] + K_2[\mathrm{NO_2}][\mathrm{F}]$$

According to steady state approximation method.

$$\frac{d[\mathrm{F}]}{dt} = 0 = K_1 \cdot [\mathrm{NO_2}] \cdot [\mathrm{F_2}] - K_2[\mathrm{NO_2}] \cdot [\mathrm{F}]$$

$$\Rightarrow \quad K_1 \cdot [\mathrm{NO_2}] \cdot [\mathrm{F_2}] = K_2[\mathrm{NO_2}] \cdot [\mathrm{F}]$$

$$\Rightarrow \quad -\frac{d[\mathrm{NO_2}]}{dt} = 2K_1[\mathrm{NO_2}] \cdot [\mathrm{F_2}]$$

$$\Rightarrow \quad r = \frac{1}{2} \times \frac{d[\mathrm{NO_2}]}{dt} = K_1[\mathrm{NO_2}] \cdot [\mathrm{F_2}]$$

Reation of fractional order:

(i) $H_2 + Br_2 \longrightarrow 2HBr$ Rate = K $[H_2]$ $[Br_2]^{1/2}$

(ii) $COCl_2 \longrightarrow CO + Cl_2$ Rate = K $[COCl_2]^{3/2}$

(iii) $CO + Cl_2 \longrightarrow COCl_2$ Rate = K $[CO]^2$ $[Cl_2]^{1/2}$

(iv) Para $H_2 \longrightarrow$ Ortho H_2 Rate = K $[P_{H_2}]^{3/2}$

(v) Thermal decomposition of acetaldehyde
Rate = K $[CH_3CHO]^{3/2}$

RADIOACTIVITY

It is a spontaneous nuclear phenomena in which certain radiations like α, β, γ are emitted by the nuclei of radioactive substances.

Radioactivity is independent of physical conditions like temperature, pressure etc.

α-rays

These consist of helium nuclei (He^{+2}). Due to each α-particle decay, atomic mass number decreases by 4 whereas atomic number decreases by 2.

$${}_{Z}^{A}X \longrightarrow {}_{Z-2}^{A-4}Y + \alpha$$

β-rays

These are composed of electrons.

$${}_{-1}e^0 \Rightarrow A = 0, Z = -1$$

$${}_{0}^{1}n \longrightarrow {}_{1}P^1 + {}_{-1}e^0$$

During the β-decay, there is no change in mass number but atomic number increases by 1 due to the conversion of neutron into proton and electron.

γ-rays

These are electro-magnetic radiation. Due to their emission, there is no change in mass number and atomic number decreases the energy level in nucleus.

Velocity: $\alpha < \beta < \gamma$

Penetration power: $\alpha < \beta < \gamma$

Ionisation power: $\alpha > \beta > \gamma$

Radioactive disintegration

All radioactive decay follow first order reaction:
Rate of disintegration or activity (A)

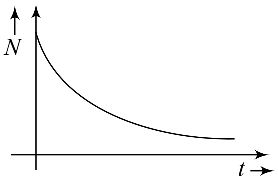
$$= \frac{-dN}{dt} \propto N$$

Where N = (Number of radioactive nuclei left at given time)

$$\frac{-dN}{dt} = \lambda N$$

$$N = N_0 e^{-\lambda t}$$

N = Number of radioactive nuclei taken initially



$$\lambda = \frac{1}{t}\ln\frac{N_0}{N} \qquad \lambda = \frac{1}{t}\ln\frac{A_0}{A}$$

$$\lambda = \frac{1}{t}\ln\frac{m_0}{m} \quad \text{and} \quad N_t = N_o\left(\frac{1}{2}\right)^n$$

m_0 : mass of nuclei initially n = Number of half-lite used

$$\therefore \qquad \frac{N_t}{N_0} = \frac{m}{m_0} = \left[\frac{1}{2}\right]^n$$

Half-life period ($t_{1/2}$):

$$t_{1/2} = \frac{0.693}{\lambda}$$

$$t_{\text{total}} = n \times t_{1/2}$$

Average Life: ($t_{\text{avg.}}$)

$$t_{\text{avg.}} = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693}$$

$$= 1.44 \times t_{1/2}$$

$$N = N_0 e^{-\lambda t}$$

$$t = t_{\text{avg}} = \frac{1}{\lambda}$$

$$\text{at} \qquad N = \frac{N_0}{e} = 0.37\,N_0$$

It is time in which 37% of the initial radioactive nuclei remain, i.e., 63% decay.

Units of activity

SI units: Disintegration per second (dps) or Becquerel (B_q)

Other units:

Curie (Ci) ⇒ 1 Ci = 3.7×10^{10} dps
Rutherford (Rd) ⇒ 1 Rd = 10^6 dps

Specific activity

It is the activity of 1 g radioactive substance.

Definitions

(1) Isotopes : Same atomic number but different mass number

(2) Isobars : Same mass number but different atomic number

(3) Isotopes : Same number of neutrons : $[A - Z] \rightarrow$ constant

(4) Isodiaphers : $(n - p) \Rightarrow$ same OR

$(A - 2Z) \Rightarrow$ same

Radioactive disintegration series

There are four natural disintegration series.

Series	Name	Starting Element	Stable End Product
$4n$	Thorium series	Th – 232	Pb – 208
$4n + 1$	Neptunium series	Np – 237	Bi – 209
$4n + 2$	Uranium series	U – 238	Pb – 206
$4n + 3$	Actinium series	U – 235	Pb – 207

Application of radioactivity

Age determination of minerals, rocks or the earth for age determination, minerals or rock sample is analysed for the amount of radioactive substance and its stable end product. When age of the mineral can be obtained from the formula.

$$\lambda = \frac{1}{t}\ln\frac{a}{a-x}$$

t = age of mineral

a = initial amount of radioactive substance

Age determination of dead animals and plants or carbon dating

$${}_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1P^1$$

This method is based on ratioactive decay of ^{14}C, which formed in the upper part of atmosphere according to above reaction. At the same time, C^{14} disintegrates so that ratio of radioactive carbon and non-radioactive carbon becomes constant. This ratio is available in all living animals and plants. After the death of animal or plant, this ratio changes due to disintegration of C^{14}. The age can be determined from the formula:

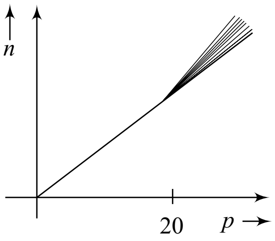
$$\lambda = \frac{1}{t}\ln\frac{a}{a-x}$$

Accuracy for this method is not good, when it is applied for very small or long time period.

Cause of radioactivity

Those nuclei whose n/p ratio is in the range 1 to 1.5 are generally stable. This range is called stability belt.

For unstable nuclei, disintegrate in order to reach to the stability best.



(1) Up to $Z = 20$; n/p ratio is 1 for most stable nuclei but above $Z = 20$, n/p ratio for stable nuclei increases because as the number of proton increases, electrostatic repulsion between these increases. In order to overcome these repulsive forces, neutrons increase number.

Above $Z = 83$; there is no stable nuclei.

Among the stable nuclei, n/p ratio is maximum for Bi bismuith (1.5).

Those nuclei which have number of neutron protons equal to magic number → 2, 8, 20, 28, 50, 82, 126 are more stable.

Maximum number of stable nuclei have even number of neutrons and even number of protons whereas very few stable nuclei have odd noumber of neutron and proton.

Favourable condition for disintegration

	Type of decay	Favourable condition	Effect
1.	α-decay for	$Z > 83$ (heavy unstable nuclei	$\frac{n}{p}\uparrow$ ${}_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}_2^4\alpha$
2.	β-decay	high n/p	$\frac{n}{p}\downarrow$ ${}_6C^{14} \longrightarrow {}_7N^{14} + {}_{-1}e^0$ $\frac{n}{p} = 1.33, \frac{n}{p} = 1.0$
3.	γ-decay	high-energy level in nuclei	decrease the energy level.
4.	Positron decay (β^+ decay)	low $\frac{n}{p}$ ratio	$\frac{n}{p}\uparrow$ ${}_7N^{13} \longrightarrow {}_6C^{13} + {}_1e^0$ $n/p = 6/7$ $n/p = 7/6$

5. *k*-capture ${}_1P^1 + {}_{-1}e^0 \longrightarrow {}_0n^1$

It is the phenomena in which lighter unstable nuclei having low n/p ratio capture the e^- from the nearest shell (i.e., K-shell) in order to increase the $\frac{n}{p}$ ratio.

$${}_4^7Be + {}_{-1}e^0 \longrightarrow {}_3^7Li$$

$$\frac{n}{p} = \frac{3}{4} \qquad \frac{n}{p} = \frac{4}{3}$$

Nuclear reactions

Reactant nuclei + Bombarding particle → product nuclei + emitted particle

Representation

Reactant nucleus (bombarding particle, emitted particle) product nucleus.

$${}_{11}Na^{24} + {}_1P^1 \longrightarrow {}_{12}Mg^{24} + {}_0n^1$$

$${}_{11}Na^{24}({}_1P^1, {}_0n^1)\ {}_{12}Mg^{24}$$

Example $\ {}_{3}^{7}\text{Li}(\alpha_2^4, {}_{2}^{3}\text{He}){}_{3}^{8}\text{Li}$

Example $\ {}_{4}^{9}\text{Be}(\gamma\ {}_0n^1){}_{4}^{8}\text{Be}$

During the nuclear fission and fusion, large amount of energy is released because of mass defect.

$$\Delta m = \text{mass defect} = m_R - m_P$$

$$E = \Delta mc^2$$

$$1 \text{ amu} = 931.5 \text{ MeV}$$

$$\text{Number of } \alpha \text{ particle emitterd} = \frac{A_1 - A_2}{4}$$

$$\text{No of } \beta \text{ particle emitted} = 2\alpha - [Z_1 - Z_2]$$

Solved Examples

1. At 10°C for any reaction rate constant = K, what will be rate constant at 90°C (given temperature coefficient 2)

Sol. $\dfrac{R_2}{R_1} = \dfrac{K_2}{K_1} = (\mu)^{\frac{\Delta T}{10}} = 2^8 \text{ K}$

2. (a) For the following reaction write down rate law:

$N_2 + 3H_2 \longrightarrow 2NH_3$

(b) If rate of dissappearance H_2 is $\dfrac{12 \text{ g}}{\ell - \sec}$. What is the rate of appearance of NH_3.

Sol. (a) $\text{Rate} = \dfrac{1}{1}\left(\dfrac{-d[N_2]}{\text{dt}}\right) = \dfrac{1}{3}\left(\dfrac{-d[H_2]}{dt}\right)$

$$= \frac{1}{2}\frac{+[d\text{NH}_3]}{dt} = K[N_2]^m[H_2]^n$$

(b) $\dfrac{d[NH_3]}{\text{dt}} = \dfrac{2}{3}\left(\dfrac{-d[H_2]}{dt}\right) = \dfrac{2}{3} \times \dfrac{12}{2} = 4\dfrac{\text{moles}}{\ell - \sec}$

$$= 4 \times 17 = 68 \text{ g}\frac{\text{gram}}{\ell - \sec}$$

3. For the reaction, $2A \to 3B + 4C$, the number of moles of B increases by 6×10^{-3} moles in 10 sec in a 10 L container. Calculate:

(a) rate of appearance of B and C.

(b) rate of disappearance of A

Sol. (a) $r_B = \dfrac{\Delta\text{Conc.}}{\Delta t} = \dfrac{6 \times 10^{-3}}{10 \times 10} = 6 \times 10^{-5}$

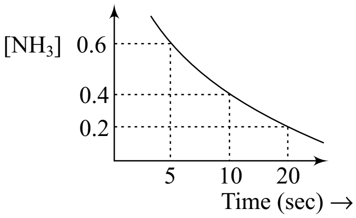
$$\frac{r_C}{4} = \frac{r_B}{3} \Rightarrow r_C = \frac{4}{3} \times r_B = 8 \times 10^{-3}$$

(b) $\dfrac{r_A}{2} = \dfrac{r_B}{3} \Rightarrow r_A = \dfrac{2}{3} r_B = 4 \times 10^{-5}$

4. For the reaction; $2NH_3 \to N_2 + 3H_2$, the curve is plotting between concentration of NH_3 v/s time. Calculate

(a) rate of decomposition of NH_3 between 5 to 10 seconds.

(b) rate of reaction between 10 to 20 seconds.



$$-\frac{\Delta[NH_3]}{\Delta t} = \frac{0.2}{5} = 0.04 \text{ M/sec}^{-1}$$

$$r = \frac{1}{2} \times \frac{0.2}{10} = 0.01 \text{ M/sec}^{-1}$$

5. $2N_2O_5 \longrightarrow 4NO_2 + O_2$, the variation of concentration of N_2O_5 with time can be expressed by $[N_2O_5] = [N_2O_5]_0\ e^{-Kt}$ and $K = 10^{-4}\ \sec^{-1}$. If initially 1 mole of N_2O_5 taken calculate.

(i) Rate of disappearance of N_2O_5 at t = 10^4 sec.

(ii) Rate of reaction during first 10^4 sec.

(iii) Variation of concentration of NO_2 with time.

(i) $\text{Rate} = -\dfrac{d[N_2O_5]}{dt} = K[N_2O_5]_0 e^{-Kt}$

$$= K[N_2O_5]_0 e^{-10^{-4} \times 10^4}$$

$$= K[N_2O_5]_0 \times \frac{1}{e}$$

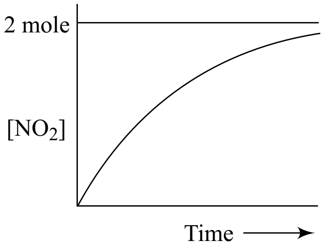
$$= 1 \times 10^{-4}[1] \times \frac{1}{e}$$

We know $\alpha = \dfrac{x}{a} = 1 - e^{-Kt}$ for first order.

(ii) $R = \dfrac{1 - 1/e}{10^4} \times \dfrac{1}{2}$

(iii)

$2N_2O_5$	$\to$	$4NO_2$	$+$	O_2
1		–		–
$1 - \alpha$		2α		$\alpha/2$



6. For the given gaseous reaction $A \rightarrow 2B + C$ pressure after sufficient time was found to be 300 mm and after time 2.303 sec, it was found to be 200 mm calculate.
(i) rate constant (ii) half-life

	A	$\rightarrow$	$2B$	$+$	C
$t = 0$	P_0		$-$		$-$
$t = t$	$P_0 - x$		$2x$		x
$t = \infty$	$-$		$2P_0$		P_0

$$P_\infty \Rightarrow 300 = 3P_0 \Rightarrow P_0 = 100 \text{ mm}$$

$$P_0 + 2x = 200 \text{ mm}$$

$$x = 50 \text{ mm}$$

$$K = \frac{2.303}{t}\log\frac{P_0}{P_0 - x}$$

$$K = \frac{2.303}{2.303}\log\frac{100}{50} = 0.3010$$

(ii) $t_{1/2} = \dfrac{0.6932}{K} = \dfrac{0.6932}{0.3010} = 2.303$

7. ${}_{20}\text{Th}^{234}$ disintegrates to gives ${}_{82}\text{pb}^{206}$ as the final product. How many α and β particles emitted.

Sol. ${}_{20}\text{Th}^{234} \longrightarrow {}_{82}\text{Pb}^{206} + x{}_2^4\alpha + y{}_{-1}^{0}\beta$

OR $\alpha = \dfrac{A_2 - A_1}{4} = \dfrac{234 - 206}{4} = 7$ [OR]

$A \Rightarrow 234 = 206 + 4x \Rightarrow x = 7$ $\quad \beta = 2 \times \alpha - [Z_1 - Z_2]$

$Z \Rightarrow 90 = 82 + 2x - y \Rightarrow y = 6$ $\quad = 2 \times 7 - [90 - 82]$

$= 14 - 8 = 6$

8. Activity of 1 g of Radium is found to be 0.5 Ci. Calculate the half-life period of radium and time required for the decay of 2 g to 0.25 g. [$A = 226$]

Sol. **Activity** $= \lambda \cdot N$

$$= \lambda \times n \times N_A$$

$$= \lambda \times \frac{1}{226} \times 6.022 \times 10^{23}$$

$$= 0.5 \times 3.7 \times 10^{10} = \lambda \frac{1}{226} \times 6.023 \times 10^{23}$$

$$t_{1/2} = \frac{0.693}{\lambda}$$

$$\lambda = 69.417 \times 10^{-13}$$

$$= 9.9 \times 10^{10} \text{ sec.}$$

$$\frac{m}{m_0} = \frac{0.25}{2} = \frac{1}{8} = \left(\frac{1}{2}\right)^3$$

$$t_{\text{taken}} = 3 \times t_{1/2} = 3 \times 9.9 \times 10^{10} \text{ sec.}$$

9. The final product of U_{238} is Pb_{206}. A sample of pitchgland is 0.0453 g of Pb_{206} for every gram U_{238} present in it, assuming that the pitch gland formed at the time of formation of the earth didn't contain any Pb_{206}. Calculate the age of earth, $t_{1/2}$ for $U_{238} = 4.5 \times 10^9$ yrs. ln 1.05234 = 0.051.

Sol. $a - x = 1$ g $\Rightarrow$ $m_{\text{pb}} = 0.0453$ g

$a = 1 + x$

$$U^{238} \longrightarrow Pb^{206} \quad \frac{0.0453}{206}$$

$$x = \frac{0.0453}{206} \times 238 = 0.05234$$

$$\frac{0.693}{4.5 \times 10^9} = \frac{1}{t}\ln\left(\frac{1.05234}{1}\right)$$

$$= 3.29 \times 10^6 \text{ yrs.}$$

10. An old piece of wood have 25% of C^{14} as much as ordinary wood today has. Find the age of wood given $t_{1/2}$ of C^{14} is 5760 yrs.

Ans. $t = 2 \times t_{1/2} = 2 \times 5760y$

11. For the elementary reaction $2A + B_2 \longrightarrow 2AB$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

Sol. $2A + B_2 \longrightarrow 2AB \left(\dfrac{dx}{dt}\right)_1 = K[A]^2[B_2]$

if V is decrease to $\dfrac{V}{3}$

$$\Rightarrow \left(\frac{dx}{dt}\right)_2 = [3A]^3[3B]\left(\frac{dx}{dt}\right)_2 = 27\left(\frac{dx}{dt}\right)_1$$

reaction increases by 27 times.

12. In the reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$ rate of formation of O_2 is 3.6 M min^{-1}.
(a) What is rate of formation of H_2O?
(b) What is rate of disappearance of H_2O_2?

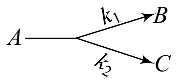
Sol. $2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad \dfrac{d_{O_2}}{dt} = 3.6 \text{ M min}^{-1}$

(a) Rate of formation of H_2O

$$\frac{d_{H_2O}}{dt} = 2 \times 3.6 = 7.2 \text{ M min}^{-1}$$

$$\frac{d_{H_2O_2}}{dt} = 7.2 \text{ M min}^{-1}$$

13. A certain organic compound A decomposes by two parallel first order mechanism



If $k_1 : k_2 = 1 : 9$ and $k_1 = 1.3 \times 10^{-5}$ s^{-1}
Calculate the concentration ratio of C to A, if experiment is started with only A and allowed to run for one hour.

Sol. Given:

$$\frac{k_1}{k_2} = \frac{1}{9}, \qquad k_1 = 1.3 \times 10^{-5}$$

$$k_2 = 9k_1$$

$$[A] = [A]_0 e^{-(k_1 + k_2)t}$$

$$[C] = \frac{k_2[A]_0}{k_1 + k_2}[1 - e^{-(k_1 + k_2)t}]$$

$$\frac{[C]}{[A]} = \frac{k_2}{k_1 + k_2}[e^{(k_1 + k_2)t} - 1] = \frac{9k_1}{10k_1}[e^{10k_1 t} - 1] = 0.537$$

14. The reaction

$$cis\text{–Cr(en)}_2\text{(OH)}_2^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} trans\text{–Cr(en)}_2\text{(OH)}_2^+$$

is first order in both directions. At 25°C, the equilibrium constant is 0.16 and the rate constant k_1 is 3.3×10^{-4} s^{-1}. In an experiment starting with the pure cis form, how long would it take for half the equilibrium amount of the trans isomer to be formed?

14. $k = 0.16, k_1 = 3.3 \times 10^{-4}$

so $k_2 = k_1/k = 2.0625 \times 10^{-3}$

$k_1 + k_2 = 0.0023925$

$$[B]_{\text{eq.}} = \frac{k_1}{k_2}[A]_{\text{eq.}} = \frac{k_1[A]_0}{k_1 + k_2}$$

Given $[B] = \dfrac{[B]_{\text{eq.}}}{2} = \dfrac{k_1[A]_0}{2(k_1 + k_2)}$

and $[B] = \dfrac{k_1[A]_0}{k_1 + k_2}[1 - e^{-(k_1+k_2)t}]$

so $\dfrac{1}{2} = 1 - e^{-(k_1+k_2)t}$ $(k_1 + k_2)t = \ln 2$

$t = 289.71$ sec. $= 4.82$ min.

15. An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was –20°. If optical rotation per mole of A, B and C are 60°, 40° and –80°, calculate half life and average life of the reaction.

Sol.

	A $\longrightarrow$	B	+	C
$t = 0$	a	–		–
$t = 20$ min.	$a - x$	x		x
$t = \infty$	–	a		a

$60(a - x) + 40x - 80x = 5$

and $40a - 80a = -20$

on solving $a = 0.5, x = 0.25$

so $t_{1/2} = 20$ min.

Average life $= 1/K = 1.443 \times t_{1/2} = 28.86$ min.

16. For the reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P$. Following data is produced:

Time/Hr.	0	1	2	3	4	∞
% A	100	72.5	56.8	45.6	39.5	30

Find k_1, k_{-1} and K_{eq}.

Sol. At $t = \infty$ when equilibrium is established

$$k = \frac{[P]}{[A]} = \frac{7}{3} = 2.33$$

and $\dfrac{k_1}{k_{-1}} = 2.33 \Rightarrow k_1 = 2.33\, k_{-1}$

$$[A] = \frac{k_2[A]_0}{k_1 + k_2}[1 - e^{-(k_1+k_2)t}]$$

$k_{-1} = 4.16 \times 10^{-5}$ sec^{-1}

$k_1 = 2.33\, k_{-1} = 9.7 \times 10^{-5}$ sec^{-1}

17. For the mechanism $A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \quad C \xrightarrow{k_3} D$

Derive the rate law using the steady-state approximation to eliminate the concentration of C. Assuming that $k_3 << k_2$, express the pre-exponential factor A and E_a for the apparent second-order rate constant in terms of A_1, A_2 and A_3 and E_{a1}, E_{a2} and E_{a3} for the three steps.

Sol. $A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C, C \xrightarrow{k_3} D$

$r = k_1[A]\,[B] - k_2[C]$

$$\frac{d[C]}{dt} = k_1[A]\,[B] - k_2[C] - k_3[C] = 0$$

$$[C] = \frac{k_1[A][B]}{k_2 + k_3}$$

$$\frac{d[D]}{dt} = r = k_1[A][B] - k_2 \times \frac{k_1[A][B]}{k_2 + k_3}$$

$$r = \frac{k_1k_3[A][B]}{k_2 + k_3}$$

since $k_2 >> k_3$

$$k_{\text{net}} = \frac{k_1k_3}{k_2}$$

so $A_{\text{net}} = \dfrac{A_1A_3}{A_2}$

$(E_a)_{\text{net}} = E_{a1} + E_{a3} - E_{a2}$

18. The decomposition of a compound P, at temperature T according to the equation $2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$ is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure is observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minute, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

Given : Vapour pressure of S(l) at temperature $T = 32.5$ mm Hg.

Sol.

	$2P_{(g)}$ $\longrightarrow$	$4Q_{(g)}$ +	$R_{(g)} + S_{(l)}$
$t = 0$	P_0		
$t = 30$ min.	$P_0 - P$	$2P$	$P/2$
$t = \infty$	–	$2P_0$	$P_0/2$

so $P_0 - P + 2P + P/2 = 317 - 32.5$

i.e., $P_0 + 1.5P = 284.5$ (i)

and $2.5P_0 = 617 - 32.5 = 584.5$

so $P_0 = 233.8$

$P = 33.8$

$$k \times 30 = \ln\frac{233.8}{200} \Rightarrow k = 0.0052$$

At $t = 75$ min

$$0.0052 \times 75 = \ln\frac{233.8}{P_0 - P}$$

$P_0 - P = 158.23 \Rightarrow P = 75.57$

$P_T = 32.5 + P_0 + 1.5P = 347.155 + 32.5$

$P_T = 379.65$ mm Hg

(ii) $0.0052 \times t = \ln 8$

$t = 399.89$ min.

19. In a nature decay chain series starts with ${}_{90}Th^{232}$ and finally terminates at ${}_{82}Pb^{208}$. A thorium ore sample was found to contain 8×10^{-5} mL of helium at STP and 5×10^{-7} g of Th^{232}. Find the age of ore sample assuming that source of He to be only due to decay of Th^{232}. Also assume complete retention of helium within the ore. (Half-life of $Th^{232} = 1.39 \times 10^{10}$ Y)

Sol. ${}_{90}Th^{232} \longrightarrow {}_{82}Pb^{208} + 6\ {}_2He^4 + 4\ {}_{-1}\beta^0$

$t = 0$ a

time t $a - x$ $6x$

given:

$$a - x = \frac{5 \times 10^{-7}}{232} = 2.155 \times 10^{-9} \text{ mole}$$

$$6x = \frac{8 \times 10^{-5}}{22400} \Rightarrow x = 5.9523 \times 10^{-10} \text{ mole}$$

so $a = 2.75 \times 10^{-9}$

$$k = \frac{0.693}{1.39 \times 10^{10}}$$

$$k \times t = \ln \frac{a}{a - x}$$

$$\frac{0.693 \times t}{1.39 \times 10^{10}} = \ln \frac{2.75 \times 10^{-9}}{2.155 \times 10^{-9}} = 0.2438$$

$t = 4.89 \times 10^9$ year

20. A sample of ${}^{131}_{53}I$, as iodine ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? ($t_{1/2} = 8$ days.)

Sol. $k = \dfrac{0.693}{8}$

$$kt = \ln \frac{A_0}{A} = \frac{0.693}{8} \times 4 = \ln \frac{A_0}{A}$$

$$\frac{A}{A_0} = 0.707$$

Total activity is 70.7% of the original activity but only 67.7% found in the thysoid so mass of stable iodide ion had migrated to the thyroid gland is

$$= \frac{67.7}{70.7} \times 0.1 = 0.09575 \text{ mg}$$

21. ${}_{84}Po^{218}$ ($t_{1/2} = 3.05$ min) decay to ${}_{82}Pb^{214}$ ($t_{1/2} = 2.68$ min) by a-emission, while Pb^{214} is a β-emitter. In an experiment starting with 1 g atom of pure Po^{218}, how much time would be required for the number of nuclei of ${}_{82}Pb^{214}$ to reach maximum.

Sol. ${}_{84}Po^{218} \xrightarrow{\lambda_1} {}_{82}Pb^{214} \xrightarrow{\lambda_2} {}_{83}Bi^{214}$

Number of nuclei of Pb^{214} at time t are $N_2 = \dfrac{\lambda_1 N_0}{(\lambda_2 - \lambda_1)}[e^{-\lambda_1 t} - e^{-\lambda_2 t}]$

For max. value of N_2 $\dfrac{dN_2}{dt} = 0$

so $t = \dfrac{1}{(\lambda_2 - \lambda_1)} \ln \dfrac{\lambda_2}{\lambda_1}$

when $\lambda_2 = \dfrac{0.693}{2.68}$, $\lambda_1 = \dfrac{0.693}{3.05}$,

on putting these values

$$t = 31.87 \ln \frac{3.05}{2.68} = 4.12 \text{ min}$$

22. A sample pitch blende is found to contain 50% Uranium (U^{238}) and 2.425% Lead. Of this Lead only 93% was Pb^{206} isotope, if the disintegration constant is 1.52×10^{-10} yr^{-1}. How old could be the pitch blende deposit?

Sol. Let the mass of sample in a g and initial mass of U^{238} is w g, then

	U^{238}	$\longrightarrow$	Pb^{206}
$t = 0$	w		
t	$w - x$		$\dfrac{206}{238}x$

given $w - x = 0.5a$

$$\frac{206x}{238} = \frac{2.425a}{100} \times 0.93 = 0.0225525a$$

$x = 0.026a$

so $w = 0.526a$

$$\lambda t = \ln \frac{w}{w - x}$$

$$1.52 \times 10^{-10} \times t = \ln \frac{0.526a}{0.5a}$$

$t = 3.33 \times 10^8$ year.

Exercise

LEVEL I

1. In a reaction involving the synthesis of ammonia by Haber's process, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the rate of reaction was measured as $= 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. The rate of change of concentration of H_2 will be

(a) 1.25×10^{-4} mol L^{-1} s^{-1}

(b) 2.50×10^{-4} mol L^{-1} s^{-1}

(c) 7.5×10^{-4} mol L^{-1} s^{-1}

(d) 5.0×10^{-4} mol L^{-1} s^{-1}

2. In the formation of sulphur trioxide by contact process, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the rate of reaction was measured as = 2.5×10^{-4} mol L^{-1} sec^{-1}. the rate of reaction expressed in terms of SO_3 will be
(a) -1.25×10^{-4} mol L^{-2} sec^{-1}
(b) 50×10^{-4} mol L^{-1} sec^{-1}
(c) -3.75×10^{-4} mol L^{-1} sec^{-1}
(d) 5.00×10^{-4} mol L^{-1} sec^{-1}

3. The rate constant of a reaction is equal to rate of reaction:
(a) When concentrations of reactants do not change with time.
(b) When concentrations of all reactants and products are equal.
(c) At time $t = 0$.
(d) When concentrations of all reactants are unity.

4. If the concentration of the reactants in the reaction $2A + B \rightarrow C + D$ is increased by three folds, the rate of the reaction will be increased by
(a) 27 times (b) 9 times
(c) 64 times (d) 01 times

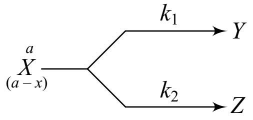
5. The rate of change in concentration of C in the reaction $2A + B \rightarrow 2C + 3D$ was reported as 1.0 mol L^{-1} sec^{-1}. Calculate the reaction rate:
(a) 0.05 mole L^{-1} sec^{-1} (b) 0.01 mol L^{-1} sec^{-1}
(c) 0.5 mol L^{-1} sec^{-1} (d) None of these

6. In a first order reaction, the initial concentration of the reactant was M/10. After 8 minutes 20 seconds the concentration becomes M/100. What is the rate constant?
(a) 5×10^{-3} sec^{-1} (b) 2.303×10^{-5} sec^{-1}
(c) 2.303×10^{-4} sec^{-1} (d) 4.606×10^{-3} sec^{-1}

7. Substance A reacts according to a first order rate law with $K = 5.0 \times 10^{-5}$ s^{-1}. If the initial concentration of A is 1.0 M, the initial rate is
(a) 1×10^{-5} Ms^{-1} (b) 5.0×10^{-5} Ms^{-1}
(c) 1×10^{-4} Ms^{-1} (d) 5.0×10^{-4} Ms^{-1}

8. The mechanism of the reaction $2NO + O_2 \rightarrow 2NO_2$ is
$NO + NO \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} N_2O_2$ (fast) ; $N_2O_2 + O_2 \xrightarrow{K_2} 2NO_2$ (slow)
The rate constant of the reaction is
(a) K_2 (b) $K_2K_1\,(K_{-1})$
(c) K_2K_1 (d) $K_2\left(\dfrac{K_1}{K_{-1}}\right)$

9. Dinitrogen pentaoxide decomposes as $2N_2O_5 \rightarrow 4NO_2 + O_2$. The rate can be given in three ways $\dfrac{-d[N_2O_5]}{dt} = K_1\,[N_2O_5]$, $\dfrac{d[NO_2]}{dt} = K_2\,[N_2O_5]$, $\dfrac{d[NO_2]}{dt} = K_3\,[N_2O_5]$
The relation between the rate constants K_1, K_2 and K_3 is
(a) $K_2 = 2K_1$ and $K_3 = 1/2\ K_1$
(b) $K_1 = 2K_2$ and $K_3 = 2K_1$
(c) $K_1 = K_2 = K_3$
(d) $K_1 = 2K_2 = 3K_3$

10. For a reaction 

, $\dfrac{d[x]}{dt}$, is equal to
(a) $k_1(a-x) - k_2(a-x)$ (b) $k_2(a-x) - k_1(a-x)$
(c) $k_1(a-x) + k_2(a-x)$ (d) $-k_1(a-x) - k_2(a-x)$

11. The mechanism of the reaction : $A + 2B + C \rightarrow D$ is
(step 1) (fast) equilibrium $A + B \rightleftharpoons X$
(step 2) (slow) $X + C \rightarrow Y$
(step 3) (fast) $Y + B \rightarrow D$
Which rate law is correct?
(a) $r = k[C]$ (b) $r = k[A]\,[B]^2\,[C]$
(c) $r = k\,[A]\,[B]\,[C]$ (d) $r = k\,[D]$

12. Mechanism of the reaction $2NO + Cl_2 \rightarrow 2NOCl$ may be written as
$2NO \overset{K}{\rightleftharpoons} (NO)_2$ …… (fast)
$(NO)_2 + Cl_2 \xrightarrow{k} 2NOCl$ …… (slow)
Rate equation would be
(a) $kK[(NO)_2]\,[Cl_2]$ (b) $kK[NO]^2\,[Cl_2]$
(c) $kK[Cl_2]$ (d) $kK[NO] \cdot [Cl_2]$

13. The half-life of decomposition of N_2O_5 is a first order reaction represented by?
$N_2O_5 \rightarrow N_2O_4 + 1/2O_2$
After 15 minutes, the volume of O_2 produced is 9 mL and at the end of the reaction 35 mL. The rate constant is equal to
(a) $\dfrac{1}{15}\log_e\dfrac{35}{26}$ (b) $\dfrac{1}{15}\log_e\dfrac{44}{26}$
(c) $\dfrac{1}{15}\log_e\dfrac{35}{36}$ (d) None of the foregoing

14. 99% at a first order reaction was completed in 32 min. When will 99.9% of the reaction complete?
(a) 48 min (b) 46 min (c) 50 min (d) 45 min

15. $T_{0.5}$ = constant, confirms the first order of the reaction as one $a^2\,T_{0.5}$ = constant confirms that the reaction is of
(a) Zero order (b) First order
(c) Second order (d) Third order

16. The half-life period for a reaction at initial concentration of 0.5 and 1.0 moles L^{-1} are 200 sec and 100 sec respectively. The order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3

17. The slope of the line for the graph of log K versus $\dfrac{1}{T}$ for the reaction, $N_2O_5 \rightarrow 2NO_2 + \dfrac{1}{2}O_2$ is – 5000. Calculate the energy of activation of the reaction – (KJ K^{-1} mol^{-1})
(a) 95.7 (b) 9.57 (c) 957 (d) None

18. For a reaction, the rate constant is expressed as, k = A.e$^{-40000/T}$. The energy of the activation is
(a) 40000 cal (b) 88000 cal
(c) 80000 cal (d) 8000 cal

19. A reaction takes place in three steps. The rate constants are k_1, k_2 and k_3. The over all rate constant $k = \dfrac{k_1k_3}{k_2}$. If (energy of activation) E_1, E_2 and E_3 are 60, 30 and 10 kJ. The overall energy of activation is:

(a) 40 (b) 30 (c) 400 (d) 60

20. For a chemical reaction $A + 3B \longrightarrow$ Product

It was observed that rate of reaction increases nine times when concentration of B increased three times by keeping concentration of A as constant. On doubling concentration of both rate increases eight times. Differential rate equation can be given as

(a) $r = k[A][B]^3$ (b) $r = k[A][B]^2$

(c) $r = k[A]^2[B]$ (d) $r = k[A]^2[B]^{1/3}$

21. A reaction is second order with respect to a reactant. If concentration of reactant is doubled the rate of reaction becomes

(a) doubled (b) halved

(c) four times (d) remains same

22. The decomposition of NH_3 is studied on platinum surface. The rate of production of N_2 and H_2 are respectively ($k = 2.5 \times 10^{-4}$ mol^{-1} L s^{-1}):

(a) 5×10^{-4} and 1.67×10^{-4}

(b) 1.67×10^{-4} and 5×10^{-4}

(c) 1.25×10^{-4} and 3.75×10^{-4}

(d) 3.75×10^{-4} and 1.25×10^{-4}

23. In a reaction between A and B, initial rate of reaction was measured for different initial concentration A and B given as

[A] inmol L^{-1}	[B] inmol L^{-1}	Initial rate in mole L^{-1} s^{-1}
0.2	0.3	5.07×10^{-5}
0.2	0.1	5.07×10^{-5}
0.4	0.05	1.43×10^{-4}

Order of reaction with respect to A and B is

(a) 1, 0 (b) 1, 1 (c) 1.5, 0 (d) 1.5, 1

24. For the reaction $R \rightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. The average rate in seconds is

(a) 4×10^{-4}M sec^{-1} (b) 4×10^{-4}M min^{-1}

(c) 6.66×10^{-6}M sec^{-1} (d) 6.66×10^{-6} M min^{-1}

25. N_2O_5 decomposes as follows: $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

If, $$\frac{-d[N_2O_5]}{dt} = k_1[N_2O_5];$$

$$\frac{d[NO_2]}{dt} = k_2[N_2O_5];$$

$$\frac{d[O_2]}{dt} = k_3[N_2O_5]$$

Which one of the following is correct for k_1, k_2 and k_3:

(a) $k_1 + k_2 = k_3$ (b) $k_1 = k_2 + K_3$

(c) $k_1 = 2k_2 + 1/2k_3$ (d) $2k_1 = k_2 = 4k_3$

26. At 27°C it was observed during a reaction of hydrogenation that the pressure of H_2 gas decreases from 2 atm to 1.1 atm in 75 minutes. The rate of reaction (molarity/sec) is: Given ($R = 0.0821$ litre atm K^{-1} mole^{-1})

(a) 8.12×10^{-6} mol L^{-1} sec^{-1}

(b) 8.12×10^{-6} mol L^{-1} min^{-1}

(c) 4.87×10^{-4} mol L^{-1} sec^{-1}

(d) 4.87×10^{-4} mol L^{-1} min^{-1}

27. The possible mechanism for the reaction : $2NO + Br_2 \rightarrow 2\ NOBr$ is

$NO + Br_2 \rightleftharpoons NOBr_2$(fast);

$NOBr_2 + NO \rightarrow 2NOBr$ (slow). Rate law is

(a) $r = k\,[NO]\,[Br_2]$ (b) $r = k\,[NO]^2\,[Br_2]^{-1}$

(c) $r = k\,[NOBr_2]\,[NO]$ (d) $r = k\,[NO]^2\,[Br_2]$

28. The reaction $2A + B + C \rightarrow D + 2E$; is found to follow the rate law as : $r = k[A][B]^2[C]^0$. If the concentration of A, B and C increases two times then rate of reaction becomes

(a) same (b) doubled

(c) eight times (d) four times

29. The following results have been obtained during the kinetic studies of the reaction: $2A + B \longrightarrow C + D$

Experiment	[A] in mol L^{-1}	[B] in mol L^{-1}	initial rate of formation of D in mol L^{-1}min^{-1}
I	0.1	0.1	6×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

The rate law and the rate constant for the reaction is

(a) $k[A]^1[B]^2$; 6 M^{-1} min^{-1}

(b) $k[A][B]$; 4 M^{-1} min^{-1}

(c) $k[A]^1[B]^2$; 6 M^{-2} min^{-1}

(d) $k[A]^2[B]$; 4 M^{-2} min^{-1}

30. From the following data for the reaction between A and B,

[A] in mol L^{-1}	[B] in mol L^{-1}	Initial rate in mole L^{-1} s^{-1}
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}

The order of the reaction with respect to A and with respect to B will be

(a) 2, 1 (b) 1, 2 (c) 2, 0 (d) 1, 3/2

31. A first order reaction takes 40 minute for 30% decomposition $t_{1/2}$ for the reaction is

(a) 66.67 min (b) 80 min

(c) 77.70 min (d) infinite time

32. A carbon radio isotope $_ZX^A$ (half life 10 days) decays to give $_{Z-2}X^{A-4}$. If 1.00 g atom of $_ZX^A$ is kept in a sealed tube, how much helium will accumulate in 20 days in STP:

(a) 22400 cc (b) 24400 cc

(c) 16800 cc (d) 17600 cc

33. A gaseous reaction $A_2(g) \longrightarrow B(g) + \frac{1}{2}C(g)$; shows increase in pressure from 100 mm to 120 mm in 5 minutes. The rate of disappearance of A_2 is

(a) 4 mm min^{-1} (b) 8 mm min^{-1}
(c) 16 mm min^{-1} (d) 2 mm min^{-1}.

34. For the reaction system $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$; volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will

(a) Diminish to one fourth of its initial value
(b) Diminish to one eighth of its initial value
(c) Increase to eight times of its initial value
(d) Increase to four times of its initial value

35. The reaction : $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ has been assigned to follow given mechanism:

I. $NO + NO \rightleftharpoons N_2O_2$ (fast)
II. $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)
III. $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

The rate constant of step II is 1.2×10^{-4} mole^{-1} L min^{-1} while equilibrium constant of step I is 1.4×10^{-2}. What is the rate of reaction when concentration of NO and H_2 each is 0.5 mole L^{-1}

(a) 2.1×10^{-7} mole L^{-1} min^{-1}
(b) 3.2×10^{-6} mole L^{-1} min^{-1}
(c) 3.5×10^{-4} mole L^{-1} min^{-1}
(d) None of these

36. The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by

Rate = $k[CH_3OCH_3]^{3/2}$

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

$$\text{Rate} = k(P_{CH_3OCH_3})^{3/2}$$

If the pressure is measured in bar and time in minutes, then the unit of rate constants is

(a) $\text{bar}^{1/2}\text{min}$ (b) $\text{bar}^{3/2}\text{min}^{-1}$
(c) $\text{bar}^{-1/2}\text{min}^{-1}$ (d) bar min^{-1}

37. A reaction involving two different reactants

(a) Can never be a second order reaction
(b) Can never be a unimolecular reaction
(c) Can never be a bimolecular reaction
(d) Can never be a first order reaction

38. Which one of the following statement for order of reaction is not correct?

(a) Order can be determined experimentally.
(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.
(c) It is not affected with the stoichiometric coefficient of the reactants.
(d) Order cannot be fractional.

39. A hypothetical reaction $A_2 + B_2 \longrightarrow 2AB$ follows the mechanism as given below:

$A_2 \longrightarrow A + A$ (fast)
$A + B_2 \longrightarrow AB + B$ (slow)
$A + B \longrightarrow AB$ (fast)

The order of the overall reaction is

(a) 2 (b) 1 (c) 3/2 (d) 0

40. The rate law for the dimerisation of NO_2 is $\frac{-d[NO_2]}{dt} = k[NO_2]^2$

Which of the following changes will change the value of the specific rate constant, k?

(a) doubling the total pressure on the system.
(b) doubling the temperature.
(c) both.
(d) none of these.

41. The temperature coefficient of a reaction is

(a) ratio of rate constants at two temperatures differing by 1°C.
(b) ratio of rate constants at temperature 35°C and 25°C.
(c) ratio of rate constants at temperature 30°C and 25°C.
(d) specific reaction rate at 25°.

42. The rate of a chemical reaction generally increases rapidly even for small temperature increase because of rapid increase in the

(a) collision frequency
(b) fraction of molecules having activation energy
(c) activation energy
(d) average kinetic energy of molecules

43. The pre-exponential factor in the Arrhenius equation of a second order reaction has the units

(a) mol L^{-1} s^{-1} (b) L mol^{-1} s^{-1}
(c) s^{-1} (d) dimensionless

44. A catalyst is a substance which

(a) increases the equilibrium concentration of the product.
(b) changes the equilibrium constant of the reaction.
(c) shortens the time to reach equilibrium.
(d) supplies energy to the reaction.

45. Which reaction characteristics is/are changing by the addition of a catalyst to a reaction at constant temperature

(a) Activation energy (b) Equilibrium constant
(c) Reaction entropy (d) Reaction enthalpy

46. A radioactive isotope having a half-life of three days was received after 12 days. It was found that there were 3 g of isotope in the container. The initial weight of the isotope when packed was

(a) 12 g (b) 24 g
(c) 36 g (d) 48 g

47. If uranium (mass number 238 and atomic number 92) emits an α-particle, the product has mass number and atomic number:

(a) 236 and 92 (b) 234 and 90
(c) 238 and 90 (d) 236 and 90

48. Consider the chemical reaction,
$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
The rate of this reaction can be expressed in terms of time derivatives of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expression:

(a) $\text{Rate} = -\dfrac{d[N_2]}{dt} = -\dfrac{1}{3}\dfrac{d[H_2]}{dt} = \dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

(b) $\text{Rate} = -\dfrac{d[N_2]}{dt} = -3\dfrac{d[H_2]}{dt} = 2\dfrac{d[NH_3]}{dt}$

(c) $\text{Rate} = \dfrac{d[N_2]}{dt} = \dfrac{1}{3}\dfrac{d[H_2]}{dt} = \dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

(d) $\text{Rate} = \dfrac{d[N_2]}{dt} = -\dfrac{d[H_2]}{dt} = \dfrac{d[NH_3]}{dt}$

49. Rate law for the following reaction:
$\text{Ester} + H^+ \rightleftharpoons \text{Acid} + \text{Alcohol}$; is
$\dfrac{dx}{dt} = k\ [\text{ester}]^1\ [H^+]^0$. What would be the effect on the rate if concentration of H^+ ion is doubled?
(a) Same (b) doubled
(c) Half (d) Data insufficient

50. Consider a reaction $aG + bH \longrightarrow$ Product. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H constant, the rate is doubled. The overall order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3

51. What is the order of a reaction which has a rate expression rate = $k[A]^{3/2}\ [B]^{-1}$
(a) 3/2 (b) 1/2
(c) 0 (d) None of these

52. The kinetic data for the reaction: $2A + B_2 \longrightarrow 2AB$ are as given below.

[A] mol L^{-1}	[B_2] mol L^{-1}	Rate mol L^{-1} min^{-1}
0.5	1.0	2.5×10^{-3}
1.0	1.0	5.0×10^{-3}
0.5	2.0	1×10^{-2}

Hence the order of reaction with respect to A and B_2 are, respectively,
(a) 1 and 2 (b) 2 and 1
(c) 1 and 1 (d) 2 and 2

53. Units of rate constant of first and zero order reactions in terms of molarity unit are respectively
(a) sec^{-1}, M sec^{-1} (b) sec^{-1}, M
(c) M sec^{-1}, sec^{-1} (d) M, sec^{-1}

54. For a reaction: $X(g) \rightarrow Y(g) + Z(g)$
The half-life period is 10 min. In what period of time would be concentration of X be reduced to 10% of original concentration?
(a) 20 min. (b) 33 min
(c) 15 min (d) 25 min.

55. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^2 sec. The rate constant of reaction in sec^{-1} is
(a) $2 \times 10^4\ s^{-1}$ (b) $3.45 \times 10^5\ s^{-1}$
(c) $1.386 \times 10^{-2}\ s^{-1}$ (d) $2 \times 10^{-4}\ s^{-1}$

56. Half-life period of a first order reaction is
(a) Inversely proportional to the concentration.
(b) Independent of the concentration.
(c) Directly proportional to the initial concentration.
(d) Directly proportional to the final concentration.

57. In the first order reaction, the concentration of the reactant is reduced to 25% in one hour. The half life period of the reaction is
(a) 2 hr (b) 4 hr (c) 1/2 hr (d) 1/4 hr

58. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio $\dfrac{(k_1)}{(k_0)}$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction is
(a) 0.5 mol^{-1} dm^3 (b) 1.0 mol^{-1} dm^3
(c) 1.5 mol^{-1} dm^3 (d) 2.0 mol^{-1} dm^3

59. A radioactive element resembling iodine in properties is
(a) Astatine (b) Lead
(c) Radium (d) Thorium

60. Taking the reaction, $A + 2B \rightarrow$ Products, to be of second order, which of the following may be the correct rate law expressions?
(a) $\dfrac{dx}{dt} = k[A][B]$ (b) $\dfrac{dx}{dt} = k[A][B]^2$
(c) $\dfrac{dx}{dt} = k[A]^2[B]$ (d) $\dfrac{dx}{dt} = k_1[A] + k_2[B]^2$

61. For a hypothetical reaction; $A + B \longrightarrow$ Product, the rate law is $r = k[B]\ [A]^0$, the order of reaction is
(a) 0 (b) 1 (c) 2 (d) 3

62. The rate of the reaction $A + B_2 \longrightarrow AB + B$; is directly proportional to the concentration of A and independent of concentration of B_2, hence, rate law is
(a) $k[A][B_2]$ (b) $k[A]^2[B_2]$
(c) $k[A]$ (d) $[B_2]$

63. Rate of a reaction; $A + B \longrightarrow$ Products, is given below as a function of different initial concentrations of A and B.

[A] mol L^{-1}	[B] mol L^{-1}	Initial rate mol L^{-1} $time^{-1}$
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

The half life of A in the reaction is
(a) 1.386 min (b) 1.386 time
(c) 0.01 min (d) 0.01 time

64. The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ and $P_B = 0.80$ atm. When $P_C = 0.2$ atm the rate of reaction relative to the initial rate is
(a) 1/48 (b) 1/24 (c) 9/16 (d) 1/6

65. Thermal decomposition of a compound is of first order. If 50% of a sample of the compound is decomposed in 120 minute, show how long will it take for 90% of the compound to decompose?
(a) 399 min (b) 410 min
(c) 250 min (d) 120 min

66. A reaction that is of the first order with respect to reactant A has a rate constant 6 min^{-1}. If we start with [A] = 0.5 mol l^{-1}, when would [A] reach the value 0.05 mol l^{-1}?
(a) 0.384 min (b) 0.15 min
(c) 3 min (d) 3.84 min

67. Calculate the half-life of the first-order reaction

$$C_2H_4O(g) \longrightarrow CH_4(g) + CO(g)$$

if the initial pressure of $C_2H_4O(g)$ is 80 mm and the total pressure at the end of 20 minutes is 120 mm.
(a) 40 min (b) 120 min
(c) 20 min (d) 80 min

68. The half life period for catalytic decomposition of AB_3 at 50 mm is found to be 4 hrs and at 100 mm it is 2.0 hrs. The order of reaction is
(a) 3 (b) 1 (c) 2 (d) 0

69. The inactivation of a viral preparation in a chemical bath is found to be a first order reaction. The rate constant for the viral inactivation if in the beginning 1.5 % of the virus is inactivated per minute is
(a) $1.25 \times 10^{-4}\ \text{sec}^{-1}$ (b) $2.5 \times 10^{-4}\ \text{sec}^{-1}$
(c) $5 \times 10^{-4}\ \text{sec}^{-1}$ (d) $2.5 \times 10^{-4}\ \text{min}^{-1}$

70. In the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, initial pressure is 500 atm and rate constant k is $3.38 \times 10^{-5}\ \text{sec}^{-1}$. After 10 minutes the final pressure of N_2O_5 is
(a) 490 atm (b) 250 atm
(c) 480 atm (d) 420 atm

71. The decomposition of formic acid on a gold surface follows first order kinetics and specific rate constants are $5.5 \times 10^{-4}\ s^{-1}$ and $9.2 \times 10^{-3}\ s^{-1}$ at 140°C and 185°C respectively. Energy of activation is
(a) 98.46 J mol^{-1} (b) 98.46 k J mol^{-1}
(c) 23.7 J mol^{-1} (d) 23.7 k J mol^{-1}

72. During a negative β-decay
(a) An atomic electron is ejected.
(b) An electron which is already present within the nucleus is ejected.
(c) A neutron in the nucleus decays emitting an electron.
(d) A part of the binding energy of the nucleus is converted into an electron.

73. Identify the missing product in the given reaction

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow ? + {}^{92}_{36}Kr + 3\,{}^{1}_{0}n$$

(a) $^{141}_{56}Ba$ (b) $^{139}_{56}Ba$ (c) $^{139}_{54}Ba$ (d) $^{141}_{54}Ba$

74. 99% of a first order reaction was completed in 32 min. When will 50% of the reaction complete?
(a) 24 min (b) 8 min (c) 4 min (d) 4.8 min

75. In which of the following case, E_a of the backward reaction is greater than that of the forward reaction?
(a) $A + 10\ \text{kcal} \longrightarrow B,\ E_a = 50$ kcal
(b) $A + 20\ \text{kcal} \longrightarrow B,\ E_a = 40$ kcal
(c) $A + 40\ \text{kcal} \longrightarrow B,\ E_a = 10$ kcal
(d) $A - 40\ \text{kcal} \longrightarrow B,\ E_a = 20$ kcal

76. A first order reaction : $A \longrightarrow$ Products and a second order reaction : $2R \longrightarrow$ Products; both have half - time of 20 minutes when they are carried out taking 4 mole L^{-1} of their respective reactants. Number of mole per litre of A and R remaining unreacted after 60 minutes from the start of the reaction, will be respectively.
(a) 1 and 0.5 (b) 0.5 and negligible
(c) 0.5 and 1 (d) 1 and 0.25

77. If 'x' is the fraction of molecules having energy greater than E_a, it will be given by
(a) $x = -\dfrac{E_a}{RT}$ (b) $\ln x = -\dfrac{E_a}{RT}$
(c) $x = e^{E_a/RT}$ (d) None of these

78. A photon of gamma radiation knocks out a proton from $_{12}Mg^{24}$ nucleus to form
(a) The isotope of parent nucleus
(b) The isobar of parent nucleus
(c) the nuclide $_{11}Na^{23}$
(d) The isobar of $_{11}Na^{23}$

79. The decay constant of a radioactive sample is 'λ'. The half-life and mean life of the sample are respectively
(a) $\dfrac{1}{\lambda}, \dfrac{\ln 2}{\lambda}$ (b) $\dfrac{\ln 2}{\lambda}, \dfrac{1}{\lambda}$
(c) $l \ln 2, \dfrac{1}{\lambda}$ (d) $\dfrac{\lambda}{\ln 2}, \dfrac{1}{\lambda}$

80. Rate of the chemical reaction : $nA \longrightarrow$ products, is doubled when the concentration of A is increased four times. If the half time of the reaction at given temperature is 16 min, then time required for 75% of the reaction to complete is
(a) 24.0 min (b) 27.3 min
(c) 48 min (d) 49.4 min

81. The rate constant of a reaction at 27°C is 2.3×10^{-3} min^{-1} and at this temperature 0.001 % of the reactant molecules are able to cross over the energy barrier existing between the reactants and the products. What can be the maximum value of rate constant achieved on raising the temperature?
(a) 23.0 min^{-1} (b) 2.3×10^{-2} min
(c) 115.0 min^{-1} (d) 230.0 min^{-1}

82. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 3.0×10^{-4} s^{-1}, 104.4 kJ mol^{-1} and 6.0×10^{14}s^{-1} respectively. The value of the rate constant as $T \longrightarrow \infty$ is

(a) 2.0×10^{18} s^{-1} (b) 6.0×10^{14}s^{-1}
(c) Infinity (d) 3.6×10^{30}s^{-1}

83. If the rate of reaction grows 15.6 times on increasing the temperature by 30 K, the temperature coefficient of the reaction will be approximately

(a) 2 (b) 3 (c) 2.5 (d) 3.5

LEVEL II

1. What will be the initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and the concentration of reactant is 0.2 mol dm^{-3} also the amount of reactant converted into products in 200 minute is

(a) 2×10^{-4} mol dm^{-3} min^{-1}, 81.97%
(b) 2×10^{-4} mol dm^{-3} min^{-1}, 18.03%
(c) 2×10^{-4} mol dm^{-3} min^{-1}, 76%
(d) 2×10^{-4} mol dm^{-3} min^{-1}, 24%

2. The half time of first order decomposition of nitramide is 2.1 hour at 15°C.

$NH_2NO_2(s) \rightarrow N_2O(g) + H_2O(l)$

If 6.2 g of NH_2NO_2 is allowed to decompose, then time taken for NH_2NO_2 to decompose 99% and volume of dry N_2O produced at this point measured at STP will be

(a) 13.95 hrs, 22.4 L (b) 13.95 hrs, 2.217 L
(c) 2.1 hrs, 22.4 L (d) 2.1 hrs, 2.217 L

3. The decomposition of N_2O_5 in CCl_4 solution at 320 K takes place as

$2N_2O_5 \rightarrow 4NO_2 + O_2$;

On the bases of given data order and the rate constant of the reaction is

Time in minutes	10	15	20	25	∞
Volume of O_2 evolved (in mL)	6.30	8.95	11.40	13.50	34.75

(a) 1, 0.198 min^{-1} (b) 3/2, 0.0198 M$^{-1/2}$ min^{-1}
(c) 0, 0.198 M min^{-1} (d) 1, 0.0198 min^{-1}

4. From the following data estimate the order for decomposition of an aqueous solution of hydrogen peroxide:

Time (minutes)	0	10	20	30
V (ml)	46.1	29.8	19.6	12.3

where V is the volume of potassium permanganate solution in mL required to decompose a definite volume of the peroxide solution.

(a) 0 (b) 1 (c) 2 (d) 1/2

5. Rate of reaction $A + B \rightarrow P$ is given as a function of different initial concentrations of A and B

S.No.	{A}	{B}	{Rate}
1.	0.01	0.01	0.005
2.	0.02	0.01	0.010
3.	0.01	0.02	0.005

order with respect to A and B

(a) 1, 0 (b) 0, 1 (c) 1, 1 (d) 1, 2

6. A drug is known to be ineffective after it has decomposed to the extent of 30%. The original concentration of a sample was 500 units/mL. When analysed 20 months later, the concentration was found to be 420 units/mL. Assuming that the decomposition is of first order, what will be the expiration time of the drug sample. What is the half life of the drug?

(a) 0.00872 month, 41 month
(b) 0.00872 month, 79.49 month
(c) 41 month, 79.49 month
(d) 79.49 month, 41 month

7. In an experiment to study hydrolysis of an ester 0.5 M HCl at 300 K was used. 5 cm^3 of the reaction mixture was withdrawn after definite intervals and titrated against 0.2 M NaOH solution. Assuming pseudo first order kintics the rate constant at 300K from the following data will be

t (sec)	0	600	1200	1800	∞
V (cm^3 of NaOH used)	11.5	12.0	12.5	13.0	25.5

(a) 6.061×10^{-5} s^{-1} (b) 6.176×10^{-5} s^{-1}
(c) 6.296×10^{-5} s^{-1} (d) 6.177×10^{-5} s^{-1}

8. The following rate data was obtained for the first order thermal decomposition of $SO_2Cl_2(g)$ at a constant volume.

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

Exp.	Time (sec^{-1})	Total pressure (atm)
1.	0	0.5
2.	100	0.6

The reaction rate when total pressure is 0.65 atmosphere will be

(a) 2.23×10^{-3} sec^{-1} (b) 0.35 atm
(c) 7.8×10^{-4} atm sec^{-1} (d) 2.33×10^{-4} atm sec^{-1}

9. The gaseous reaction, $A(g) \rightarrow 2B(g) + C(g)$ is observed to be the first order. On starting with pure A, it is found that at the end of 10 min, the total pressure of the system is 176 mm of Hg and after a long time, it is 270 mm of Hg. Which of the following is correct for the given data?

(a) The initial pressure A is 90 mm Hg.
(b) The partial pressure of A after 10 min. is 47 mm Hg.
(c) The rate constant of the reaction is 0.0649 min^{-1}.
(d) all are correct

10. For the reaction, $2NO + H_2 \rightarrow N_2O + H_2O$ the value of $-dp/dt$ is found to be 1.50 Torr s^{-1} for a pressure of 359 Torr of NO and 0.25 Torr s^{-1} for a pressure of 152 Torr, the pressure of H_2 being constant. On the other hand, when the pressure of NO is kept constant, $-dp/dt$ is 1.60 Torr s^{-1} for a hydrogen pressure of 289 Torr and 0.79 Torr s^{-1} for a pressure of 147 Torr. The overall order of the reaction is:

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

11. The optical rotation of sucrose in 0.5 N-hydrochloric acid at 308 K and at various time intervals are given below. The rate constant for the first order hydrolysis of sucrose will be

Time (minutes)	0	10	20	30	60	∞
Rotation (degrees)	+32	25.5	20.0	15.5	5.0	–10.50

(a) 0.0166 min^{-1} (b) 0.0164 min^{-1}
(c) 0.0168 min^{-1} (d) none of these

12. Bicyclohexane was found to undergo two parallel first order rearangemments. At 730 K, the first order rate constant for the formation of cyclohexene was measured as $1.26 \times 10^{-4}\text{s}^{-1}$ and for the formation of methyl cyclopentene the rate constant was $3.8 \times 10^{-5}\text{s}^{-1}$. What is the percentage of the methyl cyclopentene?
(a) 20% (b) 30% (c) 15% (d) 23%

13. ^{227}Ac has a half-life of 22 years with respect to radioactive decay. The decay follows two parallel paths, on leading to ^{222}Th and other to ^{223}Fr. The percentage yields of these two daughter nuclides are 2 and 98 respectively. The decay constant for separate paths are:
(a) $0.693\ y^{-1}$; $0.693\ y^{-1}$
(b) $0.387\ y^{-1}$; $0.63\ y^{-1}$
(c) $0.03087\ y^{-1}$; $0.00063\ y^{-1}$
(d) 2; 98

14. The decomposition of N_2O_5 is takes place as

$$N_2O_5 \rightleftharpoons 2NO_2 + \frac{1}{2}O_2$$

If the values of the rate constants are 3.45×10^{-5} and 6.9×10^{-3} at 27°C and 67°C respectively then energy of activation will be
(a) 222.5 kJ (b) 122.5 kJ
(c) 112.5 kJ (d) 450 kJ

15. The decomposition of A into product has value of K as $4.5 \times 10^3\ \text{sec}^{-1}$ at 10°C and the energy of activation 60 KJ mol^{-1}. At what temperature would K be $1.5 \times 10^4\ \text{sec}^{-1}$.
(a) 283 K (b) 293 K
(c) 297.02 K (d) 293.8 K

16. For the decomposition of dimethyl ether, A in the Arrhenious equation $k = Ae^{-Ea/RT}$ has a value of $1.26 \times 10^{13}\ \text{s}^{-1}$ and E_a value of 58.5 kcal. The half-life period for first order decomposition at 527°C is
(a) 525 sec (b) 636 sec
(c) 800 sec (d) 425 sec

17. Two substances A and B are present such that $[A_0] = 4[B_0]$ and half-life of A is 5 min and that of B is 15 min. If they start decaying at the same time following first order kinetics how much time later will the concentration of both of them would be same.
(a) 30 min (b) 60 min
(c) 15 min (d) 10 min

18. A radioactive isotope has an initial activity of 2×10^6 disintegration/min. After 4 days its activity is 9×10^5 dis/min. The activity after 40 days will be
(a) 699.31 dpm (b) 680.81 dpm
(c) 670 dpm (d) 500 dpm

19. For the first order reaction $A(g) \rightarrow 2B(g) + C(g)$, the initial pressure is $P_A = 90$ mm Hg. The pressure after 10 minutes is found to be 180 mm Hg. The half-life period of the reaction is
(a) $1.15 \times 10^{-3}\ \text{sec}^{-1}$ (b) 600 sec
(c) $3.45 \times 10^{-3}\ \text{sec}^{-1}$ (d) 200 sec

20. $A(g) \longrightarrow B(g) + C(g)$

$$\frac{-d[A]}{dt} = k[A]$$

At the start pressure is 100 mm and after 10 min, pressure is 120 mm. Hence rate constant (min^{-1}) is
(a) $\frac{2.303}{10}\log\frac{120}{100}$ (b) $\frac{2.303}{10}\log\frac{100}{20}$
(c) $\frac{2.303}{10}\log\frac{100}{80}$ (d) $\frac{2.303}{10}\log\frac{100}{120}$

21. Find out the % of the reactant molecule crossing over the energy barrier at 325 K given that $\Delta H_{325} = 0.12$ kcal $E_{a(b)} = +0.02$ cal.
(a) 41 (b) 81 (c) 71 (d) 91

22. In a endothermic equilibrium reaction if k_1 and k_2 be the rate constants of forward reaction and backward reaction respectively at temperature t°C and k_1' and k_2' be the respective rate constant at (t + 10° C) then
(a) $\frac{k_1'}{k} = \frac{k_2'}{k_2}$ (b) $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$
(c) $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$ (d) none of the above

23. A first order gaseous decomposition of $N_2O_4 \rightarrow 2NO_2$ has k value of $4.5 \times 10^3\ \text{sec}^{-1}$ at 1°C and energy of activation of 58 kJ/mole at what temperature in kelvin rate constant would be $1.00 \times 10^4\ \text{sec}^{-1}$
(a) 273 (b) 283 (c) 373 (d) 546

24. A certain reaction $A + B \rightarrow C$ is first order w.r.t to each of reactant with $K = 10^{-2}\ \text{L mol}^{-1}\ \text{sec}^{-1}$ calculate the concentration of 'A' remaining after 100 sec if initial concentration of each reactant was 0.1 M
(a) 1.11 M (b) 0.09 M
(c) 0.06 M (d) 0.07 M

25. The rate constants for two parallel reactions were found to be $1 \times 10^{-2}\ \text{dm}^{-3}\ \text{mol}^{-1}\ \text{sec}^{-1}$ and $3.0 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{sec}^{-1}$. If the corresponding energies of activation of parallel reaction are 60 kJ mol^{-1} and 70 kJ mol^{-1} respectively. The apparent overall activation energy of reaction is
(a) 130 kJ/mol (b) 135 kJ/mol
(c) 65 kJ/mol (d) 67.5 kJ/mol

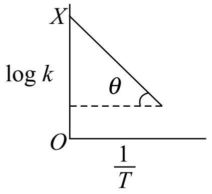
26. Number of natural lifs (T_{av}) required for a first order reaction to achieve 99.9% level of completion is
(a) 2.3 (b) 6.9 (c) 9.2 (d) 0.105

27. In zero-order reaction $t_{75\%} = xt_{1/2}$. Then the value of x =

(a) 2 (b) $\frac{3}{2}$ (c) $\frac{2}{3}$ (d) 10

28. Graph between log k and $1/T$ (k = rate constant in $\sec^{-1}$ and T is the temperature in k) is straight line

If $OX = 5$ and slope of line $= -\frac{1}{2.303}$ then E_a is



(a) 2.303×2 cal (b) $\frac{2}{2.303}$ cal
(c) 2 cal (d) none

29. Inversion of sucrose ($C_{12}H_{22}O_{11}$) is first order reaction is studied by measuring angle of rotation at different interval of time.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

if $(r_\infty - r_0) = a$ and $(r_\infty - r_t) = a - x$ where r_0, r_t and r_∞ are the angle of rotation at the start, at the time t, and at the end of reaction respectively. Then there is 50% inversion when

(a) $r_0 = 2r_t - r_\infty$ (b) $r_0 = r_t - r_\infty$
(c) $r_0 = r_t - 2r_\infty$ (d) $r_0 = r_t + r_\infty$

30. For a reaction rate constant is given by

$\ln k(\min^{-1}) = -\frac{11067k}{T} + 31.330$ then what is the effect on the rate of the reaction at 127°C if in presence of catalyst, energy of activation is lowered by 10 kJ mol^{-1}

(a) 10 times increases (b) 20 times increases
(c) 30 times increases (d) no change

31. The rate constant for the forward reaction $A(g) \rightleftharpoons 2B(g)$ is $1.5 \times 10^{-3}\ s^{-1}$ at 100 K. If 10^{-5} moles of A and 100 moles of B are present in a 10 L vessel at equilibrium then rate constant for the backward reaction at this temperature is

(a) 1.50×10^4 L $\text{mol}^{-1}\ s^{-1}$
(b) 1.5×10^{11} L $\text{mol}^{-1}\ s^{-1}$
(c) 1.5×10^{10} L $\text{mol}^{-1}\ s^{-1}$
(d) 1.5×10^{-11} L $\text{mol}^{-1}\ s^{-1}$

32. Reaction $A + B \longrightarrow C + D$ follows following rate law rate $= K \times [A]^{\frac{1}{2}}[B]^{\frac{1}{2}}$. Starting with initial concentration of one mole of A and B each, what is the time taken for amount of A becomes 0.25 mole. Given: $K = 2.31 \times 10^{-3}\ \sec^{-1}$.

(a) 300 sec (b) 600 sec
(c) 900 sec (d) None of these

33. Consider the following first order competing reactions:

$$X \xrightarrow{k_1} A + B \quad \text{and} \quad Y \xrightarrow{k_2} C + D$$

If 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants (k_2/k_1) is

(a) 4.06 (b) 0.215 (c) 1.1 (d) 4.65

34. At certain temperature, the half-life period in the thermal decomposition of a gaseous substance as follows:

P(mm Hg)	500	250
$t_{1/2}$ (in min.)	235	950

Find the order of reaction [Given: log (23.5) = 1.37; log (95) = 1.97]

(a) 1 (b) 2 (c) 2.5 (d) 3

35. A first order reaction is 50% completed in 20 min at 27°C and in 5 min at 47°C. The energy of activation of the reaction is

(a) 43.85 kJ/mol (b) 55.14 kJ/mol
(c) 11.97 kJ/mol (d) 6.65 kJ/mol

36. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4}\ s^{-1}$, 104.4 kJ mol^{-1} and $6.0 \times 10^{14}\ s^{-1}$ respectively. The value of the rate constant at $E_A \to 0$ is

(a) $2.0 \times 10^{18}\ s^{-1}$ (b) $6.0 \times 10^{14}\ s^{-1}$
(c) Infinity (d) $3.6 \times 10^{30}\ s^{-1}$

37. Given that for a reaction of order n, the integrated form of the rate equation is $k = \frac{1}{t(n-1)}\left[\frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}}\right]$ where C_0 and C are the values of the reactant concentration at the start and after time t. What is the relationship between $t_{3/4}$ and $t_{1/2}$ where $t_{3/4}$ is the time required for C to become 1/4 C_0?

(a) $t_{3/4} = t_{1/2}\,[2^{n-1} + 1]$ (b) $t_{3/4} = t_{1/2}\,[2^{n-1} - 1]$
(c) $t_{3/4} = t_{1/2}\,[2^{n+1} - 1]$ (d) $t_{3/4} = t_{1/2}\,[2^{n+1} + 1]$

38. In a reaction involving one single reactant, the fraction of the reactant consumed may be defined as $f = \left(1 - \frac{C}{C_0}\right)$ where C_0 and C are the concentrations of the reactant at the start and after time t. For a first order reaction:

(a) $\frac{df}{dt} = K(1-f)$ (b) $-\frac{df}{dt} = Kf$

(c) $-\frac{df}{dt} = K(1-f)$ (d) $\frac{df}{dt} = Kf$

39. A reaction $2A + B \xrightarrow{K} C + D$ is first order with respect to A and 2nd order with respect to B. Initial concentration ($t = 0$) of A is C_0 while B is $2C_0$. If at t as 30 minutes the concentration of C is $C_0/4$ then rate expression at t = 30 minutes is:

(a) $R = 7C_0^3 K/16$ (b) $R = 27\,C_0^3 K/32$
(c) $R = 247\,C_0^3 K/64$ (d) $R = 49\,C_0^3 K/32$

40. $A \to B$ $\qquad K_A = 10^{15}\,e^{-2000/T}$

$C \rightarrow D \qquad K_C = 10^{14}\, e^{-1000/T}$

Temperature TK at which $(K_A = K_C)$ is

(a) 1000 K (b) 2000 K
(c) (2000/2.303) K (d) (1000/2.303) K

41. The rate of a reaction gets doubled when the temperature changes from 7°C to 17°C. By which factor will it change for the temperature change from 17°C to 27°C?

(a) 1.81 (b) 1.71 (c) 1.91 (d) 1.76

42. For the reaction $A + 2B \rightarrow$ products (started with concentrations taken in stoichiometric proportion), the experimentally determined rate law is

$$-\frac{d[A]}{dt} = K\sqrt{[A]}\,\sqrt{[B]}$$

The half life time of the reaction would be

(a) $\frac{0.693}{K}$ (b) $\frac{0.693}{1/K}$
(c) $\frac{0.693}{\sqrt{2}K}$ (d) not defined

43. For a reaction $2A + B \rightarrow$ product, rate law is

$$-\frac{d[A]}{dt} = K[A]$$

At a time when $t = \frac{1}{K}$, concentration of the reactant is

(C_0 = initial concentration)

(a) $\frac{C_0}{e}$ (b) $C_0 e$ (c) $\frac{C_0}{e^2}$ (d) $\frac{1}{C_0}$

44. A hypothetical reaction, $A_2 + B_2 \longrightarrow 2AB$ follows the mechanism as given below

$A_2 \rightleftharpoons A + A$ ...(fast)
$A + B_2 \longrightarrow AB + B$ ... (slow)
$A + B \longrightarrow AB$ ...(fast)

The order of the overall reaction is:

(a) 2 (b) 1 (c) $1\frac{1}{2}$ (d) zero

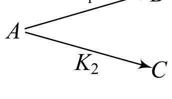
45. In the following first order competing reactions

A + Reagent $\longrightarrow$ Product and
B + Reagent $\longrightarrow$ Product

The ratio of K_1/K_2 if only 50% of B will have been reacted when 94% of A has been reacted is

(a) 4.06 (b) 0.246 (c) 2.06 (d) 0.06

46. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as



$K_1 = 1.26 \times 10^{-4}$ sec^{-1}
and $K_2 = 3.8 \times 10^{-5}$ sec^{-1}

The percentage distribution of B and C are:

(a) 80% B and 20% C
(b) 76.83% B and 23.17% C
(c) 90% B and 10% C
(d) 60% B and 40% C

47. A radioactive nuclide is produced at a constant rate of α per second. Its decay constant is λ. If N_0 be the of nuclei at time $t = 0$, then maximum number of nuclei possible are:

(a) N_0 (b) α/λ
(c) $N_0 + \frac{\alpha}{\lambda}$ (d) $\frac{\lambda}{\sigma} + N_0 s$

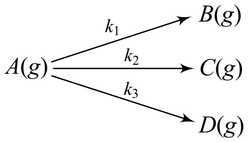
48. $A(\text{aq}) \longrightarrow B(\text{aq}) + C(\text{aq})$ is a first order reaction:

Time	t	∞
moles of reagent	n_1	n_2

Reaction progress is measure with the help of titration of reagent 'R'. If all A, B and C reacted with reagent and have 'n' factors $\left[n \text{ factors; eq. wt.} = \frac{\text{mol. wt.}}{n}\right]$ in the ratio of 1:2:3 with the reagent. The k in terms of t, n_1 and n_2 is

(a) $K = \frac{1}{t}\ln\left(\frac{n_2}{n_2 - n_1}\right)$ (b) $K = \frac{1}{t}\ln\left(\frac{2n_2}{n_2 - n_1}\right)$
(c) $K = \frac{1}{t}\ln\left(\frac{4n_2}{n_2 - n_1}\right)$ (d) $K = \frac{1}{t}\ln\left(\frac{4n_2}{5(n_2 - n_1)}\right)$

49. A gaseous compound A reacts by three independent first order processes (as shown in figure) with rate constant 2×10^{-3}, 3×10^{-3} and 1.93×10^{-3} sec^{-1} for products B, C and D respectively.



If initially pure A was taken in a closed container with P = 8 atm, then the partial pressure of B (in atm) after 100 sec from start of experiment:

(a) 0.288 (b) 0.577
(c) 1.154 (d) None of these

LEVEL III

1. Match the following:

	Column I	Column II	
(A)	$_{11}\text{Na}^{23} + \ldots \longrightarrow _{11}\text{Na}^{24} + \ldots$	(p)	$_0n^1$
(B)	$2\,_1\text{H}^3 \longrightarrow _2\text{He}^4 + 2\ \ldots$	(q)	$_1\text{H}^1$
(C)	$_{92}\text{U}^{238} \longrightarrow _{90}\text{Th}^{234} + \ldots$	(r)	$_2\text{He}^4$
(D)	$_{29}\text{Cu}^{63} \longrightarrow _{28}\text{Ni}^{63} + \ldots$	(s)	$_1e^0$
		(t)	$_1\text{H}^2$

2. Matching (For first-order reaction)

	Column I	Column II	
(A)	$t_{63/64}$	(p)	$6t_{1/2}$
(B)	$t_{15/16}$	(q)	$2t_{3/4}$

(C)	$t_{31/32}$	(r)	$\frac{5}{3}t_{7/8}$
(D)	$t_{255/256}$	(s)	$2t_{15/16}$

3. Match Column I with Column II

Column I		Column II	
(A)	Decomposition of H_2O_2	(p)	$10t_{1/2}$
(B)	$\frac{K_{308}}{K_{298}}$	(q)	first order
(C)	Arrhenius equation	(r)	Temperature coefficient
(D)	$t_{99.9\%}$ for first order	(s)	$\log\frac{K_2}{K_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$
		(t)	2 – 3

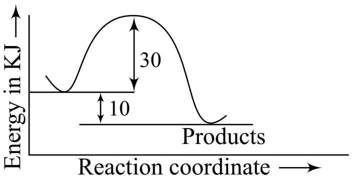
4. Match Column I with Column II

Column I Order		Column II Rate Constant	
(A)	Zeroth	(p)	$K=\frac{1}{2t}\left(\frac{1}{(a-x)^2}-\frac{1}{a^2}\right)$
(B)	First	(q)	$K=\frac{1}{t}\left(\frac{1}{(a-x)}-\frac{1}{a}\right)$
(C)	Second	(r)	$K=\frac{x}{t}$
(D)	Third	(s)	$K=\frac{1}{t}\ln\left(\frac{a}{(a-x)}\right)$

5. Match Column I with Column II

Column I Order		Column II Rate Constant	
(A)	First Order	(p)	$t_{1/2}\propto a$
(B)	Second Order	(q)	$t_{1/2}\propto\frac{1}{(a)^{n-1}}$
(C)	Zero Order	(r)	$t_{1/2}=\frac{0.693}{K}$
(D)	*n*th Order	(s)	$\log(a-x)$ v/s time graph is straight line with –ve slope
		(t)	$t_{1/2}\propto\frac{1}{a}$

Passage 1



The above graph represents the energy profile diagram for a first order reaction taking place at a constant temperature of 47°C. The specific rate constant for the forward and backward reaction is 10^{-4} min^{-1} and 10^{-6} min^{-1} respectively.

6. The energy of activation for the backward reaction is
(a) 30 kJ mol^{-1} (b) 20 kJ mol^{-1}
(c) 10 kJ mol^{-1} (d) 40 kJ mol^{-1}

7. In overall reaction heat is
(a) liberated (b) absorbed
(c) no change in heat (d) cannot be predicted

8. The maximum rate constant for the forward reaction is
(a) 5.46 (b) 7.30 (c) 1.23 (d) 9.83

Passage 2

A vessel contains gaseous dimethylether at initial pressure 'p_0' atm. Dimethyl ether decomposes on heating as per the reaction by first order kinetics.

$$CH_3-O-CH_3(g)\xrightarrow{\Delta}CH_4(g)+CO(g)+H_2(g)$$

It is observed that the half-life period for this reaction is 0.2 hour. After a very long time, pressure in the vessel is observed to be 1.2 atm. Assume ideal behaviour of all gases with constant V-T conditions.

9. What would be the approximate pressure in the vessel at 0.6 hour? [$\log_{10} 8 = 0.9$]
(a) 0.05 atm (b) 1.5 atm
(c) 2.303 atm (d) 1.1 atm

10. The initial rate of formation of CH_4 gas is
(a) 1.386 atm h^{-1} (b) 0.7 atm h^{-1}
(c) 2.07 atm h^{-1} (d) 1.4 atm h^{-1}

11. For a first order sequential reaction, $A\xrightarrow{k_1}B\xrightarrow{k_2}C$, $k_1 = 2.31\times10^{-3}$ s^{-1} and $k_2 = 1.1\times10^{2}$ s^{-1} and initial molar concentration of A is 2.0 M. The concentration of C at time t = 20 minutes is
(a) 0.75 M (b) 1.5 M
(c) 1.75 M (d) 1.875 M

Passage 3

Dideuterocyclopropane (A) undergoes a first order decomposition. The observed rate constant at a certain temperature, measured in terms of the disappearance of A, was 1.52×10^{-4} s^{-1}. Analysis of the reaction products showed that the reaction followed two parallel paths, one leading to dideuteropropene (B) and the other to *cis*-1,2-dideuterocyclopropane (C). B was found to constitute 11.2% of the reaction product, independent of the extent of reaction.

12. The order of the pathways leading to the formation of B and C respectively are

(a) 1 and 0 (b) 0 and 1
(c) 1 and 1 (d) 0 and 0

13. Rate constant for the conversion of *A* to *B* is

(a) $1.7 \times 10^{-5}\ s^{-1}$ (b) 1.7×10^{-5} mol $L^{-1}\ s^{-1}$
(c) $1.52 \times 10^{-4}\ s^{-1}$ (d) 1.35×10^{-4} mol $L^{-1}\ s^{-1}$

14. Rate constant for the conversion of *A* to *C* is

(a) 1.35×10^{-4} mol $L^{-1}\ s^{-1}$
(b) $1.7 \times 10^{-5}\ s^{-1}$
(c) $1.52 \times 10^{-4}\ s^{-1}$
(d) $1.35 \times 10^{-4}\ s^{-1}$

Passage 4

Ozone is prepared in laboratory by passing silent electric discharge through pure and dry oxygen in an apparatus known as ozoniser. This conversion from oxygen to ozone is a reversible and endothermic reaction. When oxygen is subjected to an ordinary electric discharge, most of the O_3 produced will get decomposed. When any insulating material such as glass, is inserted in the space between the two electrodes and high current density is applied, silent electric discharge passes on between the two electrodes. By this process no spark is produced and much less heat is generated, and as a result the decomposition of the produced ozone is much retarded.

The decomposition of ozone is believed to occur by the following mechanism:

$$O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O \qquad \text{(Fast step)}$$

$$O_3 + O \xrightarrow{K_f} 2O_2 \qquad \text{(Slow)}$$

15. Order of the reaction is

(a) 1 (b) 2 (c) 3 (d) 0

16. Molecularity of reaction is defined by

(a) slow step (b) reversible step
(c) from overall reaction (d) not defined

17. When the concentration of O_2 is increased, for the same concentration of ozone, its rate

(a) increases (b) decreases
(c) remains the same (d) cannot be answered

Passage 5

The rate law for the decomposition of gaseous N_2O_5 is $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$. Reaction mechanism has been suggested as follows

$$N_2O_5 \overset{Keq}{\rightleftharpoons} NO_2 + NO_3 \text{ (fast equilibrium)}$$

$$NO_2 + NO_3 \xrightarrow{k_1} NO_2 + NO + O_2 \text{ (slow)}$$

$$NO + NO_3 \xrightarrow{k_2} 2NO_2 \text{ (fast)}$$

18. Order of the reaction is

(a) 0 (b) –1 (c) 1 (d) 3/2

19. In 20 minutes 80% of N_2O_5 is decomposed. Rate constant is

(a) 0.08 (b) 0.05 (c) 0.12 (d) 0.2

20. At the equilibrium state N_2O_5, NO_2 and NO_3 concentrations are 0.2, 0.4 and 0.4 M respectively. k_1 is

(a) 0.1 (b) 0.2 (c) 1 (d) 2

Assertion and Reasoning

(a) STATEMENT-1 is True, STATEMENT-2 is True, STATEMENT-2 **is** correct explanation of STATEMENT-1
(b) STATEMENT-1 is True, STATEMENT-2 is True, STATEMENT-2 **is NOT** correct explanation of STATEMENT-1
(c) STATEMENT-1 is True, STATEMENT-2 is False.
(d) STATEMENT-1 is False, STATEMENT-2 is True.

21. Statement 1: The rate of a chemical reaction increases with increase in temperature.
Statement 2: Increase in temperature increases the number of effective collision.

22. Statement 1: Generally, the activation energy of the molecule cannot be zero.
Statement 2: Because 100% reactant molecules cannot convert into the product.

23. Statement 1: Specific activity of the same radioactive substance is same for 10 g radioactive substance as well as 50 g radioactive substance.
Statement 2: Specific activity of a radioactive substance is its activity per g.

24. Statement 1: In rate law, the exponents for concentration do not necessarily match the stoichiometry coefficients.
Statement 2: In rate law expression, exponents for concentration are determined by experiments not by balanced chemical reaction.

25. Statement 1: Half-life period of a first order reaction is independent of initial concentration.
Statement 2: Half-life period for a first order reaction is $t_{1/2} = \frac{2.303}{K}\log 2$.

26. Statement 1: The Arrhenius equation explains the temperature dependence of rate of a chemical reaction.
Statement 2: Plots of log *K* versus 1/*T* are linear and the energy of activation is obtained from such plots.

27. Statement 1: For a chemical reaction to occur, there must be collision in between reactant species.
Statement 2: All such collisions necessarily convert themselves into product formation.

28. Statement 1: $NO_2 + CO \longrightarrow CO_2 + NO \quad r = k[NO_2]$
The rate of the above reaction is independent of the concentration of CO.
Statement 2: The rate does not depend upon [CO] because it is involved in fast step.

29. Statement 1: For exothermic as well endothermic reactions; rate constant increases with increase of temperature.
Statement 2: On increasing temperature activation energy of reaction decreases.

30. **Statement 1:** For a reaction A(gas) $\rightarrow B$(gas)

$-r_A = 2.5P_A$ at 400 k

$-r_A = 2.5P_A$ at 600 k

Statement 2 : Activation energy is 4135 J/mole

31. **Statement 1:** If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.

Statement 2: Lower the activation energy, faster the reaction.

More than one correct

32. A reaction is catalysed by H^+ ion. In presence of HA, rate constant is 2×10^{-3} min^{-1} and in presence of HB rate constant is 1×10^{-3} min^{-1}, HA and HB both being strong acids, we may conclude that

(a) equilibrium constant is 2.
(b) HA is stronger acid than HB.
(c) relative acidic strength of HA and HB is 2.
(d) HA is weaker acid than HB and relative strength is 0.5.

33. Rate constant k varies with temperature as given by equation:

$\log k\ (\text{min}^{-1}) = 5 - \dfrac{2000\ \text{K}}{\text{T}}$. We can conclude

(a) pre-exponential factor A is 5
(b) E_a is 2000 kcal
(c) pre-exponential factor A is 10^5
(d) E_a is 9.152 kcal

34. For a first order reaction

(a) The degree of dissociation is equal to $1 - e^{-kt}$.
(b) A plot of reciprocal of concentration of reactant vs. time gives a straight line.
(c) The time taken for the completion of 75% of reaction is thrice the $t_{1/2}$ of the reaction.
(d) The pre-exponential factor in the Arrhenius equation has the dimensions of time.

35. The rate of change in concentration of C in the reaction $2A + B \rightarrow 2C + 3D$ was observed as 1.0 mol L^{-1} sec^{-1}. Which of the following is/are correct for the rate of reaction?

(a) Rate of change of concentration of A is 1.0 mol L^{-1} sec^{-1}.
(b) Rate of change of concentration of B is 0.5 mol L^{-1} sec^{-1}.
(c) Rate of change of concentration of D is 1.5 mol L^{-1} sec^{-1}.
(d) Rate of reaction is 0.5 mol L^{-1} sec^{-1}.

36. For the reaction: $2A + B \longrightarrow A_2B$

The rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 s^{-1}. If the initial concentration of A and B are 0.1 mol L^{-1} and 0.2 mol L^{-1} respectively then which of the following is/are correct?

(a) Initial rate of reaction is 8×10^{-9} mol L^{-1} sec^{-1}.
(b) When A is reduced to 0.06 mol L^{-1} then rate becomes 3.89×10^{-9} mol L^{-1} sec^{-1}.
(c) When A is reduced to 0.06 mol L^{-1} then B will be 0.16 mol L^{-1}.
(d) All are correct.

37. Analyse the rate expression for the following reactions:

(i) $3NO(g) \longrightarrow N_2O\ (g)$; Rate = $k[NO]^2$
(ii) $H_2O_2\ (aq) + 3I^-\ (aq) + 2H^+ \longrightarrow 2H_2O\ (l) + I_3^-$; Rate = $k[H_2O_2][I^-]$
(iii) $CH_3CHO\ (g) \longrightarrow CH_4\ (g) + CO(g)$; Rate = $k[CH_3CHO]^{3/2}$
(iv) $C_2H_5Cl\ (g) \longrightarrow C_2H_4\ (g) + HCl\ (g)$; Rate = $k[C_2H_5Cl]$

Based on the above expressions, which of the following is/are correct?

(a) Order of (i) reaction is two and unit of k is (concentration)$^{-1}$ sec^{-1}
(b) Order of (ii) reaction is one and unit of k is sec^{-1}
(c) Order of (iii) reaction is three/two and unit of k is (concentration)$^{-1/2}$ sec^{-1}
(d) Order of (iv) reaction is one and unit of k is sec^{-1}

38. $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Half-life period of the reaction is independent of concentration of zinc at constant pH. For the constant concentration of Zn, rate becomes 100 times when pH is decreased from 3 to 2. Hence

(a) $\dfrac{dx}{dt} = k[Zn]^0[H^+]^2$
(b) $\dfrac{dx}{dt} = k[Zn][H^+]^2$
(c) Rate is not affected if concentration of zinc is made four times and that of H^+ ion is halved.
(d) Rate becomes four times if concentration of H^+ ion is doubled at constant Zn concentration.

39. The basic theory behind Arrhenius equation is that

(a) the number of effective collisions is proportional to the number of molecules above a certain threshold energy.
(b) as the temperature increases, so does the number of molecules with energies exceeding the threshold energy.
(c) the rate constant is a function of temperature.
(d) the activation energy and pre-exponential factor are always temperature-independent.

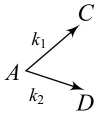
40. The calculation of the pre-exponential factor is based on the

(a) idea that, for a reaction to take place, the reactant species must come together.
(b) calculation of the molecularity of the reaction.
(c) idea that the reactant species must come together, leading to the formation of the transition state which then transforms into the products.
(d) calculation of the order of the reaction.

41. Which of the following factors affect the rate of reaction?
- (a) Nature of reactant
- (b) Pressure
- (c) Volume of reaction vessel
- (d) Radiation

42. Consider the following case of competing first order reactions.

After the start of the reaction at $t = 0$ with only A, the [C] is equal to [D] at all times. The time in which all the three concentration will be equal is given by



- (a) $t = \frac{1}{2k_1} \ln 3$
- (b) $t = \frac{1}{2k_2} \ln 3$
- (c) $t = \frac{1}{3k_1} \ln 2$
- (d) $t = \frac{1}{3k_2} \ln 2$

43. In which of the following, E_a for backward reaction is greater than E_a for forward reaction?
- (a) $A \xrightarrow{E_a = 50\,\text{kcal}} B;\ \Delta H = -10$ kcal
- (b) $A \xrightarrow{E_a = 50\,\text{kcal}} B;\ \Delta H = +10$ kcal
- (c) $A + 10$ kcal $\rightarrow B$; $E_a = 50$ kcal
- (d) $A - 10$ kcal $\rightarrow B$; $E_a = 50$ kcal

44. Which of the following statements is (are) correct?
- (a) A plot of $\log Kp$ vs $\frac{1}{T}$ is linear.
- (b) A plot of $\log[X]$ vs time is linear for a first order reaction, $X \rightarrow P$.
- (c) A plot of $\log P$ vs. $\frac{1}{T}$ is linear at constant volume.
- (d) A plot of $\log P$ vs $\frac{1}{V}$ is linear at constant temperature.

45. The rate laws for the reaction:
RCl + NaOH (aq.) $\longrightarrow$ ROH + NaCl is given by,
Rate = k_1[RCl]. The rate of the reaction will be
- (a) doubled on doubling the concentration of sodium hydroxide.
- (b) halved on reducing the concentration of alkyl halide to one half.
- (c) increased on increasing the temperature of the reaction.
- (d) unaffected by increasing the temperature of the reaction.

46. The reaction between A and B is first order with respect to A and zero order with respect to B. Analyse the given data for the same reaction.

Experiment	[A] in mol L^{-1}	[B] in mol L^{-1}	Initial rate in mole L^{-1} min^{-1}
I	0.1	0.1	2×10^{-2}
II	–	0.2	4×10^{-2}
III	0.4	0.4	–
IV	–	0.2	2×10^{-2}

Which of the following is/are correct for the above data?
- (a) Concentration of A in II experiment is 2×10^{-1} mol L^{-1}.
- (b) Half life period of B is independent of initial concentration.
- (c) Initial rate for experiment III is 3.2×10^{-2} mol L^{-1} min^{-1}.
- (d) Concentration of A in experiment IV is 1×10^{-1} mol L^{-1}.

47. Which of the following statements is/are correct?
- (a) The rate of the reaction involving the conversion of ortho-hydrogen to para-hydrogen is $-\frac{d[H_2]}{dt} = k[H_2]^{3/2}$.
- (b) The rate of the reaction involving the thermal decomposition of acetaldehyde is $k[CH_3CHO]^{3/2}$.
- (c) In the formation of phosgene gas from CO and Cl_2, the rate of the reaction is $k[CO][Cl_2]^{1/2}$.
- (d) In the decomposition of H_2O_2, the rate of the reaction is $k[H_2O_2]$.

48. Which of the following reactions is/are of the first order?
- (a) The decomposition of ammonium nitrate in an aqueous solution.
- (b) The inversion of cane-sugar in the presence of an acid.
- (c) The acidic hydrolysis of ethyl acetate.
- (d) All radioactive decays.

49. Which of the following statements about zero-order reaction is/are not true?
- (a) Unit of rate constant is sec^{-1}.
- (b) The graph between log (reactant) versus time is a straight line.
- (c) The rate of reaction increases with the increase in concentration of reactants.
- (d) Rate of reaction is independent of concentration of reactants.

50. In a pseudo first order acid catalysed hydrolysis of ester in water, the following results were obtained:

t/s	0	30	60	90
[ester]/M	0.55	0.31	0.17	0.085

Which of the following is/are correct for the given reaction?
- (a) The average rate of reaction between time interval 30 to 60 seconds is 4.67×10^{-3}mol L^{-1} s^{-1}.
- (b) Order of reaction is 2.
- (c) Pseudo first order rate constant for the acid catalysed hydrolysis of ester is 1.92×10^{-2} s^{-1}.
- (d) All are correct.

51. Which of the following statements are correct about half-life period?
   (a) It is proportional to initial concentration for zeroth order.
   (b) Average life = 1.44 × half-life; for first order reaction.
   (c) Time of 75% reaction is thrice of half-life period in first order reaction.
   (d) 99.9% reaction takes place in 100 minutes for the case when rate constant is 0.0693 min^{-1}.

52. Which of the following statements is/are correct?
   (a) The order of a reaction is the sum of the components of all the concentration terms in the rate equation.
   (b) The order of a reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentrations of all other reactants constant.
   (c) Orders of reactions can be whole numbers or fractional numbers.
   (d) The order of a reaction can only be determined from the stoichiometric equation for the reaction.

53. In Arrhenius equation, $K = Ae^{-Ea/RT}$. A may be termed as the rate constant at
   (a) very low temperature
   (b) very high temperature
   (c) zero activation energy
   (d) the boiling temperature of the reaction mixture

Integer type Question

54. Rate constant for a reaction $H_2 + I_2 \rightleftharpoons 2HI$ is 0.2, then calculate rate constant for reaction $2HI \rightleftharpoons H_2 + I_2$

55. A freshly prepared radioactive source of half-life 2 hours emits radiations of intensity which is 64 times the permissible safe level. Calculate the minimum number of half-lives after which it would be possible to work safely with this source.

56. Two reactions proceed at 25°C at the same rate, the temperature coefficient of the rate of the first reaction is 2.0 and of the second, 2.5. Find the approximate ratio of rates of these reactions at 95°C.

57. Calculate the number of neutrons accompanying the formation of ${}^{139}_{54}\text{Xe}$ and ${}^{94}_{38}\text{Sr}$ from the absorption of a slow neutron by ${}^{235}_{92}\text{U}$, followed by nuclear fission.

58. The rate constant, the activation energy and the Arhenius parameter (A) of a chemical reaction at 25°C are 3.0×10^{-4} sec^{-1}, 104.4 kJ mol^{-1} and 6.0×10^{-4} sec^{-1} respectively the value of the rate constant $T \rightarrow \infty$ is .... $\times 10^{-4}$ sec^{-1}.

59. For a first order parallel reaction $A \begin{array}{l} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{array}$ $\dfrac{k_1}{k_2} = 8$ then, at a time interval, the value of $\dfrac{(C)}{(A)}$ is given as $\dfrac{e^{xa} - 1}{x}$ what is the value of x?

60. The rate constant for the reaction $2N_2O_5 \rightarrow 4NO_2$ is 3×10^{-5} sec^{-1} if the rate 2.4×10^{-5} mol L^{-1} sec^{-1} then the concentration of N_2O_5 in mol L^{-1} is .... $\times 10^{-5}$.

Subjective Type Question

61. In a catalytic experiment involving the Haber process, $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of reaction was measured as

$$\text{Rate} = \frac{\Delta[NH_3]}{\Delta t} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

If there were no side reactions, what was the rate of reaction expressed in terms of (a) N_2, (b) H_2?

62. Dinitropentaoxide decomposes as follows:

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

Given that $-d[N_2O_5]/dt = k_1[N_2O_5]$
$d[NO_2]/dt = k_2[N_2O_5]$
$d[O_2]/dt = k_3[N_2O_5]$

What is the relation between k_1, k_2 and k_3?

63. The reaction $2A + B + C \rightarrow D + E$ is found to be first order in A second in B and zero order in C.
   (i) Give the rate law for the reaction in the form of differential equation.
   (ii) What is the effect in rate of increasing concentrations of A, B and C two times?

64. In the following reaction, rate constant is 1.2×10^{-2} M s^{-1} $A \longrightarrow B$. What is concentration of B after 10 and 20 min., if we start with 10 M of A?

65. In gaseous reactions important for understanding the upper atmosphere, H_2O and O react biomolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and $E_a = 77$ kJ mol^{-1}, then calculate E_a for the biomolecular recombination of 2OH radicals to form H_2O and O at 500 K.

66. The reaction $2NO + Br_2 \longrightarrow 2NOBr$, is supposed to follow the following mechanism:

(i) $NO + Br_2 \overset{\text{fast}}{\rightleftharpoons} NOBr_2$

(ii) $NOBr_2 + NO \xrightarrow{\text{slow}} 2NOBr$

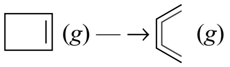
Suggest the rate of law expression.

67. A first order reaction, $A \rightarrow B$, requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature.

68. Two reactions (i) $A \rightarrow$ products (ii) $B \rightarrow$ products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 min. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half of that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K.

69. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hrs, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.025 M $KMnO_4$ solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2.

70. Isomerisation of cyclobutene into 1,3-butadine follows first order kinetics as:



The kinetic study was performed by taking same amounts of cyclobutene in three sealed flasks. First flask was broken after 20 minute and the reaction mixture was absorbed completely in bromine solution. 16.0 mL 1.0 M bromine solution was required. The second flask was broken after a very long time and the reaction mixture required 20 mL bromine solution of the same strength. If the third flask was broken after 30 minute, what volume of bromine solution of same strength would have been required?

71. Decomposition of both $A_2(g)$ and $B_3(g)$ follows 1st order kinetic as:

$$A_2(g) \xrightarrow{K_1} 2A(g) \qquad K_1(hr^{-1}) = 10^2\, e^{-\frac{14000}{RT}}$$

$$B_3(g) \xrightarrow{K_2} 3B(g) \qquad K_2(hr^{-1}) = 10^3\, e^{-\frac{20000}{RT}}$$

If one mole of each $A_2(g)$ and $B_3(g)$ are taken in a 10 L evacuated flask and heated to some temperature so that they start decomposing at the same rate, determine total pressure in the flask after 1.0 hr.

72. A first order chemical reaction was carried out for 1.0 hour in absence of a catalyst and 20% reaction was complete. A catalyst was then added and reaction was allowed to continue for next 30 min when 60% reaction was complete. A second catalyst was then added at this time and reaction was allowed to continue for further 10 min when 90% reaction was complete. If activation energy of the original path was 80 kJ, determine activation energy of catalysed pathways. Assume constant temperature throughout to be 300 K.

73. Derive an expression for the velocity of reaction:
$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$
with the help of following mechanism:

$$N_2O_5 \xrightarrow{K_a} NO_2 + NO_3$$

$$NO_3 + NO_2 \xrightarrow{K_{-a}} N_2O_5$$

$$NO_2 + NO_3 \xrightarrow{K_b} NO_2 + O_2 + NO$$

$$NO + NO_3 \xrightarrow{K_c} 2NO_2$$

74. The oxidation of certain metals is found to obey the equation $\tau^2 = \alpha t + \beta$ where t is the thickness of the oxide film at time t, α and β are constants. What is the order of this reaction?

75. The complex $[Co(NH_3)_5F]^{2+}$ reacts with water according to equation.
$[Co(NH_3)_5F]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + F^-$
The rate of the reaction = rate const. × $[complex]^a \times [H^+]^b$. The reaction is acid catalysed, i.e., $[H^+]$ does not change during the reaction. Thus rate = $k'[Complex]^a$ where $k' = k[H^+]^b$, calculate 'a' and 'b' given the following data at 25°C.

[Complex]M	$[H^+]$M	$T_{1/2}$hr	$T_{3/4}$hr
0.1	0.01	1	2
0.2	0.02	0.5	1

76. At room temperature (20°C) orange juice gets spoilt in about 64 hrs. In a refrigerator at 3°C juice can be stored three times as long before it gets spoilt. Estimate (a) the activation energy of the reaction that causes the spoiling of juice. (b) How long should it take for juice to get spoilt at 40°C?

77. A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$. The rate constant of decomposition is 4.78×10^{-3} min^{-1}. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hr of initiation of decomposition. Assume the composition of gas present and composition of gas diffusing to be same.

78. The reaction A proceeds in parallel channels $A \begin{smallmatrix} \nearrow B \\ \searrow C \end{smallmatrix}$. Suppose the half-life values for the two branches are 60 min and 90 min, what is the overall half-life value?

79. A certain reactant B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to $B^{(n-2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At $t = 0$, the volume of the reagent consumed is 25 mL and at $t = 10$ min, the volume used up is 32 mL. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

80. The catalytic decomposition of formic acid may take place in two ways:
(a) $HCOOH = H_2O + CO$
(b) $HCOOH = H_2 + CO_2$
The rate constant and activation energy for reaction (a) are 2.79×10^{-3} min^{-1} at 236°C and 12.0 kcal $mole^{-1}$ respectively and for reaction (b) are 1.52×10^{-4} min^{-1} at 237°C and 24.5 kcal $mole^{-1}$ respectively. Find the temperature which will give a product made up of equimolar quantities of water vapour, carbon monoxide, hydrogen and carbon dioxide.

81. For the reaction $A \xrightarrow{K_1} B, 2A \xrightarrow{K_1} C$ Find $\dfrac{-d[A]}{dt}$.

$$V = V_0\left[\left(\frac{n_2}{n_1}\right) - \left(\frac{n_2}{n_1} - 1\right)\exp(-n_1 kt)\right];$$

$$[A]_t = [A]_0\left[\frac{\exp(-n_1 kt)}{(n_2/n_1) - \{(n_2/n_1) - 1\}\exp(-n_1 kt)}\right]$$

82. Bicyclohexane was found to undergo two parallel first order rearrangements. At 730 K, the first order rate constant for the formation of cyclohexane was measured as $1.26 \times 10^{-4}\ s^{-1}$, and for the formation of methyl cyclopentene the rate constant was $3.8 \times 10^{-5}\ s^{-1}$. What is the percentage distribution of Cyclohexane?

83. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C.

84. The decomposition of Cl_2O_7 at 440K in the gas phase to Cl_2 and O_2 is a first order reaction.
- (i) After 55 sec at 440 K the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm., calculate that rate constant.
- (ii) Calculate the pressure of Cl_2O_7 after 100 sec of decomposition at this temperature.

85. The first order reaction has $K = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 hrs, what percentage of the initial concentration would have changed in the product? What is the half-life period of this reaction?

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. A catalyst **[IIT JEE, 1984]**
- (a) increases the average kinetic energy of reacting molecules.
- (b) decreases the activation energy.
- (c) alters the reaction mechanism.
- (d) increases the frequency of collisions of reacting species.

2. The half-life period of a radioactive element is 140 days. After 560 days, 1 g of the element will reduced to **[IIT JEE, 1986]**

(a) $\frac{1}{2}$g (b) $\frac{1}{4}$g (c) $\frac{1}{8}$g (d) $\frac{1}{16}$g

3. A first order reaction $A \longrightarrow B$ requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 min, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature. **[IIT JEE, 1993]**

4. $_{13}Al^{27}$ is a stable isotope. $_{13}Al^{29}$ is expected to disintegrate by **[IIT JEE, 1994]**

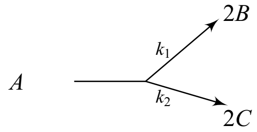
(a) α-emission (b) β-emission
(c) positron emission (d) proton emission

5. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C. **[IIT JEE, 1995]**

6. The rate constant for the first order decomposition of a certain reaction is given by the equation, $\log k(\text{sec}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$. Calculate **[IIT JEE, 1997]**
- (a) the energy of activation
- (b) the rate constant at 500 K.
- (c) At what temperature will its half-life period be 256 minute?

7. The rate constant of a reaction is $1.5 \times 10^7\ \text{sec}^{-1}$ at 50°C and $4.5 \times 10^7\ \text{sec}^{-1}$ at 100°C. Evaluate the Arrhenius parameters A and E_a. **[IIT JEE, 1998]**

8. For a hypothetical elementary reaction



where $\frac{k_1}{k_2} = \frac{1}{2}$. Initially only 2 moles of 'A' is present. Then total number of moles A, B and C at the end of 50% reaction is **[IIT JEE, 1999]**

9. The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in sec^{-1}) k_1 and k_2 respectively. The energy of activation for the two reactions are 152.30 kJ mol^{-1} and 157.7 kJ mol^{-1} as well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions. **[IIT JEE, 1999]**

10. The rate constant for an isomerisation reaction, $A \longrightarrow B$ is $4.5 \times 10^{-3}\ \text{min}^{-1}$. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 hr. **[IIT JEE, 1999]**

11. The rate constant for the reaction

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is $3 \times 10^{-5}\ s^{-1}$. If the rate at a given time is 2.40×10^{-5} mol $L^{-1}\ s^{-1}$, then concentration of N_2O_5 at that time is **[IIT JEE, 2000]**

(a) 1.4 mol L^{-1} (b) 1.2 mol L^{-1}
(c) 0.04 mol L^{-1} (d) 0.8 mol L^{-1}

12. ^{64}Cu (half-life = 12.8 h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes. **[IIT JEE, 2001]**

13. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process. $AB \xrightarrow{h\upsilon} AB^*$, the rate of formation of AB^* is directly proportional to **[IIT JEE, 2001]**

(a) C (b) I (c) I^2 (d) C.I

14. ^{23}Na is the more stable isotope of Na. Find out the process by which $^{24}_{11}Na$ can undergo radioactive decay **[IIT JEE, 2003]**

(a) β^- emission (b) α emission
(c) β^+ emission (d) K electron capture

15. The reaction, X → Product, follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 to 0.025 M. The rate of reaction, when concentration of X is 0.01 M is **[IIT JEE, 2004]**

(a) 1.73×10^{-4} M min^{-1} (b) 3.47×10^{-5} M min^{-1}
(c) 3.47×10^{-4} M min^{-1} (d) 1.73×10^{-5} M min^{-1}

16. A positron is emitted from $^{23}_{11}Na$. The ratio of the atomic mass and atomic number of the resulting nuclide is **[IIT JEE, 2007]**

(a) 22/10 (b) 22/11 (c) 23/10 (d) 23/12

17. Calculate total number of α and β particles emitted in the nuclear reaction

$_{92}U^{238} \longrightarrow {}_{82}Pb^{214}$ **[IIT JEE, 2009]**

18. For a first order reaction $A \to P$, the temperature (T) dependent rate constant (k) was found to follow the equation $\log k = -(2000)\dfrac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are **[IIT JEE, 2009]**

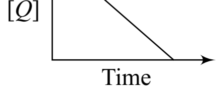
(a) 1.0×106 s^{-1} and 9.2 kJ mol^{-1}
(b) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(c) 1.0×10^{6} s^{-1} and 16.6 kJ mol^{-1}
(d) 1.0×10^{6} s^{-1} and 38.3 kJ mol^{-1}

19. An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\left[\dfrac{t_{1/8}}{t_{1/10}}\right] \times 10$? ($\log_{10}2 = 0.3$)? **[2012]**

20. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table? **[2012]**

$$^{63}_{29}Cu + {}^{1}_{1}H \longrightarrow 6\,{}^{1}_{0}n + {}^{4}_{2}\alpha + 2\,{}^{1}_{1}H + X$$

21. In the reaction, $P + Q \longrightarrow R + S$, the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is **[2013 Adv.]**



(a) 2 (b) 3 (c) 0 (d) 1

22. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be (R = 8.314 kJ^{-1} mol^{-1} and log 2 = 0.301) **[2013 Main]**

(a) 53.6 kJ mol^{-1} (b) 48.6 kJ mol^{-1}
(c) 58.6 kJ mol^{-1} (d) 60.5 kJ mol^{-1}

23. For the elementary reaction, $M \longrightarrow N$ the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is **[2014 Adv.]**

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

24. For the non-stoichiometric reaction, $2A + B \to C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K. **[2014 Main]**

Initial concentration [A]	Initial concentration [B]	Initial rate of formation of C [mol L^{-1}s^{-1}]
(i) 0.1 M	0.1 M	1.2×10^{-3}
(ii) 0.1 M	0.2 M	1.2×10^{-3}
(iii) 0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is

(a) $\dfrac{dC}{dt} = k[A][B]$ (b) $\dfrac{dC}{dt} = k[A]^2[B]$

(c) $\dfrac{dC}{dt} = k[A][B]^2$ (d) $\dfrac{dC}{dt} = k[A]$

25. Higher order (> 3) reactions are rare due to **[2015 Main]**

(a) low probability of simultaneous collision of all the reacting species.
(b) increase in entropy and activation energy as more molecules are involved.
(c) shifting of equilibrium towards reactants due to elastic collisions.
(d) loss of active species on collision.

26. Two reactions R_1 and R_2 have identical pre-exponetial factors. Activation energy of R_1 exceeds that of R_2 by 10 KJ mol^{-1}. If K_1 and K_2 are rate constants for reactions R_1 and R_2 respectively at 300 K, then ln (K_2/K_1) is equal to

(R = 8.314 J mol^{-1} K^{-1}) **[2017 Main]**

(a) 6 (b) 4
(c) 8 (d) 12

Answer Key

LEVEL I

1. (c) 2. (d) 3. (d) 4. (a) 5. (c) 6. (d) 7. (b) 8. (d) 9. (a) 10. (c)
11. (c) 12. (b) 13. (a) 14. (a) 15. (d) 16. (c) 17. (a) 18. (c) 19. (a) 20. (b)
21. (c) 22. (a) 23. (c) 24. (c) 25. (d) 26. (a) 27. (d) 28. (c) 29. (c) 30. (a)
31. (c) 32. (c) 33. (b) 34. (c) 35. (a) 36. (c) 37. (b) 38. (d) 39. (c) 40. (b)
41. (b) 42. (b) 43. (b) 44. (c) 45. (a) 46. (d) 47. (b) 48. (a) 49. (a) 50. (d)
51. (b) 52. (a) 53. (a) 54. (b) 55. (c) 56. (b) 57. (c) 58. (a) 59. (a) 60. (a)
61. (b) 62. (c) 63. (b) 64. (d) 65. (a) 66. (a) 67. (c) 68. (c) 69. (b) 70. (a)
71. (b) 72. (c) 73. (a) 74. (d) 75. (d) 76. (c) 77. (b) 78. (c) 79. (b) 80. (b)
81. (d) 82. (b) 83. (c)

LEVEL II

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

LEVEL III

1. (A) → q, t; (B) → q; (C) → r; (D) → s 2. (A) → p; (B) → p; (C) → r; (D) → s
3. (A) → q; (B) → r, t; (C) → s; (D) → p 4. (A) → r; (B) → s; (C) → q; (D) → p
5. (A) → r, s; (B) → t; (C) → p; (D) → q
6. (d) 7. (a) 8. (b) 9. (d) 10. (a) 11. (d) 12. (c) 13. (a) 14. (d) 15. (a)
16. (d) 17. (b) 18. (c) 19. (a) 20. (a) 21. (a) 22. (a) 23. (a) 24. ( ) 25. (a)
26. (a) 27. (c) 28. (a) 29. (c) 30. (a) 31. (b) 32. (b, c) 33. (c, d) 34. (a, d)
35. (a, b, c, d) 36. (a, b) 37. (a, c, d) 38. (b, c, d) 39. (a, b, c) 40. (a, c)
41. (a, b, c, d) 42. (a, b) 43. (a, d) 44. (a, b, d) 45. (b, c) 46. (a, d) 47. (a, b, c, d)
48. (a, b, c, d) 49. (a, c) 50. (a, b, d) 51. (a, b, c) 52. (a, b, c) 53. (b, c)
54. [5] 55. [6] 56. [5] 57. [3] 58. [6] 59. [9] 60. (80)
61. (i) [1×10^{-4} mol L^{-1} Sec^{-1}] (ii) [3×10^{-4} Mol L^{-1} sec^{-1}] 62. [$2K_1 = K_2 = 4K_3$]
63. (i) [$K_1 [A] [B]^2$] (ii) [rate increases by 8 times] 64. [2.8 M, 0 M] 65. [$Ea_b = 5$ kJ]
66. [Rate = $k_1 [NO]^2 [Br_2]$] 67. [67.17%] 68. [0.0327 min^{-1}] 69. [$K = 0.022$ hr^{-1}]
70. [17.47 mL] 71. [8 atm] 72. [75.44 KJ, 70.975 KJ] 73. $\left[r = \frac{-1}{2}\frac{d[N_2O_5]}{dt} = \frac{k_a k_b [N_2O_5]}{k_{-a} + 2k_b} \right]$
74. [–1] 75. [1,1] 76. (a) (43.45 kJ) (b) (20.47 hr) 77. [0.26] 78. [36 min]
79. [$K = 0.02$ min^{-1}] 80. [397.6°C] 81. $\left[\frac{-d[A]}{dt} = K_1[A] + 2K_2[A]^2 \right]$ 82. [76.8%] 83. [20.39]
84. (i) [6.23×10^{-3} Sec^{-1}] (ii) [0.033 atm] 85. [5.25% and 128.33 hr]

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (b, c) 2. (d) 3. [67.17%] 4. (b) 5. (20.358 min)
6. (a) [239.339 KJ mol^{-1}] (b) [2.18×10^{-11} sec^{-1}] (c) [669K] 7. [$A = 5.43 \times 10^{10}$, 22.01 KJ mol^{-1}] 8. [3]
9. [282 K] 10. [3.435×10^{-3} M min^{-1}] 11. (d) 12. [${}_{30}Zn^{64}$, ${}_{28}Ni^{64}$, ${}_{28}Ni^{64}$ 33.70 hr, 67.41 hr, 29.28 hr]
13. (b) 14. (a) 15. (c) 16. (c) 17. (6) 18. (d) 19. (9) 20. (8) 21. (d) 22. (a)
23. (b) 24. (d) 25. (a) 26. (b)

Hints and Solutions

LEVEL I

1. $r = \frac{-1}{3}\frac{d[H_2]}{dt}$

$$\frac{-d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4} = 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ S}^{-1}$$

2. $\frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[SO_3]}{dt}$

$$\frac{d[SO_3]}{dt} = 2 \times 2.5 \times 10^{-4} = 5 \times 10^{-4} \text{ mol L}^{-1} \text{ S}^{-1}$$

3. $aA + bB \rightarrow P$

$$\text{Rate} = \frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = K[A]^m[B]^n$$

if $[A] = 1$ M and $[B] = 1$ M

Rate = K

4. $r = K[A]^2\,[B]$

$r = K[x]^2\,[y]$

$r' = K[3x]^2\,[3y]$

$r' = 27r$

5. $r = \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{2} \times 1 = 0.5 \text{ mol L}^{-1} \text{ S}^{-1}$

6. $K = \frac{2.303}{t}\log\left[\frac{a_0}{a}\right]$

$$K = \frac{2.303}{500}\log\frac{\frac{1}{10}}{\frac{1}{100}}$$

$$= \frac{2.303}{500}\log 10 = 4.606 \times 10^{-3} \text{ sec}^{-1}$$

7. $r = K[A] = 5 \times 10^{-5}\,[1] = 5 \times 10^{-5} \text{ M s}^{-1}$

8. $r = K_2[N_2O_2]\,[O_2]$ (i)

$$\frac{K_1}{K_{-1}} = \frac{[N_2O_2]}{[NO]^2} \text{ or } [N_2O_2] = \frac{K_1}{K_{-1}}[NO]^2 \text{ from eq. (i)}$$

$$r = K_2\frac{K_1}{K_{-1}} \times [NO]^2[O_2]$$

Compare $r = K[NO]^2\,[O_2]$

$$K = K_2\frac{K_1}{K_{-1}} \times [NO]^2[O_2]$$

9. $r = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} = K[N_2O_5]$

$K_1 = 2K$

$K_2 = 4K = 2K_1$

$K_3 = K = \frac{K_1}{2}$

10. $\frac{-d[a-x]}{dt} = K_1[a-x] + K_2[a-x]$

11. $r = K[X][C]$

$$K' = \frac{[X]}{[A][B]}$$

$r = KK'[A]\,[B]\,[C]$

$= k[A]\,[B]\,[C]$

12. $r = k[(NO)_2][Cl_2]$

and $K = \frac{[(NO)_2]}{[NO]^2}$

$\therefore$ $r = kK[NO]^2[Cl_2]$

13. $K \times 15 = \ln\left(\frac{35-0}{35-9}\right)$

14. $K \times 32 = \ln\left(\frac{100}{1}\right)$ (i)

$$K \times t = \ln\left(\frac{100}{0.1}\right) \quad \text{(ii)}$$

eq. (ii)/(i)

$$\frac{t}{32} = \frac{3\ln 10}{2\ln 10}$$

$t = 48$ min

15. Given $t_{\frac{1}{2}} \propto \frac{1}{a^2}$

$\because$ $t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}$

$n - 1 = 2$

$n = 3$

16. $t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}$ $\quad \frac{200}{100} = \left(\frac{1}{0.5}\right)^{n-1}$

$2 = 2^{n-1}$ $\qquad n - 1 = 1n = 2$

17. $K = Ae^{-Ea/RT}$

$$\ln K = \ln A - \frac{Ea}{RT}$$

$$2.303 \log K = -\frac{Ea}{RT} + 2.303 \log A$$

$$\log K = -\frac{Ea}{2.303RT} + \log A$$

$$\text{slope}\frac{Ea}{2.303R} = 5000$$

$Ea = 5000 \times 8.31 \times 2.303 = 95.7 \text{ kJ K}^{-1} \text{ mol}^{-1}$

18. $-\frac{Ea}{R} = -40000$

$Ea = 40000 \times 2 = 8 \times 10^4$ cal

19. $K = Ae^{-Ea/RT}$ $\therefore$ $Ae^{-Ea/RT} = Ae^{\frac{-E_1-E_3+E_2}{RT}}$

$E_a = E_1 + E_3 - E_2 = 60 + 10 - 30 = 40$ kJ

20. **(b)** rate $= k[A]^n[B]^m$ $\therefore$ $r = k[A][B]^2$

$m = 2 \quad n = 1$

21. **(c)** $r = K[A]^2$

$r = K[A]^2 = 4K[A]^2$

22. **(a)** $2\,NH_3 \rightleftharpoons N_3 + 3H_2$

$$+\frac{d[N_2]}{dt} = +\frac{1}{3}\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$$

23. **(c)** $r = k[A]^x[B]^y$

24. **(c)** Average$= \dfrac{\text{Change in concentration}}{\text{Time}} = \dfrac{0.01}{25 \times 60}$

$= 6.66 \times 10^{-6}$ M sec^{-1}

25. **(d)** For the given change

$$\frac{-d[N_2O_5]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt} = 2\frac{d[O_2]}{dt}$$

On substituting values as given,

$$k_1[N_2O_5] = \frac{1}{2}k_2[N_2O_5] = 2k_3[N_2O_5]$$

or $\quad 2k_1 = k_2 = 4k_3$

26. **(a)** The change in molarity $= \dfrac{n}{V} = \dfrac{\Delta P}{RT}$

$$= \frac{0.9}{0.0821 \times 300} = 0.0365$$

Rate of reaction $= \dfrac{0.0365}{75 \times 60} = 8.12 \times 10^{-6}$ mol L^{-1} sec^{-1}

27. **(d)** As the slowest step is the rate determining step, therefore the rate law is , $r = k[NOBr_2]\,[NO]$

Now since $NOBr_2$ is an intermediate its concentration can be calculated from Step 1 as follows:

$$K_c = \frac{[NOBr_2]}{[NO][Br_2]};\ [K_c = \text{equilibrium constant}]$$

or $\quad [NOBr_2] = K_c[NO]\,[Br_2]$

Substituting this value in above equation,

$r = K \cdot K_c[NO]^2[Br_2]$

or $\quad$ rate $= k[NO]^2\,[Br_2]\ [k = K \cdot K_c]$

rate $= k[NO]^2\,[Br_2]$

28. **(c)**

(i) The rate law according to given information may be given as, $\dfrac{dx}{dt} = k[A]^1[B]^2[C]^0$

(ii) When concentration of A, B and C are doubled then rate will be $\dfrac{dx}{dt} = k[2A][2B]^2[C]^0 = 8k[A][B]^2[C]^2$

i.e., rate becomes 8 fold of the original rate.

29. **(c)** Let rate $= k[A]^a[B]^b$

From experiments (II) and (III)

$$\frac{[0.3]^a[0.2]^b}{[0.3]^a[0.4]^b} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}}$$

On solving $\left[\dfrac{1}{2}\right]^b = \left[\dfrac{1}{2}\right]^2 \quad \therefore \quad b = 2$

From experiments (I) and (IV)

$$\frac{[0.1]^a[0.1]^b}{[0.4]^a[0.1]^b} = \frac{6 \times 10^{-3}}{2.40 \times 10^{-2}}$$

On solving $\quad \therefore \quad a = 1$

$\because$ rate law is ; rate $= k[A]^1[B]^2$

Now rate $= 6 \times 10^{-3}$

$= k[0.1]^1[0.1]^2$

$k = 6$ M^{-2} min^{-1}

30. **(a)** Let the order with respect to A be 'a' and with respect to B be 'b'. The rate law would then be represented as

Rate $= K[A]^a[B]^b$

Therefore by (i) and (ii),

$$\frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}} = \frac{K[5.0 \times 10^{-4}]^a[6.0 \times 10^{-5}]^b}{K[2.5 \times 10^{-4}]^a[3.0 \times 10^{-5}]^b}$$

$2^3 = [2]^{a+b}$

$\therefore \quad a + b = 3$

By (ii) and (iii),

$$\frac{4.0 \times 10^{-3}}{1.6 \times 10^{-2}} = \frac{K[5.0 \times 10^{-4}]^a[6.0 \times 10^{-5}]^b}{K[1.0 \times 10^{-3}]^a[6.0 \times 10^{-5}]^b}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^a$$

$\therefore \quad a = 2$ and $b = 1$

31. **(c)** $\dfrac{0.693}{t_{1/2}} = \dfrac{2.303}{40}\log\dfrac{100}{70}$

$t_{1/2} = 77.70$ min

32. **(c)** Initial concentration (N_0) of radio-isotope is 1 g atom. Concentration remained after 20 days may be calculated as

$$N_t = N_0\left(\frac{1}{2}\right)^n$$

where n = number of half-lives = 20/10 = 2

$$N_t = 1\left(\frac{1}{2}\right)^2 = \frac{1}{4}$$

Concentration decayed to α-particles $= 1 - \dfrac{1}{4} = \dfrac{3}{4}$ g atom. An α-particle takes 2 electron from air and from helium gas. Thus,

Helium formed $= \dfrac{3}{4}$ g atom $= \dfrac{3}{4} \times 22400$ cc $= 16800$ cc

33. **(b)** $A_2 \longrightarrow B + \frac{1}{2}C$

Thus $\frac{d[C]}{dt} = \frac{120-100}{5} = 4 \text{ mm min}^{-1}$

$\therefore \quad \frac{-d[A_2]}{dt} = 2 \times 4 = 8 \text{ mm min}^{-1}$

34. **(c)** Rate = $K[NO]^2\,[O_2]$
Volume halved , concentration is doubled and the rate of reaction becomes eight times.

35. **(a)** Rate = $k_{obs}\,[NO]^2\,[H_2]$
$k_{obs} = k \cdot K_c$

36. **(c)** Unit of k = $\text{bar}^{-1/2}\,\text{min}^{-1}$

37. **(b)** Two reactant molecules are different.

38. **(d)** Order of a reaction can be fractional.

39. **(c)** Overall order is 3/2

40. **(b)** K depends only on temperature

41. **(b)** $\frac{k_{T+10}}{k_T} \approx 2$ to 3

42. **(b)** Fraction of molecules with energy more than energy barrier increases

43. **(b)** $k = Ae^{-E_a/RT}$
At $E_a = 0$
$k = A$

44. **(c)** A catalyst decreases the activation energy.

45. **(a)** A catalyst decreases the activation energy.

46. **(d)** $n = \frac{12}{3} = 4$

$$N_t = N_0\left[\frac{1}{2}\right]^n$$

$$3 = N_0\left[\frac{1}{2}\right]^4$$

$\therefore \quad N_0 = 48$ gram

47. **(b)** ${}_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}_{2}He^{4}$

48. **(a)** $N_2(g) + 3H_2(r) \rightarrow 2NH_3(g)$

$$\frac{-d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

49. **(a)** Rate equation shows that it does not depend on the concentration of (H^+)

50. **(d)** $x = 1$ $y = 2$ overall is 3

51. **(b)** Order $= 3/2 - 1 = \frac{1}{2}$

52. **(a)** Rate = $K[A]^m[B_2]^n$

53. **(a)** Rate $= \frac{\text{Concentration}}{\text{Time}}$

54. **(b)** $t_{1/2} = 10$ min $a = a_0 = 100$ and $a - x = 10$

$$K = \frac{2.303}{t}\log\frac{100}{10} = \frac{0.6932}{10}$$

55. **(c)** $K = \frac{2.303}{2 \times 10^2}\log\frac{800}{50} = 1.386 \times 10^{-2}\ \text{s}^{-1}$

56. **(b)** $t_{1/2} \propto \frac{1}{a^{n-1}} \therefore n = 1$

57. **(c)** $t_{1/2} = 0.5$ hr

58. **(a)** $t^1_{1/2} = \frac{0.693}{K_1}$

$$t^0_{1/2} = \frac{a}{2K_0}$$

59. **(a)** Astatine as it belongs to halogen

60. **(a)** rate = $K[A][B]$

61. **(b)** One

62. **(c)** Rate = $k[A]$

63. **(b)** Rate = $[A]^m[B]^n$

64. **(d)** $R_1 = K[A][B]^2 = K[0.6][0.80]^2$

$$\begin{array}{lllll} \text{After reaction} & A & +\ 2B & \longrightarrow\ C & +\ D \\ & 0.6-0.2 & 0.8-0.4 & 0.2 & 0.2 \\ & 0.4 & 0.4 & 0.2 & 0.2 \end{array}$$

$R_2 = K\,[0.4]\,[0.4]^2$

$$\frac{R_2}{R_1} = \frac{K[0.4][0.4]^2}{K[0.6][0.8]^2} = \frac{1}{6}$$

65. **(a)** $K = \frac{0.6932}{120}$ (i)

$$K = \frac{2.303}{t}\log\frac{a}{0.10a}$$

$$= \frac{2.303}{t}\log 10 \qquad \text{(ii)}$$

Equating (i) and (ii)

$$\frac{0.693}{120} = \frac{2.303}{t}$$

$t = 399$ min

66. **(a)** We know that for first order kinetics

$$K = \frac{2.303}{t}\log\frac{a}{a-x}$$

or $\quad t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6} = 0.384$ min

67. **(c)** $a = 80$ mm and $a + x = 120$ mm
$\therefore\ a - x = 40$ mm

$$K = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$= \frac{2.303}{20} \times \log\frac{80}{40}$$

$$= \frac{2.303}{20} \times 0.3010$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693 \times 20}{2.303 \times 3010} = 20 \text{ min}$$

68. **(c)** $t_{1/2} \propto a^{1-n}$

$$\frac{4 \propto (50)^{1-n}}{2 \propto (100)^{1-n}} \text{ or } 2 \propto 2^{n-1}$$

$\therefore \quad n = 2$

69. **(b)** $K = \frac{2.303}{60}\log\frac{100}{100-1.5}$

$K = 2.5 \times 10^{-4}\ \text{sec}^{-1}$

70. **(a)** $2N_2O_5 \to 4NO_2 + O_2$,

$p_0 \quad - \quad -$

$$k = \frac{2.303}{t}\log_{10}\frac{p_0}{p_t}$$

$$3.38 \times 10^{-5} = \frac{2.303}{10 \times 60}\log\frac{500}{p_t}\ ;\ p_t = 490 \text{ atm}$$

71. **(b)** $\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$;

$$\log\frac{9.2 \times 10^{-3}}{5.5 \times 10^{-4}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{413} - \frac{1}{458}\right]$$

$Ea = 98.46 \text{ kJ mol}^{-1.}$

72. **(c)** β-decay occurs by the nuclear change ${}_0n^1 \to {}_1H^1 + {}_{-1}e^0$.

73. **(a)** $92 + 0 = Z + 36 + 0 \Rightarrow Z = 56$;
and $235 + 1 \longrightarrow A + 92 + 3$;

Missing nuclide is ${}^{141}_{56}Ba$

74. **(d)** $K = \frac{2.303}{32} \times \log\frac{100}{1}$

$$K = \frac{2.303 \times 2}{32} = \frac{0.6932}{t_{1/2}}$$

$t_{1/2} = 4.8$ min

75. **(d)** $A - 40 \text{ Kcal} \to B \quad E_a = 20 \text{ Kcal}$

76. **(c)** $4 \text{ mole L}^{-1} \xrightarrow{20\,\text{min}} 2 \text{ mole L}^{-1}$

$\xrightarrow{20\,\text{min}} 1 \text{ mole L}^{-1} \xrightarrow{20\,\text{min}} 0.5 \text{ mole L}^{-1}$

and for 2nd order $t_{1/2} \propto 1/a$

77. **(b)** $x = e^{-E_a/RT}$

$$\therefore \quad \ln x = -\frac{E_a}{RT}$$

78. **(c)** ${}^{24}_{12}Mg + \gamma \longrightarrow {}^{23}_{11}Na + {}^{1}_{1}H$

79. **(b)** $t = \frac{1}{\lambda}\ln\frac{A_0}{A_t}$

at $\quad t = t_{1/2}\,;\ A_t = \frac{A_0}{2}$

$$\therefore \quad t_{1/2} = \frac{1}{\lambda}\ln 2$$

80. **(b)** $t_{1/2} \propto \frac{1}{a^{n-1}} \therefore t_{1/2} = k\sqrt{a}$ (i)

$$\frac{16}{t_{1/2(\text{II})}} = \sqrt{2} \qquad \text{(ii)}$$

$$t_{1/2(\text{II})} = \frac{16}{\sqrt{2}} = 11.3$$

$16 + 11.3 = 27.3$ min

81. **(d)** $K = Ae^{-Ea/RT}$, for 0.001% $K = 2.3 \times 10^{-3}\text{min}^{-1}$
∴ for 100% $K_{\max}$ $K_{\max} = 230\ \text{min}^{-1}$

82. **(b)** $K = Ae^{-Ea/RT}$
As $\quad T \longrightarrow \infty\ e^{(-Ea/RT)}$ 1.
Hence, $K = A = 6.0 \times 10^{14}\ \text{s}^{-1}$.

83. **(c)** $\frac{r_2}{r_1} = (\mu)^{\frac{30}{10}}$ or $15.6 = (\mu)^3$

$\log 15.6 = 3 \log \mu$
On solving $\mu = 2.5$

LEVEL II

1. **(b)** Since K has unit min^{-1} and thus, given reaction is of first order
Now, rate = K[reactant]^1
Initial rate $= 10^{-3} \times [0.2]^1$
$= 2 \times 10^{-4}$ mol dm^{-3} min^{-1}

Also $K = \frac{2.303}{t}\log\frac{a}{(a-x)}$

$$\therefore \quad 10^{-3} = \frac{2.303}{200}\log\frac{100}{(100-x)}$$

$\therefore \quad x = 18.03\%$

2. **(b)** For a first order reaction, $K = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$

Initial moles of nitramide = $\frac{6.2}{62} = 0.1$

$$\therefore \quad t = \frac{2.303 \times 2.1}{0.693}\log\frac{0.1}{0.001} = 13.95 \text{ hours}$$

Since, the decomposition is 99%, so 99% of the initial moles of NH_2NO_2 would be converted to N_2O.

Moles of N_2O = $\frac{0.1 \times 99}{100}$

∴ volume of N_2O at STP $= \frac{0.1 \times 99 \times 22.4}{100} = 2.217$ L .

3. **(d)** As discussed in the decomposition of N_2O_5

$$K=\frac{2.303}{t}\log\frac{V_\infty}{V_\infty-V_t}$$

Time	V_t	$V_\infty - V_t$	$K=\frac{2.303}{t}\log\frac{V_\infty}{V_\infty-V_t}$
10	6.30	34.75 – 6.30 = 28.45	$K=\frac{2.303}{10}\log\frac{34.75}{28.45}=0.0198$
15	8.95	34.75 – 8.95 = 25.80	$K=\frac{2.303}{15}\log\frac{34.75}{25.80}=0.0198$
20	11.40	34.75 – 11.40 = 23.35	$K=\frac{2.303}{200}\log\frac{34.75}{23.35}=0.0198$
25	13.50	34.75 – 13.50 = 21.25	$K=\frac{2.303}{25}\log\frac{34.75}{21.25}=0.0198$

Since the value of K comes out to be constant, therefore, the reaction it is of first order.
The average value of rate constant is 0.0198 min^{-1}.

4. **(b)** $K_1=\frac{2.303}{t}\log\frac{V_0}{V_t}$, we get

(i) $K_1=\frac{2.303}{10}\log\frac{46.1}{29.8}=4.364\times10^{-2}$

(ii) $K_1=\frac{2.303}{20}\log\frac{46.1}{19.6}=4.276\times10^{-2}$

(iii) $K_1=\frac{2.303}{30}\log\frac{46.1}{12.3}=4.404\times10^{-2}$

Since K_1 comes out to be nearly constant, the reaction is a first order one with K as the average value of the three.

5. In first and second sets of experiments, $[B]$ are same whereas $[A]$ is changing:

Let us suppose the rate law is $R = K[A]^m[B]^n$

$R_1 = K[0.01]^m[0.01]^n = 0.005$

$R_2 = K[0.02]^m[0.01]^n = 0.01$

$$\frac{R_1}{R_2}=\frac{1}{2}=\left(\frac{0.01}{0.02}\right)^m=\left(\frac{1}{2}\right)^m\Rightarrow m=1$$

In first and third sets of experiment, $[A]$ are same, $[B]$ is changing, therefore

$R_1 = K[0.01]^m[0.01]^n = 0.005$

$R_3 = K[0.01]^m[0.02]^n = 0.005$

$$\frac{R_1}{R_3}=1=\left(\frac{0.01}{0.02}\right)^n=\left(\frac{1}{2}\right)^n\Rightarrow n=0,$$

i.e., reaction is of first order with respect to A and of zero order with respect to B.

6. **(c)** $K=\frac{2.303}{t}\log\frac{a}{a-x}$

$$=\frac{2.303}{20}\log\left(\frac{500}{420}\right)$$

$K = 0.00872\ \text{month}^{-1}$

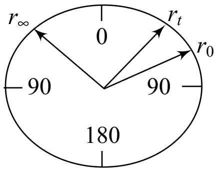
expiry $t=\frac{2.303}{0.00872}\times\log\frac{500}{350}=41$ time months

also $t_{1/2}=\frac{0.693}{0.00872}=79.49$ months

7. **(d)** From the given data, $V_0 = 11.5\ \text{cm}^3$; $V_\infty = 25.5\ \text{cm}^3$

$\therefore\quad a\propto V_\infty - V_0 = 25.5 - 11.5 = 14.0$

and $\quad (a-x)\propto V_\infty - V_t$



Putting the values of V_t = 12.0 at 600 sec; 12.5 at 1200 sec and 13.0 at 1800 sec in the equation

$$K_1=\frac{2.303}{t}\log\frac{V_\infty-V_0}{V_\infty-V_t},\text{ we get}$$

(i) $K_1=\frac{2.303}{600}\log\frac{14.0}{(25.5-12.0)}=\frac{2.303}{600}\log\frac{14.0}{13.5}$
$=6.061\times10^{-5}\ \text{s}^{-1}$

(ii) $K_1=\frac{2.303}{1200}\log\frac{14.0}{(25.5-12.5)}=\frac{2.303}{1200}\log\frac{14.0}{13.0}$
$=6.176\times10^{-5}\ \text{s}^{-1}$

(iii) $K_1=\frac{2.303}{1800}\log\frac{14.0}{(25.5-13.0)}=\frac{2.303}{1800}\log\frac{14.0}{12.5}$
$=6.296\times10^{-5}\ \text{s}^{-1}$

8. **(c)** Let us say that the pressure of SO_2Cl_2 decreases by x atm, then the increase of pressure of SO_2 and $Cl_2 = x$ atm each.

[∵ 1 mole of SO_2Cl_2 decomposes to give 1 mole of SO_2 and 1 mole of Cl_2].

	$SO_2Cl_2(g) \rightarrow$	$SO_2(g)$ +	$Cl_2(g)$
Pressure at $t = 0$	0.5 atm	0	0
Pressure at $t = t$	$(0.5 - x$ atm)	x atm	x atm

Since total pressure $(P_T) = P_{SO_2Cl_2} + P_{SO_2} + P_{Cl_2}$

$$= (0.5 - x) + x + x$$

$$P_T = 0.5 + x \text{ or } x = P_T - 0.5$$

Hence, $P_{SO_2Cl_2} = 0.5 - (P_T - 0.5)$

$$= 0.5 - P_T + 0.5 = 1.0 - P_T$$

Since, at $t = 100$ sec, $P_T = 0.6$ atm

$\therefore \quad P_{SO_2Cl_2} = 1.0 - 0.6 = 0.4$ atm

(a) Evaluation of K

$$K = \frac{2.303}{t}\log\frac{\text{initial pressure}}{\text{pressure at time } t}$$

$$K = \frac{2.303}{100}\log\frac{0.5}{0.4}$$

On solving $K = 2.23 \times 10^{-3}$ sec^{-1}

(b) Rate at $P_T = 0.65$ atm

$P_{SO_2Cl_2}$ at total pressure of 0.65 atm = 1.0 – 0.65 = 0.35 atm

Rate = $K\ P_{SO_2Cl_2} = 2.23 \times 10^{-3} \times 0.35 = 7.8 \times 10^{-4}$ atm sec^{-1}

9. **(d)** Let the initial pressure of A be P_0 mm of Hg and the pressure of A decreases in 10 min be x unit.

	A (g) $\rightarrow$	2B (g) +	C (g)
Initially	P_0	0	0
At time 10 min.	$P_0 - x$	$2x$	x
At ∞ time	0	$2P_0$	P_0

After long time interval, $P_\infty = 2P_0 + P_0 = 3P_0$

$$\therefore \quad P_0 = \frac{P_\infty}{3} = 90 \text{ mm of Hg}$$

After 10 min, $P_t = P_0 + 2x$

$176 = 90 + 2x$

$\therefore x = 43$ mm of Hg

$\therefore$ partial pressure of A after 10 min $= P_0 - x = 90 - 43$ = 47 mm of Hg.

For a first order reaction, the rate constant expression would be

$$K = \frac{2.303}{t}\log\frac{P_0}{P_0 - x}$$

$$K = \frac{2.303}{10}\log\frac{90}{47} = 0.0649 \text{ min}^{-1}$$

10. **(d)** Rate law would be represented as

$$\frac{-dp}{dt} = \text{rate} = K[P_{NO}]^a[P_{H_2}]^b$$

Using the data given in the problem, keeping pressure of H_2 constant, we get

$$1.50 = K[359]^a \quad \text{(i)}$$

$$0.25 = K[152]^a \quad \text{(ii)}$$

Dividing (i) by (ii),

$$\frac{1.50}{0.25} = \left(\frac{359}{152}\right)^a$$

Taking log of both sides,

$$\log 6 = a \log\frac{359}{152} \quad \therefore a \approx 2$$

Similarly, by keeping the pressure of NO constant, rate law is given by

$$1.60 = K[P_{NO}]^a[289]^b \quad \text{(iii)}$$

$$0.79 = K[P_{NO}]^a[147]^b \quad \text{(iv)}$$

Dividing (iii) by (iv)

$$\frac{1.60}{0.79} = \left(\frac{289}{147}\right)^b$$

Taking log of both sides

$$\log\left(\frac{1.60}{0.79}\right) = b \log\left(\frac{289}{147}\right)$$

$\therefore \quad b \approx 1$

$\therefore$ overall order of the reaction = $(a + b) = (2 + 1) = 3$

11. **(a)**

(a) Here a, the initial concentration $\propto (r_0 - r_\infty)$

x, the change in time t $\propto (r_0 - r_t)$

$\therefore (a - x) \propto (r_t - r_\infty)$

Substituting these values for different $(a - x)$ values corresponding to time t from the data in the equation for first order reaction

$$K = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{t}\log\frac{r_0 - r_\infty}{r_t - r_\infty}, \text{ we get}$$

(i) $$K_1 = \frac{2.303}{10}\log\frac{32 - (-10.5)}{25.5 - (-10.5)} = \frac{2.303}{10}\log\frac{42.5}{36.0} = 0.0166 \text{ min}^{-1}$$

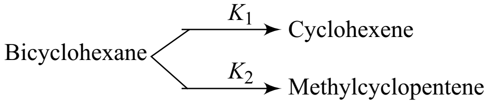
(ii) $$K_1 = \frac{2.303}{20}\log\frac{32 - (-10.5)}{20.0 - (-10.5)} = \frac{2.303}{20}\log\frac{42.5}{30.5} = 0.0166 \text{ min}^{-1}$$

(iii) $$K_1 = \frac{2.303}{30}\log\frac{32 - (-10.5)}{15.5 - (-10.5)} = \frac{2.303}{30}\log\frac{42.5}{26.0} = 0.0164 \text{ min}^{-1}$$

(iv) $$K_1 = \frac{2.303}{60}\log\frac{32 - (-10.5)}{5.0 - (-10.5)} = \frac{2.303}{60}\log\frac{42.5}{15.5} = 0.0168 \text{ min}^{-1}$$

Average value of $K_1 = 0.0166$ min^{-1}

12. **(d)**



$$\text{Percentage of cyclohexene} = \frac{K_1}{K_1 + K_2} \times 100$$

$$= \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-5}} \times 100 = 77\%$$

$\therefore$ Percentage of methylcyclopentane = 23%

13. **(c)** $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{22}$

where $K = K_1 + K_2$, which are rate constant of separate paths

Also $K_1/K_2 = 2/98$

On solving $K_2 = 0.03087\ y^{-1}$

$K_1 = 0.00063\ y^{-1}$

14. **(c)** $\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

$$\log \frac{6.9 \times 10^{-3}}{3.45 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{40}{300 \times 340}\right]$$

$E_a = 112.5$ KJ

15. **(c)** $\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60 \times 10^3}{2.303 \times 8.314}\left[\frac{T_2 - 283}{283 \times T_2}\right]$$

on solving $T_2 = 297.02$ K

16. **(a)** $\log k = \log A - \frac{E_a}{2.303RT}$ (i)

Given $A = 1.26 \times 10^{13}$

$E_a = 58.5$ kcal

$T = 527 + 273 = 800$ K

Substituting these values in Eq. (i), we get

$$\log k = \log (1.26 \times 10^{13}) - \frac{58.5 \times 10^3}{2.303 \times 1.987 \times 800}$$

$= 13.1003 - 15.9799 = -2.8796$

$k = 1.3194 \times 10^{-3}\ \text{sec}^{-1}$

$$t_{1/2} = \frac{0.693}{1.3194} \times 10^3 \text{ sec} = 525 \text{ sec}$$

17. **(c)** Amount of A left in n_1 halves $= \left(\frac{1}{2}\right)^{n_1} [A_0]$

Amount of B left in n_2 halves $= \left(\frac{1}{2}\right)^{n_2} [B_0]$

At the end, according to the question

$$\frac{[A_0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}} \Rightarrow \frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}, [[A_0] = 4[B_0]]$$

$$\therefore \quad \frac{2^{n_1}}{2^{n_2}} = 4 \Rightarrow 2^{n_1 - n_2} = (2)^2 \therefore n_1 - n_2 = 2$$

$\therefore \quad n_2 = (n_1 - 2)$ (i)

Also $t = n_2 \times t_{1/2(B)}$

(Let concentration of both become equal after time t)

$$\therefore \quad \frac{n_1 \times t_{1/2(A)}}{n_2 \times t_{1/2(B)}} = 1 \Rightarrow \frac{n_1 \times 5}{n_2 \times 15} = 1 \Rightarrow \frac{n_1}{n_2} = 3 \quad \text{(i)}$$

For Eqs. (i) and (ii)

$n_1 = 3, n_2 = 1$

$t = 3 \times 5 = 15$ minute

18. **(b)** Initial activity $a_0 = 2 \times 10^6$ dpm

Activity after four days $a_t = 9 \times 10^5$ dpm

$$\lambda = \frac{2.303}{4} \log \frac{2 \times 10^6}{9 \times 10^5} = 0.19967 \text{ day}^{-1}$$

Activity after 40 days

$$0.19967 = \frac{2.303}{40} \log \frac{2 \times 10^6}{a_t}$$

$a_t = 680.81$ dpm

19. **(b)** $K = \frac{2.303}{t} \log \frac{p}{p - x} \Rightarrow \frac{2.303}{10} \log \frac{90}{90 - 45}$

$$\Rightarrow \quad \frac{2.303}{10 \times 60} \log 2 = 1.1555 \times 10^{-3}\ \text{s}^{-1}$$

$$\therefore \quad t_{1/2} = \frac{0.693}{K} \simeq 600 \text{ sec}$$

20. **(c)** Since $P_0 + x = 120$

$$K = \frac{2.303}{10} \log \frac{100}{80}$$

21. **(b)** $\Delta H = 0.12 \times 10^3$ cal

$\Delta H = E_{af} - E_{ab}$

$E_{af} = 0.14 \times 10^3$ cal

% of molecules crossing over the barrier

$= 100 \times e^{-E_{af}/RT}$

$= 80.65 \approx 81$

22. **(c)** $E_a > E_a^1$

$$\frac{1}{k_1}\frac{d(\ln k)}{dT} = \frac{E_a}{RT_1^2}, \quad \frac{1}{k_2} = \frac{d(\ln k)}{dT} = \frac{E_a}{RT_2^2}$$

$$\frac{1}{k_1'}\frac{d(\ln k)}{dT} = \frac{E_a'}{RT_1^2}, \quad \frac{1}{k_2}\frac{d(\ln k)}{dT} = \frac{E_a}{RT_2^2}$$

$$\Rightarrow \quad \frac{k_2}{k_1} > \frac{k_2'}{k_1'} \Rightarrow \frac{k_1'}{k_1} > \frac{k_2'}{k_2}$$

Alternate method

$k_1' > k_1$ and $k_2' > k_2$ since Ea always + ve

For Endothermic reaction ΔH = + ve

$\therefore$ on increasing temperature keq $\uparrow$

$$[K_{\text{eq}}]_1 < [K_{\text{eq}}]_2 \therefore \frac{k_1}{k_2} < \frac{k_1'}{k_2'}$$

23. **(b)** $\log k = \log A - \frac{E_a}{2.303RT}$

$\log A = 14.71$

$$4 = 14.71 - \frac{3031}{T}$$

24. **(b)** $\frac{1}{[A]} = Kt + \frac{1}{[A_0]} = 1\times10^{-2}\times100 + \frac{1}{0.1} = 11$

$[A] = 0.09M$

25. **(d)** Fraction of one product $= \frac{1\times10^{-2}}{1\times10^{-2}+3\times10^{-2}} = 0.25$

Fraction of another product $= \frac{3\times10^{-2}}{1\times10^{-2}+3\times10^{-2}} = 0.75$

Overall activation energy is

$= \frac{0.25\times60+0.75\times70}{0.25+0.75} = 67.5$ kJ/mol

26. **(b)** $T_{\text{av}} = \frac{1}{K} = 1.44\times t_{1/2}$

$t_{99.9} = 10\times t_{1/2}$ in case of first order reaction $= 6.9\ T_{\text{av}}$

27. **(b)** $t_{1/2} \propto a$ in case of zero order reaction

28. **(c)** Slope $= \frac{-E_a}{2.303R} = -\frac{1}{2.303} \therefore Ea = R$

29. **(a)** At 50% inversion

$$x = \frac{a}{2}$$

$$r_\infty - r_t = \frac{r_\infty - r_0}{2}$$

$$\therefore \quad r_0 = 2r_t - r_\infty$$

30. **(b)** Conceptual

31. **(d)** $A\,(g) \rightleftharpoons 2B\,(g)$

10^{-5} mole 100 mole

$K_f = 1.5\times10^{-3}\ \text{s}^{-1}$

$$K = \frac{[100]^2}{10^{-5}\times10} = \frac{K_f}{K_b}$$

$$K_b = \frac{1.5\times10^{-3}\times10^{-7}}{10^4}$$

$K_b = 1.5\times10^{-11}\ \text{L mol}^{-1}\ \text{s}^{-1}$

32. **(b)** $A + B \longrightarrow C + D$

rate $= K[A]^{1/2}[B]^{1/2}$

$$\frac{dx}{dt} = K\sqrt{(a-x)(a-x)}$$

$$\frac{dx}{dt} = K(a-x)$$

$$\Rightarrow \quad t = \frac{2.303}{K}\log_{10}\left(\frac{a}{a-x}\right)$$

$$t = \frac{2.303}{2.31\times10^{-3}}\log_{10}\left(\frac{1}{0.25}\right)$$

$t = 600$ sec

33. **(d)** $X \xrightarrow{k_1} A + B$ and $Y \xrightarrow{k_2} C + D$

$$\frac{k_1}{k_2} = \frac{\log(2)}{\log(100/4)}$$

$$\frac{k_1}{k_2} = \frac{\log 2}{2\log 10 - 2\log 2} = \frac{0.3}{1.4}$$

$$\frac{k_2}{k_1} = \frac{1.4}{0.3} = 4.65$$

34. **(d)**

P(mm Hg)	500	250
$t_{1/2}$ (in min.)	235	950

$$\boxed{t_{1/2} \propto \frac{1}{a^{n-1}}}$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \qquad \frac{235}{950} = \left(\frac{250}{500}\right)^{n-1}$$

$$2^2 = (2)^{n-1} \qquad n-1 = 2 \Rightarrow n = 3$$

35. **(b)** $t_1K_1 = t_2K_2$ $\quad 20\times K_1 = 5\times K_2$

$$\therefore \quad \frac{K_1}{K_2} - 4$$

$$\log_{10}\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.30\times R}\left(\frac{T_2-T_1}{T_1\cdot T_2}\right)$$

$$\log_{10}(4) = \frac{Ea}{8.314\times2.3}\left(\frac{20}{300\times320}\right)$$

$Ea = 55.332$ KJ/mole

36. **(b)** $K = 3.0\times10^{-4}\ \text{s}^{-1}$; $\quad Ea = 104.4\ \text{kJ mol}^{-1}$

$A = 6.0\times10^{14}\ \text{s}^{-1}$ $\quad K_2 = Ae^{-Ea/RT}$

But when $E_a \to 0$

$$K = Ae^{-\frac{Ea}{RT}} = Ae^{\frac{-0}{RT}} = A$$

$$\therefore \quad K = A = 6\times10^{14}\ \text{S}^{-1}$$

37. **(a)** $k = \frac{1}{t(n-1)}\left[\frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}}\right]$

$$t_{1/2} = \frac{1}{k(n-1)}\left[\frac{2^{n-1}}{\text{Co}^{n-1}} - \frac{1}{\text{Co}^{n-1}}\right] \qquad \text{(i)}$$

$$t_{3/4} = \frac{1}{k(n-1)}\left[\frac{4^{n-1}}{\text{Co}^{n-1}} - \frac{1}{\text{Co}^{n-1}}\right] \qquad \text{(ii)}$$

Eq. (ii) ÷ Eq. (i)

$$\frac{t_{3/4}}{t_{1/2}} = \left[\frac{4^{n-1}-1}{2^{n-1}-1}\right] = \frac{2^{2(n-1)}-1}{(2^{n-1}-1)} = \frac{(2^{n-1}+1)(2^{n-1}-1)}{(2^{n-1}-1)}$$

$$t_{3/4} = t_{1/2}\,[2^{n-1} + 1]$$

38. **(a)** Fraction of reactant consume $f = \left(1 - \frac{C}{C_0}\right)$

for a reaction: $\frac{df}{dt} = K(1-f)$ (Remaining amount).

39. **(d)**

	$2A$	$+\ B \xrightarrow{K} C + D$
$t = 0$	C_0	$2\ C_0$
t = 30 min,	$\frac{C_0}{2}$	$\frac{7C_0}{4}$

Rate at that time $= K[A]\,[B]^2$

$$\text{Rate} = K\left[\frac{C_0}{2}\right]\left[\frac{7C_0}{4}\right]^2 = \frac{49C_0^3}{32}$$

40. **(d)** $A \to B \qquad K_A = 10^{15}\,e^{-2000/T}$

$C \to D \qquad K_A = 10^{14}\,e^{-1000/T}$

At T $(K_A = K_C)$

$$10^{15}e^{-2000/T} = 10^{14}\,e^{-1000/T}$$

$$10e^{-2000/T} = e^{-1000/T}$$

$$10 = e^{1000/T}$$

$$\log_e 10 = 1000/T \quad T = \frac{1000}{\log_e 10} \quad T = \left(\frac{1000}{2.303}\right)K$$

41. **(c)** $\log_{10}\dfrac{K_2}{K_1} = \dfrac{2.303Ea}{R}\left(\dfrac{T_2 - T_1}{T_1T_2}\right)$

$$\frac{R\log 2 \times 280 \times 290}{2.303 \times 10} = Ea$$

$$\log\frac{K_4}{K_3} = \frac{2.303 \times R\log 2 \times 280 \times 290}{2.303 \times 10 \times R}\left(\frac{10}{290 \times 300}\right)$$

$$\log_{10}\left(\frac{K_4}{K_3}\right) = \frac{280}{300}\log 2$$

$$\therefore\ \frac{K_4}{K_3} = 1.91$$

42. **(c)**

$$\begin{array}{llll} A & +\ 2B & \rightarrow & \text{products} \\ a-x & 2a-2x & & \end{array}$$

$$-\frac{d[A]}{dt} = K\sqrt{[A]}\,\sqrt{[B]}$$

Reactants are in their stoichiometric proportion

$$\Rightarrow \quad -\frac{d(a-x)}{dt} = K\sqrt{(a-x)}\sqrt{2(a-x)}$$

$$\frac{dx}{dt} = \sqrt{2}\,K(a-x) \qquad t_{1/2} = \frac{0.693}{\sqrt{2}K}$$

43. **(a)** $2A + B \rightarrow$ products $\qquad \dfrac{-d[A]}{dt} = K[A]$

$A = A_0e^{-Kt}$ $\qquad$ when $t_2 = 1/K$

$A = A_0e^{-1}$ $\qquad$ $A = A_0/e = C_0/e$

44. **(c)** Rate $= K[A][B_2]$

$$K = \frac{[A]^2}{[A_2]} \Rightarrow [A] = \{K[A_2]\}^{1/2}$$

$$r = K'[A_2]^{1/2}\,[B_2] \qquad \text{order} = 1\frac{1}{2}$$

45. **(a)** For A $\quad K_1 \times t = \ln\dfrac{100}{100-94}$ (i)

For B $\quad K_2 \times t = \ln\dfrac{100}{100-50}$ (ii)

Eqs. (i) and (ii)

$$\frac{K_1}{K_2} = \frac{\ln\frac{100}{6}}{\ln\frac{100}{50}} \Rightarrow \frac{K_1}{K_2} = 4.058$$

46. **(b)** $\%\,B = \dfrac{K_1}{K_1 + K_2} \times 100 = 76.83\%$

$\%\,C = 100 - B\% = 23.17\%$

or $\quad \%\,C = \dfrac{K_2}{K_1 + K_2} \times 100$

47. **(b)** $\dfrac{dt}{dt} = \alpha - \lambda N,$

For maximum number of nuclei $\dfrac{dN}{dt} = 0$

$$\alpha = \lambda N \Rightarrow N = \alpha/\lambda$$

48. **(d)** Let n is the moles of reagent 'R' when R is reacted with A at time $t = 0$

$$\begin{array}{lllll} & A & \longrightarrow\ B & + & C \\ t = 0 & n & 0 & & 0 \\ \text{at } t & n - x & 2x & & 3x \\ \text{at } t \to \infty & 0 & 2n & & 3n \end{array}$$

$$\therefore \quad 5n = n_2 \Rightarrow n = \frac{n_2}{5}$$

$$n + 4x = n_1 \Rightarrow x = \frac{n_1 - n}{4}$$

$$K = \frac{2.303}{t}\log\left(\frac{n}{n-x}\right)$$

so $\quad K = \dfrac{1}{t}\ln\left(\dfrac{4n_2}{5(n_2 - n_1)}\right)$

49. **(c)** Overall rate constant $= k = k_1 + k_2 + k_3 = 6.93 \times 10^{-3}$

$$t_{1/2} = \frac{0.693}{6.93 \times 10^{-3}} = 100 \text{ sec}$$

After half-life, $P_B + P_C + P_D = 4$ atm

$$\frac{P_B}{P_B + P_C + P_D} = \frac{k_1}{k_1 + k_2 + k_3} = \frac{200}{693}$$

$$P_B = 4 \times \frac{200}{693} = 1.154 \text{ atm}$$

LEVEL III

1. **(A - q, t); (B - p); (C - r); (D - s)**

(a) ${}_{11}\text{Na}^{23} + {}_1\text{H}^2 \longrightarrow {}_{11}\text{Na}^{24} + {}_1\text{H}^1$

(b) $2\,{}_1\text{H}^3 \longrightarrow {}_2\text{He}^4 + 2\,{}_0n^1$

(c) ${}_{92}\text{U}^{238} \longrightarrow {}_{90}\text{Th}^{234} + {}_2\text{He}^4$

(d) ${}_{29}\text{Cu}^{63} \longrightarrow {}_{28}\text{Ni}^{63} + {}_1e^0$

2. **(A - p); (B - q); (C - r); (D - s)**

$$k = \frac{2.303}{\text{t}}\log\frac{A_0}{A_t}$$

3. **(A - q); (B - r, t); (C - s); (D - p)**

(A – q): Decomposition of H_2O_2 follows first order kinetics.

(B – r, t): It is temperature coefficient and lies between 2-3.

(C – s): $\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$ is Arrhenius equation

(D - p): $t_{99.9\%} = 10t_{1/2}$

$$t_{99.9\%} = \frac{2.303}{K}\log\frac{R_0}{R_0\times\frac{0.1}{100}}$$

$$= \frac{2.303}{K}\times\log 1000 = \frac{2.303\times 3}{K} = \frac{6.909}{K}$$

$$\mathrm{t}_{99.0\%} = 10\times\left[\frac{0.693}{K}\right] = 10\times t_{1/2}$$

4. **A-r, B-s, C-q, D-p**

for n^{th} order ($n \neq 1$)

$$K = \frac{1}{(n-1)t}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

5. **A-rs, B-t, C-p, D-q**

$t_{1/2}$ of nth order $= \frac{1}{(a)^{n-1}}$

6. **(d)** $(E_a)_b = 30 + 10 = 40$ kJ/mole
7. **(a)** $\Delta H = -10$ KJ

∴ reaction is exothermic

8. **(b)** $K_f = A_f e^{-\frac{Ea}{RT}}$

$$A_f = \frac{K_f}{e^{-\frac{Ea}{RT}}} = \frac{10^{-4}}{e^{-\frac{30\times1000}{8.314\times320}}} = \frac{10^{-4}}{e^{-11.27}}$$

$$= 10^{-4}\times e^{11.27}$$

∴ $\log A_f = -4 + 4.8614 = 0.8614 = \log 7.3$

∴ $A_f = K_f = 7.3$

9. **(d)**

	$CH_3OCH_3(g) \longrightarrow$	$CH_4(g)$ +	$CO(g)$ +	$H_2(g)$
Initial	p_0	–	–	–
at time t	$p_0 - x$	x	x	x
after long time	–	p_0	p_0	p_0

given $3p_0 = 1.2$ ∴ $p_0 = 0.4$ atm

also $K = \frac{0.693}{0.2}\mathrm{h}^{-1}$

$$K = \frac{2.303}{t}\log\frac{p_0}{p_0 - x}$$

∴ $x = 0.35$

∴ $P_T = 0.4 - 0.35 + 0.35 + 0.35 + 0.35 = 1.1$ atm

10. **(a)** $\text{Rate} = K\times P^{\circ}$

$$= \frac{0.693}{0.2}\times 0.4$$

$$= 1.386\ \text{atm h}^{-1}$$

11. **(d)** Since $k_2 >> k_1$, therefore given sequential reaction converts as follows:

$$A \xrightarrow{k_1} C$$

∵ $[A]_0 = [A]_t + [C]_t$

$$K_1 = \frac{0.6932}{t_{1/2}}\ \therefore t_{1/2} = 300\ \text{sec.} = 5\ \text{min}.$$

half-life of the reaction is 5 min.

In four half-lives the amount of C formed is 1.875 M.

12. **(c)** Formation of B is independent of initial concentration it is first order, fraction of 'c' also does not change, it is also first order
13. **(a)** $\frac{K_1}{1.52\times10^{-4}} = 0.112 \Rightarrow K_1 = 1.7\times10^{-5}\ \mathrm{s}^{-1}$
14. **(d)** $\frac{K_2}{1.52\times10^{-4}} = 0.888 \Rightarrow K_2 = 1.35\times10^{-4}\ \mathrm{s}^{-1}$
15. **(a)** Rate = $k_f[O_3][O]$

$$K_{eq} = \frac{[O_2][O]}{[O_3]};\ [O] = \frac{K_{eq}[O_3]}{[O_2]}$$

Rate = $k_f K_{eq}[O_3]^2\ [O_2]^{-1}$

∴ order = 2 + (–1) = 1

16. **(a)** moleculatiry of complex reaction has no signifance
17. **(b)** Rate = $k'[O_3]^2\ [O_2]^{-1}$

It means as concentration of O_2 increases rate decreases.

18. **(c)** Rate = $k_1[NO_2][NO_3]$

$$K_{eq} = \frac{[NO_2][NO_3]}{[N_2O_5]}$$

$K_{eq}[N_2O_5] = [NO_2]\ [NO_3]$

∴ Rate = $k_1\ K_{eq}\ [N_2O_5]$

∴ order = 1

19. **(a)** $K = \frac{2.303}{t}\log\frac{A_0}{A_t} = \frac{2.303}{20}\log\frac{100}{20}$

$$= \frac{2.303}{20}\times 0.6990 = 0.08$$

20. **(a)** $N_2O_5 \rightleftharpoons NO_2 + NO_3$

$$K_{eq} = \frac{0.4\times0.4}{0.2} = 0.8$$

Since $K = K_1\times K_{eq} = 0.08$

∴ $k_1 = 0.1$

21. **(a)** On increasing temperature number of effective collision increases which increases rate of chemical reaction.
22. **(a)** Molecular collisions are random and hence it is not possible that 100% reactant molecule can convert into product.
23. **(a)** Specific activity is defined as decay per second per gram of radioactive isotope.
24. **(a)** Order of reaction is an experimental quantity.
25. **(a)** Half-life is independent of initial concentration.
26. **(a)** Like $y = mx + c$
27. **(c)** When reactant molecules collide among themselves then, only they can convert themselves in to product if

Effective collision occur for Effective collision Reactant must have minimum threshold Energy and molecule should be properly oriented.

28. **(a)**

$$NO_2 \xrightarrow{\text{slow}} NO + O$$

$$CO + O \xrightarrow{\text{Fast}} CO_2$$

29. **(c)** Activation energy does not depend on temperature.

30. **(a)** $-r_A = (2.5R(400))C_A$ at 400 K

$-r_A = (2.5R(600))C_A$ at 600 K

Since $[A] = C_A = \dfrac{n_A}{V} = C_A = \dfrac{P_A}{RT}$

then $\log\left(\dfrac{6}{4}\right) = \dfrac{Ea}{2.303R}\left(\dfrac{1}{400} - \dfrac{1}{600}\right)$

$Ea = 4135$ J

31. **(b)** $K = Ae^{-\frac{Ea}{RT}}$

If $Ea = 0$ then $K = A$

32. **(b, c)** $\dfrac{2 \times 10^{-3}}{1 \times 10^{-3}} = 2$

33. **(c, d)** $\log k = \log A - \dfrac{E_a}{2.303RT} = 5 - \dfrac{2000}{T}$

$\therefore$ $\log A = 5$

$A = 10^5$

$E_a = 9.152$ kcal

34. **(a, d)** $k = \dfrac{1}{t}\ln\dfrac{1}{1-\alpha} \Rightarrow -kt = \ln(1-\alpha)$

$\therefore$ $1 - \alpha = e^{-kt}$

$\therefore$ $\alpha = 1 - e^{-kt}$

also $k = Ae^{-E_a/RT}$

35. **(a, b, c, d)**

Rate of reaction $= -\dfrac{1}{2}\dfrac{d[A]}{dt} = -\dfrac{d[B]}{dt} = \dfrac{1}{2}\dfrac{d[C]}{dt} = \dfrac{1}{3}\dfrac{d[D]}{dt}$

As $\dfrac{d[C]}{dt} = 1.0 \text{ mol L}^{-1}\text{ sec}^{-1}$

$$-\frac{d[A]}{dt} = \frac{d[C]}{dt} = 1.0 \text{ mol L}^{-1}\text{ sec}^{-1}$$

$$-\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = 0.5 \text{ mol L}^{-1}\text{ sec}^{-1}$$

$$\therefore \quad \frac{d[D]}{dt} = \frac{3}{2}\frac{d[C]}{dt} = 1.5 \text{ mol L}^{-1}\text{ sec}^{-1}$$

Rate of reaction $= \dfrac{1}{2}\dfrac{d[C]}{dt} = 0.5 \text{ mol L}^{-1}\text{ sec}^{-1}$.

36. **(a, b)** Rate $= k[A][B]^2$

Initial rate $= 2 \times 10^{-6}\,[0.1][0.2]^2$

$= 8 \times 10^{-9} \text{ mol L}^{-1}\text{ sec}^{-1}$

Now as [A] is reduced to 0.06 mol L^{-1}, i.e., 0.04 mol L^{-1} of [A] is reacted

$\because$ 2 moles A reacts with 1 mole B.

$\therefore$ 0.04 moles of A reacts with 0.02 moles of B

$\therefore$ $[B]_{\text{left}} = 0.2 - 0.02 = 0.18$

$\therefore$ rate $= 2 \times 10^{-6}\,[0.06][0.18]^2$

$= 3.89 \times 10^{-9} \text{ mol}^{-2}\text{ L}^{-1}\text{sec}^{-1}$

37. **(a, c, d)**

(i) As Rate $= k[NO]^2$ order = 2 and unit of k = (concentration)$^{-1}$ sec^{-1}

(ii) As Rate $= k[H_2O_2][I^-]$ overall order = 2 and unit of k = (concentration)$^{-1}$ sec^{-1}

(iii) As Rate $= k[CH_3CHO]^{3/2}$ order = 3/2 and unit of k = (concentration)$^{-1/2}$ sec^{-1}

(iv) As Rate $= k[C_2H_5CI]$ order = 1 and unit of k = sec^{-1}

38. **(b, c, d)** For first order, $t_{1/2}$ is independent of initial concentration.

$$\frac{dx}{dt} = k[4\text{Zn}]\left[\frac{1}{2}\text{H}^+\right]^2 = \text{K}[\text{Zn}][\text{H}^+]$$

$$\frac{dx}{dt} = k[\text{Zn}][2\text{H}^+]^2 = 4\text{K}[\text{Zn}][\text{H}^+]^2$$

39. **(a, b, c)** $K = Ae^{-Ea/RJ}$

40. **(a, c)** Collisions are necessary to bring about the chemical reaction.

41. **(a, b, c, d)** Factors affecting the rate of reaction

42. **(a, b)** $k_1 = k_2$

$\Rightarrow$ $\dfrac{2}{3}$rd of A has reacted for $[A] = [C] = [D]$

$$k_1 + k_2 = \frac{1}{t}\ln\frac{[A_0]}{1/3[A_0]}$$

$$\Rightarrow \quad t = \frac{1}{k_1 + k_2}\ln 3 = \frac{1}{2k_1}\ln 3 = \frac{1}{2k_2}\ln 3$$

43. **(a, c)** $\Delta H = E_{af} - E_{ab}$ if $\Delta H = -$ ve

$E_{ab} > E_{af}$ and If $\Delta H = +$ ve $E_{ab} < E_{af}$.

44. **(a, b, d)** use

$PV = nRT$

and $K_P = Ae^{-\frac{\Delta H}{RT}}$

45. **(b, c)** $R \propto K$

$K = Ae^{-\frac{Ea}{RT}}$

$\therefore$ on increasing temperature rate constant increases

$\therefore$ Rate increased.

46. **(a, d)** Rate $= K[A]^1\,[B]^0$

For I $\quad 2 \times 10^{-2} = K[0.1]\,[0.1]^0$

For II $\quad 4 \times 10^{-2} = K[x]\,[0.2]^0$

$\therefore$ $x = 0.2$ M

For IV $\quad 2 \times 10^{-2} = K\,[y]\,[0.2]^0$

$\therefore$ $y = 0.1$ M

47. **(a, b, c, d)** See Example of fractional order in theory

48. **(a, b, c, d)** See Example of first order in theory

49. **(a, c)** See zero order in theory.

50. **(a, c)** Use $K = \dfrac{2.303}{t}\log\dfrac{a}{a-x}$ –

$$\text{rate} = \frac{0.31 - 0.17}{60 - 30} = 4.67 \times 10^{-3}$$

51. **(a, b, d)**

(a) $t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}$

(b) $T_{\text{av}} = \frac{1}{K} = 1.44 \times t_{1/2}$

(c) $t_{3/4} = 2 \times t_{1/2}$ for 1st order

(d) $t_{99.9} = 10 \times t_{1/2}$ for 1st order

52. **(a, b, c)** Order is experimental and determined by experiment only.

In the expression of rate law, order is defined as (coefficient) of active mass.

$aA + bB \longrightarrow P$

Rate $= K[A]^m\,[B]^n$

m = Order w.r.t. A

n = Order w.r.t. B

$(m + n)$ = overall order of reaction

Order of any reaction can be obtained only by experiment methods.

Order of reaction may have –ve, +ve, zero or fractional value

53. **(b, c)** At $E_a = 0$, $K = A$

Also at very high temperature $K = A$

Since $K = Ae^{-\frac{Ea}{RT}}$

54. **(5)** For reversible reaction rate constant is also reverse.

$$K_r = \frac{1}{K_f} = \frac{1}{0.2} = 5$$

55. **(6)** $N = \frac{N_0}{64} = \frac{N_0}{2^6} \therefore n = 6$

We known $N_t = N_0\left(\frac{1}{2}\right)^n$

56. **(5)** $\frac{(r_2)_{95}}{(r_1)_{95}} = \left(\frac{\mu_2}{\mu_1}\right)^{\frac{\Delta T}{10}} = \left(\frac{2.5}{2.0}\right)^7$

$= 4.76 \approx 5$

OR

at temp	rx_n (I)	rx_n (II)
25°C	r	r
35°C	$2r$	$2.5r$
45°C	$(2)^2r$	$(2.5)^2r$
55°C	$(2)^3r$	$(2.5)^3r$
65°C	$(2)^4r$	$(2.5)^4r$
75°C	$(2)^5r$	$(2.5)^5r$
85°C	$(2)^6r$	$(2.5)^6r$
95°C	$(2)^7r$	$(2.5)^7r$

$$\text{Ratio of rates} = \frac{\text{Rate of reaction (II)}}{\text{Rate of reaction (I)}}$$

$$= \frac{(2.5)^7 r}{(2)^7 r} = 4.77 \approx 5$$

57. **(3)** The sum of mass number and atomic numbers of reactants = The sum of mass number and atomic number of product in a nuclear reaction.

Hence the given nuclear fission reaction is

$$^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{139}_{54}\text{Xe} + {}^{94}_{38}\text{Sr} + 3{}^{1}_{0}n$$

58. **(6)**

$$\log K = \log A - \frac{Ea}{2.303RT}$$

$(T \rightarrow \infty)$

When $\log K = \log A$

59. **(9)** $\ln\frac{A_0}{A} = (k_1 + k_2)t$

$$\ln\frac{A+B+C}{A} = 9a$$

$$\ln\frac{A+8C+C}{A} = 9a$$

$$\therefore \quad \frac{(C)}{(A)} = \frac{e^{9a}-1}{9}$$

60. **(80)** Since it is a first order

$\therefore$ rate $= K[\text{N}_2\text{O}_5] = 3 \times 10^{-2}\,[\text{N}_2\text{O}_5]$

$= 2.4 \times 10^{-5}$

$$\therefore \quad [\text{N}_2\text{O}_5] = \frac{2.4 \times 10^{-5}}{3 \times 10^{-2}} = 80 \times 10^{-5}$$

61. (a) $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

$$\text{Rate} = \frac{\Delta[\text{NH}_3]}{\Delta t} = 2 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}$$

$$-\frac{\Delta[\text{H}_2]}{dt} = \frac{-1}{3}\frac{\Delta[\text{H}_2]}{dt} = \frac{1}{2}\frac{\Delta[\text{NH}_3]}{dt}$$

$$\frac{\Delta[\text{N}_2]}{dt} = 1 \times 10^{-4}\text{mol l}^{-1}\text{ sec}^{-1}$$

(b) $-\frac{\Delta[\text{H}_2]}{dt} = -\frac{3}{2} \times 2 \times 10^{-4}\text{mol L}^{-1}\text{s}^{-1}$

$= -13 \times 10^{-4}\text{ Mol L}^{-1}\text{S}^{-1}$

62. $\text{N}_2\text{O}_5\text{ (g)} \longrightarrow 2\text{NO}_2\text{ (g)} + \frac{1}{2}\text{O}_2\text{ (g)}$

$-d[\text{N}_2\text{O}_5]/dt = k_1[\text{N}_2\text{O}_5]$

$d[\text{NO}_2]/dt = k_2[\text{N}_2\text{O}_5]$

$d[\text{O}_2]/dt = k_3[\text{N}_2\text{O}_5]$

$$-\frac{d\,\text{N}_2\text{O}_5}{dt} = \frac{1}{2}\frac{d\,\text{NO}_2}{dt} = 2\frac{d\,\text{O}_2}{dt}$$

$$K_1 = \frac{K_2}{2} = 2K_3$$

$$2K_1 = K_2 = 4K_3$$

63. $2A + B + C \rightarrow D + E$

(i) $\frac{dx}{dt} = K_1[A][B]^2[C]^0 = K_1[A][B]^2$

(ii) if concentration increases two times.

$$\frac{dx}{dt} = K_1[2A][2B]^2[2C]^0 = 8K_1\,[A][B]^2$$

⇒ rate increases by 8 times

64. $A \longrightarrow B \qquad K = 1.2 \times 10^{-2}\ \text{M s}^{-1}$

Initially = 10 M

From the unit of rate constant, we find that reaction is of zero order $X_1 = kt$.

$\therefore$ remaining $= (10 - 1.2 \times 10^{-2} \times 10 \times 60) = (10 - 7.2)$ M

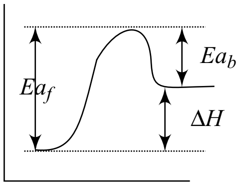
[Remaining mole = 2.8 M]

If $10 = 1.2 \times 10^{-2}\, t$

$$\therefore t = \frac{1000}{60 \times 1.2} \quad \text{at } t = 13.88 \text{ min reaction complete}$$

$\therefore$ after 20 min (13.88 min) contraction of reactant 0 M

65. $H_2O + O \underset{Eb}{\overset{Ea}{\rightleftharpoons}} 2HO°\quad \Delta H = 72$ kJ



$T = 500$ K

$Ea_f = 77$ kJ/mole $\quad \Rightarrow \quad \Delta H = Ea_f - Ea_b$

$72 = 77 - Eb$

$Ea_b = 77 - 72$

$Ea_b = 5$ kJ

66. $2NO + Br_2 \longrightarrow 2NOBr$

(i) $NO + Br_2 \rightleftharpoons NOBr_2$ (Fast)

(ii) $NOBr_2 + NO \xrightleftharpoons{\text{Slow}} 2NOBr$

Rate is determined by the slowest step

⇒ Rate = $K[NOBr_2][NO]$

But $NOBr_2$ here exist inform of intermediate.

$$\therefore \quad K_C = \frac{[NOBr_2]}{[NO][Br_2]} \Rightarrow \text{Rate} = k_1[NO]^2[Br_2]$$

⇒ Rate = $k_1[NO]^2\,[Br_2]$ and $k_1 = K \times K_C$

⇒ 3rd order Reaction

67. $A \longrightarrow B \quad Ea = 70$ kJ/mole $\quad t_{1/2} = 40$ min

$$K_1 = \frac{2.303}{20}\log\frac{100}{0.75} = 0.01438\ \text{min}^{-1}$$

$$\log_{10}\frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$= \frac{70 \times 10^3}{2.303 \times 8.314}\left[\frac{15}{298 \times 313}\right]$$

$$\frac{k_2}{k_1} = 5.88 \times 10^{-4} \times 10^3 = 10^{0.588}$$

$$\frac{k_2}{k_1} = 3.87$$

$\therefore \quad k_2 = 3.87 \times 0.01438 = 0.05571$

$$k_2 = 0.05571 = \frac{2.303}{20}\log\frac{100}{100 - y}$$

$y = 67.17$

68. (i) $A \longrightarrow$ product

(ii) $B \longrightarrow$ product

$$\log\left(\frac{k_2}{k_1}\right) = \frac{Ea}{2.303R}\left[\frac{10}{310 \times 300}\right]$$

$\log 2 \times 2.303 \times 8.314 \times 310 \times 300 = Ea$

$Ea = 53.6$ kJ/mole

$$k_{A_2} = \left(\frac{0.693}{30}\right)\text{min}^{-1}$$

$$k_{B_2} = \left(\frac{0.693}{15}\right)\text{min}^{-1}$$

$$Ea = 26.8 \text{ kJ/mole} = \frac{53.6}{2}$$

$$\log\frac{k_2}{k_B} = \frac{Ea}{2.303R}\left[\frac{-10}{310 \times 300}\right]$$

$$\log\left(\frac{k_2}{k_B}\right) = \frac{-26.8 \times 1000}{2.303 \times 8.314 \times 300 \times 310}$$

$$\log\frac{k_2}{k_B} = -0.151 = \log(0.706)$$

$$\therefore \quad k_2 = \left(\frac{0.706 \times .693}{15 \times 60}\right)\text{sec}^{-1}$$

$k_2 = 0.0327\ \text{min}^{-1}$

69. $2H_2O_2 \longrightarrow 2H_2O + O_2$

mili equivalent of H_2O_2 in 10 mL diluted solution

= mili equivalent of $KMnO_4$ titrated = 25 × .025 × 5 = 3.125

mili equivalent in 100 mL solution = 31.25

but 22400 mL O_2 = 68 gm H_2O_2

$$1\text{ mL} = \frac{68}{22400}$$

$$20\text{ mL} = \frac{68 \times 20}{22400} \text{ In 1 mL } H_2O_2 \text{ solution}$$

$$= \frac{68 \times 20 \times 10}{22400} \text{ in 10 mL } H_2O_2$$

Number of mili in 10 ml of 20 volume H_2O_2 solution

$$\text{Initially} = \frac{68 \times 20 \times 10 \times 1000}{17 \times 22400} = 35.71$$

$$\Rightarrow \quad K = \frac{2.303}{6}\log\left(\frac{35.71}{31.25}\right)$$

$K = 0.022\ \text{hr}^{-1}$

70. Initial *m* mol of cyclobutene = 10

Let after 20 min, *x m* mol cyclobutene isomerised.

m mol of cyclobutene left = 10 – *x* and *m* mol of diene formed = *x*

No of millimoles of Br_2 required
= No of millimoles of π bond in substance
m mol of Br_2 required after 20 min = $10 - x + 2x = 10 + x = 16$ $\therefore$ $x = 6$
$\Rightarrow$ $2a = 20$ (only 1, 3 butadiene present)

$$\therefore \quad a = 10, 20\text{ K} = \ln\frac{10}{4} \qquad \text{(i)}$$

If y m mol of cyclobutene isomerized after 30 min.

$$30\text{ K} = \ln\frac{10}{10 - y} \qquad \text{(ii)}$$

From Eqs. (i) and (ii) $y = 7.47$
$\Rightarrow$ m mol of Br_2 required = $10 + y = 17.47$
$\Rightarrow$ Volume of bromine solution required = 17.47 mL

71. $10^2 e^{-\frac{14000}{RT}} = 10^3 e^{-\frac{20000}{RT}}$ Solving

$T = 313.42$ K
$\Rightarrow$ Rate constant $K_1 = K_2 = 0.464\ \text{hr}^{-1}$

$$\Rightarrow \quad K_1 t = \ln\frac{n_0(A_2)}{n_0(A_2) - n_1} \Rightarrow n_1 = 0.37$$

$$K_2 t = \ln\frac{n_0(B_3)}{n_0(B_3) - n_2} \Rightarrow n_2 = 0.37$$

$\Rightarrow$ Total moles of gases after 1.0 hr. = 1.37 + 1.74 = 3.11

$$P = \frac{n_T RT}{V} = \frac{3.11 \times 0.0821 \times 313.42}{10} = 8\text{ atm}$$

72. Let rate constant in absence of catalyst is k_1
Let rate constant in presence of first catalyst is k_2
Let rate constant in presence of second catalyst is k_3

$$k_1 \times 1 = \ln\frac{100}{80} \Rightarrow k_1 = 0.2231\ \text{hr}^{-1} \qquad \text{(i)}$$

$$k_2 \times 0.5 = \ln\frac{80}{40} \Rightarrow k_2 = 1.3862 \qquad \text{(ii)}$$

$$\frac{k_3 \times 1}{6} = \ln\frac{40}{10} \Rightarrow k_3 = 8.317 \qquad \text{(iii)}$$

$$k_1 = Ae^{-80{,}000/RT}$$

$k_2 = Ae^{-E_{a_1}/RT}$ E_{a_1} → Activation energy in presence of First catalyst

$$\ln\frac{k_2}{k_1} = \frac{80{,}000 - E_{a_1}}{RT} = \ln\frac{1.3862}{0.2231}$$

$$E_{a_1} = 75443.8\text{ J} = 75.44\text{ kJ}$$

$k_3 = Ae^{-E_{a_2}/RT}$ E_{a_2} → Activation energy in presence of Second catalyst

$$\ln\frac{k_3}{k_1} = \frac{80{,}000 - E_{a_2}}{RT} = \ln\frac{8.317}{0.2231}$$

$$E_{a_2} = 70974.9\text{ J} = 70.975\text{ J}$$

73. $N_2O_5 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} NO_2 + NO_3$

$NO_2 + NO_3 \xrightarrow{k_b} NO_2 + O_2 + NO$

$NO + NO_3 \xrightarrow{k_c} 2NO_2$

$$\frac{-d[N_2O_5]}{dt} = k_a[N_2O_5] - k_{-a}[NO_2][NO_3] \qquad \text{(i)}$$

$$\frac{d[NO_3]}{dt} = k_a[N_2O_5] - k_{-a}[NO_2][NO_3] - k_b[NO_2]$$

$$[NO_3] - k_c[NO][NO_3] = 0 \qquad \text{(ii)}$$

$$\frac{d[NO]}{dt} = k_b[NO_2][NO_3] - k_c[NO][NO_3] = 0 \qquad \text{(iii)}$$

From Eq. (iii)

$$[NO] = \frac{k_b}{k_c}[NO_2]$$

Putting this in Eq. (ii)

$$k_a[N_2O_5] = [NO_3]\{k_a[NO_2] + 2k_a[NO_2]$$

$$[NO_3] = \frac{k_a[N_2O_5]}{k_{-a}[NO_2] + 2k_b[NO_2]}$$

Putting this in equation (i)

$$\frac{-d[N_2O_5]}{dt} = ka[N_2O_5] - \frac{k_a k_{-a}[N_2O_5]}{k_{-a} + 2k_b}$$

$$\frac{-d[N_2O_5]}{dt} = \frac{2k_a k_b[N_2O_5]}{k_{-a} + 2k_b}$$

$$r = \frac{-1}{2}\frac{d[N_2O_5]}{dt} = \frac{k_a k_b[N_2O_5]}{k_{-a} + 2k_b}$$

74. $\tau^2 = \alpha t + \beta$

$$2\tau\frac{d\tau}{dt} = \alpha \Rightarrow \frac{d\tau}{dt} = \frac{\alpha}{2\tau} = \frac{\alpha}{2}(\tau)^{-1}$$

order = –1

75. Given: $r = k'$ [complex]^a
and since $t_{3/4} = 2t_{1/2}$
so $a = 1$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[H^+]^b}$$

On doubling concentration of $[H^+]$ ion $t_{1/2}$ gets half so $b = 1$

76. Let at 20°C rate constant = K
Then at 3°C rate constant = $K/3$

$$\ln\frac{K}{K/3} = \frac{E_a}{R}\left[\frac{1}{276} - \frac{1}{293}\right] \Rightarrow E_a = 43.45\text{ kJ}$$

Let at 40°C rate constant is K_1 then

$$\ln\frac{K_1}{K} = \frac{43.45 \times 10^3}{8.314}\left[\frac{1}{293} - \frac{1}{313}\right]$$

$$K_1 = 3.125\text{ k}$$

So time required for juice to get spoil at 40°C = $\frac{64}{3.125}$ = 20.47 hr.

77.

$$\begin{array}{llllll} & CH_3OCH_3 & \longrightarrow & CH_4 + & CO + & H_2 \\ t = 0 & 0.4 & & & & \\ t = 4.5\text{hr.} & 0.11 & & 0.29 & 0.29 & 0.29 \end{array}$$

$$kt = \ln\frac{P_0}{P} \Rightarrow 4.78 \times 10^{-3} \times 4.5 \times 60 = \ln\frac{0.4}{P}$$

$P = 0.11$ atm

at $t = 0$ $P_0 = 0.4$

$M_0 = 46$

at $t = 4.5$ hr. $P = 0.11 + 0.29 \times 3 = 0.98$ atm

$$M = \frac{0.11 \times 46 + 0.29(16 + 28 + 2)}{0.98} = 18.77$$

$$\frac{R_0}{R} = \frac{P_0}{P}\sqrt{\frac{M}{M_0}} = \frac{0.4}{0.98}\sqrt{\frac{18.77}{46}} = 0.26$$

78.

$$\begin{tikzcd} & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd} \qquad k = k_1 + k_2$$

$$\frac{0.693}{t_{1/2}} = \frac{0.693}{60} + \frac{0.693}{90}$$

$t_{1/2} = 36$ min.

79.

$$\begin{array}{lll} & B^{n+} \longrightarrow & B^{(n+4)+} \\ t = 0 & a & - \\ t = 10\text{ min.} & a - x & x \end{array}$$

v.f. of $B^{n+} = |(n - 2) - n| = 2$

v.f. of $B^{(n+4)+} = |(n + 4) - (n - 1)| = 5$

Let normality of reducing agent $= N$

so $2a = 25N$ $\therefore$ $a = 12.5$ N

$2(a - x) + 5x = 32N$

$$2a + 3x = 32N \qquad x = \frac{7}{3}N$$

$$K \times 10 = \ln\frac{a}{a - x} = \ln\frac{12.5\text{ N}}{12.5\text{ N} - \frac{7}{3}\text{N}}$$

$K = 0.02$ min^{-1}.

80. For reaction 1

$$k_2 = k_1 e^{+E_a/R\left(\frac{1}{T_1} - \frac{1}{T}\right)} = 2.79 \times 10^{-3}\, e^{6000\left(\frac{1}{509} - \frac{1}{T}\right)}$$

For reaction 2

$$k_2 = 1.52 \times 10^{-4}\, e^{12250\left(\frac{1}{510} - \frac{1}{T}\right)}$$

For given condition

$$2.79 \times 10^{-3}\, e^{6000\left(\frac{1}{509} - \frac{1}{T}\right)} = 1.52 \times 10^{-4}\, e^{12250\left(\frac{1}{510} - \frac{1}{T}\right)}$$

$$18.355 = e^{12250\left(\frac{1}{510} - \frac{1}{T}\right) - 6000\left(\frac{1}{509} - \frac{1}{T}\right)}$$

$$\ln 18.355 = 12.33 - \frac{6250}{T} = 2.9$$

$T = 670.6$, $K = 397.6$°C

81. $$\frac{-d[A]}{dt} = K_1[A] + 2K_2[A]^2$$

82. 76.8%

$$\begin{tikzcd} & \text{Cyclohexane} \\ \text{Bicyclohexane} \arrow[ur, "K_1"] \arrow[dr, "K_2"'] & \\ & \text{Methylcyclopentene} \end{tikzcd}$$

$K_{AV} = K_1 + K_2 = 1.26 \times 10^{-4} + 0.38 \times 10^{-4} = 1.64 \times 10^{-4}$

$K_1 \times$ % of Cyclohexane $= K$

$$\text{Fraction of cyclohexane} = \frac{K_1}{K} = \frac{1.26 \times 10^{-4}}{1.64 \times 10^{-4}} = 0.768$$

Fraction of methyl cyclopentene

$$= \frac{K_2}{K} = \frac{0.38 \times 10^{-4}}{1.64 \times 10^{-4}} = 0.232.$$

83. 20.39

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

84. (i) 6.23×10^{-3} sec^{-1} (ii) 0.033 atm

$$\therefore \quad K = \frac{2.303}{55}\log_{10}\frac{0.062}{0.044}$$

$$K = 6.23 \times 10^{-3}\text{ sec}^{-1} = \frac{2.303}{100}\log\frac{0.062}{P_{Cl_2O_7}}$$

85. 5.25% and 128.33 hr

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{1.5 \times 10^{-6}} = 462000\text{ sec} = 128.33\text{ hr.}$$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. **(b, c)** Characteristic of catalyst

2. **(d)** $\frac{1}{16}$g or $N_t = N_0\left(\frac{1}{2}\right)^n = 1 \times \left(\frac{1}{2}\right)^4$

$$1 \xrightarrow{140} \frac{1}{2} \xrightarrow{140} \frac{1}{4} \xrightarrow{140} \frac{1}{8} \xrightarrow{140} \frac{1}{16}$$

3. $A \longrightarrow B$ $\qquad Ea = 70$ kJ/mole

$$K_1 = \frac{2.303}{20}\log\frac{100}{75} = 0.01438\text{ min}^{-1}$$

$$\log_{10}\frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$= \frac{70 \times 10^3}{2.303 \times 8.314}\left[\frac{15}{298 \times 313}\right]$$

$$\frac{k_2}{k_1} = 5.88 \times 10^{-4} \times 10^3 = 10^{0.588}$$

$$\frac{k_2}{k_1} = 3.87$$

$\therefore$ $k_2 = 3.87 \times 0.01438 = 0.05571$

$$k_2 = 0.05571 = \frac{2.303}{20}\log\frac{100}{100 - y}$$

$y = 67.17$

4. **(b)** The species $_{13}\text{Al}^{29}$ contains more neutrons than the stable isotope $_{13}\text{Al}^{27}$
(means high n/p $\therefore$ β decay)

5. At 380°C $K_1 = \dfrac{0.6932}{(t_{1/2})_1} = \dfrac{0.6932}{360}$

At 380°C $K_2 = \dfrac{0.6932}{(t_{1/2})_2}$

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

$$\log\frac{K_2}{\frac{0.6932}{360}} = \frac{200 \times 1000}{2.303 \times 8.314}\left[\frac{1}{653} \times \frac{1}{723}\right]$$

$$K_2 = 6.18 \times 10^{-2}\ \text{min}^{-1}$$

$$\therefore \quad K_2 = \frac{2.303}{t}\log\frac{a}{0.25a}$$

$t = 20.358$ min

6. (a) $E_a = 239.339$ kJ mol^{-1}
(b) $K = 2.18 \times 10^{-11}$ sec^{-1}
(c) $T = 669$ K
(i) $E_a = (1.25 \times 10^4\ \text{K})(2.303)(8.314\ \text{kJ}^{-1}\ \text{mol}^{-1})$
$= 239.339$ KJ mol^{-1}

(ii) $\log K = 14.34 - \dfrac{1.25 \times 10^4}{500}$

$\log K = -10.66 \quad \therefore K = 2.18 \times 10^{-11}$ sec^{-1}

(iii) $t_{1/2} = \dfrac{0.693}{K} \Rightarrow K = 4.51 \times 10^{-5}\ \text{s}^{-1}$

or $\quad -4.346 = 14.34 - \dfrac{1.25 \times 10^{-5}\ \text{K}}{T}$, $T = 669$ K

7. $E_a = 22.01$ k mol^{-1} and $A = 5.43 \times 10^{10}$ sec^{-1}

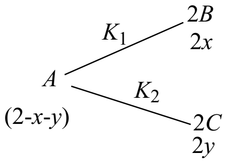
$$\log\frac{K_2}{K_1} = \log\frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{2.303 \times 8.314}\left(\frac{50}{323 \times 373}\right)$$

$\therefore \quad Ea = 22.01$ kJ mol^{-1}
$A = 5.43 \times 10^{10}$ sec^{-1}

8. **(3)** $\dfrac{d[B]}{dt} = 2K_1[A]$

$\dfrac{d[C]}{dt} = 2K_2[A]$

$\therefore \quad \dfrac{[B]}{[C]} = \dfrac{K_1}{K_2} = \dfrac{1}{2}$



$\therefore \quad [C]_t = 2[B]_t$
Total No of moles after 50% reaction
$= [A_t] + [B_t] + [C_t] = (2 - x - y) + 2x + 2y$
But $x + y = 1$
$\therefore \quad 2x + 2y = 2$
$\therefore \quad [A_t] + [B_t] + [C_t] = 1 + 2x + 2y = 3$

9. **282 K** $\qquad k = Ae^{-E_a/RT}$

$$2.303 \log 10 = \frac{157700 - 152300}{8.314 \times T}$$

$\therefore \quad T = 282$ K

10. 3.4353×10^{-3} M min^{-1}
$k(a - x) = 4.5 \times 10^{-3} \times 0.7634$
$= 3.4353 \times 10^{-3}$ M min^{-1}

11. **(d)** As unit of k is sec^{-1}, reaction is of the first order.

$$r = k[N_2O_5]; \therefore [N_2O_5] = \frac{2.4 \times 10^{-5}}{3 \times 10^{-5}} = 0.8\ \text{mol L}^{-1}$$

12. 33.70 hr, 67.41 hr, 29.28 hr
$_{30}\text{Zn}^{64}$, $_{28}\text{Ni}^{64}$, $_{28}\text{Ni}^{64}$

$t_{1/2}$ for β^--emission $= \dfrac{0.693}{2.056 \times 10^{-2}} = 33.70$ hr

$t_{1/2}$ for β^+-emission $= \dfrac{0.693}{1.028 \times 10^{-2}} = 67.41$ hr

$t_{1/2}$ for electron capture $= \dfrac{0.693}{2.327 \times 10^{-2}} = 29.28$ hr

13. **(b)** The rate of photochemical reaction ∝ intensity of light.

14. **(a)** $_0n^1 + _1p^1 + _{-1}e^0$ or β^-
Since $n/p \uparrow$
$\therefore$ β emission.

15. **(c)** Rate $= K[X] = \dfrac{0.693}{t_{1/2}} \times [X] = \dfrac{0.693}{20} \times 0.01$

$= 3.47 \times 10^{-4}$ M min^{-1}
0.1 M → 0.05 → 0.025 M
40 minute $= 2 \times t_{1/2}$
$\therefore \quad t_{1/2} = 20$ min.

16. **(c)** $^{23}_{11}\text{Na} \longrightarrow {}^{23}_{10}X + {}^{0}_{1}\beta$

17. **(8)** $_{92}\text{U}^{238} \longrightarrow {}_{82}\text{Pb}^{214}$

Number of α particle $= \dfrac{238 - 214}{4} = 6a$

Number of β particle $= 2 \times 6 - [92 - 82] = 2$
Total particles $= 6 + 2 = 8$

18. **(d)** Given $\log K = -2000 \times \dfrac{1}{T} + 6.0$

We know $\log K = -\dfrac{Ea}{2.303RT} + \log A$

$\therefore \quad A = 10^6$ and $\dfrac{-Ea}{2.303RT} = \dfrac{-2000}{T}$

$\therefore \quad E_a = 2000 \times 2.303 \times 8.3\ \text{J} = 38.3$ KJ mol^{-1}

19. **(9)** For a first order process $Kt = \ln\dfrac{[A]_0}{[A]}$

where $[A]_0$ = initial concentration.
$[A]$ = concentration of reactant remaining at time "t".

$$\Rightarrow \quad Kt_{1/8} = \ln\frac{[A]_0}{[A]_0/8} = \ln 8 \qquad \text{(i)}$$

and $Kt_{1/10} = \ln\dfrac{[A]_0}{[A]_0/10} = \ln 10$ (ii)

Therefore, $\dfrac{t_{1/8}}{t_{1/10}} = \dfrac{\ln 8}{\ln 10} = \log 8 = 3 \log 2$

$= 3 \times 0.3 = 0.9$

$\Rightarrow \quad \dfrac{t_{1/8}}{t_{1/10}} \times 10 = 0.9 \times 10 = 9$

20. **(8)** Balancing the given nuclear reaction in terms of atomic number (charge) and mass number.

$${}_{29}Cu^{63} + {}_1H^1 \longrightarrow {}_{60}n^1 + {}_1He^4(\alpha) + 2\,{}_1H^1 + {}_{26}X^{52}$$

The atomic number 26 corresponds to transition metal Fe which belongs to 8th group of modern periodic table.

21. **(d)** Time of 75% reaction is twice the time taken for 50% reaction if it is first order reaction w.r.t. *P*. From graph [*Q*], decreases linearly with time, thus it is zeroth order reaction w.r.t. *Q*.

$$\frac{dx}{dt} = K[P]^a[Q]^b$$

Order w.r.t. $P = a = 1$

Order w.r.t. $Q = b = 0$

Thus, overall order of the reaction = 1 + 0 = 1.

22. **(a)** From Arrhenius equation,

$$\log\frac{K_2}{K_1} = \frac{-E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Given, $\dfrac{K_2}{K_1} = 2$

$T_2 = 310$ K and $T_1 = 300$ K

On putting values,

$$\Rightarrow \quad \log 2 = \frac{-E_a}{2.303 \times 8.314}\left(\frac{1}{310} - \frac{1}{300}\right)$$

$$\Rightarrow \quad E_a = 53598.6 \text{ KJ/mol} = 53.6 \text{ KJ mol}^{-1}$$

23. **(b)** For the elementary reaction, $M \longrightarrow N$

Rate law can be written as

Rate $\propto [M]^n$

Rate $= K[M]^n$

When we double the concentration of [*M*],

Rate becomes 8 times, hence new rate law can be written as

$8 \times \text{Rate} = K[2M]^n$

$$\frac{\text{Rate}}{8 \times \text{Rate}} = \frac{K[M]^n}{K[2M]^n}$$

$$\frac{1}{8} = \frac{1}{[2]^n}$$

$$\Rightarrow \quad [2]^n = 8 = [2]^3 \quad \Rightarrow \quad n = 3$$

24. **(d)** This problem can be solved by determining the order of reaction w.r.t. each reactant and then writing rate law equation of the given equation accordingly as

$$R = \frac{dC}{dt} = k[A]^x[B]^y$$

where, x = order of reaction w.r.t. *A*

y = order of reaction w.r.t. *B*

$1.2 \times 10^{-3} = k[0.1]^x[0.1]^y$ (i)

$1.2 \times 10^{-3} = k[0.1]^x[0.2]^y$ (ii)

$2.4 \times 10^{-3} = k[0.2]^x[0.1]^y$ (iii)

$$\frac{\text{(ii)}}{\text{(i)}} = 1 = \left(\frac{2}{1}\right)^y \quad \therefore y = 0$$

$$\frac{\text{(iii)}}{\text{(i)}} = 2 = \left(\frac{2}{1}\right)^x \quad \therefore x = 1$$

$$\therefore \quad R = k[A]^1[B]^0$$

As shown above, rate of reaction remains constant as the concentration of reactant (B) changes from 0.1 M to 0.2 M and becomes double when concentration of A change from 0.1 to 0.2. (i.e., doubled).

25. **(a)** The main conditions for the occurrence of a reaction is proper orientation and effective collision of the reactants.

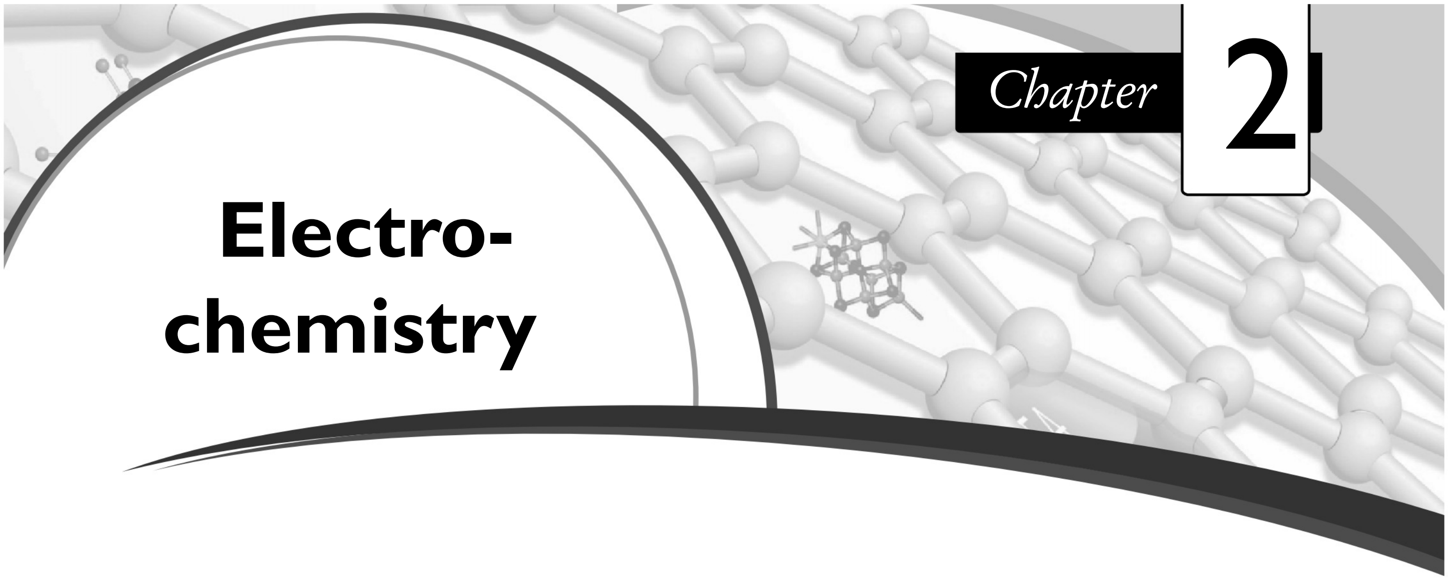
Since, the chances of simultaneous collision with proper orientation between two species in high order reactions are very rare, so reaction with order greater than 3 are rare.

25. $\dfrac{R_2}{R_1} = \dfrac{K_1}{K_2}$

$$\therefore \quad \ln\frac{K_2}{K_1} = \ln\left[\frac{Ae^{-\frac{Ea}{RT}}}{Ae^{-\frac{Ea+10}{RT}}}\right]$$

$$\ln\frac{K_2}{K_1} = \ln\left[e^{-\frac{10}{RT}}\right]$$

$$= \frac{-10 \text{ KJ}}{RT} = \frac{-10 \times 1000}{8.314 \times 300} = 4.0093$$



Chapter 2

Electro-chemistry

Key Concepts

This branch of chemistry deals with two types of conversion:

Conversion of chemical energy into electrical energy ⇒ electrochemical cell

Conversion of electrical energy into chemical ⇒ electrolytic cell

Electrochemical cell/Galvanic cell/voltaic cell

⇒ Electrical energy is produced from the chemical changes

⇒ Maximum electrical work obtained from the electrochemical cell = decrease in Gibb's free energy.

Max. electrical work = $-\Delta G = nF\,E_{cell}$

n = Number of mole of e^- involved in the transfer.

F = Faraday constant

= 96500 c

E_{cell} = E.M.F. of the cell/cell-voltage

⇒ In Galvanic cell, spontaneous redox reaction takes place.

Daniel Cell: When Zn is anode and copper is cathode, electro chemical cell is called *Daniel* cell.

⇒ Oxidation occurs at anode, reduction occurs at cathode.

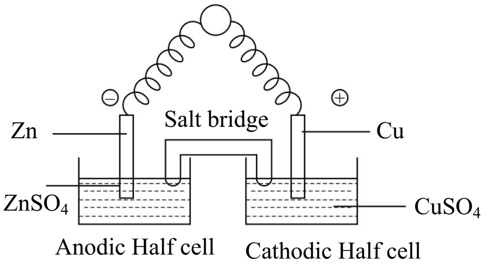
At anode: $Zn \rightarrow Zn^{+2} + 2e-$

At cathode: $Cu^{+2} + 2e^- \rightarrow Cu$

$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$ (cell reaction)

⇒ Flow of e^- from anode to cathode

⇒ Flow of i (current) from cathode to anode



Salt Bridge

It is the U-tube filled with inert electrolytes like KNO_3, KCl, NH_4NO_3, etc., mixed with gelatin or agar-agar.

Characteristics of electrolyte used in salt Bridge

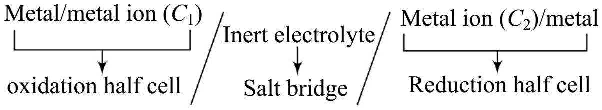
1. Electrolyte should not be able to react with any ion in either of the half-cell.
2. Velocities of the cations and anions of the salt should be similar.

Importance of salt-Bridge

1. It completes the circuit by connecting two half cell.
2. Maintain the electrical neutrality in two half cell.
3. It does not allow the intermixing of solution ion in the half cells.

Representation of Galvanic Cell

1. When metal electrode is dipped into its metal ion.



Example $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$

$Zn/Zn^{+2}\,//\,Cu^{+2}/Cu$

Example $Zn + 2Ag^+ \rightarrow 2Ag + Zn^{+2}$

$Zn/Zn^{+2}//Ag^+/Ag$

2. When some gaseous species exist in the half cell reaction then Pt electrode is used.

Example $Cu^{+2} + H_2 \rightarrow 2H^+ + Cu$

$Pt(H_2)/H^+//Cu^{+2}/Cu$

P_1 atm

Example $2H^+ + 2e^- \rightarrow H_2$

$H^+/Pt(H_2)$

Example $2Cl^- \rightarrow Cl_2 + 2e^-$

$Pt(Cl_2)/Cl^-$

3. When only ions are present in the half-cell reaction then, use the Pt electrode.

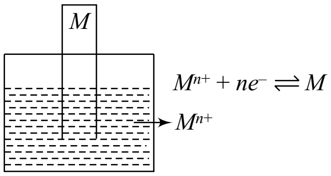
   Example $Fe^{+2} \rightarrow Fe^{+3} + 1e^-$

   $(Pt)/Fe^{+2}/Fe^{+3}$ or $Pt/Fe^{+2}, Fe^{+3}$

   Example $MnO_4^- \xrightarrow{5e^-} Mn^{+2}$

   $MnO_4^-/Mn^{+2}\,(Pt)$

Electrode Potential (E)



It is the Potential difference between the metal and ions in the solution when a metal is dipped into its metal ion.

It is the measurement of tendency of species for oxidation or reduction. It can be of two types:

1. Reduction Potential (E_R):

   $E_R \uparrow \Rightarrow$ tendency for reduction$\uparrow$

   $E_R = -E_0$

2. Oxidation Potential (E_0):

   $E_0 \uparrow \Rightarrow$ tendency for oxidation$\uparrow$

   $E_R = -E_0$

   Standard Electrode Potential (E°):

   It is the electrode potential at S.T.P.

   T = 298 K

   C = 1 M

   P = 1 atm or 1 bar

Note:

1. **Electrode potential is intensive quantity:**

   $Ag^+ + 1e^- \rightarrow Ag;\qquad E^o_{Ag^+/Ag} = +0.80$ volt

   $2Ag^+ + 2e^- \rightarrow 2Ag;\qquad E° = +0.80$ volt

   $\Delta G_1 = -1 \times F \times 0.80$ and $\Delta G_2 = -2 \times F \times 0.80$

2. **If direction of any cell reaction is reversed, magnified of E remains same but sign will change:**

   $Ag^{+1} + 1e- \rightarrow Ag;\quad E° = +0.80$ V

   $Ag \rightarrow Ag^+ + 1e^-;\quad E° = -0.80$ V

3. **Whenever two or more half-cell reactions are added. E is not additive in nature. So, it obtained by ΔG:**

   $Fe^{+3} + 1e^- \rightarrow Fe^{+2};\quad E_1^o = +0.77$ V

   $Fe^{+2} + 2e^- \rightarrow Fe;\quad E_2^o = -0.44$ V

   $Fe^{+3} + 3e^- \rightarrow Fe;\quad E^o = ?$

   $$\Delta G = \Delta G_1 + \Delta G_2$$

   $$-nFE = -(n_1FE_1 + n_2FE_2)$$

   $$nE = n_1E_1 + n_2E_2$$

   $$\Rightarrow \quad 3 \times E = 1 \times 0.77 + 2 \times -0.44$$

   $$\Rightarrow \quad E = -\frac{0.11}{3}\text{V}$$

Difference between E.M.F. of Cell and Potential Difference

	E.M.F.		Potential Difference
(1)	It is difference of two electrode potentials of the galvanic cell when there is no current flow in the circuit, i.e., open circuit.	(1)	It is difference of two electrode potential, when there is current flow in the circuit.
(2)	It is the maximum voltage obtained from the cell.	(2)	It is lesser than maximum.
(3)	It is measured by potentiometer.	(3)	It is measured by voltmeter.

E.M.F. of Cell or Cell Voltage

$$E^0_{cell} = (E^0_A)_{\text{oxidation potential}} + (E^0_C)_{\text{Reduction Potential}}$$

$$E^0_{cell} = E^0_{(cathode)} - E^0_{(anode)} \text{ if data in SRP}$$

$$= E^0_{(anode)} - E^0_{(cathode)} \text{ if data in SOP}$$

Electro-Chemical Series

In this series, different species are arranged in the increasing order of their standard reduction potential (E_R^o).

$$\underset{\xleftarrow[\text{E}_\text{R}^\text{o} = -\text{ve}]{\hspace{6cm}}}{\text{Li K Ba Ca Na Mg Al Zn Fe Ni Sn Pb}} \Big/ \begin{matrix}\text{H} \\ \text{0 volt}\end{matrix} \Big/ \underset{\xrightarrow[\text{E}_\text{R}^\text{o} = +\text{ve}]{\hspace{2cm}}}{\text{Cu Mg Ag Au}}$$

Halogens

$$\xrightarrow[E_R^o = \text{increases}]{I_2 \quad Br_2 \quad Cl_2 \quad F_2}$$

APPLICATION OF ELECTRO-CHEMICAL SERIES

1. **Oxidising Power ($\propto E_R^o$):**

   $F_2 > Cl_2 > Br_2 > I_2$ (order of oxidising power)

   $2x^- + Cl_2 \rightarrow 2Cl^- + x_2$

   x = Br, 1

2. **Reducing Power** ($\propto E_0^o$) OR ($\propto 1/E_R^o$):

   HF < HCl < HBr < HI (order of reducing power)

3. **Displacement Reaction:**

   Generally, reactivity of metals $\propto \dfrac{1}{E_R^o}$

   (a) More reactive metal can displace lesser reactive metal from its salt solution:

   $Zn + CuSO_4$ (Blue) $\rightarrow ZnSO_4 + Cu$

   (Colour less)

   $Ag + CuSO_4 \rightarrow$ NO reaction

   (b) Only those metals can displace the H from dilute acids whose reactivity is more than H, i.e., having $-E_R^o$.

$Zn + H_2SO_4$ (dil) $\rightarrow ZnSO_4 + H_2 \uparrow$

$Cu + H_2SO_4$ (dil) $\rightarrow$ No reaction

4. **Feasibility or Spontaneity of Cell reaction:**

For spontaneity $\Delta G = -ve = -nFE_{cell}$

$\Rightarrow \quad E_{cell} = +ve$

If $E_{cell} = -ve \Rightarrow$ non-spontaneous in the given direction but spontaneous on opposite direction.

$\therefore \quad E_R^o$ lesser $\Rightarrow$ anode

E_R^o more $\Rightarrow$ cathode

If four elements w, x, y, z form diatomic molecule and also form singly charged –ve ions. Following observations are made:

(a) $2x^- + y_2 \rightarrow 2y^- + x_2$

(b) $2w^- + y_2 \rightarrow$ no reaction

(c) $2z^- + x_2 \rightarrow 2i^- + z_2$

then the correct order of reduction potential and oxidising power.

$w > y > x > z$

Whether under standard condition, following reaction are possible or not:

(i) Fe reduce Fe^{+3} to Fe^{+2}

Given:

$$\text{(i)} \begin{cases} Fe^{+3} + 1e^- \rightarrow Fe^{+2}; & E^\circ = 0.77\ V \quad \text{(cathode)} \\ Fe^{+2} + 2e^- \rightarrow Fe; & E^\circ = -0.44\ V \quad \text{(anode)} \end{cases}$$

If $E^o_{cell} = +ve \Rightarrow$ Reaction Spontaneous

$Fe^{+3} + Fe \rightarrow Fe^{+2} + Fe^{+2}$

$E^o_{Fe^{+3}/Fe^{+2}} + E^o_{Fe/Fe^{+2}}$

$E^o_{cell} = [0.77] + [+0.44] = +1.21\ V$

(ii) MnO_4^- ion literate O_2 from H_2O in presence of acid

$$\begin{cases} MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O;\ E^\circ = 1.51\ V & \text{(Cathode)} \\ 2H^+ + 1/2\,O_2 + 2e^- \rightarrow H_2O;\ E^\circ = 1.223\ V & \text{(anode)} \end{cases}$$

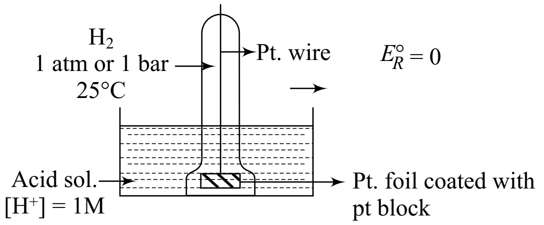
$$E^o_{cell} = E^o_{MnO_4^-/Mn^{+2}} + E^0_{H_2O/O_2} = 1.51 + (-1.223) = 0.287\ V$$

Since $E^o_{cell} = +ve \Rightarrow$ Spontaneous

REFERENCE ELECTRODE

Electrode potential of any electrode is measured with respect to refrence electrode.

1. **Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE):**

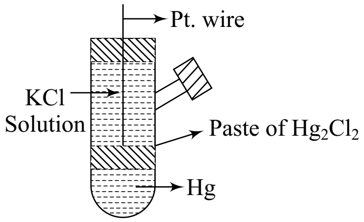


Half-Cell Reaction

$2H^+ + 2e^- \rightleftharpoons H_2$

$H^+/Pt(H_2)$ or $H^+/H_2/pt$

2. **Calomel (Hg_2Cl_2) Electrode:**



Half-Cell Reaction

$$\frac{1}{2}Hg_2Cl_2(s) + 1e^- \rightleftharpoons Hg(l) + Cl^-(aq.)$$

E.M.F. of this electrode depends on the concentration of KCl.

Representation

$Cl^-/Hg_2Cl_2/Hg/Pt$ When act as cathode

Factors Affecting Electrode Potential

$\Rightarrow$ Nature of electrode

$\Rightarrow$ Temperature

$\Rightarrow$ Concentration

$\Big]\Rightarrow$ Effect is given by Nernst equation

Nernst Equation

$\Delta G = \Delta G^\circ + 2.303\ RT \log Q$

$-nFE_{cell} = -nFE^o_{cell} + 2.303RT \log Q$

$$\Rightarrow \quad E_{cell} = E^o_{cell} - \frac{2.303RT}{nF}\log Q$$

at 298 K

$R = 8.314,\ F = 96500\ C$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log Q$$

For pure solids and pure liquids activity is taken as 1 and for gas phase activity will be written in terms of partial pressure in atm or bar,

1. $Zn + 2Ag^+ \longrightarrow Zn^{+2} + 2Ag$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$$

and $\quad E^o_{cell} = E^o_{Zn/Zn^{+2}} + E^o_{Ag^+/Ag}$

2. $Cu^{+2} + 2e^- \longrightarrow Cu$

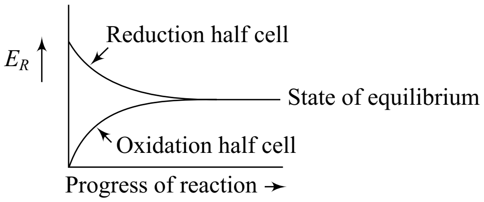
$$E_{Cu^{2+}/Cu} = E^o_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{[Cu^{+2}]}$$

3. $Zn \longrightarrow Zn^{+2} + 2e^-$

$$E_{Zn/Zn^{+2}} = E^o_{Zn/Zn^{+2}} - \frac{0.0591}{2}\log[Zn^{+2}]$$

Application of Nerst Equation

1. **To find the equilibrium constant of cell reaction:**



at equilibrium:

⇒ $\Delta G = 0 \Rightarrow E_{cell} = 0$

⇒ No current flow in the circuit

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log Q$$

⇒ $$E^o_{cell} = \frac{0.0591}{n} \log K_{eq.}$$

2. **To find P^H of solution:**

If the E_{CELL} of following half-cell.
$Pt(H_2)1$ atm/HCl; E = 0.25 V P_H can be calculated as
$H_2 \longrightarrow 2H^+ + 2e^-$

Since $E^o_{H_2/H^+} = 0$

⇒ from Nenst equation

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[H^+]}{P_{H_2}}$$

$$0.25 = 0 - \frac{0.0591}{2} \log \frac{[H^+]^2}{1\,atm}$$

⇒ 0.25 = 0.0591 × Ph Since Ph = –log[H$^+$]

⇒ $$Ph = \frac{0.25}{0.0591} = 4.23$$

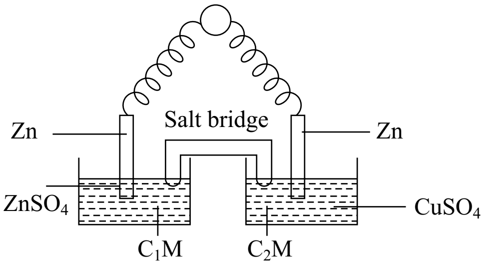
CONCENTRATION CELLS

These are the galvanic cell in which both the two electrodes are composed of same material so that always $E^o_{cell} = 0$. These can be of two types:

1. Electrolyte concentration cell
2. Electrode concentration cell

Electrolyte concentration cells

In these concentration cells, two identical electrodes are dipped into metal ions of different concentration.



Example (i) $Zn/Zn^{+2}(C_1)//Zn^{+2}(C_2)/Zn$

$$\rightarrow Zn + \underset{C_2M}{Zn^{+2}} \longrightarrow \underset{C_1M}{Zn^{+2}} + Zn$$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log Q$$

$$E_{cell} = \frac{-0.0591}{2} \log \frac{C_1}{C_2} = \frac{0.0591}{2} \log \frac{C_2}{C_1}$$

$$E_{cell} = \frac{0.0591}{n} \log \frac{[\text{concentration}]\ \text{cathode}}{[\text{concentration}]\ \text{anode}}$$

$C_2 > C_1$

Example (ii) Pt/H_2 1 atm/$H^+(C_1)//H^+(C_2)/H_2$ 1 atm/ Pt. ⇒ $C_2 > C_1$

Electrode Concentration Cell

In these cells, driving force for the current flow is pressure difference

Example $Pt/H_2\ (P_1\ atm)/H^+(1M)//H^+(1M)/H_2\ (P_2\ atm)/Pt$

$$\underset{P_1}{H_2} + \underset{1M}{2H^+} \longrightarrow \underset{1M}{2H^+} + \underset{P_2}{H_2}$$

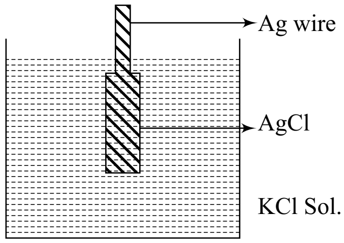
$$E_{cell} = \frac{-0.0591}{n} \log \frac{P_2}{P_1} = \frac{0.0591}{2} \log \frac{P_1}{P_2}$$

$P_1 > P_2$

Metal-Metal sparingly (insoluble) soluble salt electrode

Example Silver-silver chloride electrode

In this electrode, silver wire is coated with AgCl then, dipped into chloride ion solution.



Reduction half-cell reaction: (when act as cathode)

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^- \quad ; \quad \Delta G^o_1$$

$$Ag^+ + 1e^- \rightleftharpoons Ag \quad ; \quad \Delta G^o_2$$

$$AgCl(s) + 1e^- \rightleftharpoons Ag(s) + Cl^-\ (aq.) \quad ; \quad \Delta G^o_3$$

Representation

$Cl^-/AgCl/Ag$ (when it acts as cathode)
$Ag/AgCl/Cl^-$ (when acts as anode)

$$E_{Cl^-/AgCl/Ag} = E^o_{Cl^-/AgCl/Ag} - \frac{0.0591}{1} \log[Cl^-] \qquad (1)$$

Electrode potential of this half-cell will depend only on concentration of KCl solution

$$\Delta G^o_3 = \Delta G^o_1 + \Delta G^o_2$$

⇒ $$-1 \times F \times E^o_{Cl^-/AgCl/Ag} = -2.303\,RT \log K_{SP}(AgCl) + (-1 \times F \times E^o_{Ag^+/Ag})$$

$$\Rightarrow \quad E^{o}_{Cl^-/AgCl/Ag} = E^{o}_{Ag^+/Ag} + \frac{2.303RT}{F} \log K_{sp}(AgCl)$$

$$\Rightarrow \quad E^{o}_{Cl^-/AgCl/Ag} = E^{o}_{Ag^+/Ag} + \frac{0.0591}{1} \log K_{sp}(AgCl) \quad (2)$$

From (1)

$$E_{Cl^-/AgCl/Ag} =$$

$$E^{o}_{Ag^+/Ag} + \frac{0.0591}{1} \log K_{SP}(AgCl) - 0.0591 \log (Cl^-)]$$

$$\Rightarrow \quad E_{Cl^-/AgCl/Ag} = E^{o}_{Ag+/Ag} + \frac{0.0591}{1} \log \frac{K_{SP}[AgCl]}{[Cl^-]}$$

$$= E^{o}_{Ag^+/Ag} + \frac{0.0591}{1} \log[Ag^+]$$

$$E_{Cl^-/AgCl/Ag} = E_{Ag^+/Ag}$$

If Ag^+ ion concentration on both electrode are same.

$$Ag^+ + 1e^- \rightarrow Ag$$

$$E_{Ag^+/Ag} = E^{o}_{Ag^+/Ag} + 0.0591 \log [Ag^+]$$

Heat of reaction (ΔH) in electrochemical cell

$$\Delta G = \Delta H - T\Delta S$$

$$dG = V\,dP - SdT$$

For chemical reaction:

$$d(\Delta G) = \Delta V\,dP - \Delta SdT$$

At constant Pressure $dP = 0$

$$d(\Delta G) = -\Delta SdT$$

$$\frac{d}{dT}(\Delta G) = -(\Delta S)$$

$$\Delta S = \frac{-d}{dT}(-nFE)$$

$$\Delta S = nF\left(\frac{dE}{dT}\right)_P$$

Entropy change in electrochemical cell:

$$\left(\frac{dE}{dT}\right)_P = \text{Temperature coefficient of cell.}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \Delta H - T \cdot nF\left(\frac{dE}{dT}\right)_P$$

$$\Rightarrow \quad -nFE + TnF\left(\frac{dE}{dT}\right)_P = \Delta H$$

$$\therefore \quad \Delta H = nF\left[T\left(\frac{dE}{dT}\right)_P - E\right]$$

Battery

These are the galvanic cells without salt bridge.

Types of Battery

1. Primary Cells:

These are the cells which cannot be recharged after using once. Their cell reaction are irreversible in nature.

Example Dry cell or leclanche cell

anode: Zn

Cathode: graphite

Electrolyte: $ZnCl_2 + NH_4Cl + C + MnO_2$ (depolariser)

Cell reaction

Anode: $Zn \longrightarrow Zn^{+2} + 2e^-$

Cathode:

$$2\overset{+4}{Mn}O_2(s) + 2NH_4^+ + 2e \rightarrow \overset{+3}{Mn_2}O_3(s) + 2NH_3 + H_2O$$

E.M.F. of cell = 1.5 V

2. Secondary Cells:

These are the cells which can be recharged and can be used again and again as their cell reaction are reversible in nature.

Example, Lead storage battery

Anode: Pb

Cathode: PbO_2

Electrolyte: Conc. H_2SO_4

E.M.F. depends on the concentration of H_2SO_4.

Cell reaction

(a) Discharging

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode:

$$PbO_2(s) + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O$$

Net Cell Reaction

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq.) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

(b) Charging

During charging it act like electrolytic cell and all the cell reaction are reversed.

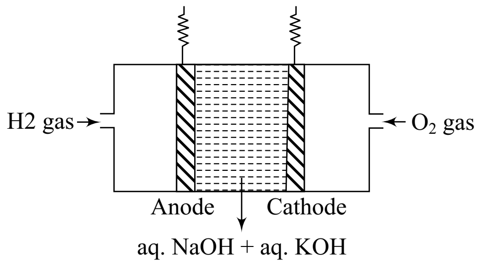
$$2PbSO_4 + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq.)$$

On passing IF charge, 1 mole of H_2SO_4 is produced during the reaction.

3. Fuel Cell:

In this cell, heat of combution is converted into electrical energy.

Example $H_2 - O_2$ cell. (Bacon's cell)



Anode: $2H_2 + 4OH^- \rightarrow 4H_2O(l) + 4e^-$

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq.)$

Net reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Fuel cells are used in aircraft because

1. These are lighter so, convenient to use.
2. No harmful product is formed.
3. Efficiency is relatively high.

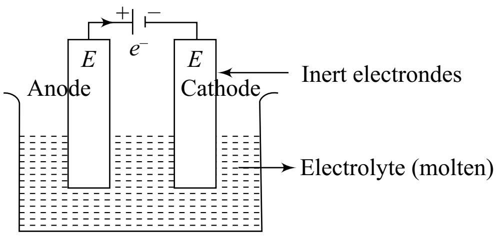
Efficiency of fuel cell

$$\eta = \frac{\text{Electrical work produced}}{\text{Heat of combustion}}$$

$$= \frac{-\Delta G}{\Delta H_C} = \frac{nFE}{\Delta H_C}$$

ELECTROLYTIC CELL

1. It converts electrical energy into chemical energy.
2. In this cell, non-spontaneous cell reaction ($\Delta G = +ve$) are carried out with the help of electric work.



at anode: oxidation occurs

$$2Cl^- \rightarrow Cl_2\uparrow + 2e^-$$

at cathode: reduction occurs

$$2Na^+ + 2e^- \rightarrow 2Na$$

- Flow of electron from anode to cathode in outer circuit.
- Flow of current from anode of cathode through the solution.
- For the working of electrolytic cell, minimum voltage required is slightly more than the E_{cell}.

PRODUCT OF ELECTROLYSIS (USING INERT ELECTRODE)

1. **Electrolysis of Water:**

At Anode

$$2H_2O \longrightarrow O_2\uparrow + 4H^+ + 4e^- \quad E_0^o = -1.23\text{ V}$$

$$[H^+] = [OH^-] = 10^{-7} \text{ at ph} = 7$$

$$E_{o(\text{at }P^H=7)} = -1.23 - \frac{0.0591}{4}\log[H^+]^4$$

$$= -1.23 + 0.42$$

$$= -0.81\text{ V}$$

At Cathode

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-;\ E_R^o = -0.8277\text{ V}$$

$$E_R\ (\text{at } P^H = 7) = -0.8277 - \frac{0.0591}{2}\log[OH^-]^2$$

$$= -0.41\text{ V}$$

Net cell reaction:

$$2H_2O(l) \rightleftharpoons O_2\uparrow + 2H_2O\uparrow$$

$$E_{cell} = -0.41 - 0.81$$

$$= -1.22\text{ V}$$

2. **Electrolysis of aq. NaCl:**

At cathode

1. $Na^+ + 1e^- \rightarrow Na; E° = -2.71\text{ V}$
2. $H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-; E_R = -0.41\text{ V}$

Because of more reduction potential.

At anode

(i) $2Cl^- \rightarrow Cl_2\uparrow + 2e^-; E_o = -1.36\text{ V}$

(ii) $2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-; E_o = -0.81\text{ V}$

Inspite of high oxidation potential (E_o) at anode, O_2 is not released because of its high over voltage.

Over voltage = actual potential required – theoretical potential required

If solution is diluted then, O_2 is released at anode.

> ***Note:***
>
> - In the aqueous solution if active metal ions like alkali metal ions, alkaline earth metal ions are present then, H_2O is reduced and produces H_2 gas at cathode.
> - If low reactive metal like Cu, Ag are present in the solution then, these metal ions are reduced, not water.
> - If halide ions (except F^-) are present in the aqueous solution then, halogen is produced at anode. But, if dilute solution of halide ions is there then, H_2O is oxidised to produce O_2 at anode.
> - If CO_3^{2-}, PO_4^{3-}, NO_3^-, SO_4^{2-} are present in the aqueous solution then, H_2O is oxidised and O_2 is produced.

Example 1. Aq. $CuSO_4$ solution:

Anode: $2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$

Cathode: $Cu^{+2} + 2e^- \rightarrow Cu$

2. 1 M HCl solution:

Anode: $2Cl^- \rightarrow Cl_2\uparrow + 2e^-$

Cathode: $2H^+ + 2e^- \rightarrow H_2\uparrow$

3. Aq. H_2SO_4 solution

Anode: $2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$

Cathode: $2H^+ + 2e^- \rightarrow H_2\uparrow$

If highly concentrated solution of H_2SO_4 is taken then, at anode following reaction takes place: $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$

ELECTROLYSIS USING THE REACTIVE ELECTRODE OR ATTACKED ELECTRODE

Whenever metal electrodes of electrolytic cell are dipped into their metal ion solution, metal is oxidised and metal is reduced so that there will be not net reaction.

For example Electrolysis of $CuSO_4$ solution using Cu electrodes

At Anode:

$$Cu \longrightarrow Cu^{+2} + 2e^-$$

At Cathode:

$$Cu^{+2} + 2e^- \rightarrow Cu$$

In this electrolysis, concentration of electrolyte remain unchanged.

Faraday's law of electrolysis

Ist Law: Mass of the substance reacted on liberated at any electrode is directly proportional to the charge passed.

$$w \propto Q$$

$$w = ZQ$$

w = mass of substance in grams

Q = charge passed in coulomb

Z = electrochemical equivalent

$$= \frac{E}{96500}$$

E = Equal weight of the substance.

$$E = \frac{\text{Molecular weight}}{n\text{-factor}} = \frac{\text{Mwt}}{n_f}$$

n-factor = Number of moles of e^- transferred for 1 mole of the substance.

$$w = \frac{E}{96500}Q = \frac{E}{96500}.i \times t$$

$$\text{Number of gm equivalent} = \frac{w}{E} = \frac{\text{it}}{96500} = \frac{Q}{96500}$$

= Number of Faraday

= Number of moles of e^- transferred

= moles of substance × *n* factor

$$= \frac{V}{V_{eq}}.$$

$V_{eq.}$= It is the volume occupied by 1 g equivalent of the gas.

$$V_{eq} = \frac{\text{molar volume}}{n_f}$$

Volume of gas formed = gram Equivalent × V_{eq}

2^nd^ Law: Whenever two or more electrolytic cells are connected in series then, mass of the substance reacted or produced at any electrode is directly proportional to its equivalent weight.

$$w = \frac{E}{96500}Q \Rightarrow w \propto E$$

$$\frac{w_1}{E_1} = \frac{w_2}{E_2} = \text{............}$$

ELECTROLYTIC CONDUCTANCE

1. **Conductance (C):**

$$C = \frac{1}{R} \text{ unit} \Rightarrow \text{ohm}^{-1}\ (\Omega^{-1}) \text{ or mho } (\mho) \text{ or Seimen}$$

2. **Specific conductance or Conductivity [K]:**

$$K = \frac{1}{\rho} = \frac{1}{R}\cdot\frac{1}{A} = \frac{C\cdot l}{A} \text{ represented by Kork}$$

$l \rightarrow$ distance between two electrodes in the cell.

A → cross-sectional area of the electrodes

$\frac{l}{A} \rightarrow$ cell constant (cm^{-1}) represented by G*

unit of 'K' = ohm^{-1}, cm^{-1}

> ***Note:***
>
> ⇒ If l = 1 cm and A = 1 cm^2 ⇒ K = C
>
> So, specific conductance is the conductance of all the ions present in 1 cm^3 of solution:
>
> ⇒ K is additive in nature.
>
> $$K_{\text{solution}} = K_{\text{solute}} + K_{\text{solvent}}$$

3. **Molar conductance (λ_m) or Λ_m:** It is the conductance of all the ions produced by 1 mole of electrolyte present in the given volume of solution.

$$\lambda_m = (K)_{\text{solute}} \times V$$

$$\lambda_m = K_{\text{solute}} \times \frac{1000}{M}\text{Scm}^2\text{Mole}^{-1} = \frac{K}{\text{Concentration}}$$

$$\lambda_m = K_{\text{solute}} \times \frac{1}{1000M}\text{Sm}^2\,\text{Mole}^{-1}\text{If K in Sm}^{-1}$$

V = volume (in cm^3) of the solution containing 1 mole of electrolyte

units = Ω^{-1} cm^2/mole

4. **Equivalent conductance ($\lambda_{eq.}$) or Λ_{eq}:**

It is the conductance of all the ions given by 1 gram equivalent of electrolyte in the given solution.

$$\lambda_{eq} = K_{\text{solute}} \times V$$

$$= K_{\text{solute}} \times \frac{1000}{N}$$

V-vol. (in cm^3) of solution containing 1 gram equivalent of electrolyte.

Unit = ohm^{-1} cm^2 g eq.^{-1}

Relation between λ_m amd $\lambda_{eq.}$

$$\lambda_{eq} = \frac{\lambda_m}{n\text{-factor}}$$

n-factor = total +Ve charge or total –Ve charge in the electrolyte.

$$\text{for} \quad Al_2(SO_4)_3 \Rightarrow \lambda_{eq} = \frac{\lambda_m}{6}$$

$$\text{for} \quad Na_3PO_4 \Rightarrow \lambda_{eq} = \frac{\lambda_m}{3}$$

Example The resistance of 0.01 N solution of electrolyte was found to be 200 Ω at 298 K. If cell constant is 0.82/cm. Then, calculated eq. conductance.

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

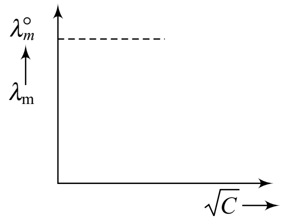
$$K = \frac{1}{R}\frac{l}{A}$$

$$\therefore \quad \Lambda_{eq} = \frac{1}{R}\frac{l}{A} \times \frac{1000}{N}$$

Sol. $\lambda_{eq} = \frac{1}{200} \times 0.82 \times \frac{1000}{0.01} = 410 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq.}^{-1}$

Factors affecting electrolytic conductance

1. **Nature of Electrolyte:** Strong electrolytes provide more ions so, their conductance is more compared to weak electrolytes.
2. **Nature of solvent:** More the polarity of solvent; more will be the conductance.
3. **Temperature:** On increasing the temperature, interionic interaction decreased and average Kinetic Energy of ions increases ↑ so, conductance increases.
4. **Concentration:** With increase in concentration conductance decreases.



(a) For strong electrolytes:

With increase in dilution incre in conductance for strong electrolyte is very small. This effect is given by Debye Huckel On sagar equation.

$$\lambda_m^c = \lambda_m^o - b\sqrt{c} \qquad \lambda_m^o \text{ or } \lambda_m^\infty$$

$\lambda_m^c \rightarrow$ molar conductance at given concentration c

λ_m^o molar conductance at 0 concentration.

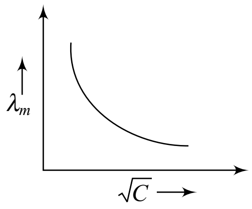
λ_m^∞ molar conductance at ∞ dilution

b = constant

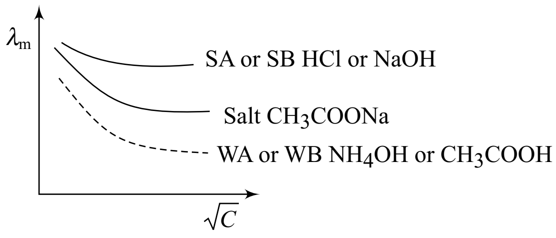
(b) For weak electrolytes

There is rapid increment in the conductance of weak electrolyte w.r.t. increase in dilution because degree of dissociation increases appreciably.

⇒ λ_m^o cannot be obtained graphically for weak electrolytes.



⇒ λ_m and λ_{eq} increase with dilution but K decreases with dilution.



Kohlraauch's law

At ∞ dilution, when dissociation is complete all the ions more independently and contributes towards molar or equivalent conductance irrespective of the other ions present.

Example $Al_2(SO_4)_3$

$$\lambda_m^o[Al_2(SO_4)_3] = 2\,\lambda_m^o(Al^{+3}) + 3\lambda_m^o(SO_4^{2-})$$

$$\lambda_{eq.}^o[Al_2(SO_4)_3] = \lambda_{eq.}^o(Al^{+3}) + \lambda_{eq.}^o(SO_4^{2-})$$

$$= \frac{\lambda_m^o(Al^{+3})}{3} + \frac{\lambda_m^o(SO_4^{2-})}{2}$$

$$n_f = 6 \;\therefore\; \lambda_{eq} = \frac{\lambda_m}{6}$$

Example $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

$$\lambda_m^\infty = 2 \cdot \lambda_m^\infty(K^+) + 2\lambda_m^\infty(Al^{+3}) + 4 \cdot \lambda_m^o(SO_4^{2-})$$

$$n_f = 8 \;\therefore\; \lambda_{eq} = \frac{\lambda_m}{8}$$

$$\lambda_{eq.}^\infty = \frac{1}{4}\lambda_m^\infty(K^+) + \frac{1}{4}\lambda_m^\infty(Al^{+3}) + \frac{1}{2}\lambda_m^o(SO_4^{2-})$$

Applications

1. To find λ_m^∞ for weak electrolytes from strong electrolyte:

Example $\lambda_m^o(CH_3COOH) = \lambda_m^\infty(CH_3COO^-) + \lambda_m^\infty(H^+)$

$$= \lambda_m^\infty(CH_3COONa) + \lambda_m^\infty(HCl) - \lambda_m^\infty(NaCl)$$

Given that λ_m^∞ for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 523.28, 280, 129.8 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ Molar conductance of NH_4OH can be calculated as

$$\lambda_m^\infty(NH_4OH) = \lambda_m^\infty(NH_4^+) + \lambda_m^\infty(OH^-)$$

$$= \lambda_m^\infty(NH_4Cl) + \frac{1}{2}\lambda_m^\infty[Ba(OH)_2] - \frac{1}{2}\lambda_m^\infty(BaCl_2)$$

$$= 251.44$$

2. To find degree of dissociation for weak electrolyte:

$$\alpha = \frac{\lambda_m^c}{\lambda_m^\infty} = \frac{\lambda_{eq.}^c}{\lambda_{eq.}^\infty} = \frac{K \times \frac{1000}{M}}{\lambda_m^\infty}$$

3. To find solubility of sparingly soluble salts:

For sparingly soluble salts, solution is always saturated so their molar concentration = solubility

$$\lambda_m = K_{solute} \times \frac{1000}{S}$$

A 18°C, specific conductivity of saturated solution of AgCl is $1.19 \times 10^{-6}\ \Omega^{-1} \text{ cm}^{-1}$. If equivalent conductivity of Ag^+ and Cl^- at this temperature if 53.8 and 65.9 $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$. Then, K_{sp} of AgCl. can be calculated as

$$1.19 \times 10^{-6} \times \frac{1000}{S} = \lambda_m = (53.8 + 65.9) = 119.1$$

$$S = 10^{-5}$$

$$K_{SP} = S^2 = 10^{-10}$$

Ionic Mobility (U)

$$U = \frac{\text{Velocity of ion}}{\text{Potential gradient}}$$

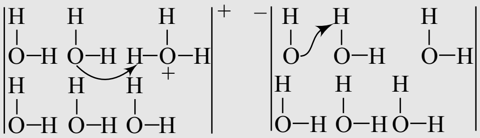
$$\text{Potential gradient} = \frac{\text{Potential applied}}{\text{Distance between two electrodes}}$$

Unit of ‘U’ = $m^2\ volt^{-1}\ sec^{-1}$

$$\lambda_{eq} = FU \rightarrow \text{experimental}$$

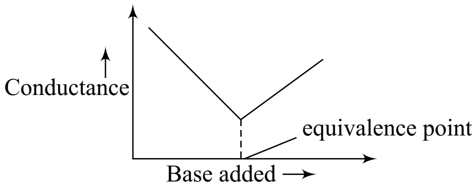
Note:

- Conductance depends on both number of ions and mobility of ion as ionic mobility.
- Ionic mobility of H^+ and OH^- ions, abnormally high and so their conductance is too high. It is due to Grothus type of conductance for H^+ and OH^- ion.



i.e., jumping of H^+ or OH^- ions from one molecule of water to another.

Graph for titration of strong acid VS strong Base



$$HCl + NaOH \rightarrow NaCl + H_2O$$

Solved Examples

1. Calculate the maximum electrical work obtained from the cell reaction in its S.T.P.:

$$Zn + 2Ag^+ \rightarrow 2Ag + Zn^{+2}$$

$$E^o_{Zn^{+2}/Zn} = -0.76\ V; \quad E^o_{Ag^+/Ag} = 0.80\ V$$

Sol. $W = -\Delta G$

$$= nFE^o_{cell} \text{ and } E^o_{cell} = E^o_{Ag^+/Ag} + E^o_{Zn/Zn^{+2}}$$

$$= 2 \times 96500 \times (0.80 + 0.76)$$

$$= 2 \times 96500 \times 1.56\ J$$

2. Calculate the standard electrode potential of Ni^{+2}/Ni if E.M.F. of the cell $Ni/Ni^{+2}(0.01M)//Cu^{+2}(0.1M)/Cu$; $E_{cell} = 0.59$ V and $E^o_{Cu^{+2}/Cu} = 0.34$ V.

Sol. $Ni + \underset{(0.1M)}{Cu^{+2}} \rightarrow \underset{(0.01M)}{Ni^{+2}} + Cu$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log Q$$

$$\Rightarrow \quad E_{cell} = 0.59 = E^o_{cell} - \frac{0.0591}{2} \log\left[\frac{0.01}{0.1}\right]$$

$$E^o_{cell} = 0.59\ \text{volt} - 0.03 = 0.56\ V$$

$$E° = 0.56 = 0.34 - E^o_{Ni^{+2}/Ni}$$

$$E^o_{Ni^{+2}/Ni} = -0.22\ V$$

3. At 298 K; find equilibrium constant for the reaction

$$2Fe^{+3} + Sn^{+2} \longrightarrow 2Fe^{+2} + Sn^{+4}$$

$$E^o_{Fe^{+3}/Fe^{+2}} = 0.77\ V; E^o_{Sn^{+4}/Sn^{+2}} = 0.15\ V$$

Sol. $E° = E^o_{Fe^{+3}/Fe^{+2}} + E^o_{Sn^{+2}/Sn^{+4}}$

$$= 0.77 + (-0.15) = 0.62$$

$$0.62 = \frac{0.0591}{2} \log K_{eq.}$$

$$Keq = 10^{21}$$

4. The standard reduction potential Cu^{+2}/Cu is 0.34V calculate the reduction potential at $P^H = 14$ for the above couple. $K_{SP}\ (Cu(OH)_2) = 1 \times 10^{-19}$.

Sol. $Cu^{+2} + 2e^- \longrightarrow Cu$

$$E = 0.34 - \frac{0.0591}{2} \log \frac{1}{[Cu^{+2}]} \qquad P^H = 14 \text{ or } P^{OH} = 0$$

$$K_{SP} = 1 \times 10^{-19} = [Cu^{+2}][OH^-]^2$$

Since $P^{OH} = 0 \therefore [OH^-] = 1$ M

$\therefore \quad K_{sp} = 1 \times 10–19 = [Cu^{+2}]\ [OH^-]^2$

$\Rightarrow \quad [Cu^{+2}] = 10^{-19}\ [OH^-] = 1$ M

$$E = 0.34 - \frac{0.0591}{2} \log \frac{1}{10^{-19}}$$

$$= 0.34 - \frac{0.0591}{2} \times 19 = -0.22\ \text{volt.}$$

5. E.M.F. of the cell given below is 0.767 V.
$Ag/AgI(s)$, 0.05 M KI//0.05 M $AgNO_3/Ag$
Calculate solubility product of AgI.

Sol. $K_{SP} = [Ag^+][I^-]$ (1)

$$= [Ag^+]_{anode} \times 0.05$$

$$Ag + Ag^+_{cathode} \longrightarrow Ag^+_{anode} + Ag$$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log Q$$

$$\Rightarrow \quad 0.767 = 0 - \frac{0.0591}{1}\log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$$

$$\Rightarrow \quad \log\frac{[Ag^+]}{0.05} = \frac{-0.767}{0.0591} = -13$$

$$\Rightarrow \quad [Ag^+]_{anode} = 0.05 \times 10^{-13}\ M$$

From (1) $KsP = [Ag^+]_{Anode} \times 0.05 = 25 \times 10^{-17}$

6. The standard reduction potential of Ag^+/Ag electrode at 298 K is 0.8 V.

Given that $KspAgI = 10^{-16}$. Evaluate the

(i) Potential of Ag^+/Ag electrode in a saturated solution of AgI.

(ii) S.R.P. of $I^-/AgI/Ag$ electrode.

Sol. (i) $Ag^+ + 1e^- \rightarrow Ag$

$$E = 0.8 - 0.0591 \log [Ag^+]$$

$\Rightarrow E = 0.32$ V by putting $[Ag^+] = 10^{-8}$M

$$AgI \rightleftharpoons Ag^+ + I^-$$

$$[Ag^+]^2 = K_{SP} = 10^{-16} \Rightarrow [Ag^+] = 10^{-8}$$

(ii) $E^o_{I^-/AgI/Ag} = 0.8 + 0.0591 \log 10^{-16}$

$= 0.8 - 0.0591 \times 16$

$= -0.16$ V

7. For a cell, $Mg(s) + 2Ag^+ (0.0001\ M) \longrightarrow Mg^{2+} (0.130\ M) + 2Ag(s)$.

Calculate its E_{cell} if $E^o_{cell} = 3.17$ V

(a) 1.96 V
(b) 2.96 V
(c) –2.96 V
(d) 3.24 V

Sol. **(b)** The cell can be written as Mg | Mg^{2+} (0.130 M) || Ag^+ (0.0001 M) | Ag

$$E_{(cell)} = E^e_{(cell)} - \frac{RT}{2F}\ln\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$= 3.17\ V - \frac{0.059\ V}{2}\log\frac{0.130}{(0.0001)^2}$$

$$= 3.17\ V - 0.21\ V = 2.96\ V$$

8. Given the overall formation constant of the $[Fe(CN)_6]^{4-}$ ion as 10^{35} and the standard potentials for the half reactions,

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$; E° = 0.77 V

$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$; E° = 0.36 V

Calculate the overall formation constant of the $[Fe(CN)_6]^{3-}$ ion.

(a) 8.59×10^{41}
(b) 7.59×10^{41}
(c) 5.59×10^{41}
(d) 9.59×10^{41}

Sol. **(a)**

Let K_f be the formation constant of $[Fe(CN)_6]^{3-}$ ion.

$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$; $K_f = 10^{35}$;

$$\Delta G^o_1 = -2.303RT \log K_f = -199704.69\ J$$

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$; E° = 0.77V;

$$\Delta G^o_2 = -96500 \times 0.77 = -74305\ J$$

$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-} + e^-$;

$$E° = -0.36\ V;\ \Delta G^o_3 = +96500 \times 0.36 = 34740\ J$$

$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$;

$$\Delta G^o_4 = \Delta G^o_1 + \Delta G^o_2 + \Delta G^o_3 = -239269.69\ J$$

$$\Delta G^o_4 = -2.303\ RT \log K'_f$$

$\therefore \quad K'_f = 8.59 \times 10^{41}$

9. For the reaction, $4Al\ (s) + 3O_2(g) + 6H_2O + 4OH^- \longrightarrow 4[Al(OH)_4]^-$; $E^o_{cell} = 2.73$ V. If $\Delta G^o_f(OH^-) = -157$ kJ mol^{-1} and $\Delta G^o_f(H_2O) = -237.2$ kJ mol^{-1}, determine $\Delta G^o_f(Al(OH)_4^-)$.

(a) 1.30103 kJ mol^{-1}
(b) –1.30103 kJ mol^{-1}
(c) 3.30103 kJ mol^{-1}
(d) –3.30103 kJ mol^{-1}

Sol. **(b)**

The ΔG° and E^o_{cell} are related by $\Delta G° = -nFE^o_{cell} = -12 \times 96500 \times 2.73 = -3.16 \times 10^3$ kJ

(since ΔG^o_f of Al(s) and O_2 (g) are zero)

$$\Delta G^o_f(Al(OH)_4^-) = \frac{-3.16 \times 10^3 + (6 \times -237.2) + (4 \times -157)}{4}$$

$$= -1.30 \times 10^3\ kJ\ mol^{-1}$$

10. What is the equilibrium constant (Kc) of the reaction?

$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{+2}(aq) + 2Ag(s)$; $E^o_{cell} = 0.46$ V

(a) 2.02×10^{13}
(b) 3.92×10^{14}
(c) 2.02×10^{14}
(d) 3.92×10^{15}

Sol. (d) $E^o_{cell} = \frac{0.059\ V}{2}\log K_C = 0.46$ V or

$$\log K_C = \frac{0.46\ V \times 2}{0.059\ V} = 15.6$$

$$K_C = 3.92 \times 10^{15}$$

11. The standard electrode potential for Daniel cell is 1.1 V. Find the standard Gibbs energy for the reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

(a) –212.3 kJ/mol
(b) –2.123 kJ/mol
(c) 21.23 kJ/mol
(d) 21230 J/mol

Sol. (a) $\Delta_r G^o = -nFE^o_{(cell)}$

n in the above equation is 2, F = 96500 C mol^{-1} and $E^o_{cell} = 1.1$ V

Therefore, $\Delta_r G^o = -2 \times 1.1\ V \times 965000\ C\ mol^{-1}$
$= -212300\ J\ mol^{-1}, = -212.3\ kJ\ mol^{-1}$.

12. What is the potential of hydrogen electrode in contact with a solution whose pH is 10 at 1 atm?

(a) 0.581 (b) –0.591 V

(c) 0.059 V (d) 5.91 V

Sol. (b) For hydrogen electrode, $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

Applying Nernst equation,

$$E_{H^+/H_2} = E^o_{H^+/H_2} - \frac{0.0591}{n}\log\frac{1\text{atm}}{[H^+]}$$

$$= 0 - \frac{0.0591}{1}\log\frac{1}{10^{-10}}\{\text{pH} = 10 \text{ means } [H^+] = 10^{-10}\text{M}\}$$

$$= -0.0591 \times 10 = -0.591 \text{ V}$$

13. The emf of the cell for the reaction

$Ni(s) + 2Ag^+(0.0002M) \longrightarrow Ni^{2+}(0.160M) + 2Ag(s)$

Given that E^o_{cell} = 1.05 V

(a) 0.75 V (b) –0.45 V

(c) 0.91 V (d) –0.82 V

Sol. (c) Applying Nernst equation to the given cell reaction

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.05 \text{ V} - \frac{0.0591}{2}\log\frac{0.160}{(0.0002)^2}$$

$$1.05 - \frac{0.0591}{2}\log\frac{1600}{2\times 2}\times 10^4$$

$$1.05 - \frac{0.0591}{2}\log(4\times 10^6)$$

$$1.05 - 0.03[6 - 0.06] = 5.4 \times 0.03$$

$$1.05 - 0.162 = 0.888 \text{ V}$$

14. For reaction, $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$ has E^o_{cell} = 0.236 V at 298 K. The standard Gibbs energy and the equilibrium constant of the cell reaction

(a) 45.55 kJ/mol, 8.5×10^8

(b) 50.12 kJ/mol, 7.2×10^7

(c) –50.12 kJ/mol, 8.5×10^8

(d) –45.55 kJ/mol, 9.6×10^7

Sol. (d) $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ and $2I^- \longrightarrow I_2 + 2e^-$

Hence, for the given cell reaction, $n = 2$.

$$\Delta_r G^\circ = -nFE^o_{cell} = -2 \times 96500 \times 0.236 \text{ J}$$

$$= -45.55 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\circ = -2.303RT \log K_c$$

$$\text{or} \quad \log K_c = \frac{\Delta_r G^o}{2.303RT}$$

$$= \frac{-45.55 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{kJ K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}$$

$$= 7.983$$

$\therefore$ K_c = Antilog (7.983) = 9.616 10^7

15. In the bottom cells widely used in watches and other decrease the following reaction take place.

$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-_{(aq)}$

the $\Delta_r G^\circ$ and E° for the reaction is

Given $Ag^+ + e \rightarrow Ag E^o = +0.344$ V

$Zn^{+2} + 2e^- \rightarrow Zn \ E^o = -0.76$ V

(a) -2.13×10^5 J, 1.104 V

(b) -2.13×10^5 J, –1.104 V

(c) 2.13×10^5 J, 1.104 V

(d) -1.13×10^5 J, –2.104 V

Sol. (a)

(a) Zn is oxidised and Ag_2O is reduced (as Ag^+ ions change into Ag).

(b) $E^o_{cell} = E^o_{Ag_2O/Ag}(\text{Red}) + E^o_{Zn/Zn^{2+}}$ (Ox)

$$= 0.344 + 0.76 = 1.104 \text{ V}$$

$$\Delta G = -nFE^o_{cell} = -2 \times 96500 \times 1.104 \text{ J}$$

$$= -2.13 \times 10^5 \text{ J}$$

16. Calculate the EMF of the electrode concentration cell

Hg-Zn (c_1 M) | Zn^{2+} (c M) | Hg-Zn (c_2 M)

at 25°C, if the concentration of the zinc amalgam are 2 g per 100 g of mercury and 1 g per 100 g of mercury in anode and cathode half-cell respectively.

(a) 6.8×10^{-2} V (b) 8.8×10^{-3} V

(c) 5.7×10^{-2} V (d) 7.8×10^{-3} V

Sol. (b) The reactions at the two half-cells are

At cathode: $Zn^{2+}(c) + 2e^- \longrightarrow Zn(c_2)$

At anode: $Zn(c_1) \longrightarrow Zn^{2+}(c) + 2e^-$

Net cell reaction: $Zn(c_1) \longrightarrow Zn(c_2)$

Applying Nernst equation to the net cell reaction gives

$$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{c_2}{c_1} = \frac{0.059}{2}\log\frac{c_1}{c_2}(\text{since } E^o_{cell} = 0)$$

$$E_{cell} = \frac{0.059}{2}\log\left(\frac{2/65.4}{1/65.4}\right) = 8.8 \times 10^{-3} \text{ V}$$

17. Calculate the EMF of the following galvanic cell

Zn | Zn^{2+} (0.01 M) || Zn^{2+} (0.1 M) | Zn

at 298 K.

(a) 0.0395 V (b) –0.0395 V

(c) 0.0295 V (d) 1.0345 V

Sol. (c) The reactions at the two half-cells are

At cathode: $Zn^{2+}_c + 2e^- \longrightarrow Zn$

At anode: $Zn \longrightarrow Zn^{2+}_A + 2e^-$

Net cell reaction: $Zn^{2+}_C \longrightarrow Zn^{2+}_A$

Applying Nernst equation to the net cell reaction gives

$$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}_A]}{[Zn^{2+}_C]}$$

$$E_{cell} = \frac{0.059}{2}\log\frac{[Zn^{2+}_A]}{[Zn^{2+}_C]} \quad (\text{since } E^o_{cell} = 0)$$

$$E_{cell} = \frac{0.059}{2}\log\frac{0.1}{0.01} = 0.0295 \text{ V}$$

18. The Ksp of CuI is 1.1×10^{-12} M^2. Determine EMF of the cell, represented as

Cu | CuI | I^- (1 M) || Cu^+ (1 M) | Cu.

(a) 0.502 V (b) 1.203 V

(c) 0.705 V (d) 0.115 V

Sol. (c) The anode of the given cell is metal-insoluble metal salt-anion type half-cell while cathode is of the type metal-metal ion. The half-cell reactions at anode are

$$Cu(s) \longrightarrow Cu^+ + e^-;\ \Delta G_1 = -FE^o_{Cu|Cu^+}$$

$$Cu^+ + I^- \rightleftharpoons CuI(s);\ \Delta G_2 = 0$$

Net anode reaction: $Cu(s) + I^- \rightleftharpoons CuI(s) + e^-;\ \Delta G_3 = -FE_{Cu|CuI|I^-}$

According to Hess's law, we know

$$\Delta G_1 + \Delta G_2 = \Delta G_3$$

$$\therefore\quad \Delta G_1 = \Delta G_3 \quad (\text{as } \Delta G_2 = 0)$$

$$\therefore\quad -FE_{Cu|Cu^+} = -FE_{Cu|CuI|I^-}$$

So, $E_{Cu|Cu^+} = E_{Cu|CuI|I^-}$

Since, the E value of $Cu \longrightarrow Cu^+ + e^-$ and E value of $Cu + I^- \longrightarrow CuI + e^-$ are same, the representation of anode can be changed from metal-insoluble metal salt-anion half-cell to metal-metal ion half-cell, provided the concentration of Cu^+ in both the half-cells is same. So, the complete cell can now be represented as

$$Cu|Cu^+\left(\frac{K_{sp}}{[I^-]}\right)||Cu^+(1M)|Cu$$

Reactions occurring at the two electrodes are

At anode: $Cu \longrightarrow Cu^+_A + e^-$

At cathode: $Cu^+_C + e^- \longrightarrow Cu$

Net cell reaction: $Cu^+_C \longrightarrow Cu^+_A$

Applying Nernst equation gives

$$= E^o_{Cu^+_C|Cu} - E^o_{Cu^+_A|Cu} - \frac{RT}{F}\ln\frac{[Cu^+_A]}{[Cu^+_C]}$$

$$E_{cell} = E^o_{cell} + \frac{RT}{F}\ln\frac{[Cu^+_C]}{[Cu^+_A]}$$

$$E_{cell} = \frac{RT}{F}\ln\frac{[Cu^+_C]}{[Cu^+_A]} \qquad (\text{as } E^o_{cell} = 0)$$

$$E_{cell} = \frac{RT}{F}\ln\frac{[Cu^+_C]\times[I^-]}{K_{SP}} = 0.059\log\frac{1\times1}{1.1\times10^{-12}}$$

$$E_{cell} = 0.70$$

19. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 S/m. What is the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution?

(a) 0.31 Sm^{-1}, 124×10^{-4} Sm^2 mol^{-1}

(b) 0.248 Sm^{-1}, 124×10^{-4} S m^2 mol^{-1}

(c) 1.12 Sm^{-1} , 221×10^4 Sm^2 mol^{-1}

(d) 0.196 Sm^{-1}, 248×10^{-4} S m^2 mol^{-1}

Sol. (b) The cell constant is given by the equation

Cell constant = G* = conductivity × resistance

= 1.29 S/m 100 Ω = 129 m^{-1} = 1.29 cm^{-1}.

Conductivity of 0.02 mol L^{-1} KCl solution = cell constant/resistance

$$= \frac{G^*}{R} = \frac{129\ m^{-1}}{520\ \Omega} = 0.248\ Sm^{-1}$$

Concentration = 0.02 mol L^{-1} = 1000 × 0.02 mol m^{-3} = 20 mol m^{-3}

$$\text{Molar conductivity} = \Lambda_m = \frac{K}{\text{Concentration}}$$

$$= \frac{248\times10^{-3}\,Sm^{-1}}{20\ mol\ m^{-3}} = 124\times10^{-4}\,Sm^2mol^{-1}$$

$$\text{Alternatively, } K = \frac{1.29\ cm^{-1}}{520\ \Omega} = 0.248\times10^{-2}\,S\ cm^{-1}$$

$$\text{and}\quad \Lambda_m = K\times1000\ cm^3\ L^{-1}\ molarity^{-1}$$

$$\Lambda_m = \frac{K\times1000}{M}$$

$$= \frac{0.248\times10^{-2}\,S\ cm^{-1}\times1000\ cm^3L^{-1}}{0.02\ mol\ L^{-1}}$$

$$= 124\ S\ cm^2\ mol^{-1}$$

20. The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 Ω. Its resistivity, conductivity and molar conductivity.

(a) 87.135 Ω, 0.1148 S cm^{-1}, 229.6 S cm^2 mol^{-1}

(b) 77.123 Ω, 0.241 S cm^{-1}, 119.5 S cm^2 mol^{-1}

(c) 92.29 Ω, 0.124 S cm^{-1}, 272.3 S cm^2 mol^{-1}

(d) 83.92 Ω , 0.1192 S cm^{-1}, 220.3 S cm^2 mol^{-1}

Sol. (a) $A = \pi r^2 = 3.14 \times 0.5^2\ cm^2 = 0.785\ cm^2 = 0.785 \times 10^{-4}\ m^2$

l = 50 cm = 0.5 m

$$R = \frac{\rho l}{A} \text{ or } \rho = \frac{RA}{l} = \frac{5.55\times10^3\,\Omega\times0.785\ cm^2}{50\ cm}$$

$$= 87.135\ \Omega\ cm$$

$$\text{Conductivity} = K = \frac{1}{\rho} = \left(\frac{1}{87.135}\right)S\ cm^{-1}$$

$$= 0.01148\ S\ cm^{-1}$$

$$\Lambda m = \frac{0.01148\ S\ cm^{-1}\times1000\ cm^3\ L^{-1}}{0.05\ mol\ L^{-1}}$$

$$= 229.6\ S\ cm^2\ mol^{-1}$$

If we want to calculate the values of different quantities in terms of 'm' instead of 'cm'.

$$\rho = \frac{RA}{l} = \frac{5.55\times10^{3}\,\Omega\times0.785\times10^{-4}\,\mathrm{m}^{2}}{0.5\ \mathrm{m}}$$

$$= 87.135\times10^{-2}\,\Omega\mathrm{m}$$

$$K = \frac{1}{\rho} = \frac{100}{87.135}\Omega\mathrm{m} = 1.148\ \mathrm{Sm}^{-1}$$

and

$$\Lambda_m = \frac{K}{C} = \frac{1.148\ \mathrm{S\,m}^{-1}}{50\ \mathrm{mol\,m}^{-3}} = 229.6\times10^{-4}\,\mathrm{S\,m^{2}\,mol^{-1}}$$

21. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Its molar conductivity is:

(a) 120 S cm^2 mol^{-1} (b) 115 S cm^2/mol

(c) 124.0 S cm^2 mol^{-1} (d) 1105 cm^2/mol

Sol. (c) $\Lambda_m = \dfrac{K\times1000}{\text{Molarity}} = \dfrac{0.0248\ \mathrm{S\,cm^{-1}}\times1000\ \mathrm{cm^3L^{-1}}}{0.20\ \mathrm{mol\,L^{-1}}}$

$$= 124\ \mathrm{S\,cm^2\,mol^{-1}}$$

22. The resistance of a conductivity cell containing 0.0001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146 × 10^{-3} S cm^{-1}.

(a) 0.200 cm^{-1} (b) 0.219 cm^{-1}

(c) 0.195 cm^{-1} (d) 0.190 cm^{-1}

Sol. (b) Cell constant $= \dfrac{\text{Conductivity}}{\text{Conductance}}$

= Conductivity × Resistance

$$0.146\times10^{-3}\ \mathrm{S\,cm^{-1}}\times1500\ \Omega = 0.219\ \mathrm{cm^{-1}}$$

23. Λ^{o}_{m} for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. What is the for Λ^{o}_{m} (in S cm^2 mol^{-1})

(a) 426.9 (b) 390.5 (c) 517.9 (d) 552.2

Sol. (b) $\Lambda^{o}_{m(HAc)} = \lambda^{o}_{H^+} + \lambda^{o}_{Ac^-}$

$$= \lambda^{o}_{H^+} + \lambda^{o}_{Cl^-} + \lambda^{o}_{Ac^-} + \lambda^{o}_{Na^+} - \lambda^{o}_{Cl^-} - \lambda^{o}_{Na^+}$$

$$= \Lambda^{o}_{m(HCl)} + \Lambda^{o}_{m(NaAc)} - \Lambda^{o}_{m(NaCl)}$$

$$= (425.9 + 91.0 - 126.4)\ \mathrm{S\,cm^2\,mol^{-1}}$$

$$= 390.5\ \mathrm{S\,cm^2\,mol^{-1}}$$

24. The conductivity of 0.001028 mol L^{-1} acetic acid is 4.95 × 10^{-5} S cm^{-1}. Its dissociation constant is ________. if Λ^{o}_{m} for acetic acid is 390.5 S dm^2 mol^{-1}.

(a) 48.15 × 10^{-3} mol L^{-1}

(b) 2.75 × 10^{-5} mol/L

(c) 1.78 × 10^{-5} mol L^{-1}

(d) 3.2 × 10^{-3} mol/L

Sol. (c) $\Lambda_m = \dfrac{K}{C} = \dfrac{4.95\times10^{-5}\mathrm{S\,cm^{-1}}}{0.001028\ \mathrm{mol\,L^{-1}}}\times\dfrac{1000\ \mathrm{cm^3}}{\mathrm{L}}$

$$= \frac{K\times1000}{M}$$

If K in S cm^{-1}

$$= 48.15\ \mathrm{S\,cm^3\,mol^{-1}}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^{o}_{m}} = \frac{48.15\ \mathrm{S\,cm^2\,mol^{-1}}}{390.5\ \mathrm{S\,cm^2\,mol^{-1}}} = 0.1233$$

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^-} + \mathrm{H^+}$$

C O O

C – Cα Cα Cα

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

$$\kappa = \frac{c\alpha^2}{a(1-\alpha)} = \frac{0.001028\ \mathrm{mol\,L^{-1}}\times(0.1233)^2}{1-0.1233}$$

$$= 1.78\times10^{-5}\,\mathrm{mol\,L^{-1}}$$

25. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^{-1} mol^{-1}. Its degree of dissociation (α) and dissociation constant. Given $\lambda^{o}(\mathrm{H^+})$ = 349.6 S cm^2 mol^{-1} and $\lambda^{o}(\mathrm{HCOO^-})$ = 54.6 S cm^2 mol^{-1}.

(a) $K_a = 3.67\times10^{4}$ $\alpha = 0.214$

(b) $K_a = 3.67\times10^{-4}$ $\alpha = 0.114$

(c) $K_a = 2.25\times10^{-4}$ $\alpha = 0.150$

(d) $K_a = 2.25\times10^{-2}$ $\alpha = 0.314$

Sol. (b) Λ^{o}_{m} (HCOOH) = $\lambda^{o}(\mathrm{H^+})$ + $\lambda^{o}(\mathrm{HCCO^-})$ = 349.6 + 54.6 S cm^2 mol^{-1}

= 404.2 S cm^2 mol^{-1}

Λ^{c}_{m} = 46.1 S cm^2 mol^{-1} (Given)

$$\alpha = \frac{\Lambda^{c}_{m}}{\Lambda^{0}_{m}} = \frac{46.1}{404.2} = 0.114$$

$$\mathrm{HCOOH} \rightleftharpoons \mathrm{HCOO^-} + \mathrm{H^+}$$

Initial concentration C mol L^{-1}

Conc. at eqm. C(1 – α) Cα Cα

$$K_\alpha = \frac{C\alpha\cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = \frac{0.025\times(0.114)^2}{1-0.114} = 3.67\times10^{-4}$$

26. Conductivity of 0.00241 M acetic acid is 7.896 10^{-5} S cm^{-1}. It has Λ^{o}_{m} is 390.5 S cm^2 mol^{-1}. What is its molar conductivity and dissociation constant.

(a) 1.85 × 10^{-5} mol L^{-1} (b) 2.86 × 10^{-4} mol L^{-1}

(c) 1.92 × 10^{-4} mol L^{-1} (d) 3.52 × 10^{-2} mol L^{-1}

Sol. **(a)**

$$\Lambda^{c}_{m} = \frac{K\times1000}{\text{Molarity}} = \frac{(7.896\times10^{-5}\mathrm{S\,cm^{-1}})\times1000\ \mathrm{cm^3L^{-1}}}{0.00241\ \mathrm{mol\,L^{-1}}}$$

$$= 32.76\mathrm{S\,cm^2mol^{-1}}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^o} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times (8.4 \times 10^{-2})^2}{1 - 0.084} = 1.86 \times 10^{-5}$$

27. A solution of $CuSO_4$ is electrolysed for 10 min with a current of 1.5 amp. The mass of copper deposited at the cathode is

(a) 0.2938 g (b) 0.325 g

(c) 1.752 g (d) 0.92 c

Sol. (a) t = 600 s charge = current × time = 1.5 A × 600 s = 900 C

According to the reaction:

Cu^{2+} (aq) + $2e^-$ = Cu(s)

We require 2F or 2 × 96500 C to deposit 1 mol or 63 g of Cu.

For 900 C, the mass of Cu deposited

= (63 g mol^{-1} × 900 C)/(2 × 96500 C mol^{-1}) = 0.2938 g.

28. Consider the reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?

(a) 6 F (b) 5 F

(c) 4 F (d) 3 F

Sol. (a) 1 mole of $Cr_2O_7^{-2}$ corresponds to 6 moles of electrons = 6 F of electricity

as 1 mole of electron = 1 Faraday

29. If a current of 0.5 amp flows through a metallic wire for 2 hrs, then how many electrons flow through the wire?

(a) 2.24×10^{21} (b) 2.39×10^{21}

(c) 2.246×10^{22} (d) 3.23×10^{22}

Sol. (c) Q (coulombs) = i(ampere) × t (sec) = (0.5 ampere) × (2 × 60 × 60 s) = 3600 C.

A flow of 1 F, i.e., 96500 C is equivalent to flow of 1 mole of electrons, i.e., 6.02×10^{23} electrons.

∴ 3600 C is equivalent to flow of electrons = $\frac{6.02 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22}$ electrons.

30. How much current is necessary to produce H_2 gas at the rate of 224 cm^3/s at NTP?

Sol. $2H^+ + 2e^- \rightarrow H_2$

2F charge required for deposition of 1 mole H_2

= 22400 ml H_2 at STP

∴ 22400 ml H_2 liberated by 2 × 96500 C

∴ 1 ml H_2 liberated by $\frac{2 \times 96500}{22400}$

∴ 224 ml liberated by

$$= \frac{2 \times 96500}{22400} \times 224 = i \times t = i \times 1$$

i = 1930 Amp.

OR

$$w = \frac{E}{96500} it \Rightarrow \frac{w}{E} = \frac{i}{96500}$$

$$\Rightarrow \frac{224}{22400} \times 2 = \frac{i}{96500} \quad \therefore i = 1930 \text{ Amp.}$$

31. Calculate the quantity of electricity in Faraday that will be required to liberate 710 g of gas by electrolysis of concentration NaCl and also calculate the weight of NaOH produced during the process.

Sol. $F = \frac{w}{E} = \frac{710}{71} \times 2 = 20$ F

$$w_{NaOH} = 20 \times \frac{40}{1} = 800 \text{ g}$$

$NaCl \rightarrow Na^+ + Cl^-$

$2Cl^- \rightarrow Cl_2 + 2e^-$

for 1 mole Cl_2 electricity required = 2F

∴ for $\frac{710}{71}$ = 10 mole Cl_2 required = 2F × 10 = 20F

∴ Mole of NaCl used = 2 × Moles of Cl_2 evolved = 20 mole

∴ Moles of NaOH formed = 20 Mole = 20 × 40 = 800 gram

32. An acidic solution of $Cu(NO_3)_2$ salt containing 0.4 g of Cu^{+2} is electrolysed until all the Cu is deposited. The electrolysis continues for 7 more minutes with volume of solution kept at 100 ml and current at 1.2 A. Calculate the volume of gases evolved at NTP during the entire process.

Sol. 1st electrolysis:

At anode: $2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$

At cathode: $Cu^{+2} + 2e^- \rightarrow Cu$

$$\text{g eq. of } O_2 = \text{g of Cu} = \frac{0.4}{63.5} \times 2$$

$$V_1 = V_{O_2} = \frac{0.4}{63.5} \times 2 \times \frac{22400}{4} \text{ ml} = 70.55 \text{ ml}$$

2nd electrolysis:

Cathode: $2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$

Anode: $2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$

$$\text{gm eq. of } H_2 = \text{gm eq. of } O_2 = \frac{1.2 \times 7 \times 60}{96500}$$

$$V_2 = V_{H_2} = \text{g eq.} \times V_{eq.}$$

$$= \frac{1.2 \times 7 \times 60}{96500} \times \frac{22400}{2} \text{ ml} = 58.495 \text{ ml}$$

$$V_3 = V_{O_2} = \frac{1.2 \times 7 \times 60}{96500} \times \frac{22400}{4} \text{ ml} = 29.247 \text{ ml}$$

∴ Total volume of gases

= 70.55 + 58.495 + 29.247 = 159.292 ml

33. The molar conductivity of mono-basic acid at ∞ dilution is 380 mho cm^2 mol^{-1} and 0.01 M. acid specific conductivity is 9.5×10^{-4} mho cm^{-1}.

Calculate

(i) degree of dissociation of monobasic acid.

(ii) K_A of acid.

Sol. (i) $$\alpha = \frac{\Lambda_m^C}{\Lambda_m^\infty} = \frac{K\times\frac{1000}{M}}{\Lambda_m^\infty}$$

$$\alpha = \frac{9.5\times10^{-4}\times\frac{1000}{0.01}}{380} = 0.25$$

(ii) $$\begin{array}{lccc} HA & \rightleftharpoons & H^+ & +A^- \\ C-C\alpha & & C\alpha & C\alpha \end{array}$$

$$K_a = \frac{\alpha^2 C}{1-\alpha} = \frac{0.01\times225\times0.25}{0.75} = 8.3\times10^{-4}$$

34. The conductivity of a saturated solution of $BaSO_4$ is 3.06×10^{-6} $ohm^{-1}cm^{-1}$ and its equivalent conductance is 1.53 $ohm^{-1}cm^2\,eq^{-1}$. The K_{sp} for $BaSO_4$ will be

(a) 4×10^{-6} (b) 2.5×10^{-9}

(c) 2.5×10^{-13} (d) 1×10^{-6}

Variation of conductivity and molar conductivity with concentration

Sol. **(d)** n_f of $BaSO_4 = 2$

$$\Lambda_{eq} = \frac{\Lambda_m}{2}$$

$$\therefore \quad \Lambda_m = 2\times\Lambda_{eq}$$

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{-2}$$

$$K(BaSO_4) = 3.06\times10^{-6}$$

$$\lambda(BaSO_4) = 1.53$$

Let the aq. solution contain x moles of Ba^{+2} and x moles the of SO_4^{-2} and they are produced from x moles/L of $BaSO_4$

$$\Lambda_m = 3.06\times10^{-6}\times\frac{1000}{X} = 1.53\times2$$

$$x = 1\times10^{-3}$$

$$[Ba^{2+}] = 1\times10^{-3} \quad \therefore \quad K_{sp} = S^2$$

$$= 1\times10^{-6}$$

35. An aquous solution containing one mole per litre of each $Cu(NO_3)_2$ $AgNO_3$, $Hg(NO_3)_2$ and $Mg(NO_3)_2$ is being electrolysed using inert electrodes. The values of the standard electrolysed electrode potentials in volts (reduction potentials) are Ag $|Ag^+ = +0.80$, $Hg|Hg^{2+} = +0.79$, $Cu|Cu^{+2} = +0.34$, $Mg|Mg^{2+} = -2.37$ With increasing voltage ,the sequence of deposition of metals on cathode will be

(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag

(c) Ag, Hg, Cu (d) Cu, Hg, Ag

Sol. **(c)** Higher the reduction potential, more will be the tendency of deposition ($M^{n+} + ne^- \longrightarrow M$) but Mg^{2+} ions will not be deposited because H_2O is reduced more easily than Mg^{2+} ions.

36. The resistance of N/10 solution is found to be 2.5 10^3 ohms. The equivalent conductance of the solution is (cell constant =1.25 cm^{-1})

(a) 25 ohm^{-1} cm^2 eq^{-1}

(b) 5.0 ohm^{-1} cm^2 eq^{-1}

(c) 2.5 ohm^{-1} cm^2 eq^{-1}

(d) 2.5 ohm^{-1} cm^{-2} eq^{-1}

Sol. (b)

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

$$= \frac{1}{R}\frac{\ell}{A}\times\frac{1000}{N}$$

$$= \frac{1}{2.5\times10^3}\times1.25\times\frac{1000}{0.1}$$

$$= 5\ Ohm^{-1}cm^2eq^{-1}$$

Exercise

LEVEL I

1. Electrolysis of a solution of SO_4^{2} ions produces $S_2O_8^{-2}$. Assuming 75% current efficiency, what current should be employed to achieve a production rate of 1 mole S_2O_8 per hour?

(a) 43.3 A (b) 71.5 A (c) 35.2 A (d) 58.3 A

2. How much will the potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7

(a) increase by 0.0591 V (b) decrease by 0.0591 V

(c) increase by 0.413 V (d) decrease by 0.413 V

3. The $E^0_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are –0.41, +1.57, +0.77 and +1.97 V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest?

(a) Co (b) Mn (c) Fe (d) Cr

4. For the redox change;

$$\underset{0.1\,M}{Zn(s) + Cu^{2+}} \longrightarrow \underset{0.1\,M}{Zn^{2+}} + Cu(s)$$, taking place

In a cell E^0_{cell} is 1.10 volt. E_{cell} for the cell would be

(a) 1.07 V (b) 0.82 V (c) 2.14 V (d) 180 V

5. An aqueous solution containing Na^+, Sn^{2+}, Cl^- and SO_4^{2-} ions, all at unit concentration, is electrolysed between a silver anode and a platinum cathode. What changes occur at the electrodes when current is passed through the cell? Given: $E^o_{Ag^+|Ag} = 0.799$ V

$$E^o_{Sn^{2+}|Sn} = -0.14\text{ V}, E^o_{Cl_2|Cl^-} = 1.36\text{ V},$$

$$E^o_{S_2O_8^{2-}|SO_4^{2-}} = 2\text{V}, E^o_{Sn^{4+}|Sn^{2+}} = 0.13\text{ V}$$

(a) Sn^{2+} is reduced and Cl^- is oxidised.
(b) Ag is oxidised and Sn^{2+} is reduced.
(c) Sn^{2+} is reduced and Sn^{2+} is oxidised
(d) H^+ is reduced and Sn^{2+} is oxidised.

6. The limiting molar conductivities Λ^o for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1} respectively. The Λ^o for NaBr (S cm^2 mol^{-1}) is
(a) 302 (b) 176 (c) 278 (d) 128

7. In the electrolysis of $CuCl_2$ solution using Cu electrodes, the weight of Cu anode increased by 2 g at cathode. In the anode
(a) 0.2 mole of Cu^{2+} will go into solution.
(b) 560 mL O_2 liberate
(c) No loss in weight
(d) 2 g of copper goes into solution as Cu^{2+}

8. The density of Cu is 8.94 g cm^{-3}. The quantity of electricity needed to plate an area 10 cm × 10 cm to a thickness of 10^{-2} cm using $CuSO_4$ solution would be
(a) 13586 C (b) 27155 C
(c) 40758 C (d) 20348 C

9. A current of 9.65 A is drawn from a Daniel cell for exactly 1 hr. The loss in mass at anode and gain in mass at cathode, respectively are
(a) 11.43 g, 11.77 g (b) 11.77 g, 11.43 g
(c) 22.86 g, 23.54 g (d) 23.54, 22.86 g

10. An electrochemical cell stops working after some time because
(a) one of the electrodes is eaten away.
(b) electrode potentials of both the electrodes become equal in magnitude.
(c) electrode potentials of both electrodes go on decreasing.
(d) electrode potentials of both the electrodes go on increasing.

11. Four alkali metals A, B, C and D are having respectively standard electrode potentials as –3.05, –1.66, –0.40 and 0.80 V. Which one will be most reducing?
(a) A (b) B (c) C (d) D

12. $Zn(S) + Cl_2$ (1 atm) $\rightarrow Zn^{2+} + 2Cl^-$ The E° of the cell is 2.12 V. To increase E
(a) Zn^{2+} concentration should be increased.
(b) Zn^{2+} concentration should be decreased.
(c) Cl^- concentration should be increased.
(d) partial pressure Cl_2 should be decreased.

13. $Cr_2O_7^{2-} + I^- \rightarrow I_2 + Cr^{3+}$, $E°_{cell} = 0.79$ V, E°$Cr_2O_7^{-2}Cr^{+3}$ = 1.33 V, $E^o_{I_2|I^-}$?
(a) 0.54 (b) –0.054 (c) +0.18 V (d) –0.18 V

14. The standard emf of the cell $Cd(s)|CdCl_{2(0.1M)}||AgCl(s)|Ag(s)$ in which the cell reaction is
$Cd(s) + 2AgCl(s) \rightarrow 2Ag(s) + Cd^{2+}(aq) + 2Cl^-(aq)$ is 0.6915 V at 0°C and 0.6753 V at 25° C. ΔH of the reaction is
(a) –176 kJ (b) –334.7 kJ
(c) +123.5 kJ (d) –167 kJ

15. On the basis of information available from the reaction

$$\frac{4}{3}Al + O_2 \longrightarrow \frac{2}{3}Al_2O_3, \Delta G = -827 \text{ kJ}$$

mol^{-1} of O_2, the minimum emf required to carry out electrolysis of Al_2O_3 is
(a) 2.14 V (b) 4.28 V (c) 6.42 V (d) 8.56 V

16. If half-cell reaction $A + e^- \rightarrow A^-$ has a large negative reduction potential, it follows that
(a) A is readily reduced
(b) A is readily oxidised
(c) A^{-1} is readily reduced
(d) A^{-1} is readily oxidised

17. A standard hydrogen electrode has zero electrode potential because
(a) hydrogen is easier to oxidise.
(b) this electrode potential is assumed to be zero.
(c) hydrogen atom has only one electron.
(d) hydrogen is the lightest element.

18. What will be the emf of the given cell? $Pt|H_2(P_1)|H^+(aq)|H_2(P_2)|Pt$
(a) $\frac{RT}{F}\ln\frac{P_1}{P_2}$ (b) $\frac{RT}{2F}\ln\frac{P_1}{P_2}$
(c) $\frac{RT}{F}\ln\frac{P_2}{P_1}$ (d) None of these

19. Value of E H_2O/H_2(1atm)Pt at 298 K would be
(a) –0.207 V (b) +0.207 V
(c) –0.414 V (d) +0.414 V

20. Conductivity (units Siemen's S) is directly proportional to the area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is
(a) S m mol^{-1} (B) S m^2 mol^{-1}
(c) S^{-2} m^2 mol (d) S^2m^2 mol^{-2}

21. For strong electrolytes, the plot of molar conductance vs $\sqrt{c}$ is
(a) parabolic (b) linear
(c) sinusoidal (d) circular

22. If the molar conductance values of $Ca^{2+}$and Cl^- at infinite dilution are respectively

118.88×10^{-4} m^2 mhosmol^{-1} and 77.33×10^{-4} m^2 mhos mol^{-1},then that of CaCl$_2$ is (m^2 mhosmol^{-1}).

(a) 118.88×10^{-4} (b) 154.66×10^{-4}
(c) 273×10^{-4} (d) 196.21×10^{-4}

23. Which of the following statements is true for the electrochemical Daniell cell?

(a) Electrons flow from copper electrode to zinc electrode.
(b) Current flows from zinc electrode to copper electrode.
(c) Cations move towards copper electrode.
(d) Cations move towards zinc electrode.

24. Best way to prevent rusting of iron is by

(a) making iron cathode.
(b) putting it in saline water.
(c) Both of these
(d) None of these

25. Time required to deposit one millimole of aluminium metal by the passage of 9.65 amp through aqueous solution of aluminium ion is

(a) 30 s (b) 10 s (c) 30,000 s (d) 10,000 s

26. The cell Pt (H$_2$) (1 atm) |H$^+$ (pH = ?), I$^-$ (a = 1) AgI(s), Ag has emf, E_{298} = 0. The electrode potential for the reaction AgI + e^- $\rightarrow$ Ag + I$^{\ominus}$ is –0.151 volt. Calculate the pH value:-

(a) 3.37 (b) 5.26 (c) 2.56 (d) 4.62

27. The standard EMF of the cell in which the reaction $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ occurs is 0.59 V at 25°C. The equilibrium constant for the given reaction is approximately

(a) 50 (b) 10 (c) 10^{50} (d) 10^5

28. If the pressure of H$_2$ gas is increased from 1 atm to 100 atm keeping H$^+$ concentration constant at 1 M, the change in reduction potential of hydrogen half-cell at 25°C will be

(a) 0.059 V (b) 0.59 V
(c) 0.0295 V (d) 0.118 V

29. During electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP, liberated at cathode would be

(a) 1.2 L (b) 2.4 L (c) 2.6 L (d) 4.8 L

30. Using the information in the preceding problem, calculate the solubility product of AgI in water at 25°C [$E^o_{(Ag+,\, Ag)}$ = +0.799 volt] :- given AgI + e^- $\rightarrow$ Ag + I$^{\ominus}$
$E^o = -0.151$

(a) 1.97×10^{-17} (b) 7.91×10^{-17}
(c) 1.79×10^{-17} (d) 9.17×10^{-17}

31. A current of 9.65 amp is passed through the aqueous solution NaCl using suitable electrodes for 1000 s. The amount of NaOH formed during electrolysis is

(a) 2.0 g (b) 4.0 g (c) 6.0 g (d) 8.0 g

32. Using the data $E^o_{Zn^{+2}/Zn} = 0.76\text{ V}, E^o_{Cu^{+2}/Cu} = +0.34\text{ V}$ calculate the equilibrium constant of the reaction at 25°C.

$$Zn + Cu^{++} \rightleftharpoons Zn^{++} + Cu,\ K = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

(a) 8.314×10^{24} (b) 4.831×10^{-31}
(c) 8.314×10^{36} (d) 4.831×10^{44}

33. The standard electrode potential (reduction) of Ag$^+$|Ag is 0.800 V at 25°C. Its electrode potential in a solution containing 10^{-3} M ion of Ag$^+$ ions is

(a) 0.623 V (b) –0.977 V
(c) 0.892 V (d) 1.246 V

34. The number of Faradays required to produce one mole of water from hydrogen-oxygen fuel cell containing aqueous alkali as electrolyte is

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

35. The solubility product of silver iodide is 8.3×10^{-17} and the standard potential (reduction) of Ag, Ag$^+$ electrode is +0.800 volts at 25°C. The standard potential of Ag, AgI/I$^-$ electrode (reduction) from these data is

(a) –0.30 V (b) +0.15 V
(c) +0.10 V (d) –0.15 V

36. The standard electrode potentials (reduction) of Pt/Fe^{3+}, Fe^{+2} and Pt/Sn^{4+}, Sn^{+2} are +0.77 V and 0.15 V respectively at 25°C. The standard EMF of the reaction $Sn^{4+} + 2Fe^{2+} \rightarrow Sn^{2+} + 2Fe^{3+}$ is

(a) –0.62 V (b) –0.92 V (c) +0.31 V (d) +0.85 V

37. The emf of the following cell
Ni(s)/NiSO$_4$ (1.0 M) || H$^+$ (1.0 M)|H$_2$ (1 atm), Pt at 25°C is 0.236 V. The electrical energy which can be produced is

(a) 22.73 kJ (b) 45.55 kJ
(c) 19.30 kJ (d) 23.60 kJ

38. The reduction potential of a half-cell consisting of a Pt electrode immersed in 1.5 M Fe^{2+} and 0.015 M Fe^{3+} solution at 25°C is ($E^o_{Fe^{3+}/Fe^{2+}} = 0.770\text{ V}$) :

(a) 0.652 V (b) 0.88 V
(c) 0.710 V (d) 0.850 V

39. The specific conductance of a N/10 KCl solution at 18°C is 1.12×10^{-2} mho cm^{-1}. The resistance of the solution contained in the cell is found to be 65 ohms. Calculate the cell constant.

(a) 0.912 cm^{-1} (b) 0.512 cm^{-1}
(c) 0.728 cm^{-1} (d) 0.632 cm^{-1}

40. Calculate the dissociation constant of water at 25°C from the following data:
Specific conductance of H$_2$O = 5.8×10^{-8} mho cm^{-1}
$\lambda^{\infty}_{OH^-} = 198.0$ mho cm^2.

(a) 3.2×10^{-15} mol L^{-1} (b) 4×10^{-15} mol L^{-1}
(c) 1.62×10^{-16} mol L^{-1} (d) data in sufficient

41. Which of the following represents the reduction potential of silver wire dipped into 0.1 M AgNO$_3$ solution at 25°C:

(a) E°$_{red}$ (b) (E°$_{red}$ + 0.059)
(c) (E°$_{ox}$ – 0.059) (d) (E°$_{red}$ – 0.059)

42. If the solution of the $CuSO_4$ in which copper rod is immersed is diluted to 10 times, the electrode reduction potential ($T = 298$ K):
(a) increases by 0.030 V
(b) decreases by 0.030 V
(c) increases by 0.059 V
(d) decreases by 0.0059 V

43. The oxidation potential of a hydrogen electrode at pH = 1 is ($T = 298$ K):
(a) 0.059 volt (b) 0 volt
(c) –0.059 volt (d) 0.59 volt

44. The electrode potential becomes equal to standard electrode potential when reactants and products concentration ratio is
(a) equal to 1 (b) greater than 1
(c) less than 1 (d) None of the above

45. Given standard electrode potentials:

$$Fe^{3+} + 3e^- \longrightarrow Fe;\ E^\circ = -0.036\text{ V}$$
$$Fe^{2+} + 2e^- \longrightarrow Fe;\ E^\circ = -0.440\text{ V}$$

The standard electrode potential E° for

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}\text{ is}$$

(a) –0.476 V (b) –0.404 V
(c) 0.440 V (d) 0.772 V

46. The reduction potential of a hydrogen electrode at pH 10 at 298 K is: ($p = 1$ atm)
(a) 0.51 volt (b) 0 volt
(c) –0.591 volt (d) 0.059 volt

47. The emf of the cell, $Ni|Ni^{2+}$ (1.0 M)$||Ag^+$ (1.0 M)$|Ag$[E° for $Ni^{2+}/Ni = -0.25$ V, E° for $Ag^+/Ag = 0.80$ V] is given by [E° for $Ag^+/Ag = 0.80$ V]
(a) $-0.25 + 0.80 = 0.55$ V
(b) $-0.25 - (+0.80) = -1.05$ V
(c) $0 + 0.80 - (-0.25) = +1.05$ V
(d) $-0.80 - (+0.25) = -0.55$ V

48. E° (Ni^{2+}/Ni) = –0.25 V, E° (Au^{3+}/Au) = 1.50 V. The emf of the voltaic cell $Ni|Ni^{2+}$ (1.0 M)$||Au^{3+}$ (1.0 M)$|Au$ is
(a) 1.25 V (b) –1.75 V
(c) 1.75 V (d) 4.0 V

49. A chemist wants to produce Cl_2(g) from molten NaCl. How many grams could be produced if he uses a steady current of 2 amp for 2.5 minutes?
(a) 3.55 g (b) 1.775 g (c) 0.110 g (d) 0.1775 g

50. Consider the reaction: ($T = 298$ K)

$$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$$

The emf of the cell, when $[Cl^-] = [Br_2] = [Br^-] = 0.01$ M and Cl_2 gas is at 1 atm pressure, will be (E° for the above reaction is = 0.29 volt):
(a) 0.54 V (b) 0.35 V
(c) 0.24 V (d) –0.29 V

51. Three Faradays of electricity was passed through an aqueous solution of iron (II) bromide. The mass of iron metal (atomic mass 56) deposited at the cathode is
(a) 56 g (b) 84 g (c) 112 g (d) 168 g

52. Three moles of electrons are passed through three solutions in succession containing $AgNO_3$, $CuSO_4$ and $AuCl_3$ respectively. The molar ratio of amounts of cations reduced at cathode will be
(a) 1:2:3 (b) 2:1:3 (c) 3:2:1 (d) 6:3:2

53. The emf of the cell involving the following reaction, $2Ag^+ + H_2 \longrightarrow 2Ag + 2H^+$ is 0.80 V. The standard oxidation potential of silver electrode is
(a) –0.80 V (b) 0.80 V
(c) 0.40 V (d) –0.40 V

54. For the net cell reaction of the cell $Zn(s)|Zn^{2+}||Cd^{2+}|Cd(s)$ ΔG° in kilo joules at 25°C is ($E^\circ_{cell} = 0.360$ V):
(a) 112.5 (b) 69.47 (c) –34.73 (d) –69.47

55. How many faradays are required to reduce one mol of MnO_4^- to Mn^{+2}?
(a) 1 (b) 2 (c) 3 (d) 5

56. $Cu^+ + e^- \longrightarrow Cu$, $E^\circ = X_1$ V;

$Cu^{2+} + 2e^- \longrightarrow Cu$, $E^\circ = X_2$ volt, then for

$Cu^{2+} + e^- \longrightarrow Cu^+$, E° (volt) will be

(a) $X_1 - 2X_2$ (b) $X_1 + 2X_2$
(c) $X_1 - X_2$ (d) $2X_2 - X_1$

57. $M^{2+} + 2e \longrightarrow M$. 0.275 g of metal M is deposited at the cathode due to passage of 1 A of current for 965 s. Hence atomic weight of the metal M is
(a) 27.5 (b) 55.0 (c) 110.0 (d) 13.75

58. A certain metal salt solution is electrolysed in series with a silver coulometer. The weight of silver and the metal deposited are 0.5094 g and 0.2653 g. Calculate the valency of the metal if its atomic weight is nearly that of silver.
(a) 1 (b) 2 (c) 3 (d) 4

LEVEL II

1. Consider the standard reduction potentials (in volts) as shown in figure. Find E°.

$$\begin{tikzcd} SO_4^{2-} \arrow[r, "-0.936"] \arrow[rr, bend right, "E^\circ = ?"'] & SO_3^{2-} \arrow[r, "-0.576"] & \frac{1}{2}S_2O_3^{2-} \end{tikzcd}$$

(a) 0.326 V (b) 0.425 V (c) 0.756 V (d) 0.512 V

2. Calculate the electrode potential at 25°C of Cr^{3+}, $Cr_2O_7^{2-}$ electrode at pOH = 11 in a solution of 0.01 M both in Cr^{3+} and $Cr_2O_7^{2-}$. E° value for the cell

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$

E° = 1.33 V.
(a) 0.725 V (b) 0.936 V
(c) 0.652 V (d) 0.213 V

3. The standard oxidation potential for the half-cell $NO_2^-(g) + H_2O \longrightarrow NO_3^-(aq) + 2H^+(aq) + 2e$ is –0.78 V.

Calculate the reduction potential in 9 molar H^+ assuming all other species at unit concentration.

(a) 0.235 V (b) –0.0142 V
(c) 0.836 V (d) –0.0474 V

4. The emf of the cell $M|M^{n+}$ (0.02 M) || H^+ (1 M) | H_2 (g) (1 atm), Pt at 25°C is 0.81 V. The valency of the metal if the standard oxidation potential of the metal is 0.76 V?

(a) 5 (b) 2 (c) 4 (d) 3

5. In two vessels each containing 500 mL water, 0.5 m mol of aniline ($K_b = 10^{-9}$) and 25 m mol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.

(a) 0.395 V (b) 0.792 V (c) 0.452 V (d) 0.312 V

6. The EMF of the standard weston cadmium cell
Cd (12.5%) in Hg | 3 $CdSO_4$, $8H_2O$ (solid) | standard solution of $CdSO_4$ | Hg_2SO_4 (s) | Hg is 1.0180 volts at 25°C and the temperature coefficient of the cell emf, $\left(\frac{\partial E}{\partial T}\right)_P = -4.0 \times 10^{-5}\,\text{V deg}^{-1}$. Calculate ΔG, ΔH and ΔS for the reaction in the cell when $n = 2$.

(a) ΔG = –196.5 kJ, ΔH = 198.8 kJ, ΔS = –7.72 J/deg
(b) ΔG = 196.5 kJ, ΔH = 198.8 kJ, ΔS = –7.72 J/deg
(c) ΔG = 196.5 kJ, ΔH = 198.8 kJ, ΔS = –7.72 J/deg
(d) ΔG = –196.5 kJ, ΔH = 198.8 kJ, ΔS = 7.72 J/deg

7. The standard electromotive force of the cell:
Fe | Fe^{2+}(aq) || Cd^{2+} | Cd is 0.0372 V
The temperature coefficient of emf is –0.125 V K^{-1}. Calculate the quantities ΔG°, ΔH° and ΔS° at 25°C.

(a) ΔG° = –7179.6 J, ΔH° = –7196.43 kJ, ΔS° = –24.125 kJ/K
(b) ΔG° = 7179.6 J, ΔH° = –7196.43 kJ, ΔS° = –24.125 kJ/K
(c) ΔG° = 7179.6 J, ΔH° = 7196.43 kJ, ΔS° = 24.125 kJ/K
(d) ΔG° = 7179.6 J, ΔH° = 7196.43 kJ, ΔS° = 24.125 kJ/K

8. A current of 0.193 amp is passed through 100 mL of 0.2M NaCl for an hour. Calculate pH of solution after electrolysis. Assume no volume change.

(a) 11.9 (b) 12.82 (c) 12.0 (d) 11.5

9. The emf of the cell is ________for this reaction

$$Mg(s) \mid Mg^{2+}\,(0.1\text{ M}) \parallel Ag^+\,(1\times10^{-4}\text{ M}) \mid Ag$$

$$E^o_{Ag^+/Ag} = 0.8\text{ V},\ E^o_{Mg^{2+}/Mg} = -2.37\text{ V}$$

(a) 2.96 V (b) 3.2 V (c) 1.9 V (d) 4.4 V

10. Silver is electrodeposited on a metallic vessel of surface area 800 cm^2 by passing a current of 0.20 amp for 3.0 hrs. The thickness of silver deposited ___.
Given its density is 10.47g/cc [Atomic weight of Ag = 108]

(a) 3.2×10^{-4} cm (b) 1.29×10^{-4} cm
(c) 2.88×10^{-4} cm (d) 4.2×10^{-3} cm

11. The standard oxidation potential of Ni/Ni^{2+} electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured emf be zero at 25°C? Assume $[Ni^{-2+}]$ = 1 M.

(a) 3 (b) 6.5 (c) 5.5 (d) 4

12. The equivalent conductance of silver nitrate solution at 250°C for an infinite dilution was found to be 133.3 $ohm^{-1}\ cm^2 eq^{-1}$. The transport number of Ag^+ ions in very dilute solution of $AgNO_3$ is 0.464. The equivalent conductance of Ag^+ at infinite dilution is

(a) 34.6 $\Omega^{-1}\ cm^{-1} eq^{-1}$
(b) 61.9 $\Omega^{-1}\ cm^{-1} eq^{-1}$
(c) 52.7 $\Omega^{-1}\ cm^{-1} eq^{-1}$
(d) 49.2 $\Omega^{-1}\ cm^{-1} eq^{-1}$

13. Same quantity of electricity is being used to liberate iodine (at anode) and a metal *x* (at cathode). The mass of x deposited is 0.617 g and the iodine is completely reduced by 46.3 cc of 0.124 M sodium thiosulphate. Find the equivalent mass of *x*.

(a) 213.5 (b) 108.2 (c) 111.2 (d) 310.6

14. Dal lake has water 8.2×10^{12} L approximately. A power reactor produces electricity at the rate of 1.5×10^6 coulomb per second at an appropriate voltage. How many years would it take to electrolyse the lake?

(a) 2.4 million years (b) 5.3 million years
(c) 1.9 million years (d) 4.6 million years

15. Calculate the emf of the cell
Pt, H_2 (1.0 atm) | CH_3COOH (0.1 M) || NH_3 (aq, 0.01 M) | H_2 (1.0 atm), Pt,
K_a (CH_3COOH) = 1.8×10^{-5}, K_b (NH_3) = 1.8×10^{-5}

(a) –0.92 V (b) –0.46 V
(c) –0.35 V (d) –0.20 V

16. Calculate E° for the following reactions at 298 K:

$$Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag + 2NH_3$$

$$Ag(CN)_2^- + e^- \rightleftharpoons Ag + 2CN^-$$

Given: $E^o_{Ag^+|Ag} = 0.7991$ V, $K_{Ins}[Ag(NH_3)_2^+] = 6.02 \times 10^{-8}$ and $K_{Ins}[Ag(CN)^-{}_2] = 1.995 \times 10^{-19}$

(a) 0.372 V, –0.307 V (b) 0.214 V, –0.21 V
(c) –0.21 V, 0.372 V (d) –4.12 V, 0.307 V

17. The equivalent conductance of 0.10 N solution of $MgCl_2$ is 97.1 mho $cm^2 eq^{-1}$ at 25°C. A cell with electrode that are 1.5 cm^2 in surface area and 0.5 cm apart is filled with 0.1 N $MgCl_2$ solution. How much current will flow when potential difference between the electrodes is 5 V?

(a) 0.1432 amp (b) 0.214 amp
(c) 0.321 amp (d) 0.1456 amp

18. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amp for 20 minutes. What mass of Ni is deposited at the cathode?

(a) 2.2 g (b) 3.5 g (c) 1.6 g (d) 1.803 g

19. Three electrolytic cells, A, B, C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively are connected in series. A steady current of 1.5 amp was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of Cu and Zn were deposited?
(a) 14.40 min, Cu = 0.427 g, Zn = 0.437 g
(b) 15.2 min, Cu = 0.52 g, Zn = 0.247 g
(c) 13.3 min, Cu = 0.437 g, Zn = 0.427 g
(d) 12.5 min, Cu = 0.534 g, Zn = 0.232 g

20. In a fuel cell H_2 and O_2 react to produce electricity. In the process H_2 gas is oxidised at the anode and O_2 is reduced at the cathode. If 67.2 L of H_2 at NTP reacts in 15 min, what is the average current produced? If the entire current is used for electro-deposition of Cu from Cu^{2+}, how many g of Cu are deposited?
(a) $I = 443.3$ A , $M_{Cu} = 190.5$ g
(b) $I = 643.3$ A , $M_{Cu} = 190.5$ g
(c) $I = 643.3$ A , $M_{Cu} = 180.5$ g
(d) $I = 543.3$ A, $M_{Cu} = 190.\ 5$ g

21. During the discharge of a lead storage battery, density of H_2SO_4 fell from 1.294 to 1.139 g/mL. Sulphuric acid of density 1.294 is 39% H_2SO_4 by weight and that of density 1.139 g/mL is 20% H_2SO_4 by weight. The battery holds 3.5 L of the acid and volume remains practically constant during discharge. Calculate ampere-hour of which the battery must have been used. The charging and discharging reactions are:

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^- \quad \text{(charging)}$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$$
(discharging)

(a) 245.04 A Hr (b) 255.04 A Hr
(c) 235.04 A Hr (d) 265.04 A Hr

22. By how much would the oxidising power of the $(MnO_4^-|Mn^{2+})$ couple change if the H^+ ions concentration is decreased 100 times at 25ºC?
(a) Increases by 189 mV
(b) Decreases by 189 mV
(c) Will increase by 19 mV
(d) Will decrease by 19 mV

23. The useful work done during the reaction

$$Ag(s) + \frac{1}{2}Cl_2(g) \longrightarrow AgCl(s)$$

Would be
(a) 110 kJ mol^{-1} (b) 220 kJ mol^{-1}
(c) 55 kJ mol^{-1} (d) 100 kJ mol^{-1}
Given:

$$E^0_{Cl_2/Cl^-} = 1.36V, E^0_{AgCl/Ag/Cl^-} = 0.220 \text{ V}, P_{Cl_2} = 1 \text{ atm}$$

and $T = 298$ K

24. Construct the cell corresponding to the reaction:

$$3Cr^{2+} (1M) \longrightarrow 2Cr^{3+} (1M) + Cr(s)$$

and predict if the reaction is spontaneous. Also calculate the following: ΔH and ΔS of the reaction at 25°C.

Given: $E^o_{Cr^{3+},Cr} = 0.5$ V, $E^o_{Cr^{3+},Cr^{2+}} = -0.41$ V

ΔG of the reaction at 35°C = –270.50 kJ
(a) ΔH = –51.05 kJ, ΔS = 700 kJ K^{-1}
(b) ΔH = –31.05 kJ, ΔS = 700 kJ K^{-1}
(c) ΔH = –51.05 kJ, ΔS = 706 kJ K^{-1}
(d) ΔH = –53.05 kJ, ΔS = 706 kJ K^{-1}

25. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing Ag(l) for a period of 8.0 hrs at a current of 8.46 amp? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3.
(a) 124.18 g, 1.02×10^{-5} cm^2
(b) 124.18 g, 1.02×10^{-2} cm^2
(c) 272.18 g, 1.02×10^{-4} cm^2
(d) 272.18 g, 1.02×10^{-2} cm^2

26. The solubility product of $Fe(OH)_3$ at 25°C is $10^{-36.4}$ mol^4 dm^{-12} and E° (Fe^{3+}/Fe) = –0.036 V. The standard emf of the reaction $Fe(OH)_3(s) \longrightarrow Fe^{3+} + 3OH^-$.
(a) –0.586 V (b) –1.786 V
(c) –0.786 V (d) –0.286 V

27. The solubility product and solubility of AgCl in the following cell which has an emf of 0.455 V at 25°C is
Ag/AgCl in 0.1 M KCl | 0.1 M $AgNO_3$ | Ag
(a) 1.95×10^{-9}, 1.396×10^{-5} mol/L
(b) 1.95×10^{-10}, 1.396×10^{-9} mol/L
(c) 1.95×10^{-10}, 1.396×10^{-4} mol/L
(d) 1.95×10^{-4}, 1.396×10^{-4} mol/L

28. For a saturated solution of AgCl at 25°C, specific conductance is 3.41×10^{-6} ohm^{-1} cm^{-1} and that of water used for preparing the solution was 1.60×10^{-6} ohm^{-1} cm^{-1}. What is the solubility product of AgCl? $\lambda_{eq(AgCl)} = 138.3$ ohm^{-1} cm^{-1} $equiv^{-1}$.
(a) 2.51×10^{-6} mol^2/L^2 (b) 1.21×10^{-6} mol/L^2
(c) 2.71×10^{-5} mol/L (d) 1.72×10^{-10} mol^2/L^2

29. A hydrogen electrode placed in a buffer solution of CH_3COONa and acetic acid in the ratio's x:y and y:x has oxidation potential values E_1 volts and E_2 volts respectively at 25° C. The pK_a values of acetic acid would be (where pressure of H_2 is 1 atm).

(a) $\dfrac{E_1 + E_2}{0.118}$ (b) $\dfrac{E_2 - E_1}{0.118}$

(c) $-\dfrac{E_1 + E_2}{0.118}$ (d) $\dfrac{E_1 - E_2}{0.118}$

30. $E^o_{I_2|I^-} = 0.6197$ V and $E^0_{I_3^-|I^-} = 0.5355$ V

What is the equilibrium constant for the formation of triiodide ion $I_2 + I^- \rightleftharpoons I_3^-$ at 298 K?

(a) 614.9 (b) 71.49 (c) 714.9 (d) 61.49

31. A current was passed in series through a solution of a salt of a metal X and solution of $ZnSO_4$ using zinc electrodes. After a certain time, 0.348 g of X and 1.264 g of zinc has been deposited. If the salt is represented as XCl, what is the molar mass of X?

(a) 18 g mol^{-1} (b) 27 g mol^{-1}
(c) 36 g mol^{-1} (d) 9 g mol^{-1}

32. Given, E° = –0.268 V for the $Cl^- | PbCl_2 | Pb$ couple and –0.126 V for the $Pb^{2+} | Pb$ couple, determine K_{sp} for $PbCl_2$ at 25°C?

(a) 2.312×10^5 M^3 (b) 1.536×10^{-5} M^3
(c) 1.214×10^{-4} M^3 (d) 2.416×10^{-4} M^3

33. Consider the cell $\underset{1\text{ atm}}{H_2(Pt)}\left|\begin{matrix}H_3O^+(aq)\\ pH = 5.5\end{matrix}\right|\left|\begin{matrix}Ag^+\\ xM\end{matrix}\right|$ Ag. The measured emf of the cell is 1.023 V. What is the value of x? $E^0_{Ag^+, Ag} = +0.799$ V. [$T = 25°C$]

(a) 0.25 M (b) 2×10^{-3} M
(c) 1.5×10^{-3} M (d) 1.5×10^{-2} M

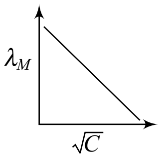
34. Hg_2Cl_2 is produced by the electrolytic reduction of Hg^{2+} ion in presence of Cl^- ion is $2Hg^{2+} + 2Cl^- + 2e^{\ominus} \rightarrow Hg_2Cl_2$. Calculate the current required to have a rate production of 44 g per hour of Hg_2Cl_2 [Atomic weight of Hg = 200.6]:

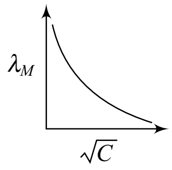
(a) 5 amp (b) 4 amp
(c) 6.5 amp (d) 3.5 amp

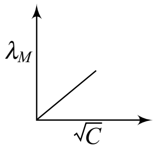
35. The ionisation constant of a weak electrolyte is 25×10^{-6} while the equivalent conductance of its 0.01 M solution is 19.6 S cm^2 eq^{-1}. The equivalent conductance of the electrolyte at infinite dilution (in S cm^2 eq^{-1}) will be:

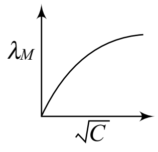
(a) 250 (b) 196 (c) 392 (d) 384

36. Which of the following curve represents the variation of λ_M with $\sqrt{C}$ for $AgNO_3$?

(a)


(b)


(c)


(d)


37. Four moles of electrons were transferred from anode to cathode in an experiment on electrolysis of water. The total volume of the two gases (dry and at STP) produced will be approximately (in litres):

(a) 22.4 (b) 44.8 (c) 67.2 (d) 89.4

38. Equivalent conductance of $BaCl_2$, H_2SO_4 and HCl at infinite dilution are A_∞^1, A_∞^2 and A_∞^3 respectively. Equivalent conductance of $BaSO_4$ solution is

(a) $A_\infty^1 + A_\infty^2 - 2A_\infty^3$ (b) $A_\infty^1 + A_\infty^2 + A_\infty^3$
(c) $A_\infty^1 + A_\infty^2 - A_\infty^3$ (d) $A_\infty^1 - A_\infty^2 + A_\infty^3$

39. Salts of *A* (atomic weight = 7), *B* (atomic weight = 27) and *C* (atomic weight = 48) were electrolysed under identical conditions using the same quantity of electricity. It was found that when 2.1 g of *A* was deposited, the weights of *B* and *C* deposited were 2.7 g and 7.2 g. The valencies of *A*, *B* and *C* respectively are:

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

40. The cost at 5 paise/KWH of operating an electric motor for 8 hours which takes 15 amp at 110 V is

(a) ₹66 (b) 66 paise
(c) 37 paise (d) ₹6.60

41. A silver wire dipped in 0.1 M HCl solution saturated with AgCl develops a potential of –0.25 V. If $E°_{Ag/Ag+}$ = –0.799 V, the K_{sp} of AgCl in pure water will be:

(a) 2.95×10^{-11} (b) 5.1×10^{-11}
(c) 3.95×10^{-11} (d) 1.95×10^{-11}

42. Consider the reaction of extraction of gold from its ore

$Au + 2CN^-(aq.) + O_2(g) + H_2O \longrightarrow Au(CN)_2^- + OH^-$

Use the following data to calculate ΔG° for the reaction

$K_f\,[Au(CN)_2^-] = X$

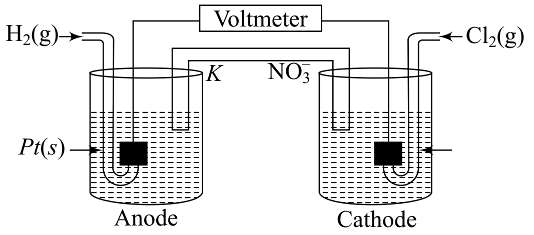
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$: E° = +0.41 V

$Au^{3+} + 3e^- \longrightarrow Au$: E° = +1.5 V

$Au^{3+} + 2e^- \longrightarrow Au^+$: E° = +1.4 V

(a) –RT ln X + 1.29 F (b) –RT ln X – 2.11 F
(c) –RT ln + 2.11 F (d) –RT ln X – 1.29 F

43. Consider the following Galvanic cell:



By what value the cell voltage when concentration of ions in anodic and cathodic compartments both increased by factor of 10 at 298 K.

(a) +0.0591 (b) –0.0591
(c) –0.1182 (d) 0

44. For the fuel cell reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$; $\Delta_fH°_{298}$ (H_2O, l) = –285.5 kJ/mol. What is $\Delta S°_{298}$ for the given fuel cell reaction? Given

$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$ E° = 1.23 V

(a) –0.322 J/K (b) –0.635 kJ/K
(c) 3.51 kJ/K (d) –0.322 kJ/K

45. The resistance of 0.5 M solution of an electrolyte in a cell was found to be 50 Ω. If the electrodes in the cell are 2.2 cm apart and have an area of 4.4 cm^2 then the molar conductivity (in S m^2 mol^{-1}) of the solution is

(a) 0.2 (b) 0.02
(c) 0.002 (d) None of these

46. The dissociation constant of n-butyric acid is 1.6×10^{-5} and the molar conductivity at infinite dilution is 380×10^{-4} Sm^2mol^{-1}. The specific conductance of the 0.01 M acid solution is
(a) 1.52×10^{-5} Sm^{-1} (b) 1.52×10^{-2} Sm^{-1}
(c) 1.52×10^{-3} Sm^{-1} (d) none

LEVEL III

1. For the galvanic cell

$$Ag|Ag^+_{(aq)}(0.1M)\,||\,Cd^{2+}_{(aq)}\ (0.1M)|Cd$$

$$(E^\circ_{Ag^+/Ag} = 0.80\ V,\ E^\circ_{Cd^{2+}/Cd} = -0.40\ V),$$

	Column I		Column II
(A)	The cell reaction	(p)	–1.17 V
(B)	Reaction quotient	(q)	–1.20 V
(C)	The cell potential	(r)	Non-spontaneous
(D)	The standard cell potential	(s)	1/10
		(t)	$E^\circ_{cell} = E^\circ_C - E^\circ_A$ data in SRP

2. Consider the reduction reactions:
(i) $Sn^{2+} + 2e^- \longrightarrow Sn$; E° = –0.14 V
(ii) $Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$; E° = 0.13 V

	Column I		Column II
(A)	$E^\circ_{Sn^{4+}/Sn}$	(p)	–0.00 5 V
(B)	Standard oxidation potential of Sn to Sn (+IV)	(q)	+0.005 V
(C)	Disproportionation of Sn^{2+}	(r)	Spontaneous
(D)	Oxidation of Sn to Sn^{4+}	(s)	Non-spontaneous
		(t)	$E^\circ = \dfrac{x_1E_1^\circ + x_2E_2^\circ}{x_3}$

3.

	Column I		Column II
(A)	Cathode	(p)	Primary cell
(B)	1 Coulomb	(q)	Secondary cell
(C)	Dry cell	(r)	6.24×10^{18} electrons
(D)	Lead storage cell	(s)	Concentration cell
(E)	$Zn \mid Zn^{2+}$ (0.01 M) $\|\|$ Zn^{2+} (0.1 M) $\mid Zn$	(t)	Positive terminal of electrochemical cell

4.

	Column I (Quantities)		Column II (Factors on which dependency exist)
(A)	Molar conductance	(p)	Temperature
(B)	emf of a cell in operation	(q)	Concentration of species involved
(C)	Electrode potential	(r)	Nature of substance involved
(D)	Standard reduction potential	(s)	No. of electrons lost or gained in the reaction
		(t)	Dilution

Comprehension I

The standard reduction potentials of some half-reactions are given as below:

$$Cu^{2+} + e \longrightarrow Cu^+;\ E_1^\circ = 0.15\ V$$

$$Cu^+ + e \longrightarrow Cu;\ E_2^\circ = 0.05\ V$$

$$Ag^+ + e \longrightarrow Ag;\ E_3^\circ = 0.799\ V$$

The decrease in Gibbs energy (–ΔG) is responsible for the production of equivalent amount of electrical work. Thus, ΔG = nFE

5. The E° for $Cu|Cu^{2+}$ in volt is
(a) 0.35 (b) –0.35 (c) +0.325 (d) –0.066 V

6. The E°_{cell} for $Cu|Cu^{2+} \,||\, Ag^+|Ag$ in volt is
(a) +0.449 (b) 0.733 V (c) –0.339 (d) –0.474

7. The E cell for $Cu|Cu^{2+}$ (0.1 M) || (0.1 M) $Ag^+|Ag$ the reaction is
(a) 0.7034 V (b) 0.374 V
(c) –0.415 V (d) –0.10945 V

Comprehension II

E°_{RP} and their respective half-reactions for some change are given below:

(i) $MnO_4^-\,(aq) + 8H^+ + 5e \longrightarrow Mn^{+5}(aq) + 4H_2O(l)$; E° = +1.52 V
(ii) $MnO_4^-\,(aq) + 4H^+ + 2e \longrightarrow MnO_2(s) + 2H_2O(l)$; E° = +2.26 V
(iii) $MnO_4^-\,(aq) + 2e \longrightarrow Mn^{+5}(aq)$; E° = +0.56 V (acid med.)
(iv) $Mn^{3+} + e \longrightarrow Mn^{2+}$; E° = +1.51 V (acid med.)
(v) $Mn^{4+} + e \longrightarrow Mn^{3+}$; E° = +0.95 V (acid med.)

8. The most stable oxidation state of Mn is
(a) Mn^{2+} (b) Mn^{4+} (c) Mn^{7+} (d) Mn^{6+}

9. Which is the least stable oxidation state of Mn?
(a) Mn^{2+} (b) Mn^{4+} (c) Mn^{7+} (d) Mn^{6+}

10. The E° for, $Mn^{4+} + 2e \longrightarrow Mn^{2+}$; is equal to
(a) 1.23 V (b) 2.46 V (c) 0.56 V (d) –0.56 V

Comprehension III

The potential of an electrode when each species involved in it exists in the standard state is called its standard potential. The standard reduction potential of a couple is the measure of its tendency to get reduced. A series obtained by arranging the various couples in order of their decreasing standard potential is called electrochemical series. Any of the two couples of this series joined together gives an electrochemical cell in which reduction occurs at the electrode which occupies the higher position. The standard potential of hydrogen electrode is taken to be zero by convention. Given below are the sequence of half-reactions (acidic media) with relevant E^0 values in volt at 298K.

$$MnO_4^- \xrightarrow{0.560} MnO_4^{2-} \xrightarrow{2.26} MnO_2 \xrightarrow{0.95}$$
$$Mn^{3+} \xrightarrow{1.50} Mn^{2+} \xrightarrow{-1.18} Mn$$

Also given some more data are:

$$Fe^{2+} \xrightarrow{-0.44} Fe_{(s)} \xrightarrow{+0.036} Fe^{3+}$$

11. The E° for $MnO_4^- \longrightarrow Mn^{2+}$ is equal to
(a) 1.054 V (b) 1.506 V
(c) 5.27 V (d) 7.53 V

12. The value of E° for the reaction:

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$,

is equal to
(a) 0.734 V
(b) 0.284 V
(c) 4.498 V
(d) Cannot be calculated as concentrations of species are not given.

13. For the cell

$Fe_{(s)} \mid Fe^{2+}$ (0.1M) || 100 mL 0.3M HA (pKa =5.2) mixed with 50 mL 0.4M NaOH | H_2 (1 atm), Pt

the E_{cell} at 298 is equal to
(a) –0.15 V (b) +0.185 V
(c) –0.44 V (d) +0.1623 V

Comprehension IV

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cells reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values.

$I_2 + 2e^- \longrightarrow 2I^-$; E° = 0.54
$Cl_2 + 2e^- \longrightarrow 2Cl^-$; E° = 1.36
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$; E° = 1.50
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; E° = 0.77
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$; E° = 1.23

14. Among the following, identify the correct statement.
(a) Chloride ion is oxidised by O_2.
(b) Fe^{2+} is oxidised by chloride ion.
(c) Iodide ion is oxidised by chlorine ion.
(d) Mn^{2+} is oxidised by chlorine.

15. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because
(a) O_2 oxidises Mn^{2+} to Mn^{3+}
(b) O_2 oxidises both Mn^{2+} and Fe^{2+}
(c) Fe^{3+} oxidises H_2O to O_2
(d) Mn^{3+} oxidises H_2O to O_2

Comprehension IV

The molar conductance of NaCl varies with the concentration as shown in the following table and all values follows the equation

$\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$ Where λ_m^C = molar specific conductance

λ_m^∞ = molar specific conductance at infinite dilution

C = molar concentration

Molar Concentration of NaCl	Molar Conductance in ohm^{-1} cm^2 $mole^{-1}$
4×10^{-4}	107
9×10^{-4}	97
16×10^{-4}	87

When a certain conductivity cell was filled with 25×10^{-4} (M) NaCl solution. The resistance of the cell was found to be 1000 ohm. At infinite dilution, conductance of Cl^- and SO_4^{-2} are 80 ohm^{-1} cm^2 $mole^{-1}$ and 160 ohm^{-1} cm^2 $mole^{-1}$ respectively.

16. What is the molar conductance of NaCl at infinite dilution?
(a) 147 ohm^{-1} cm^2 $mole^{-1}$
(b) 107 ohm^{-1} cm^2 $mole^{-1}$
(c) 127 ohm^{-1} cm^2 $mole^{-1}$
(d) 157 ohm^{-1} cm^2 $mole^{-1}$

17. What is the cell constant of the conductivity cell:
(a) 0.385 cm^{-1} (b) 3.85 cm^{-1}
(c) 38.5 cm^{-1} (d) 0.1925 cm^{-1}

18. If the cell (C) is filled with 5×10^{-3} (N) Na_2SO_4 the observed resistance was 400 ohm. What is the molar conductance of Na_2SO_4.
(a) 19.25 ohm^{-1} cm^2 $mole^{-1}$
(b) 96.25 ohm^{-1} cm^2 $mole^{-1}$
(c) 385 ohm^{-1} cm^2 $mole^{-1}$
(d) 192.5 ohm^{-1} cm^2 $mole^{-1}$

Comprehension VI

In a lead storage battery, Pb (anode) and PbO_2 (cathode) are used. Concentrated H_2SO_4 is used as electrolyte. The battery holds 3.5 L acid with it. In the discharge process, the density of acid fell from 1.294 to 1.139 g/mL. The sulphuric acid of density 1.294 g mL^{-1} is 39% by mass and that of density 1.139 g/mL is 20% by mass.

19. Equivalent mass of sulphuric acid in lead storage battery is

(a) 49 (b) 98
(c) 24.5 (d) None of these

20. Normalities of sulphuric acid before and after discharge are

(a) 5.15, 2.32 (b) 2.32, 5.15
(c) 5.15, 5.15 (d) 2.32, 2.32

21. Number of ampere-hours for which the battery must have been used is

(a) 26504 amp-hrs (b) 2650.4 amp-hrs
(c) 265.04 amp-hrs (d) 26.504 amp-hrs

22. The amount of charge which the battery must have been used is

(a) 9.88 F (b) 8.98 F (c) 8.89 F (d) 7.88 F

23. Which of the following takes place in discharge process at anode?

(a) $PbO_2 + 4H^+ + SO_4^{-2} + 2e^- \longrightarrow PbSO_4 + 2H_2O$

(b) $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{-2} + 2e^-$

(c) $Pb + SO_4^{-2} \longrightarrow PbSO_4 + 2e^-$

(d) $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{-2}$

Comprehension VII

Chemical reaction involves interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large number conveniently, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept. A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass: Na = 23, Hg = 200; 1 Faraday = 96500 coulombs).

24. The total number of moles of chlorine gas evolved is

(a) 0.5 (b) 1.0 (c) 2.0 (d) 3.0

25. If the cathode is Hg electrode, the maximum weight (g) of amalgam formed in this solution is

(a) 200 (b) 225 (c) 400 (d) 446

26. The total charge (coulomb) required for complete electrolysis is

(a) 24125 (b) 48250 (c) 96500 (d) 193000

Comprehension VIII

Copper reduces NO_3^- into NO and NO_2 depending upon concentration of HNO_3 in solution. Assuming $[Cu^{2+}] = 0.1$ M, and $P_{NO} = P_{NO_2} = 10^{-3}$ atm and using given data answer the following questions:

$$E^o_{Cu^{2+}/Cu} = +0.34 \text{ volt};$$

$$E^o_{NO_3^-/NO} = +0.96 \text{ volt}$$

$$E^o_{NO_3^-/NO_2} = +0.79 \text{ volt};$$

$$\text{at 298 K}(2.303)\frac{RT}{F} = 0.06 \text{ volt}$$

27. E_{Cell} for reduction of $NO_3^- \longrightarrow$. NO by Cu(s), when $[HNO_3] = 1$ M is [At $T = 298$]

(a) = 0.61 (b) = 0.71 (c) = 0.51 (d) = 0.81

28. At what HNO_3 concentration thermodynamic tendency for reduction of NO_3^- into NO and NO_2 by copper is same?

(a) $10^{1.23}$ M(b) $10^{0.56}$ M (c) $10^{0.66}$ M (d) $10^{0.12}$ M

(Assertion and Reason)

(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

29. **Statement 1:** (E°)SRP value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}

Statement 2: The third ionisation energy of Mn is very high as it requires change from d^5 to d^4 configuration.

30. **Statement 1:** Specific conductance decreases with dilution whereas equivalent conductance increases.

Statement 2: On dilution, number of ions per millilitre decreases but total number of ions increases considerably.

31. **Statement 1:** Calomel electrode especially saturated with KCl solution is used as a reference electrode, i.e., secondary standard electrode.

Statement 2: The potential of calomel electrode depends upon the concentration of Cl^- ions.

32. **Statement 1:** The electrolytic cell during electrolysis of NaCl (aq.) on addition of little red litmus shows a blue colour.

Statement 2: At cathode: $2H^+ + 2e \longrightarrow H_2$

The reaction at cathode gives rise to an increase in pH ranging in alkaline medium.

33. **Statement 1:** If an aqueous solution of NaCl is electroysed, the product obtained at the cathode is H_2 gas and not Na.

Statement: Gases are liberated faster than the metals.

Multiple correct Question

34. The electrolysis of aqueous solution of $CuBr_2$ using platinum electrode would lead to the evolving of

(a) Br_2 gas at anode
(b) Br_2 gas at anode and O_2 gas at cathode
(c) Copper(s) at cathode
(d) H_2 gas at cathode

35. Which of the following statements is (are) correct?

(a) The reactivity of metals decreases in going down the electrochemical series.

(b) A metal can displace any other metal placed above it in the electrochemical series from its salt solution.
(c) The oxidising power of the substances decrease from the top to the bottom in the electrochemical series.
(d) A redox reaction is feasible when the substance having higher reduction potential gets reduced and the one having lower reduction potential gets oxidised.

36. When a nickel spatula is used to stir an aqueous copper sulphate solution
(a) the solution is stirred well without any chemical change.
(b) nickel spatula gets partly oxidized into Ni^{2+} ions.
(c) Cu^{2+} ions present in the solution get partly reduced into Cu.
(d) copper gets deposited on the spatula.

37. Which among the following statement(s) is/are correct?
(a) If $E^0_{A^{n+}/A}$ is negative, H^+ will be reduced to H_2 by the element 'A'
(b) Compounds of (Zn, Na, Mg) are reduced by hydrogen (H_2) whereas those of noble metals (Cu, Ag, Au) are not reducible.
(c) If $E^0_{A^{n+}/A}$ is positive, A^{n+} will be reduced to A by H_2
(d) M | M^{n+} || H^+ | H_2 (Pt) will be spontaneous if $E^0_{M^{n+}/M}$ is negative

38. Electrode potential data are given below.

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq);\ E^o = +0.77\ V$$

$$Al^{3+}(aq) + 3e^- \longrightarrow Al(s);\ E^o = -1.66\ V$$

$$Br_2(aq) + 2e^- \longrightarrow Br^-(aq);\ E^o = +1.08\ V$$

Based on the given data which statement/s is/are true?
(a) Fe^{2+} is stronger reducing agent than. Br^-.
(b) Fe^{2+} is stronger reducing agent than Al.
(c) Al is stronger reducing agent than Fe^{2+}.
(d) Br^- is stronger reducing agent than Al.

39. We observe blue colour if
(a) Cu electrode is placed in the $AgNO_3$ solution.
(b) Cu electrode is placed in the $ZnSO_4$.
(c) Cu electrode is placed in the dil HNO_3.
(d) Cu electrode is placed in the $NiSO_4$.

40. The emf of the following cell
Fe(s) | Fe^{2+} (0.1M) || Cu^{2+} (0.01M) | Cu
is found to be equal to 0.75V. The emf of the cell can be increased by
(a) diluting concentration Fe^{2+} solution.
(b) diluting Cu^{2+} solution.
(c) increasing the concentration of Fe^{2+} ions.
(d) increasing the concentration of Cu^{2+}.

41. The standard emf of the cell,

$$Cd(s)|\underset{0.1M}{CdCl_2(aq)}||AgCl(s)|Ag(s)$$

in which the cell reaction is 0.6195 V at 0°C and 0.6753 V at 25° C. The value of ΔH of the reaction at 25°C is
(a) 167.26 kJ/mol
(b) –1.961 kJ/mol
(c) 40 K/mol
(d) –0.469 Kcal/mol

42. The standard electrode potentials, $E^o_{I_2/I^-}$, $E^o_{Br^-/Br_2}$ and $E^o_{Fe/Fe^{2+}}$ are respectively +0.54 V, –1.09 V and 0.44 V as the basis of given data which of the following is/are spontaneous?
(a) $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$
(b) $Fe + Br_2 \longrightarrow Fe^{2+} + 2Br^-$
(c) $Fe + I_2 \longrightarrow Fe^{2+} + 2I^-$
(d) $I_2 + 2Br^- \longrightarrow 2I^- + Br_2$

43. Which of the following statements is (are) not correct?
(a) Metallic conduction is due to the movement of electrons whereas the electrolytic conduction is due to the movement of ions.
(b) Both metallic and electrolytic conductions involve transfer of matter.
(c) Electrolytic conduction decreases with rise in temperature.
(d) Metallic conduction involves no chemical change.

44. Which of the following aqueous solution turn(s) alkaline after electrolysis?
(a) NaCl
(b) $CuCl_2$
(c) CH_3COONa
(d) K_2SO_4

45. In which of the following cell(s): $E_{cell} = E^o_{cell}$?
(a) Cu(s) | Cu^{2+} (0.01 M) || Ag^+ (0.1 M) | Ag(s)
(b) Pt(H_2) | pH = 1 || Zn^{2+} (0.01 M) | Zn (s)
(c) Pt(H_2) | pH = 1 || Zn^{2+} (1 M) | Zn (s)
(d) Pt(H_2) | H^+ = 0.01 M || Zn^{2+} (0.01 M) | Zn(s)

46. Fuel cell involves following reaction(s):
(a) $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$ (at cathode)
(b) $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$ (at anode)
(c) $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$ (at anode)
(d) $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$ (at cathode)

47. In lead storage battery, during discharging process. Which of the following is not the correct statement?
(a) PbO_2 gets oxidised.
(b) H_2SO_4 is produced.
(c) density of H_2SO_4 solution decreases.
(d) density of H_2SO_4 solution increases.

48. 100 mL of a buffer of 1 M NH_3 and 1 M NH_4^+ are placed in two voltaic cells separately. A current of 1.5 A is passed through both cells for 20 min. If electrolysis of water only takes place, what is not true regarding the pH of

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-\ (R.H.S.)$$

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-\ (L.H.S.)$$

(a) half-cell on L.H.S. will increase.
(b) half-cell on R.H.S. will increase.
(c) Both the half-cells will increase.
(d) Both the half-cells will decrease.

49. A current of 2.68 A is passed for one hour through an aqueous solution of $CuSO_4$ using copper electrodes. Select the correct statement (s) from the following:
(a) Increase in mass of cathode = 3.174 g.
(b) Decrease in mass of anode = 3.174 g.
(c) No change in masses of electrodes.
(d) The ratio between the change of masses of cathode and anode is 1:2.

50. Fe is reacted with 1.0 M HCl. E° for $Fe/Fe^{2+} = +0.34$ volt. The correct observation(s) regarding this reaction is/are:
(a) Fe will be oxidised to Fe^{2+}.
(b) Fe^{2+} will be reduced to Fe.
(c) since emf is positive, the reaction shall occur.
(d) since emf is positive, the reaction shall not occur.

Integer and Subjective Type Question

51. At equimolar concentration of Fe^{2+} and Fe^{3+}, what must $[Ag^+]$ be so that the voltage of the galvanic cell made from Ag^+/Ag and Fe^{3+}/Fe^{2+} electrodes equals zero? The reaction is $Fe^{2+} + Ag^+ \rightleftharpoons Fe^{3+} + Ag$. Determine the equilibrium constant at 25°C for the reaction. Given: $E^o_{Ag^+/Ag} = 0.799$ volt and $E^o_{Fe^{+3}/Fe^{2+}} = 0.771$ V.

52. Calculate the volume of Cl_2 at NTP produced during electrolysis of $MgCl_2$ which produces 6.50 g Mg. At. wt. of Mg = 24.3.

53. An ammeter and copper volt meter are connected in series in an electric circuit through which a constant direct current flows. The ammeter shows 0.525 amp. If 0.6354 g of Cu is deposited in one hour, what is percentage error of ammeter? [At. wt. of Cu = 63.54.]

54. Cd amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. How many minute long should a current of 5 amp is passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2.56 g mercury? [At.wt. of Cd = 112.40.]

55. The standard oxidation potential of Ni/Ni^{2+} electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured emf be zero at 25^0C? Assume $[Ni^{2+}] = 1$ M and $P_{H_2} = 1$ atm.

56. 3 amp current was passed through an aqueous solution of an unknown salt of Pd^{n+} for 1 hr. 2.977 g of Pd was deposited at cathode. Find n. (At. wt. of Pd = 106.4)

57. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the Cu is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 ampere. Calculate the volume of gases evolved at NTP during entire electrolysis.

58. In the cell,

$$Tl \mid Tl^+ (0.1\ M) \parallel Sn^{+2} (0.01\ M) \mid Sn$$

$$E^o_{T\ell/T\ell^+} = 0.34V,\ E^o_{Sn^{+2}/Sn} = -0.14$$

a current of 40 mA is flowing from tin to thallium electrode. An external battery of 1.2 V emf is connected to the cell so that its polarity is opposite to the natural polarity of the cell. If 0.38 g of thallium is deposited in one hour at 25°C, determine % efficiency of thallium electrode. (Tl = 204).

59. The given cell,
$Ag \mid AgCl \mid HCl\ (0.1\ M) \mid H_2\ (1\ atm) \mid Pt \parallel Pt \mid H_2\ (1\ atm) \mid H^+\ (c\ M) \mid KCl\ (1\ M) \mid Hg_2Cl_2 \mid Hg$ () is used to measure pH of solution. Given E° = 0.2873 V for $Cl^- \mid AgCl \mid Ag$ couple and E° = 0.2415 V for $Cl^- \mid Hg_2Cl_2 \mid Hg$ couple, determine the concentration of H^+ in the right cell if the potential of the given cell is 0.1256 V.

60. Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride in M/32 solution of salt at 298 K from the following cell data at 298 K:
$Pt \mid H_2\ (1\ atm) \mid H^+\ (1\ M) \parallel M/32\ C_6H_5NH_3Cl \mid H_2\ (1\ atm) \mid Pt$; $E_{cell} = -0.188$ V.

61. Calculate E° for the following reactions at 298 K:

$$Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag + 2NH_3$$
$$Ag(CN)_2^- + e^- \rightleftharpoons Ag + 2CN^-$$

Given:
$$E^o_{Ag^+/Ag} = 0.7991\ V,\ K_{lns}[Ag(NH_3)_2^+] = 6.02 \times 10^{-8}$$

and $K_{lns}[Ag(CN)_2^-] = 1.995 \times 10^{-19}$.

62. The resistance of a N/10 KCl solution is 245 ohms. Calculate the specific conductance and the equivalent conductance of the solution if the electrodes in the cell are 4 cm apart and each having an area of 7.0 sq. cm.

63. The resistance of a solution 'A' is 50 ohms and that of solution 'B' is 100 ohms, both solutions being taken in the same conductivity cell. If equal volumes of solution A and B are mixed, If the resistance of the mixture using the same cell is R find 3R. (Assume that there is no increase in the degree of dissociation of A and B on mixing.)

64. In a conductivity cell the two platinum electrodes, each of area 10 sq. cm. are fixed 1.5 cm apart. The cell contained 0.05 N solution of a salt. If the two electrodes are just half-dipped into the solution which has a resistance of 50 ohms, find equivalent conductance of the salt solution.

65. A big irregular shaped vessel contained water, the sp. conductance of which was 2.56×10^{-5} mho cm^{-1}. 500 g of NaCl was then added to the water and the specific conductance after the addition of NaCl, was found to be 3.10×10^{-5} mho cm^{-1}. Find the capacity of the vessel if it is fulfilled with water. (λ^∞ NaCl = 149.9)

66. The equivalent conductance of 0.10 N solution of $MgCl_2$ is 97.1 mho cm^2 eq^{-1}. A cell with electrodes that are 1.50 cm^2 in surface are and 0.50 cm apart is filled with 0.1 N $MgCl_2$ solution. How much current will flow when the potential difference between the electrodes is 5 V?

67. At 18°C the mobilities of NH_4^+ and ClO_4^- ions are 6.6×10^{-4} and 5.7×10^{-4} cm^2 V^{-1} sec^{-1} at infinite dilution. Calculate equivalent conductance of ammonium chlorate solution.

68. For H^+ and Na^+ the values of λ^{∞} are 349.8 and 50.11. Calculate the mobilities of these ions and their velocities if they are in a cell in which the electrodes are 5 cm apart and to which a potential of 2 V is applied.

69. The equivalent conductance of an infinitely dilute solution NH_4Cl is 150 and the ionic conductances of OH^- and Cl^- ions are 198 and 76 respectively. What will be the equivalent conductance of the solution of NH_4OH at infinite dilution. If the equivalent conductance of a 0.01 N solution NH_4OH is 9.6, what will be its degree of dissociation?

70. Calculate the dissociation constant of water at 25°C from the following data:

Specific conductance of $H_2O = 5.8 \times 10^{-8}$ mho cm^{-1},

$\lambda^{\infty}_{H^+} = 350.0$ and $\lambda^{\infty}_{OH^-} = 198.0$ mho cm^2

71. Calculate K_a of acetic acid if its 0.05 N solution has equivalent conductance of 7.36 mho cm^2 at 25°C.

($\lambda^{\infty}_{CH_3COOH} = 390.70$)

72. The specific conductance of a saturated solution of AgCl at 25°C after substracting the specific conductance of water is 2.28×10^{-6} mho cm^{-1}. Find the solubility product of AgCl at 25°C. ($\lambda^{\infty}{}_{AgCl} = 138.3$ mho cm^2)

73. An excess of liquid Hg was added to 10^{-3} M acidified solution of Fe^{3+} ions. It was found that only 5% of the ions remained as Fe^{3+} at equilibrium at 25°C. Calculate $E^{o}_{Hg|Hg_2^{2+}}$ at 25°C. The equilibrium reaction is

$$2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$$

and $E^{o}_{Fe^{2+}|Fe^{3+}} = -0.77$ V

(a) 0.023 V (b) –0.793 V

(c) –0.029 V (d) 7.93 V

74. Equinormal solution of two weak acids, HA ($pK_a = 3$) and HB ($pK_a = 5$) are each placed in contact with standard hydrogen electrode at 25°C. When a cell is constructed by interconnecting them through a salt bridge find the emf of the cell.

75. Estimate the cell potential of a Daniel cell having 1.0 M Zn^{++} and originally having 1.0 M Cu^{++} after sufficient NH_3 has been added to the cathode compartment to make NH_3 concentration 2.0 M. Given K_f for $[Cu(NH_3)_4]^{2+} = 1 \times 10^{12}$, E° for the reaction, $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ is 1.1 V.

76. K_d for dissociation of $[Ag(NH_3)_2]^+$ into Ag^+ and NH_3 is 6×10^{-8}. Calculate E° for the following half reaction;

$Ag(NH_3)_2^+ + e^- \longrightarrow Ag + 2NH_3$

Given $Ag^+ + e^- \longrightarrow Ag$, E° = 0.799 V

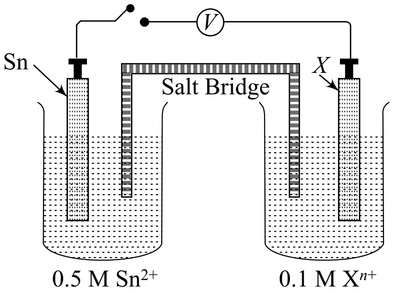
77. The overall formation constant for the reaction of 6 mole of CN^- with cobalt (II) is 1×10^{19}. The standard reduction potential for the reaction $[Co(CN)_6]^{3-} + e^- \rightarrow [Co(CN)_6]^{4-}$ is –0.83 V. Calculate the formation constant of $[Co(CN)_6]^{3-}$.

Given $Co^{3+} + e^- \rightarrow Co^{2+}$; E° = 1.82 V

78. The emf of cell: $H_2(g)$|Buffer||Normal calomal electrode is 0.6885 V at 40°C when the barometric pressure is 725 mm of Hg. What is the pH of the solution. E°calomal = 0.28?

79. A direct current of 1.25 A was passed through 200 mL of 0.25 M $Fe_2(SO_4)_3$ solution for a period of 1.1 hour. The resulting solution in cathode chamber was analysed by titrating against acidic $KMnO_4$ solution. 25 mL permaganate solution was required to reach the end point. Determine molarity of $KMnO_4$ solution. If E^o for $Fe^{+3} + e \rightleftharpoons Fe^{+2}$ is 0.77 Volt.

80. An electrochemical cell is constructed with an open switch as shown below.



When the switch is closed, mass of tin-electrode increases. If E° (Sn^{2+}/Sn) = –0.14 V and for E° (X^{n+}/X) = – 0.78 V and initial emf of the cell is 0.65 V, determine n and indicate the direction of electron flow in the external circuit.

81. 10 g fairly concentrated solution of $CuSO_4$ is electrolyzed using 0.01 F of electricity. Calculate

(a) the weight of resulting solution.

(b) equivalents of acid or alkali in the solution.

82. One of the methods of preparation of per disulphuric acid, $H_2S_2O_8$, involve electrolytic oxidation of H_2SO_4 at anode ($2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of H_2 and 2.35 L of O_2 were generated at STP. What is the weight of $H_2S_2O_8$ formed?

83. Assume that impure copper contains only iron, silver and a gold as impurities. After passage of 140 A, for 482.5 sec, of the mass of the anode decreased by 22.260 g and the cathode increased in mass by 22.011 g. Estimate the % iron and % copper originally present.

84. For the galvanic cell: Ag|AgCl(s)|KCl(0.2 M)||KBr(0.001 M)|AgBr(s)|Ag, Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.

$[K_{sp(AgCl)} = 2.8 \times 10^{-10}; K_{sp(AgBr)} = 3.3 \times 10^{-13}]$

85. An aqueous solution of NaCl on electrolysis gives $H_{2(g)}$, $Cl_{2(g)}$ and NaOH according to the reaction:

$$2Cl^-(aq) + 2H_2O \rightleftharpoons 2OH^-_{(aq)} + H_2(g) + Cl_2(g)$$

A direct current of 25 amperes with a current efficiency of 62% is passed through 20 L of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1 kg of Cl_2? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation).

86. A sample of water from a large swimming pool has a resistance of 9200 Ω at 25°C when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of 85 Ω at 25°C. 500 g of NaCl were dissolved in the pool, which was throughly stirred. A sample of this solution gave a resistance of 7600 Ω. Calculate the volume of water in the pool.

Given: Molar conductance of NaCl at that concentrations is 126.5 $\Omega^{-1}cm^2mol^{-1}$ and molar conductivity of KCl at 0.02 M is 138 Ω^{-1} cm^2mol^{-1}.

87. In the refining of silver by electrolytic method what will be the weight of 100 g Ag anode if 5 ampere current is passed for 2 hrs? Purity of silver is 95% by weight.

88. Hydrogen peroxide can be prepared by successive reactions:

$$2NH_4HSO_4 \rightarrow H_2 + (NH_4)_2S_2O_8$$

$$(NH_4)_2S_2O_8 + 2H_2O \rightarrow 2NH_4HSO_4 + H_2O_2$$

The first reaction is an electrolytic reaction the second is steam distillation. What amount of current would have to be used in first reaction to produce enough intermediate to yield 100 g pure H_2O_2 per hour? Assume 50% anode current efficiency.

89. Determine at 298 for cell:

$$Pt|Q, QH_2, H^+||1M\ KCl|Hg_2Cl_2|Hg(l)|Pt$$

(a) it's emf when pH = 5.0
(b) the pH when $E_{cell} = 0$
(c) the positive electrode when pH = 7.5
given $E^o_{RP(RHS)} = 0.28$, $E^o_{RP(LHS)} = 0.699$

90. Calculate the cell potential of a cell having reaction $Ag_2S + 2e^- \rightleftharpoons 2\ Ag + S^{2-}$ in a solution buffered at pH = 3 and which is also saturated with 0.1 M H_2S. For H_2S : $K_1 = 10^{-8}$ and $K_2 = 1.1 \times 10^{-13}$, $K_{sp}(Ag_2S) = 2 \times 10^{-49}$, $E^o_{Ag^+|Ag} = 0.8$.

91. At 25°C, $\Delta H_f(H_2O, l) = -56700$ J/mol and energy of ionization of $H_2O(l) = 19050$ J/mol. What will be the reversible EMF at 25°C of the cell,

$Pt|H_2(g)(1\ atm)|H^+||\ OH^-|O_2(g)(1\ atm)|Pt$, if at 26°C the emf increase by 0.001158 V.

92. A dilute aqueous solution of KCl was placed between two electrodes 10 cm apart, across which a potential of 6 V was applied. How far would the K^+ ion move in 2 hrs at 25°C? Ionic conductance of K^+ ion at infinite dilution at 25°C is 73.52 ohm^{-1} cm^2 $mole^{-1}$?

93. Calculate the equilibrium concentration of all ions in an ideal solution prepared by mixing 25.00 mL of 0.100 M Tl+with 25.00 mL of 0.200 M Co^{3+}.

$E°(Tl^+/Tl^{3+}) = -1.25$ V, $E°\ (Co^{3+}/Co^{2+}) = 1.84$ V

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. Find the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for $Fe^{3+} | Fe^{2+}$ and $I_3^- | I^-$couples. **[1998]**

(a) 5.2×10^8
(b) 6.26×10^7
(c) 3.8×10^7
(d) 4.3×10^7

2. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell Ag | Ag^+ (standard Ag_2CrO_4 soln.) || Ag^+(0.1M) | Ag is 0.164 V at 298 K. **[1998]**

(a) 1.45×10^{-12}
(b) 2.2×10^{-11}
(c) 3.2×10^{-11}
(d) 2.44×10^{-12}

3. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than the other. The concentration of $CuSO_4$ in the cell with higher emf value is 0.5 M. Find out the concentration of $CuSO_4$ in the other cell (2.203 RT/F = 0.06). **[2003]**

(a) 0.09 M
(b) 0.2 M
(c) 0.05 M
(d) 0.3 M

4. Find the equilibrium constant for the reaction,
$In^{2+} + Cu^{2+} \longrightarrow In^{3+} + Cu^+$ at 298 K

Given: $E^o_{Cu^{2+}/Cu^+} = 0.15$ V; $E^o_{In^{2+}/In^+} = -0.40$ V,

$E^o_{In^{3+}/In^+} = -0.42$ V **[2004]**

(a) 10^{11}
(b) 10^{10}
(c) 10^{12}
(d) 10^8

5. We have taken a saturated solution of AgBr. Ksp of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 L of this solution find conductivity (specific conductance) of this solution in terms of 10^{-7} S m^{-1} units. Given, molar conductance of Ag^+, Br^- and NO^{3-} are 6×10^{-3} Sm^2mol^{-1}. 8×10^{-3} Sm^2 mol^{-1} and 7×10^{-3} Sm^2 mol^{-1}. **[2006]**

(a) 55
(b) 45
(c) 58
(d) 60

6. Given, $E^o_{Cr^{3+}/Cr} = -0.74$ V; $E^o_{MnO_4^-/Mn^{2+}} = 1.51$ V,

$E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V, $E^o_{Cl/Cl^-} = 1.36$ V

Based on the data given above strongest oxidising agent will be **[2013 Main]**

(a) Cl
(b) Cr^{3+}
(c) Mn^{2+}
(d) MnO_4^-

7. In a galvanic cell, the salt-bridge **[2014 Adv.]**
(a) does not participate chemically in the cell reaction.
(b) stops the diffusion of ions from one electrode to another.
(c) is necessary for the occurrence of the cell reaction.
(d) ensures mixing of the two electrolytic solutions.

8. Given below are the half-cell reactions. **[2014 Main]**
$Mn^{2+} + 2e^- \longrightarrow Mn$; $E^o = -1.18$ eV $2(Mn^{3+} + e^- \longrightarrow Mn^{2+})$; $E^o = +1.51$ eV
The E° for $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ will be
(a) –2.69 V; the reaction will not occur.
(b) –2.69 V; the reaction will occur.
(c) –0.33 V; the reaction will not occur.
(d) –0.33 V; the reaction will occur.

9. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞, respectively. The correct relationship between λ_C and λ_∞ is given as (where, the constant B is positive) **[2014 Main]**
(a) $\lambda_C = \lambda_\infty + (B)C$ (b) $\lambda_C = \lambda_\infty - (B)C$
(c) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$ (d) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$

10. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution of 0.5 M solution of same electrolyte is 1.4 S m^{-1} and resistance of same solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in $Sm^2\ mol^{-1}$ is **[2014 Main]**
(a) 5×10^{-4} (b) 5×10^{-3}
(c) 5×10^{3} (d) 5×10^{2}

11. The standard reduction potential data at 25°C is given below: **[2013 Adv.]**
$E^o(Fe^{3+}/Fe^{2+}) = +0.77$ V; $E^o(Fe^{+2}/Fe) = -0.44$ V;
$E^o(Cu^{2+}/Cu) = +0.34$ V; $E^o(Cu^{2+}/Cu) = +0.52$ V;
$E^o(O_2(g) + 4H^+ + 4e^-) \longrightarrow 2H_2O) = +1.23$ V;
$E^o(O_2(g) + 2H_2O + 4e^-) \longrightarrow 4OH^-) = +0.40$ V;
$E^o(Cr^{3+}/Cr) = -0.74$ V; $E^o(Cr^{2+}/Cr) = +0.91$ V;
Match E° of the rebox pair in Column I with the values given in Column II and select the correct answer using the code given below the lists.

	Column I		Column II
P.	$E^o(Fe^{3+}/Fe)$	1.	–0.18 V
Q.	$E^o(4H_2O \rightleftharpoons 4H^+ + 4OH^-)$	2.	–0.4 V
R.	$E^o(Cu^{2+} + Cu \longrightarrow 2Cu^+)$	3.	–0.04 V
S.	$E^o(Cr^{3+}, Cr^{2+})$	4.	–0.83 V

Codes:

	P	Q	R	S
(a)	4	1	2	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	3	4	1	2

12. Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is (atomic mass of Cu = 63.5u) **[2015 Main]**
(a) 0 g (b) 63.5 g (c) 2 g (d) 127 g

Answer Key

LEVEL I

1. (b)	2. (d)	3. (d)	4. (a)	5. (c)	6. (d)	7. (d)	8. (b)	9. (b)	10. (b)
11. (a)	12. (b)	13. (a)	14. (d)	15. (a)	16. (d)	17. (b)	18. (b)	19. (c)	20. (b)
21. (b)	22. (c)	23. (c)	24. (a)	25. (a)	26. (c)	27. (c)	28. (a)	29. (d)	30. (b)
31. (b)	32. (c)	33. (a)	34. (c)	35. (d)	36. (a)	37. (b)	38. (a)	39. (c)	40. (d)
41. (d)	42. (b)	43. (a)	44. (a)	45. (d)	46. (c)	47. (c)	48. (c)	49. (c)	50. (b)
51. (b)	52. (d)	53. (a)	54. (d)	55. (d)	56. (d)	57. (b)	58. (b)		

LEVEL II

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

LEVEL III

1. (A) → r; (B) → s; (C) → p, t; (D) → q   2. (A) → p, t; (B) → q, t; (C) → s, t; (D) → r
3. (A) → t; (B) → r; (C) → p; (D) → q; (E) → s   4. (A) → p, q, r, t; (B) → p, q, r, s, t; (C) → p, q, r, s, t; (D) → r, s
5. (d)   6. (b)   7. (a)   8. (a)   9. (c)   10. (a)   11. (b)   12. (a)   13. (d)   14. (c)
15. (d)   16. (c)   17. (d)   18. (d)   19. (b)   20. (a)   21. (c)   22. (a)   23. (c)   24. (b)
25. (d)   26. (d)   27. ( )   28. ( )   29. (a)   30. (a)   31. (b)   32. (a)   33. (c)   34. (a, c)
35. (a, d)   36. (b, c, d)   37. (a, c, d)   38. (a, c)   39. (a, c)   40. (a, d)   41. (b, d)   42. (a, b, c)
43. (b, c)   44. (a, c)   45. (a, b)   46. (a, c)   47. (a, b, d)   48. (a, c, d)   49. (a, b)   50. (a, c)
51. [3]   52. [6]   53. [2]   54. [2]   55. [4]   56. [4]   57. 228.735 mL and 158.285 mL,   58. [25%]
59. 1.24×10^{-5} M   60. 6.5×10^{-4} M, 1.352×10^{-5} M   61. –0.301 V   62. 23.32 $\Omega^{-1}cm^2eq^{-1}$ 63. [200]
64. 120 $\Omega^{-1}cm^2eq^{-1}$ 65. 2.37×10^8 cc.   66. 0.1456 Amp.   67. [118.695 mho cm^2]
68. [$H^+ = 1.45 \times 10^{-3} cms^{-1}$, $Na^+ = 2.08 \times 10^{-4} cms^{-1}$]   69. [0.0353]   70. ($2 \times 10^{-16}$)
71. [1.76×10^{-5}]   72. [2.70×10^{-10} (mole/L)^2]   73. (b)   74. [0.059]   75. [$E_{cell} = 0.71$ V]
76. [0.373 V]   77. 4.7×10^{63} 78. = 6.6   79. 0.41 M   80. [3]
81. (a) = 9.6025g, (b) = 0.01   82. 43.45 g   83. Cu = 98.88%, Fe = 0.847 %
84. – 0.037 V,   85. 48.74 hr., 1.408 M   86. 2.014×10^5L   87. 57.58g   88. 315.36 Amp.
89. (a) – 0.1235 V (b) pH = 7.1 (c) Calomal electrode   90. – 0.1674V   91. 0.44137
92. 3.29 cm   93. [Tl^+] = 10^{-8} M, [Co^{+3}] = 2×10^{-8} M, [Tl^{+3}] = 0.0025 M, [Co^{+2}] =0.005 M

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (b)   2. (d)   3. (c)   4. (b)   5. (a)   6. (d)   7. (a, b)   8. (a)   9. (c)   10. (a)
11. (d)   12. (b)

Hints and Solutions

LEVEL I

1. (b) $2SO_4^{--} \rightarrow S_2O_8^{-2} + 2e^-$
For 1 mole of $S_2O_8^{-2}$
Electricity required = 2F

$$= 2 \times 96500 = i \times t \times \frac{75}{100}$$

$$2 \times 96500 = i \times 3600 \times \frac{75}{100}$$

$i = 71.48$ Amp.

2. (d) $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2(g)$, $\left[E = E^0 - \frac{0.0591}{n}\log Q\right]$

$$= 0.0 - \frac{0.0591}{1}\log\frac{[P_{H_2}]^{1/2}}{[H^+]} = \frac{0.591}{1}\log\frac{1}{10^{-7}}$$

$$= –0.0591 \times 7 \times \log 10 = –0.413 \text{ V}$$

3. (d) More the E^0_{RP}, more is the tendency to get reduced or lesser is tendency to get oxidised. $E^0_{RP(Cr^{3+}/Cr^{2+})}$ is lowest or $E^0_{OP(Cr^{2+}/Cr^{3+})}$ is maximum among all.

4. (a) $E = E^0_{cell} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$

Since $E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$

$$= 1.10 + \frac{0.059}{2}\log\frac{0.1}{1} = 1.07 \text{ V}$$

5. (c) At anode, either Ag can get oxidised to Ag^+ or Sn^{2+} to Sn^{4+} or Cl^- to Cl_2 or SO_4^{2-} to $S_2O_8^{2-}$. Their respective oxidation potential values are –0.799 V, –0.13 V, –1.36 V and –2 V. From these values, it is evident that Sn^{2+} would be oxidised first, followed by Ag at anode. At cathode, either Na^+ can get reduced to Na or Sn^{2+} to Sn or H^+ to H_2. The reduction potential value of Na^+ is highly negative while for Sn^{2+} | Sn is –0.14 V and for $H^+ + e^- \longrightarrow \frac{1}{2}H_2 \left(E_{H^+|H_2} = -0.059 \log\frac{1}{10^{-7}}\right)$ is –0.41 V. Thus, Sn^{2+} will get reduced at cathode followed by H^+.

6. (d) $\Lambda^0_{NaBr} = \Lambda^0_{NaCl} + \Lambda^0_{KBr} - \Lambda^0_{KCl} = 126 + 152 – 150 =$ 128 S cm^2 mol^{-1}

7. **(d)** During electrolysis of $CuSO_4$ solution using Cu electrodes, the cell reaction is

Anode: $Cu(s) \longrightarrow Cu^{++} + 2e^-$

Cathode: $Cu^{++}(aq) + 2e^- \longrightarrow Cu(s)$

The loss in weight of anode is equal to gain in weight of cathode.

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

8. **(b)** Weight of copper deposited $= 10 \times 10 \times 10^{-2} \times 8.94 = 8.94$ g

Number of moles of copper deposited $= \dfrac{8.94}{63.54}$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Number of Faradays needed to deposit 1 mole of Cu is two.

$$\therefore \text{ charge} = \frac{2 \times 8.94}{63.54}\text{F} = \frac{2 \times 8.94 \times 96500}{63.54}\text{C} = 27155 \text{ C}$$

9. **(b)** At anode $Zn \rightarrow Zn^{+2} + 2e^-$

At cathode $Cu^{+2} + 2e \rightarrow Cu$

2F required for 1 mole Zndisolution into Zn^{+2} (means weight loss) and 1 mole Cu deposite means weight Gain

$$\therefore \quad \frac{9.65 \times 60 \times 60}{96500} = 0.36 \text{ F}$$

$$\Rightarrow \quad \frac{1}{2} \times 0.36 \text{ Mole Zn (Loss in wt.)} = 11.77 \text{ gram}$$

$$\Rightarrow \quad \frac{1}{2} \times 0.36 \text{ Mole Cu (Loss in wt.)} = 11.43 \text{ gram}$$

10. **(b)**
$$\begin{aligned} E_{\text{cell}} &= E_{\text{ox}} + E_{\text{red}} \\ &= E_{\text{ox}} - E_{\text{ox}} \\ &= 0 \end{aligned}$$

11. **(a)** Best reducing agent is one which is itself oxidised most easily, viz, A. SinceAlkali metal have –ve SRP

$\therefore$ given data are in SRP.

12. **(b)** $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \dfrac{\text{RT}}{\text{nF}} \text{ in } \dfrac{[\text{Zn}^{2+}][\text{Cl}^-]^2}{\text{P}_{\text{Cl}_2}}$

13. **(a)** In the given reaction, I^- has been oxidised to I_2 and $Cr_2O_7^{2-}$ ions have been reduced to Cr^{+3}

$$\therefore \quad E^{\circ}_{\text{cell}} = E^{\circ}_{Cr_2O_7^{2-}/Cr^{+3}} - E^{\circ}_{I_2/I^-}$$

i.e., $0.79 = 1.33 - E^{\circ}_{I_2/I^-}$ or $E^{\circ}_{I_2/I^-} = 0.54$ V

14. **(d)**
$$\begin{aligned} \Delta G &= -nFE_{\text{cell}} \\ &= -2 \times 96500 \times 0.6753 \text{ (at 25°C)} \\ &= -130333 \text{ J} \end{aligned}$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right) \left[\frac{\partial E}{\partial T} \text{ is called temperature coefficient of cell}\right]$$

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{E_2 - E_1}{T_2 - T_1}$$

$$= \frac{0.6753 - 0.6915}{298 - 273} = -6.48 \times 10^{-4}$$

$\therefore \quad \Delta S = 2 \times 96500 \times (-6.48 \times 10^{-4})$

$-125.064 \text{ J mol}^{-1}$

$\Delta G = \Delta H - T\Delta S$. Substituting the values, we get

$\Delta H = 167.6$ kJ.

15. **(a)** For 1 mole of O_2, $O_2 \longrightarrow \dfrac{2}{3} \times 3O^{2-}$

so that $n = \dfrac{2}{3} \times 6 = 4$.

Hence, $\Delta G = -nFE$ given

$$E = \frac{\Delta G}{-nF} = \frac{-827000}{-4 \times 96500} = 2.14 \text{ volt.}$$

16. **(d)** Large negative reduction potential means large positive oxidation potential which implies that A– is easily oxidised.

17. **(b)** Just because of a convention.

18. **(b)**

At cathode: $2H^+ + 2e^- \rightleftharpoons H_2(P_2)$

At anode: $H_2(P_1) \rightleftharpoons 2H^+ + 2e^-$

Oveall reaction: $H_2(P_1) \rightleftharpoons H_2(P_2)$

$$E = E^{\circ} - \frac{RT}{nF}\ln\frac{P_2}{P_1} = 0 - \frac{RT}{2F}\ln\frac{P_2}{P_1} = \frac{RT}{2F}\ln\frac{P_1}{P_2}$$

19. **(c)** For water at 298 K, $[H^+] = 10^{-7}$ M

Reduction reaction is $H^+ + e^- \longrightarrow \dfrac{1}{2}H_2$

$$\therefore \quad E = -\frac{\text{RT}}{\text{F}}\ln\frac{P_{\text{H}}^{1/2}}{[\text{H}^+]} = -0.0591 \log\frac{P_{\text{H}_2}^{1/2}}{[\text{H}^+]}$$

$$= -0.0591 \log\frac{1}{10^{-7}}$$

$$= -0.4137 \simeq -0.414 \text{ V}$$

20. **(b)** $\text{Conductivity} \propto \dfrac{\text{Area} \times \text{Concentration}}{\text{Length}}$

or $\quad \text{Conductivity} = K \times \dfrac{\text{Area} \times \text{Concentration}}{\text{Length}}$

or $\quad K = \dfrac{\text{Conductivity} \times \text{Length}}{\text{Area} \times \text{Conc.}}$

$$= \frac{S \times m}{m^2 \times \text{mol m}^{-3}} = \text{S m}^2 \text{ mol}^{-1}.$$

21. **(b)** The plot of $\wedge_m$ vs $\sqrt{c}$ is linear according to Debye-Huckel onsager equation.

22. **(c)** $\wedge^{\circ}_m(\text{CaCl}_2) = \lambda^{\circ}_m(\text{Ca}^{2+}) + 2\lambda^{\circ}_m(\text{Cl}^-)$

$= 118.88 \times 10^{-4} + 2(77.33 \times 10^{-4})$

$= 273.54 \times 10^{-4} \text{ m}^2 \text{ mho mol}^{-1}$.

23. **(c)** Cu^{2+} ions gain electrons and are deposited on copper.

24. **(a)** Iron loscs electrons to form Fe^{2+} only when it acts as anode.

25. **(a)** $Al^{3+} + 3e^- \longrightarrow Al$

$\therefore$ 1 millimole require

$\therefore$ $3 \times 96.5\ C = 9.6\ A \times$ time in sec.

$$\text{Time} = \frac{3 \times 96.5}{9.65} = 30\ s$$

26. **(c)** $\frac{1}{2}H_2 + AgI \longrightarrow H^+ + Ag + I^- \qquad E = 0$

$\because$ $AgI + I^- \rightarrow Ag + I^-\ E = -0.151$

$\therefore$ $\frac{1}{2}H_2 \longrightarrow H^+ + e^- \quad E = 0.151$

$$0.151 = -\frac{0.059}{1}\log[H^+] = 0.059 \times pH$$

$$pH = \frac{0.151}{0.059} = 2.5$$

27. **(c)** For the given cell reaction,

$$\Delta G^o = -nFE^o_{cell} = -RT \ln K_{eq}$$

$$-5 \times 96500 \times 0.59 = -2.303 \times 8.314 \times 298 \log K_{eq}$$

$$K_{eq} = 7.8 \times 10^{49} \approx 10^{50}$$

28. **(a)** The half-cell reaction for hydrogen half-cell acting as cathode is

$$2H^+ + 2e^- \longrightarrow H_2$$

$$E_{H^+|H_2} = E^o_{H^+|H_2} - \frac{0.059}{2}\log\frac{P_{H_2}}{[H^+]^2}$$

$\therefore$ $E_{H^+|H_2} = -\frac{0.059}{2}\log\frac{1}{[H^+]^2}$

Now, when the pressure of H_2 gas is changed to 100 atm without changing $[H^+]$, the reduction potential becomes

$\therefore$ $E'_{H^+|H_2} = -\frac{0.059}{2}\log\frac{100}{[H^+]^2}$

$\therefore$ change in reduction potential =

$$E_{H^+|H_2} - E'_{H^+|H_2} = \frac{0.059}{2}\log\frac{100}{[H^+]^2} \times \frac{[H^+]^2}{1} = 0.059\ V$$

29. **(d)** During electrolysis of an aqueous solution of Na_2SO_4, the following reactions occur at the electrodes.

Anode: $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$

Number of Faradays needed to liberate 1 mole of O_2 = 4.

$\therefore$ charge $= \frac{2.4 \times 4}{22.4} F$

Number of moles of H_2 liberated by 1 F of charge $= \frac{1}{2}$

Number of mole of $H_2 = \frac{2.4 \times 4}{2 \times 22.4}$

Volume of H_2 of STP $= \frac{2.4 \times 4 \times 22.4}{2 \times 22.4} = 4.8\ L$

30. **(b)** $AgI + e^- \longrightarrow Ag + I^-\ E° = -0.151$ (i)

$Ag^+ + e^- \longrightarrow Ag\ E° = 0.799$ (ii)

$\therefore$ (i) – (ii)

$AgI \rightleftharpoons Ag^+ + I^- \qquad E° = -0.151 - 0.799$

$E° = -0.95 \qquad E = E° - \frac{0.0591}{1}\log K_{sp}$

$-16.074 = \log_{10} K_{sp}$, $\therefore K_{sp} = 7.91 \times 10^{-17}$

31. **(b)** $W = Zit = \frac{40}{96500} \times 9.65 \times 10^3 = 4\ g$

32. **(c)** $E° = \frac{0.0591}{2}\log K \qquad 1.1 \times 2 = 0.06 \log K$

$36.22 = \log K \qquad 10^{36.22} = K_f$

$8.314 \times 10^{36} = K$

33. **(a)** $E_{cell} = 0.80 - \frac{0.0591}{1}\log\left[\frac{1}{10^{-3}}\right] = 0.623\ V$

34. **(c)** $\overset{0}{H_2} + \frac{1}{2}O_2 \longrightarrow \overset{+1}{H_2}O^{-2} = 2F$

35. **(d)** See derivation of metal metal sparingly soluble electrode.

When act as cathode (reduction half cell)

(Result)

$$E_{I^-/AgI/Ag} = E^o_{Ag^+/Ag} + \frac{0.0591}{1}\log[Ag^+] = E^o_{Ag^+/Ag}$$

and

$$E^o_{I^-/AgI/Ag} = E^o_{Ag^+/Ag} + \frac{0.0591}{1}\log Ksp\ AgI$$

$= 0.80 + 0.0591 \log [8.3 \times 10^{-17}]$

$+ 0.80 - 0.95 = -0.15\ V$

36. **(a)** $2Fe^{2+} + Sn^{+4} \longrightarrow 2Fe^{3+} + Sn^{+3}$

$E° = E_C° - E_A° = 0.15 - 0.77 = -0.62\ V$

37. **(b)** $Ni(s) + 2H_2 \longrightarrow NiSO_4 + H_2$

$$0.236 = E° - \frac{0.0591}{1}\log\frac{1}{1}$$

$-nFE° = \Delta G°$

$\Delta G° = -2 \times 96500 \times 0.236 = 45.55\ kJ$

38. **(a)** $Fe^{3+} \longrightarrow Fe^{2+}$

$$E_{cell} = 0.770\ V - \frac{0.0591}{1}\log\frac{1.5}{0.015}$$

$= 0.770 - 0.059 \times 2 = 0.652\ V$

39. **(c)** $K = 1.12 \times 10^{-2}$ mho – cm^{-1}

N/10 KCl solution

$$K = \frac{1}{R} \cdot \frac{l}{A}$$

$$1.12 \times 10^{-2} = \frac{1}{65} \times \frac{l}{A}$$

$l/A = 0.728\ cm^{-1}$

40. **(d)** $K_{(H_2O)} = 5.8 \times 10^{-8}$ mho – cm^{-1}

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$C - C\alpha \qquad C\alpha \quad C\alpha$$

$\text{Kd} = \text{C}\alpha^2$

$C = 55.55\ \text{M}$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$$

$$\alpha = \frac{\text{K} \times \dfrac{1000}{\text{M}}}{\Lambda^\infty_{mH^+} + \Lambda^\infty_{mOH^-}}$$

Data insufficient

λ_∞ (H^+) must be given

41. (d) $Ag^+ + e^- \longrightarrow Ag$

$$E_{cell} = E° - \frac{0.059}{1}\log\left[\frac{1}{0.1}\right]$$

$$= E°_{red} - 0.059$$

42. (b) $Cu^{2+} + 2e^- \longrightarrow Cu$

$V_1 = 1, \quad C_1 = 1\ \text{M}$

$V_2 = 10, \quad C_2 = 0.1\ \text{M}$

$$E_{cell} = E° - \frac{0.0591}{2}\log\frac{1}{1} \qquad E_{cell} = E°$$

$$E_{cell} = E° - \frac{0.0591}{2}\log\left[\frac{1}{0.1}\right]$$

$$= E° - 0.059/2 = E° - 0.030$$

43. (a) $H_2 \longrightarrow 2H^+ + 2e^-$

$\text{pH} = 1, [H^+] = 10^{-1} \qquad E° = 0$

$$E = \frac{0.0591}{2}\log\frac{[H_2]}{[H^+]^2} = \frac{0.0591}{2}\log\left[\frac{1}{10^{-1}}\right]^2$$

$$= \frac{0.0591}{2} \times 2 = 0.0591\ \text{V}$$

44. (a) $E = E^o_{cell} - \dfrac{0.0591}{n}\log\left[\dfrac{P}{R}\right]$ if $\left[\dfrac{P}{R}\right] = 1$ then $E_{cell} = E^o_{cell}$

45. (d) $Fe^{3+} + 3e^- \longrightarrow Fe \quad \Delta G_1 = -nF\,E°_{cell} = -3F\,E°_{cell}$

$Fe^{2+} + 2e^- \longrightarrow Fe \quad \Delta G_2 = -2F\,E°_{cell}$

$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad \Delta G_3 = -F\,E°_{cell}$ required

$\because \quad \Delta G_3 = \Delta G_1 - \Delta G_2$

$-F\,E_{cell} = -3F\,E°_{cell} + 2F\,E_{cell}$

$-E_{cell} = -3 \times (-0.036) + 2\,(-0.440)$

$-E_{cell} = -\,0.772 \qquad E_{cell} = +\,0.772\ \text{V}$

46. (c) $2H^+ + 2e^- \longrightarrow H_2 \qquad \text{pH} = 10, [H^+] = 10^{-10}$

$E° = 0$

$$E_{red} = \frac{0.0591}{2}\log\frac{[H^+]^2}{P_{H_2}(g)} = \frac{0.0591}{2} \times 2\log[10^{-10}]$$

$$= \frac{0.0591}{2} \times 2 \times [-10] = -0.591\ \text{V}$$

47. (c) $E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.80 - (-0.25) = 1.05\ \text{V}$

48. (c) $E^o_{cell} = E^o_{cathode} - E^o_{anode} = 1.50 - (-0.25) = 1.75\ \text{V}$

49. (c) $2Cl^- \longrightarrow Cl_2 + 2e^-$

$$W = Zit = \frac{F}{F}i \times t$$

$$= \frac{71}{2 \times 96500} \times 2 \times 2.5 \times 60 = 0.110\ \text{g}$$

50. (b) $E_{cell} = 0.29 - \dfrac{0.0591}{2}\log\dfrac{[Cl^-]^2[Br_2]}{[Br^-]^2[Cl_2]}$

$$= 0.29 - \frac{0.0591}{2}\log\frac{[10^{-2}]^2[10^{-2}]}{[10^{-2}]^2[1]}$$

$$= 0.29 + \frac{0.0591}{2} \times 2 = 0.349 \approx 0.35\ \text{V}$$

51. (b) $Fe^{+2} + 2e^- \to Fe$

2F charge = 1 mole Fe = 56 gram

$\therefore \quad$ 1 F charge = $\dfrac{56}{2}$ gram

$\therefore \quad$ 3 F charge = $\dfrac{56}{2} \times 3 = \dfrac{168}{2}$ = 84 gram

52. (d) $Ag^+, \quad Cu^{2+}, \quad Au^{3+}$

$$\frac{1}{1} : \frac{1}{2} : \frac{1}{3}$$

$$= 6 : 3 : 2$$

53. (a)

$E^o_{cell} = E^o_{cathode} - E_{anode} \qquad 0.80 = E^o_{Ag^+/Ag} - E^o_{H^2/H^+}$

$0.80 = E^o_{Ag^+/Ag} - 0$

$E^o_{oxidation} = -E^o_{red} = -0.80\ \text{V}$

54. (d) $\Delta G° = -nF\,E°_{cell} \qquad (\because 1\ F = 96500\ C)$

$= -2 \times 0.360 \times 96500 = -69480\text{J} = -69.48\ \text{kJ}$

55. (d) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O = 5\ F$

56. (d) $Cu^+ + e^- \longrightarrow Cu \qquad \Delta G_1 = -F\,E° = -\,FX_1$

$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \Delta G_2 = -2F\,E° = -2FX_2$

$Cu^{2+} + e^- \longrightarrow Cu^+ \qquad \Delta G_3 = -F\,E°$

$\Delta G_3 = \Delta G_2 - \Delta G_1 \qquad -FE° = -2FX_2 + FX_1$

$E° = 2X_2 - X_1$

57. (b) $W = \text{Zit} = \dfrac{E}{F}it = \dfrac{\text{Atomic wt.} \times i \times t}{n \times F}$

$$0.275 = \frac{\text{atomic wt.} \times 14 \times 965}{2 \times 96500}$$

Atomic wt. = 0.550 × 100 = 55

58. (b) $\dfrac{w_1}{w_2} = \dfrac{(E_1)_{Ag}}{(E_2)_{metal}} \quad \dfrac{0.5094}{0.2653} = \dfrac{\left(\dfrac{\text{atomic weight}}{\text{valency factor}}\right)_{Ag}}{\left(\dfrac{\text{atomic weight}}{\text{valency factor}}\right)_{metal}}$

$\dfrac{0.5094}{0.2653} = \dfrac{(\text{valence factor})_{Metal}}{1}$ valence factor $1.9 \approx 2$

LEVEL II

1. (c)

$$\overset{+6}{SO_4^{-2}} + 2e \longrightarrow \overset{+4}{SO_3^{-2}}\ E_1^o = -0.936$$

$$\overset{+4}{SO_4^{-2}} + 2e \longrightarrow \frac{1}{2}\overset{+2}{S_2O_3^{-2}}\ E_2^o = -0.576$$

$$\therefore \quad SO_4^{-2} + 4e \longrightarrow \frac{1}{2}S_2O_3^{-2}$$

$$nE^\circ = n_1E_1^o + n_2E_2^o \qquad E^\circ = \frac{-2\times 0.936 - 2\times 0.576}{4}$$

$$= -0.756\ \text{V}$$

2. (b)

$$\underset{0.01}{Cr_2O_7^{-2}} + \underset{10^{-3}}{14H^+} + 6e \longrightarrow \underset{0.01}{2\,Cr^{3+}} + 7H_2O \qquad E^\circ = 1.33\ \text{V}$$

$P_{OH} = 11$

$PH = 3$

$[H^+] = 10^{-3}$

$$E_{cell} = E^o{}_{cell} - \frac{0.0591}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{-2}][H^+]^{14}}$$

$$= 1.33 - \frac{0.0591}{6}\log\frac{[0.01]^2}{[0.01]\times[10^{-3}]^{14}} = 0.936\ \text{V}$$

3. (d) $NO_2^-(g) + H_2O \longrightarrow NO_3^-(aq) + 2H^+(aq) + 2e$

$E^o = 0.78$ V

$$E_{cell} = E_{cell}^o - \frac{0.0591}{2}\log\frac{1}{[H^+]^2}$$

$$= 0.78 - \frac{0.0591}{2}\times\log\left(\frac{1}{9}\right)^2$$

$$= 0.78 - \frac{0.0591}{2}\times 2[-\log 9]$$

$$= 0.78 + 0.056 = 0.836\ \text{V}$$

4. (b) $A: M - ne \longrightarrow \underset{(0.02\,M)}{M^{n+}} \qquad E^o = +0.76$

$$C: \underset{(1m)}{nH^+} + ne \longrightarrow \frac{n}{2}H_2(g) \qquad E^o = 0$$

$$M + nH^+ \longrightarrow M^{n+} + \frac{n}{2}H_2(g). \quad E^o = +0.76$$

$$E_{cell} = 0.81 = +0.76 - \frac{0.0591}{n}\log\frac{[M^{n+}]}{[H^+]^n}$$

$$= +0.76 - \frac{0.0591}{n}\log\frac{0.02}{1}$$

$$= +0.76 + \frac{0.0591}{n}\log\frac{1}{0.02}$$

$$= +0.76 + \frac{0.0591}{n}\times 1.7$$

$$\frac{0.0591}{n}\times 1.7 = 0.81 - 0.76$$

$$n = \frac{0.0591\times 1.7}{0.05}$$

$$= 2$$

5. (a) $E_{cell} = E_{cell}^o \dfrac{-0.0591}{n}\log Q$

$E_{cell}^o = 0$

At Anode: $H_2 - 2e \longrightarrow 2H^+\ (aq)$

At Cathode: $2H^+(aq) + 2e \longrightarrow H_2(g)$

$$E_{cell} = 0 - \frac{0.0591}{2}\log\frac{[H^+]_A^2}{[H^+]_C^2}$$

At cathode:

$$[H^+] = \frac{25\times 10^{-3}}{500\times 10^{-3}} = \frac{25}{500} = (5\times 10^{-2})$$

At Anode:

$$PhNH_2 + H_2O \rightleftharpoons PhNH_3^+ + OH^-$$

$$[OH^-] = \sqrt{\frac{K_b}{C}}$$

$$\therefore \quad [OH^-]^2 = \frac{10^{-9}}{\frac{0.5}{500}} = 10^{-6}$$

$$\therefore \quad [H^+] = 10^{-8}$$

$$\therefore \quad E_{cell} = +\frac{0.0591}{2}\log\frac{(5\times 10^{-2})^2}{(10^{-8})^2}$$

$$= +\frac{0.0591}{2}\log[5\times 10^6]^2$$

$$= +0.0591[6 + 0.7]$$

$$= 0.0591\times[6.7]$$

$$= +0.395\ \text{V}$$

6. (a) $\left(\dfrac{dE}{dT}\right)_p = -4\times 10^{-5}\ \text{V/deg}$

$n = 2$

$E_{cell}^o = 1.0181\ \text{V}$

$\Delta G^o = -2FE_{cell}^o$

$= -2\times 96500\times 1.018$

$= -196474$ J

$= -196.5$ kJ

$$\Delta S^o = nF\left(\frac{dE}{dT}\right) = -2\times 96500\times 4\times 10^{-5}$$

$$= -7.72\ \text{J/deg}$$

$$\Delta H^o = nF\left(T\left(\frac{dE}{dT}\right)_p - E_{cell}^o\right) = 198.8\ \text{KJ}$$

7. **(a)** Use the formula $\Delta H^o = nF\left(T\left(\frac{dE}{dT}\right)_p - E^o_{cell}\right)$

$n = 1$

$\frac{dE}{dT} = -0.125\ V/K$

$E^o_{cell} = 0.0732\ V$

8. **(b)** $Q = it$

$i = 0.193$ A, $t = 1$ hr $= 60 \times 60$ sec

$\therefore \quad Q = 0.193 \times 3600$

$= 694.8C = \frac{694.8}{96500}F$

$= 7.2 \times 10^{-3}$ F

$= 7.2 \times 10^{-3}$ Mole Na^+

$= 7.2 \times 10^{-3}$ Mole (NaOH)

$[OH^-] = \frac{7.2 \times 10^{-3}}{0.1} = 7.2 \times 10^{-2} M$

$POH = 2 - \log 7.2\ ;\ p^H = 14 - p^{OH}\ ; = 12 + \log 7.2 = 12.82$

9. **(a)** $E_{cell} = 3.17 - \frac{0.059}{2}\log\frac{(10^{-1})}{(10^{-4})^2}$

$= 3.170 \times 0.02951 \log 10^7$

$= 3.17 - 0.21 = 2.96\ V$

10. **(c)** Thickness of silver deposited $= x$ cm

Weight of Ag deposited = density × V = $10.47 \times 800x$ g

Now $800 \times 10.47x = \frac{108}{96500} \times 0.2 \times 3 \times 3600$

$x = 2.88 \times 10^{-4}$ cm

11. **(d)** $E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Ni^{+2}]}{[H^+]^2}$

$0 = 0.236 + 0.0591 \log[H^+]$

$0.236 = -0.591 \log[H^+]$

$= 0.0591\ Ph$

$P^H = 3.99 = 4.00$

12. **(b)** Equivalent conductance at infinite dilution for $AgNO_3 = 133.3\ ohm^{-1}cm^2eq^{-1}$

$t_{Ag^+} = 0.464$

$\therefore \quad \lambda_{Ag^+} = 133.3 \times 0.464$

$= 61.85$

13. **(b)** Number of equivalent of I_2 reduced

$= 46.3 \times 10^{-3} \times 0.124$

$= 5.7 \times 10^{-3}$

Number of equivalent of I_2 = Number of equivalent of metal

$5.7 \times 10^{-3} = \frac{0.617}{E}$

$E = 108.2$

14. **(c)** Volume $= 8.2 \times 10^{12}$ L

Taking density app 1 g/c.c

Mass of H_2O in the lake $= 8.2 \times 10^{12}$ kg

$= 8.2 \times 10^{15}$ g

$H_2O \rightarrow H^+ + OH^-$

At cathode: $2H^+ + 2e^- \rightarrow H_2(g)$

At anode: $2OH^- - 2e \rightarrow H_2O + \frac{1}{2}O_2(g)$

$W = \frac{E}{F} \times i \times t$

$\therefore \quad t = \frac{W \times F}{E \times i}$

$t = \frac{8.2 \times 10^{15} \times 96500}{1.5 \times 10^6 \times 9 \times 3600 \times 24 \times 365}$

$= 1.9 \times 10^6$ years

$= 1.9$ million years

15. **(b)** Pt, H_2 (1 atm)/CH_3COOH (0.1 M)//NH_3 (aq, 0.01 M)/H_2 (1 atm) Pt

$K_a(CH_3COOH) = 1.8 \times 10^{-5}$

$K_b(NH_3) = 1.8 \times 10^{-5}$

At anode: $\frac{1}{2}H_2 - e \longrightarrow H^+ \qquad E^o = 0$

At Cathode: $H^+ + e \longrightarrow \frac{1}{2}H_2(g) \qquad E^o_{cell} = 0$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{1}\log\frac{[H^+]_A}{[H^+]_C} \qquad (1)$$

$[OH^-]^2 = 0.01 \times 1.8 \times 10^{-5}$

$[OH^-] = 4.2 \times 10^{-4}$

$[H^+]_C = \frac{10^{-14}}{4.2 \times 10^{-4}}$

Similarly,

$[H^+]^2 = 1.8 \times 10^{-5} \times 0.1$

$[H^+]_A = \sqrt{1.8 \times 10^{-6}}$

From equation (1)

$E_{cell} = -0.0591 \times 7.78$

$= -0.46\ V$

16. **(a)** $Ag(NH_3)_2^+ + e \rightleftharpoons Ag + 2NH_3 \qquad E^o = X volt$

$Ag - e \rightleftharpoons Ag^+ \qquad E^o = -0.7991$

$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3 \quad E^o = X - 0.791$

At Equilibrium

$E_{cell} = 0 \quad K_{[Ag(NH_3)_2]^+} = 6.02 \times 10^{-8}$

$E^o = X - 0.7991 = \frac{0.06}{1}\log K$

$$\Rightarrow \quad X = 0.7991 + 0.06 \times \log(6 \times 10^{-8})$$
$$= 0.372 \text{ V}$$

Similar method applies to second question.

17. **(d)** $\lambda_{(aq)} = 97.1$ mho – cm^2/eq.

$A = 1.5$

$l = 0.5$

Normality = 0.1 N

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

$$97.1 = \frac{\frac{1}{R}\frac{l}{A} \times 1000}{N}$$

$$97.1 \times 0.1 = \frac{1}{R} \times \frac{0.5}{1.5} \times 1000$$

$$\therefore \quad R = \frac{1000}{9.71 \times 3} = 34.32\ \Omega$$

$$\therefore \quad i = \frac{V}{R} = \frac{5}{34.32} = 0.1456 \text{ Amp.}$$

18. **(d)** Quantity of electricity passed = (5 A) × (20 × 60 s) = 6000 C; $Ni^{2+} + 2e^- \longrightarrow Ni$

Thus, 2F, i.e., 2 × 96500 C deposit Ni = 1 mol, i.e., 58.7 g

$\therefore$ 6000 C will deposit Ni = $\frac{58.7}{2 \times 96500} \times 6000$ g = 1.825 g

19. **(a)** $Ag^+ + e^- \longrightarrow Ag$, i.e., 108 g of Ag are deposited by 1 F = 96500 C

1.45 g of Ag will be deposited by $\frac{96500}{108} \times 1.45$ C = 1295.6 C

$Q = i \times t$ or $t = Q/i$ = 1295.6/1.50 = 863.7 s = 14.40 Min

i.e., 2 × 96500 C deposit Cu = 63.5 g

$\therefore$ 1295.6 C will deposit Cu = $\frac{63.5}{2 \times 96500} \times 1295.6$

$$= 0.426 \text{ g}$$

$$Zn^{2+} + e^- \longrightarrow Zn$$

$$\therefore \quad \text{Zn deposited} = \frac{65.3}{2 \times 96500} \times 1295.6 = 0.438 \text{ g}$$

20. **(b)** Reaction at anode of fuel cell,

$$\begin{array}{lcl} H_2(g) & \longrightarrow & 2H^+ + 2e^- \\ 1 \text{ mole} & & 2 \text{ mole} \\ 22.4 \text{ L} & & 2 \text{ F} \end{array}$$

67.2 L of H_2 correspond = $\frac{2 \times 96500}{22.4} \times 67.2$ coulomb

Time = 15 × 60 sec

$$\text{Average current} = \frac{2 \times 96500 \times 67.2}{22.4 \times 15 \times 60} = 643.3 \text{ amp}$$

Mass of copper deposited by $\frac{2 \times 96500}{22.4} \times 67.2$ coulomb

$$= \frac{63.5}{2 \times 96500} \times \frac{96500 \times 67.2}{22.4} = 190.5 \text{ g}$$

21. **(d)** Weight of solution before discharge

= 3500 × 1.294 = 4529 g

Weight of H_2SO_4 before discharge

$$= \frac{39}{100} \times 4529 = 1766.31 \text{ g}$$

Weight of solution after discharge

= 3500 × 1.139 = 3986.5 g

Weight of H_2SO_4 after discharge

$$= \frac{20}{100} \times 3986.5 = 797.3 \text{ g}$$

Loss in mass of H_2SO_4 during discharge = 1766.31 – 797.3 = 969.01 g

Now from first law of electrolysis,

$$W = \frac{Q \times E}{96500};\ 969.01 = \frac{Q \times 98}{96500};$$

Q = 954178.21 coulomb

$$\text{Ampere-hour} = \frac{\text{Coulomb}}{3600} = \frac{954178.21}{3600}$$

= 265.04 ampere-hour.

22. **(b)** $MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

According to Nernst equation,

$$E_{red} = E^o_{red} - \frac{0.0591}{5}\log\left[\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right]$$

Let $[H^+]_{initial} = X$

$$E_{red(initial)} = E^o_{red} - \frac{0.0591}{5}\log\left[\frac{[Mn^{2+}]}{[MnO_4^-][X]^8}\right]$$

$$[H^+]_{final} = \frac{X}{100} = \frac{X}{10^2}$$

$$E_{red(final)} = E^o_{red} - \frac{0.0591}{5}\log\frac{[Mn^{2+}] \times 10^{16}}{[MnO_4^-] \times [X]^8}$$

$$E_{\,red(final)} - E_{\,red(initial)} = \frac{-0.0591}{5}\ \log 10^{16} = -0.1891 \text{ V}$$

This E_{red} decreases by 0.189 V. The tendency of the half-cell to get reduced is its oxidising power. Hence the oxidising power decreases by 0.189 V.

23. **(a)** For the cell reaction

$$Ag(s) + \frac{1}{2}Cl_2(g) \longrightarrow AgCl(s)$$

$$E^0 = 1.36 - 0.22 = +1.14\text{V}$$

$$\text{or} \quad E = E^\circ - \frac{0.0591}{1}\log\frac{1}{(P_{Cl_2})^{1/2}}$$

Under standard conditions $P_{Cl_2} = 1$,

$$\therefore \quad \log P_{Cl_2}^{1/2} = 0$$

Useful work = $-\Delta G = +nFE$

$= 1 \times 96500 \times 1.14 \times 10^{-3}$ kJ = 110 kJ mol^{-1}

24. **(d)** The cell corresponding to the given reaction is as follows.

$$Cr^{2+}(1\text{ M}) \mid Cr^{3+}(1\text{ M}) \parallel Cr^{2+}(1\text{ M}) \mid Cr(s)$$

$$\text{I } Cr^{3+} + 3e \longrightarrow Cr(s),\ \Delta G^{o}_{I} = -3FE^{o}_{Cr^{3+},Cr}$$

$$\text{II } Cr^{3+} + e \longrightarrow Cr^{2+},\ \Delta G^{o}_{II} = -FE^{o}_{Cr^{3+},\,Cr^{2+}}$$

Eq. I - Eq. II: $Cr^{2+} + 2e \longrightarrow Cr(s)$, $\Delta G^{o} = -3 \times 0.5\text{ F} - 0.41\text{ F} = -1.91\text{ F}$

$$\Delta G^{o} = -2FE^{o}_{Cr^{2+},Cr} = -1.91\text{ F}$$

$$\therefore\ E^{o}_{Cr^{2+},Cr} = \frac{1.91}{2} = 0.955\text{ V}$$

$$E^{o}_{cell} = E^{o}_{Cr^{2+},\,Cr} - E^{o}_{Cr^{3+},Cr^{2+}} = 0.955 + 0.41 = 1.365\text{ V}$$

E^{o}_{cell} is +ve so $\Delta G°$ is –ve and hence the given reaction is spontaneous

$\therefore \Delta G° = -nF\ E^{o}_{cell} = -2 \times 96500 \times 1.365\text{ J} = -263.44\text{ kJ}$

From Gibb's-Helmholtz equation

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_{P}$$

$$-263.44 = \Delta H + 298\frac{(-270.50 + 263.44)}{10}$$

$$= \Delta H - 298 \times 0.706$$

$$\therefore \quad \Delta H = -53.05\text{ kJ}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-53.05 + 263.44}{298}$$

$= 0.706$ kJ K^{-1} = 706 kJ K^{-1}.

25. **(c)**

$$w_{Ag} = \frac{\text{E.i.t}}{96500} = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500} = 272.18\text{g}$$

$$\text{Volume of Ag} = \frac{272.18}{10.5} = 25.92\text{ mL}$$

$$\text{Surface area } \frac{25.92}{0.00254} = 1.02 \times 10^{4}\text{ cm}^{2}$$

26. **(c)** The cell can be formed as $Fe|Fe^{3+}$; $OH^{-} \parallel Fe(OH)_3(s) \mid Fe$

The electrode reactions can be written as

$$Fe(s) \longrightarrow Fe^{3+} + 3e^{-}$$

$$Fe(OH)_3(s) + 3e^{-} \longrightarrow Fe(s) + 3OH^{-}$$

Overall reaction is, i.e., by adding

i.e., $E^{0} = E^{0}_{OH^{-}/Fe(OH)_3/Fe} - E^{0}_{Fe^{3+}/Fe}$ (i)

$E^{o}_{OH^{-}/Fe(OH)_3/Fe}$ can be calculated if we know E° and E° can be calculated as follows

$$E^{o} = \frac{0.0591}{3}\log 10^{-36.4} = \frac{0.0591 \times (-36.4)}{3} = 0.75\text{ V}$$

From (i)

$E^{o}_{OH^{-}/Fe(OH)_3/Fe} = -0.75 - 0.036 = -0.786$ V From (i)

27. **(b)** $Ag \longrightarrow Ag^{+}_{(a_1)} + e^{-}$

$$Ag^{+}_{(a_2)} + e^{-} \longrightarrow Ag$$

$$Ag^{+}_{(a_2)} \longrightarrow Ag^{+}_{(a_1)}$$

$$E = -\frac{0.0591}{1}\log\frac{a_1}{a_2}$$

$$= 0.0591\log\frac{a_2}{a_1} = 0.059\log\frac{0.1}{a_1} = 0.455$$

$$\log\frac{0.1}{a_1} = \frac{0.455}{0.059} = 7.71$$

$$\frac{0.1}{a_1} = \text{anti } 7.71 = 5.129 \times 10^{7}$$

$$a_1 = [Ag^{+}] = \frac{0.1}{5.129 \times 10^{7}} = 1.95 \times 10^{-9}$$

$[Cl^{-}] = 10^{-1}$

Solubility product of AgCl = $[Ag^{+}][Cl^{-}] = 1.95 \times 10^{-9} \times 10^{-1} = 1.95 \times 10^{-10}$

Solubility of AgCl = $[Ag^{+}] = [Cl^{-}] = \sqrt{1.95 \times 10^{-10}} = 1.396 \times 10^{-5}$ moles/L

28. **(d)** For AgCl, molarity = normality ∵ $n_f = 1$

actual specific conductance = (specific conductance of AgCl – specific conductance of water)

$= (3.41 - 1.60) \times 10^{-6}$

$= 1.81 \times 10^{-6}\ ohm^{-1}\ cm^{-1}$

For saturated solution of sparingly soluble salt

$\Lambda_{eq} = \Lambda^{\infty}_{eq}$, and solubility = concentration

$$\Lambda^{\infty}_{eq} = \frac{\text{Ksolute} \times 1000}{\text{S}}$$

$$\therefore \quad 138.3 = \frac{1.81 \times 10^{-6} \times 1000}{\text{S}}$$

$$S(\text{mol } L^{-1}) = \frac{1000 \times 1.81 \times 10^{-6}}{138.3} = 1.31 \times 10^{-5}\text{ mol L}^{-1}$$

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

$\therefore$ $K_{sp} = [Ag^{+}][Cl^{-}] = S^{2} = (1.31 \times 10^{-5})^{2} = 1.72 \times 10^{-10}\ mol^{2}\ L^{-2}$

29. **(a)** $CH_3COOH \rightleftharpoons CH_3COO^{-} + H^{+}$

$$K_a = \frac{[CH_3COO^{-}][H^{+}]}{[CH_3COOH]}$$

$$\therefore \quad [H^{+}] = \frac{Ka[CH_3COOH]}{[CH_3COO^{-}]}$$

For the first cell, $[H^{+}] = \dfrac{K_a \times y}{x}$

$$E_1 = E_{H_2|2H^{+}} = -\frac{0.0591}{2}\log\left(\frac{yK_a}{x}\right)^{2}$$

$$= -0.0591\log\left(\frac{yK_a}{x}\right)$$

For the second cell, $[H^+] = \dfrac{xK_a}{y}$

$$E_2 = E_{H_2|2H^+} = -\frac{0.0591}{2}\log\left(\frac{xK_a}{y}\right)^2$$

$$= -0.0591\log\left(\frac{xK_a}{y}\right)$$

$$E_1 + E_2 = -0.0591\log K_a^2$$

$$pK_a = \frac{E_1 + E_2}{0.118}$$

30. **(c)** The standard emf of the cell in which the following equilibrium is established

$$I_2 + I^- \rightleftharpoons I_3^-$$

is given by $(E^o_{I_2|I^-} - E^o_{I_3^-|I^-}) = \dfrac{0.059}{2}\log K_c$

Substituting the values of $E^o_{I_2|I^-}$ = 0.619 V, $E^o_{I_3^-|I^-}$ = 0.5355 V

$$(0.6197 - 0.5355) = \frac{0.059}{2}\log K_c$$

On solving, $K_c = 714.9$

31. **(d)** For the same charge,
equivalents of X = equivalents of Zn

$\dfrac{0.348}{E} = \dfrac{1.264 \times 2}{65.4}$, where E is equivalent weight of X.

On solving, $E = 9$.

Since, n-factor of X in XCl is 1, the molar mass of X = 9 g mol^{-1}.

32. **(b)** Given that E° = –0.268 V for Cl^- $|PbCl_2|$ Pb and

$E°$ = –0.126 V for Pb^{2+} | Pb

The $E°$ values of the two half-cells are related to each other as

$$E^o_{Cl^-|PbCl_2|Pb} = E^o_{Pb^{2+}|Pb} + \frac{0.0591}{2}\log K_{sp}(PbCl_2)$$

$$-0.268 = -0.126 + \frac{0.0591}{2}\log K_{sp}(PbCl_2)$$

On solving, $K_{sp}(PbCl_2) = 1.536 \times 10^{-5}\ M^3$.

33. **(a)** $2Ag^+ + H_2 \longrightarrow 2H^+ + 2Ag$

$$1.023 = (E^o_C - E^o_A) - \frac{0.0591}{2}\log\frac{[H^+]^2}{P_{H_2}[Ag^+]^2}$$

$$1.023 = (0.799 - 0) - \frac{0.591 \times 2}{2}\log[H]^+ + \frac{0.591 \times 2}{2}\log[X]^2$$

$$0.294 = 0.06 \times 5.5 + \frac{0.06}{2}\log[X]^2$$

$$= -0.036 = \frac{0.06}{2} \times 2\log X$$

$$= -0.6 = \log X$$

$$0.6 = \log\frac{1}{(X)},\ \log 4 = \log\frac{1}{X}$$

$$X = \frac{1}{4}M$$

$$= 0.25\ M$$

34. **(a)** $w = Z\,i\,t$ $\qquad w = \dfrac{E}{96500} \times i \times t$

$$\frac{w}{t} = \frac{200.6 \times 2 + 71}{2 \times 96500} \times i$$

$$= \frac{44}{3600} = \frac{236.1}{96500} \times i$$

$i = 5$ amp.

35. **(c)** $K_a = 25 \times 10^{-6}$ $\quad \Lambda^C_{eq.} = 19.6\ s\ cm^2\ eq^{-1}$

$$C = 0.01\ M \qquad \alpha = \sqrt{\frac{K_a}{C}} = \frac{\Lambda^C_{eq}}{\Lambda^\infty_{eq}}$$

$$\sqrt{\frac{25 \times 10^{-6}}{0.01}} = \frac{19.6}{\Lambda^\infty_{eq}} \Rightarrow \frac{5 \times 10^{-3}}{0.1} = \frac{19.6}{\Lambda^\infty_{eq}}$$

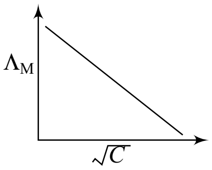
$$\Lambda_{eq} = \frac{19.6 \times 0.10}{5 \times 10^{-3}}$$

$$\frac{1960}{5} = 392\ Scm^2eq^{-1}$$

36. **(a)** $\Lambda_M = \Lambda^\circ_M - b\sqrt{C}$

$y = C - mx$

slope = –ve



37. **(c)** $H_2O \longrightarrow H_2 + \frac{1}{2}O_2 + 2e^-$

$$2H_2O \longrightarrow 2H_2 + O_2 + 4e^-$$

gases $[H_2 + O_2] = 2 \times 22.4 + 22.4 = 67.2$

38. **(c)**

$$A^1_\infty = \Lambda^\infty_{BaCl_2} = \frac{1}{2}\Lambda^\infty_{eq\,Ba^{2+}} + \Lambda^\infty_{eq\,Cl^-} \qquad (i)$$

$$A^2_\infty = \Lambda^\infty_{H_2SO_4} = \Lambda^\infty_{eq\,H^+} + \frac{1}{2}\Lambda^\infty_{eq\,SO_4^{-2}} \qquad (ii)$$

$$A^3_\infty = \Lambda^\infty_{HCl} = \Lambda^\infty_{H^+} + \Lambda^\infty_{Cl^-} \qquad (iii)$$

$$\Lambda^\infty_{eq\,BaSO_4} = \frac{1}{2}\Lambda^\infty_{eq\,Ba^{2+}} + \frac{1}{2}\Lambda^\infty_{eq\,SO_4^{2-}} \qquad (iv)$$

eq. (iv) = eq. (i) + eq. (ii) – eq. (iii)

$$= A^1_\infty + A^2_\infty - A^3_\infty$$

39. **(b)** From 2nd Law $W \propto E$

$$\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$$

$$n_1 \times \frac{2.1}{7} = n_2 \times \frac{2.7}{27} = n_3 \times \frac{7.2}{48}$$

$$0.3n_1 = 0.1n_2 \text{ and } 0.1n_2 = \frac{3}{2}n_3$$

$$n_2 = 3n_1 \quad \text{and} \quad 2n_2 = 3n_3$$

$$n_3 = \frac{2}{3}n_2 = \frac{2}{3}(3n_1) = 2n_1$$

$$n_1 : n_2 : n_3 = 1:3:2$$

40. **(b)** Cost = $\frac{5 \text{ paise}}{\text{KWH}} \times \text{hour} \times 15 \text{ amp} \times 110$

$$= \frac{5}{10^3 \times \text{WH}} 8 \times 15 \times 110 = \frac{66000}{10^3} = 66 \text{ paise}$$

41. **(b)** $\text{Ag} + \text{Cl}^- \longrightarrow \text{AgCl} + e^-$

$E = E° + 0.0591 \log [\text{Cl}^-]$

$-0.25 = E° + 0.0591 \log 0.1 \qquad \therefore\ E° = -0.1909$

Now for reaction

$\text{Ag} + \text{Cl}^- \longrightarrow \text{AgCl} + e^-$

$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$

$\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl}$

$$E = E^{\circ}_{\text{Ag/AgCl/Cl}-} + E^{\circ}_{\text{Ag+/Ag}} + 0.0591 \log \text{K}_{\text{sp}}$$

since $E = 0$ at equilibrium and $K_{\text{SP}} = \text{K}_{\text{eq}}$

$\text{O} = -0.1909 + 0.799 + 0.0591 \log \text{K}_{\text{sp}}$

$\text{K}_{\text{sp}} = 5.13 \times 10^{-11}$

42. **(a)** Given: $\text{Au}^{+3} + 3e^- \longrightarrow \text{Au} \rightleftharpoons \quad E_1^{\circ} = 1.5$

$\text{Au}^{+3} + 2e^- \longrightarrow \text{Au}^+ \rightleftharpoons \quad E_2^{\circ} = 1.4$

so for reaction $nE = n_1E_1 + n_2E_2$

$\text{Au} \longrightarrow \text{Au}^+ + e^- \quad \text{E}° = 2E_2^{\circ} - 3E_1^{\circ} \Rightarrow \text{E}° = -1.7$

$\text{Au} + 2\text{CN}^- \longrightarrow \text{Au(CN)}_2^- + e^- \qquad \text{E}° = x$

$\text{Au}^+ + e^- \longrightarrow \text{Au} \qquad \text{E}° = 1.7$

$$\text{O} = x + 1.7 - \frac{RT}{F}\ln X$$

$$x = \frac{RT}{F}\ln X - 1.7$$

For reaction

$\text{O}_2 + \text{H}_2\text{O} + 4e^- \longrightarrow 4\text{OH}^- \qquad \text{E}° = 0.41$

$$\text{Au} + 2\text{CN}^- \longrightarrow \text{Au(CN)}_2^- + e^- \quad \text{E}° = \frac{RT}{F}\ln X - 1.7$$

so for reaction

$$\text{Au} + 2\text{CN}^- + \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} \longrightarrow \text{Au(CN)}_2^- + \text{OH}^-$$

$$\text{E}° = 0.41 + \frac{RT}{F}\ln\text{X} - 1.7 = -1.29 + \frac{RT}{F}\ln\text{X}$$

$\Delta\text{G}° = -\text{nFE}° \ (n = 1)$

$\Delta\text{G}° = 1.29 \text{ F} - \text{RT} \ln\text{X}$

43. **(c)**

Anode: $\text{H}_2 \to 2\text{H}^+ + 2e^-$

Cathode: $\text{Cl}_2 + 2e^- \to 2\text{Cl}^-$

$\text{E} = \text{E}° - 0.0591 \log [\text{H}^+][\text{Cl}^-]$

on increasing concentration by 10 E will increase by a factor of $-0.0591 \log 100 = -0.0591 \times 2 = -0.1182$ V

44. **(d)**

$2\text{H}_2 + \text{O}_2 \to 2\text{H}_2\text{O} \qquad \Delta\text{H} = 2 \times (-285.5 \text{ kJ})$

$\text{O}_2 + 4\text{H}^+ + 4e^- \to 2\text{H}_2\text{O} \qquad \text{E}° = 1.23$

$2\text{H}_2 \to 4\text{H}^+ + 4e^- \qquad \text{E}° = 0$

for reaction:

$\text{O}_2 + 2\text{H}_2 \to 2\text{H}_2\text{O} \qquad \text{E}° = 1.23$

$\Delta\text{G}° = -\text{nFE}° = -4 \times 96500 \times 1.23 = -474780$

$\Delta\text{G}° = \Delta\text{H}° - \text{T}\Delta\text{S}°$

$-474780 = -571000 - 298\ \Delta\text{S}°$

$\Delta\text{S}° = -322.8$ J/K

45. **(c)** $\lambda_{\text{M}} = \frac{K \times 1000}{M}$

$$K = \frac{1}{R}\left(\frac{l}{a}\right) = \frac{1}{50}\left(\frac{2.2}{4.4}\right) = \frac{1}{100} = 0.01$$

$$\lambda_{\text{M}} = \frac{0.01 \times 1000}{0.5} = 20 \text{ S cm}^2 \text{ mole}^{-1}$$

$$= 20 \times 10^{-4} \text{ S m}^2 \text{ mole}^{-1} = 0.002 \text{ S m}^2 \text{ mole}^{-1}$$

46. **(b)** $K_a = 1.69 \times 10^{-5} = \text{C}\alpha^2 = 0.01\ \alpha^2 = \alpha = 0.04$

$$\alpha = \frac{\lambda_M}{\lambda_M^{\infty}} \Rightarrow \qquad \lambda_M = 0.04 \times 380$$

$$\lambda_M = 15.2 \text{ S cm}^2 \text{ mole}^{-1} \qquad \lambda_M = \frac{K \times 1000}{M}$$

$$15.2 = \frac{K \times 1000}{0.01}$$

$K = 1.52 \times 10^{-4} \text{ S cm}^{-1}$

$K = 1.52 \times 10^{-2} \text{ S m}^{-1}$

LEVEL III

(Match the Column)

1. **(A-r), (B-s), (C-p,t), (D-q)**

$\text{Ag/Ag}^+ \text{ (0.1 M)} \parallel \text{Cd}^{2+} \text{ (0.1 M)/Cd}$

0.1 M (0.1 M)

At anode: $2\text{Ag} - 2e \longrightarrow 2\text{Ag}^+ \qquad -0.8$ V

At cathod: $\text{Cd}^{2+} + 2e \longrightarrow Cd \qquad -0.4$ V

$2\text{Ag} + \text{Cd}^{2+} \longrightarrow 2\text{Ag}^+ + Cd \qquad -1.2$ V

(0.1 M) (0.1 M)

$$Q = \frac{[\text{Ag}^+]^2}{[\text{Cd}^{2+}]} = \frac{1}{10}$$

Due to –ve cell potential, reaction is non-spontaneous.

$$E_{\text{cell}} = -1.2 - \frac{0.0591}{2}\log\frac{1}{10}$$

$$= -1.2 + \frac{0.0591}{2}$$

$$= -1.17 \text{ V}$$

2. **(A-p,t), (B-q,t), (C-s,t), (D-r)**

$$Sn^{2+} + 2e \longrightarrow Sn \qquad E° = -0.14\ V$$

$$Sn^{4+} + 2e \longrightarrow Sn^{2+} \qquad E° = 0.13\ V$$

$$Sn^{4+} + 4e \longrightarrow Sn$$

Use $nE° = n_1E_1^o + n_2E_2^o$

$$E^o = \frac{-2 \times 0.14 + 2 \times 0.13}{4} = \frac{-0.01}{2}$$

$$E^o_{Sn^{+4}/Sn} = -0.005V$$

$$\therefore \quad E^o_{Sn/Sn^{+4}} = +0.005V$$

$$Sn^{2+} + 2e \longrightarrow Sn \qquad E° = -0.14\ V$$

$$Sn^{+2} - 2e \longrightarrow Sn^{4+} \qquad E° = -0.13\ V$$

$$\therefore Sn^{2+} + Sn^{2+} \longrightarrow Sn + Sn^{4+} \quad E° = -0.27\ V$$

If the potential of a cell is +ve, the cell reaction is spontaneous, otherwise non-spontaneous.

3. **(A -t), (B-r), (C-p), (D-q), (E-s)**

96500Coulomb = charge on N_A e–

$$\therefore \quad 1coulomb = \frac{N_Ae^-}{96500} = \frac{6.022 \times 10^{23}}{96500}$$

$$= \frac{6022}{965} \times 10^{18}$$

$$= 6.24 \times 10^{18} e^-$$

and see theory for cell

4. **(A - p,q,r,t), (B - p, q, r, s, t), (C - p, q, r, s, t), (D - r, s)**

(A) $\Lambda_m = \dfrac{K \times 1000}{M}$

and M = Number of moles in one liter solution

$$M \propto \frac{1}{V(dilution)}$$

$$M \propto \frac{1}{Temperature}$$

and K depend on Nature of substance

(B) and (C) $E_{cell} = E^o_{cell} - \dfrac{2.303RT}{n} \log Q$

(D) P, T and C constant at standard condition.

Comprehension

Comprehension I

5. **(d)** $Cu \longrightarrow Cu^{+1} + e^- \quad E_1^o = -0.05\ V$

$$Cu^+ \longrightarrow Cu^{+2} + e^- \quad E_2^o = -0.15\ V$$

$$Cu \longrightarrow Cu^{+2} + 2e^- \quad E° = ?$$

$$2 \times E^o_{Cu/Cu^{+2}} = 1 \times -0.05 + 1 \times -0.15$$

$$\therefore \quad E^o_{Cu/Cu^{+2}} = -\frac{0.20}{3} = -0.066\ V$$

6. **(b)** $Cu - 2e \longrightarrow Cu^{2+} \qquad E^o_{cell} = -0.066$

$$\underline{2Ag^+ + 2e \longrightarrow 2Ag \qquad E^o_{cell} = +0.799}$$

$$2Ag^+ + Cu \longrightarrow Cu^{+2} + 2Ag \quad E^o_{cell} = +0.733V$$

7. **(a)** $E_{cell} = E^o_{cell} - \dfrac{0.0591}{2} \log \dfrac{0.1}{(0.1)^2}$

$$= 0.733 - \frac{0.0591}{2} \times 1$$

$$= 0.7034\ V$$

Comprehension II

8. **(a)** The highest reduction potential for the formation of Mn^{2+} ions indicate, Mn^{++} is the most stable form.

9. **(c)** The three case Mn^{7+} dissociates to give Mn^{2+}, Mn^{4+} and Mn^{5+} respectively. Thus it is least stable.

10. **(a)** $Mn^{4+} + e \longrightarrow Mn^{2+} \qquad E° = 1.51\ V$

$$Mn^{4+} + 1e \longrightarrow Mn^{3+} \qquad E° = 0.95\ V$$

use $nE^o = n_1E_1^o + n_2E_2^o$

$$Mn^{4+} + 2e \longrightarrow Mn^{2+} \quad E° = \frac{1.51 + 0.95}{2}$$

$$= \frac{2.46}{2} = 1.23V$$

Comprehension III

11. **(b)**

$$\overset{+7}{M}nO^-_4 + e \longrightarrow MnO^{-2}_4 \qquad 0.56$$

$$\overset{+6}{M}nO^{-2}_4 + 2e \longrightarrow \overset{+4}{M}nO_2 \qquad 2.26$$

$$MnO_2 + e \longrightarrow Mn^{3+} \qquad 0.95$$

$$Mn^{3+} + e \longrightarrow Mn^{2+} \qquad 1.5$$

$$MnO^-_4 + 5e \longrightarrow Mn^{2+}$$

$$E^0 = \frac{0.56 + 2 \times 2.26 + 0.95 + 1.5}{5}$$

$$= \frac{7.53}{5} = 1.506V$$

12. **(a)**

$$MnO_4^- + 5e \longrightarrow Mn^{2+} \qquad 1.506V$$

$$Fe^{2+} \longrightarrow Fe + 2e^- \qquad -0.44.....\ ..(i)$$

$$Fe \longrightarrow Fe^{3+} + 3e^- \qquad 0.036.......(ii)$$

– – – – – – – – – – – – – – – – – – – –

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \qquad E° = ?$$

use $nE^o = n_1E_1^o + n_2E_2^o$

$$\frac{-2 \times 0.44 + 3 \times 0.036}{1} = -0.772V = E^o_{Fe^{+2}/Fe^{+3}}$$

$$\therefore \quad E^o_{cell} = (1.506) + -(0.772) = 0.734V$$

13. **(d)**

$$Fe|Fe^{2+}(0.1M) \| \underset{(10^{-52}M)}{H^+} / H_2, pt$$

$$HA + NaOH \longrightarrow BA + H_2O$$

m-moles	30	20	–	–
	10	0	10	–

Acidic buffer,

$$\text{Ph} = \text{PKa} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 5.2 + \log\frac{10}{10} = 5.2$$

$$\therefore\ [\text{H}^+] = 10^{-5.2}\ \text{M}$$

$$\text{At anode}: \text{Fe} - 2\text{e} \longrightarrow \text{Fe}^{2+} \qquad E^{\circ}_{\text{cell}} = x$$

$$\text{At Cathod}: 2\text{H}^+ + 2\text{e} \longrightarrow \text{H}_2(\text{g}) \quad E^{\circ}_{\text{cell}} = 0$$

$$\text{Fe} + 2\text{H}^+_{(\text{aq.})} \longrightarrow \text{Fe}^{2+} + \text{H}_2(\text{g})$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2}\log\frac{0.1}{[\text{H}^+]^2}$$

$$E^{\circ}_{\text{cell}} = x = +0.44\ \text{V}$$

$$\therefore\ \text{E}_{\text{cell}} = 0.44 - \frac{0.0591}{2}\log\frac{[0.1]}{[10^{-5.2}]^2}$$

$$= 0.44 - \frac{0.0591}{2}\log[10^{+9.4}]$$

$$= 0.44 - 0.277 = 0.1623\text{V}$$

Comprehension IV

14. **(c)** Species with greater reduction potential, oxidises other with lower reduction potential.

15. **(d)** Mn^{3+} oxidises H_2O to O_2 because the standard reduction potential of ($\text{Mn}^{3+} \longrightarrow \text{Mn}^{2+}$) is greater than that of ($\text{O}_2 \longrightarrow \text{H}_2\text{O}$).

Write up V

16. **(d)** $R = 1000\ \Omega$

$$\lambda_\infty(\text{Cl}^-) = 80$$

$$\lambda_\infty(\text{SO}_4^{-2}) = 160$$

$$\lambda_\infty = \lambda_m + b\sqrt{C}$$

$$\lambda_\infty = 107 + b\sqrt{4\times10^{-4}} \qquad (1)$$

$$\lambda_\infty = 97 + b\sqrt{9\times10^{-4}} \qquad (2)$$

Eq (1) – Eq (2)

$0 = 10 + b(2 \times 10^{-2}) - b \times (3 \times 10^{-2})$

$0 = 10 - b \times 10^{-2}$

$10 = b \times 10^{-2}$

$b = 10^{+3}$

$\lambda_\infty = 107 + 10^3 \times 2 \times 10^{-2}$

$(\text{NaCl}) = 107 + 20 = 127$

17. **(d)** $\lambda_\text{m} = \text{K}\times\dfrac{1000}{\text{M}}$

$$\lambda_m = \lambda_\infty - b\sqrt{C} = 127 - 10^3\sqrt{25\times10^{-4}}$$

$$\lambda_m = 127 - 10^3 \times 5 \times 10^{-2}$$

$$= 77 = K \times V = K \times \frac{1000}{25\times10^{-4}}$$

$$\Rightarrow\quad K = 77 \times 25 \times 10^{-7} = 1925 \times 10^{-7} = \frac{1}{R}\frac{l}{A}$$

$$\therefore\ \frac{\ell}{\text{A}} = 1925\times10^{-7}\times1000 = 0.1925\text{cm}^{-1}$$

18. **(d)** $N = M \times 2$

$$\Rightarrow\quad M = \frac{5\times10^{-3}}{2}$$

$$\frac{l}{A} = 0.1925$$

$$\lambda = K \times V = K \times \frac{1000\times2}{5\times10^{-3}}$$

$$= \frac{1}{R}\cdot\frac{1}{\text{A}}\cdot\frac{1000\times2}{5\times10^{-3}}$$

$$\lambda = \frac{1}{400}\times0.1925\times\frac{1000\times2}{5\times10^{-3}}$$

$$= 192.5\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

Comprehension VI

19. **(b)** $\text{Pb} + \text{SO}_4^{-2} \rightarrow \text{PbSO}_4 + 2e^-$

$$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{-2} + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$$

$$\text{Pb} + \text{PbO}_2 + 4\text{H}^+ + 2\text{SO}_4^{-2} \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$$

During charging on passing 1F charge 1 mole of H_2SO_4 is produced

$\therefore\ n_f = 1$

$$E_{\text{H}_2\text{SO}_4} = \frac{98}{1}$$

20. **(a)** Weight of H_2SO_4 before discharging

$$= 1.294\times\frac{39}{100}\times3500$$

$= 1766.31$ g

Weight of H_2SO_4 after discharging

$$= 1.139\times\frac{20}{100}\times3500$$

$= 797.3$ g

Normality of H_2SO_4 before discharging

$$= \frac{1766.31}{98}\times\frac{1}{3.5} = 5.15$$

Normality of H_2SO_4 after discharging

$$= \frac{797.3}{98}\times\frac{1}{3.5} = 2.32$$

21. **(c)** $\Delta(\text{NV}) \times \text{F}$ = Total charge

$$\text{Ampere-hour} = \frac{\text{Coulomb}}{3600\text{s}}$$

$$= \frac{(5.15 - 2.32)\times3.5\times96500}{3600}$$

$$= \frac{955832.5}{3600} = 265.5$$

22. **(a)**

Loss in mass of H_2SO_4 during discharge

$= 1766.31 - 797.3 = 969.01$ g

Moles of H_2SO_4 lost during discharge

$$= \frac{969.01}{98} = 9.88786$$

During the discharge reaction, 4 moles of H^+ ions, i.e., 2 moles of H_2SO_4 require 2F, 2 × 96500 coulombs.

∴ 9.88786 moles will require

$$= \frac{2 \times 96500 \times 9.88786}{2} = 954178 \text{ Coulombs}$$

$$\text{Total charge} = \frac{954178}{96500} \text{F} = 9.9\text{F}$$

23. **(c)** See lead storage battery discharge reaction.

Comprehension VII

24. **(b)** $\frac{1}{2}$ litre of 4 M NaCl is electrolysed.

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

$$\frac{1}{2} \times 4 = 2 \text{mole gives 1 moles } Cl_2 \text{gas}$$

OR

∴ Number of equivalents of NaCl electrolysed = 2 eq

Amount of Cl_2 produced = 2 eq = 1 mole

25. **(d)** Amount of Na formed = 2 eqNa = 46 gNa

∴ *ωt* of amalgm (NaHg) = 2 mole × [223]

= 446 gram

26. **(d)** Total Charge = 2F = 193000C

Passage VIII

27. **(b)** $(3e^- + 4H^+ + NO_3^- \longrightarrow NO + 2H_2O) \times 2$

$(Cu \longrightarrow Cu^{+2} + 2e^-) \times 3$

$8H^+ + 2NO_3^- + 3Cu \longrightarrow 3Cu^{+2} + 2NO + 4H_2O$

$$E = 0.96 - 0.34 - \frac{0.06}{6} \log \frac{P_{NO}^2[Cu^{+2}]^3}{[NO_3^-]^2[H^+]^8} \quad \text{(i)}$$

since $[HNO_3] = 1$ M so $[H^+] = [NO_3^-] = 1$

$$E = 0.62 - \frac{0.06}{6} \log (10^{-3})^2 (0.1)^3 = 0.71 \text{ V}$$

28. $(e^- + 2H^+ + NO_3^- \longrightarrow NO_2 + H_2O) \times 2$

$Cu \longrightarrow Cu^{+2} + 2e^-$

$4H^+ + 2NO_3^- + Cu \longrightarrow Cu^{+2} + 2NO_2 + 2H_2O$

$$E = 0.79 - 0.34 - \frac{0.06}{2} \log \frac{[P_{NO_2}]^2[Cu^{+2}]}{[NO_3^-]^2[H^+]^4} \quad \text{(ii)}$$

Let $[HNO_3] = x$M so $[H^+] = [NO_3^-] = x$

equation (i) and (ii)

$$0.62 - \frac{0.06}{2}\log\frac{10^{-9}}{x^{10}} = 0.45 - \frac{0.06}{2}\log\frac{10^{-7}}{x^6}$$

$$0.17 = \frac{0.06}{6}[-9 - 10 \log x] - \frac{0.06}{2}[-7 - 6 \log x]$$

$$x = 10^{0.56} \text{ M}$$

Assertion and Reasoning

29. **(a)** Assertion is correct (Can be checked from electrochemical series).
Reason B also the correct explanation.

30. **(a)** For specific conduction, the number of charge carrying particles are less compared to the increases in Area. For equivalent conductance the increases in volume is more comparable to the decrease in specific conductance.

31. **(b)** Assertion is correct and Reason is correct but not the proper explanation . Assertion is convention based but reason is related to Nernst equation.

32. **(a)** Due to discharge of H^+, the concentration of OH^- ion increases and thus the solution become alkaline

33. **(c)** $NaCl \longrightarrow Na^+ + Cl^-$

$H_2O \longrightarrow H^+ + OH^-$

At Cathode: $2H^+ + 2e \longrightarrow H_2(g)$

At Anode: $2Cl^- - 2e \longrightarrow Cl_2(g)$

34. **(a, c)** $CuBr_2 \longrightarrow Cu^{+2} + 2Br^-$

$H_2O \longrightarrow H^+ + OH^-$

At Cathode $Cu^{+2} + 2e^- \longrightarrow Cu$

At Anode $2Br^- \longrightarrow Br_2 + 2e^-$

35. **(a, d)** Reduction potential means the means the ability of the species to accept electrons. Metals are good contributor of electrons. That is why down the group (which is arranged in order of increasing reduction potential) reactivity decreases

36. **(b, c, d)** $CuSO_4 \longrightarrow Cu^{2+} + SO_4^{-2}$

$H_2O \longrightarrow H^+ + OH^-$

At Cathod: $Cu^{2+} + 2e \longrightarrow Cu(s)$

At Anode: $Ni - 2e \longrightarrow Ni^{2+}(aq)$

37. **(a, c, d)** Hints: Top members in the electrochemical series are having the tendency to lose electrons I hence oxidised. For a spontaneous cell reaction E_{cell} must be positive.

38. **(a, c)** SRP – 1.66 < 0.77 < 1.08 for Al, Fe^{+2}, Br^-

∴ Reducing power

$Al > Fe^{+2} > Br^-$

39. **(a, c)** Due to formation of Cu^{2+} ions in the solution.
Hints: Refer electrochemical series and
$Cu + \text{dil. } HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

40. **(a, d)** $Fe(s) + Cu^{2+} (0.01 \text{ M}) \longrightarrow Fe^{2+} (0.1 \text{ M}) + Cu$

$$E^o_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]}{[Cu^{2+}]}$$

41. **(b, d)** $T_1 = 273$ K

$T_2 = 298$ K

$$\frac{dE}{dT} = \frac{0.6753 - 0.6195}{298 - 273}$$

$= 0.002232$ V/K

$$\Delta H = nF\left(T\left(\frac{dE}{dT}\right) - E\right)$$

$= 2 \times 96500(298 \times 0.002232 - 0.6753)$

$= -1961.6 \text{ J} = -1.9616 \text{ KJ}$

42. (a, b, c) Refer electrochemical series.
SRP + 1.09 > + 0.54 > – 0.44 for Br_2/Br^-, I_2/I^- and Fe^{+2}/Fe
∴ Fe can reduced Br_2 and I_2 into Br^- and I– and I– can reduce Br_2 into Br^-

43. (b, c) Electrolytic conduction increases with rise in temperature because due to formation of more ions. Also check Nernst esn.

44. (a, c) In first case, H^+ and Cl^- discharges, which increases the amount of OH^-.
In second case, CH_3COO^- hydrolyses with water giving a solution of PH > 7.

45. (a, b)

(a) $$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{[Cu^{+2}]}{[Ag^+]^2}$$

$$= E^o_{cell} - \frac{0.059}{2}\log\frac{0.01}{(0.1)^2}$$

$$\therefore \quad E_{cell} = E^o_{cell}$$

(b) $$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{0.01}{(0.1)^2}$$

at Ph = 1 and $[H^+] = 0.1$

46. (a, c) See theory fuel cell

47. (a, b, d) The following reactions take place in a lead storage battery during discharging process:

At Anode: $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At Cathode:

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

∴ net cell reaction

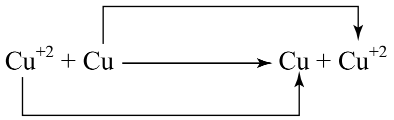
$$Pb + PbO_2 + 4H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

In the overall reaction H_2SO_4 is consumed and water is formed. (Pb, $PbSO_4$ and PbO_2 are solids). Therefore, the density of H_2SO_4 solution decreases.

48. (a, c, d) Since OH^- is produced in R.H.S., hence the pH of R.H.S. increases, whereas H^+ is produced in the L.H.S, hence the pH of L.H.S. decreases.

49. (a, b)

Oxidation at anode ∴ mass ↓



Reduction at cathode ∴ mass ↑

$$W = \frac{E}{96500} \times i \times t = \frac{63.5 \times 2.68 \times 3600}{2 \times 96500} = 3.174 \text{ g}$$

50. (a, c) $2H^+ + Fe \longrightarrow Fe^{2+} + H_2$

$E°_{cell} = E°_{cathode} - E°_{anode} = 0 - (-0.34) = 0.34$ V

Fe will oxidised emf is +ve, the reaction shall occur.

51. (3) $E^o_{cell} = E^o_{Fe^{2+}/Fe^{3+}} + E^o_{Ag^+/Ag}$

$= -0.771 + 0.799 = 0.028$ volt

At equilibrium, $E_{cell} = 0$

$$0 = E^o_{cell} - \frac{0.0591}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]}$$

$$E^o_{cell} = 0.0591 \log\frac{1}{[Ag^+]} = 0.028$$

$$\log\frac{1}{[Ag^+]} = 0.4737 = \log 3$$

$$\therefore \quad \frac{1}{[Ag^+]} = 3 \quad \text{and}$$

$[Ag^+] = 0.34$

$$\log K = \frac{nE^o}{0.0591} = 0.4737 = \log 3$$

$K = 3.0$

52. (6) At cathode: $Mg^{2+} + 2e^- \longrightarrow Mg$
at anode: $2Cl^- \longrightarrow Cl_2 + 2e$
∵ equivalent of Mg at cathode = Equivalent of Cl_2 at anode

$$\therefore \quad \frac{6.5}{24.3/2} = \frac{w_{Cl_2}}{35.5}$$

$$\therefore \quad w_{Cl_2} = 18.99 \text{ g}$$

At NTP $\quad PV = nRT = \frac{\text{weight}}{\text{molarmass}}RT$

$$1 \times V = \frac{18.99}{71} \times 0.0821 \times 273$$

Volume of Cl_2 = 6.0 L

53. (2) Current flown = 0.525 amp as shown by ammeter
Actual current flown

$$(i) = \frac{w}{E \times t} \times 96500 = \frac{0.6354 \times 96500}{(63.54/2) \times 60 \times 60}$$

∴ $i = 0536$ ampere

Thus error in (i) = 0.536 – 0.525 = 0.011

∴ % error in ammeter = $\frac{0.011 \times 100}{0.536}$ = 2.05% = 2.0% approx.

54. (2) 88 g Hg has 12 g Cd

∴ 2.56 g Hg require = $\frac{12 \times 2.56}{88}$ = 0.349 gram Cd

Cd = 0.349

since $Cd^{2+} + 2e \longrightarrow Cd \left[\therefore E_{Cd} = \frac{112.40}{2}\right]$

Now, $w = \frac{E.i.t}{96500}$

$$0.349 = \frac{112.4 \times 5 \times t}{2 \times 96500} = 120 \text{ sec} = 2 \text{ min}$$

55. (4) $Ni \longrightarrow Ni^{2+} + 2e \qquad E^o_{OP} = 0.236$ V

$2H^+ + 2e \longrightarrow H_2 \qquad E^o_{RP} = 0$

∵ $E_{cell} = 0$

$$\therefore \quad E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[Ni^{2+}]}$$

$$0 = 0.236 + \frac{0.059}{2}\log_{10}[H^+]^2$$

$$\Rightarrow \quad +0.236 = \frac{0.059}{2}\times 2\left[-\log\left[H^+\right]\right]$$

$4 = -\log[H^+] = \text{Ph}$

$\therefore$ pH = 4

56. **(4)** Since $Pd^{n+} + ne \longrightarrow Pd$

For Pd, $\frac{w}{E} = \frac{i \times t}{96500}$

$$\frac{2.977}{106.4/n} = \frac{3\times 1\times 60\times 60}{96500}$$

$n = 4$

57. The problem does not mention about the acidic salt of Cu^{2+}, i.e., what kind of acidic salt is this? Does the acidic salt have chloride, sulphate or nitrate as anion against the cation Cu^{2+} and the answer will solely depend on the assumption we make in the beginning about the acidic salt. First, let us assume that the salt is of cupric chloride ($CuCl_2$).

In the first part of electrolysis, the reaction occurring at the two electrodes are

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

At anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

[The reaction occurring at anode is the oxidation of Cl^- in preference to OH^- since the standard oxidation potential of $Cl^- > OH^-$].

Mole of Cu^{2+} reduced at cathode $= \frac{0.4}{63.5}$

Mole of electrons required at cathode $= \frac{2\times 0.4}{63.5} =$ Mole of electrons released at anode

$\therefore$ mole of Cl_2 liberated at anode $= \frac{2\times 0.4\times 1}{63.5\times 2} = \frac{0.4}{63.5}$

Volume of Cl_2 liberated at STP at anode

$$= \frac{0.4}{63.5}\times 22400 = 141 \text{ mL}$$

In second part of electrolysis, when current is passed for 7 more minutes, the H^+ will be reduced at cathode since Cu^{2+} ions are discharged completely and OH^- ions are oxidised at anode since Cl^- is also completely oxidised. The reactions occurring are:

At cathode: $2H^+ + 2e^- \longrightarrow H_2$

At anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Mole of electrons passed $= \frac{1.2\times 7\times 60}{96500}$

Volume of H_2 at STP released at cathode

$$= \frac{1.2\times 7\times 60}{96500\times 2}\times 22400 = 58.49 \text{ mL}$$

Volume of O_2 at STP released at anode

$$= \frac{1.2\times 7\times 60}{96500\times 4}\times 22400 = 29.245 \text{ mL}$$

Total of gases ($Cl_2 + O_2 + H_2$) liberated at STP during entire electrolysis

$= 141 + 58.49 + 29.245 = 228.735$ mL

Second, let us assume that the that of $CuSO_4$

In first part of electrolysis, the ions discharged at cathode and anode are Cu^{2+} and OH^- respectively.

At cathode: $Cu^{2+} + 2e^+ \longrightarrow Cu$

At anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

$\therefore$ mole of O_2 liberated at anode $= \frac{2\times 0.4}{63.5\times 4} = \frac{0.4}{63.5\times 2}$

$\therefore$ volume of O_2 at STP liberated at anode

$$= \frac{0.4}{63.5\times 2}\times 22400 = 70.55 \text{ mL}$$

In second part of electrolysis, the H^+ and OH^- ions are discharged at cathode and anode respectively.

At cathode: $2H^+ + 2e^- \longrightarrow H_2$

At anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Volume of H_2 at STP released at cathode

$$= \frac{1.2\times 7\times 60}{96500\times 2}\times 22400 = 58.49 \text{ mL}$$

Volume of O_2 at STP released at anode

$$= \frac{1.2\times 7\times 60}{96500\times 4}\times 22400 = 29.245 \text{ mL}$$

$\therefore$ total of gases ($H_2 + O_2$) liberated at STP during entire electrolysis

$= 70.55 + 58.49 + 29.245 = 158.285$ mL

[Note: If we assume the salt to be $Cu(NO_3)_2$, the volume of gases liberated (at STP) still remains same as in the case of $CuSO_4$ (158.235 mL) as NO_3^- is also resistant to oxidation (just like SO_4^{2-}) and OH^- oxidises in preference to NO_3^-].

58. **(25%)** For reversible cells, if an external voltage of opposing polarity is attached to the cell, a current flowing from thallium to tin electrode is given as

$$I = \frac{E - E_b}{R} \qquad \text{(i)}$$

where E = Applied voltage = 1.2 V, Eb = Back emf (i.e., reversible emf of cell) and R = cell resistance.

Calculation of R:

For cell: Tl | Tl^+ (0.1 M) || Sn^{+2} (0.01 M) | Sn

$$E_b = E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{1}\log\frac{[Tl^+]}{[Sn^{+2}]^{1/2}}$$

$$= (0.340 - 0.140) - 0.059\log\frac{0.1}{(0.01)^{1/2}} \Rightarrow E_b = 0.2 \text{ V}$$

$$I=\frac{E_{\text{cell}}}{R} \Rightarrow R=\frac{E_{\text{cell}}}{\text{I}}=\frac{0.2}{40\times10^{-3}};\quad R=5\Omega$$

Using the value in equation (i), $I=\frac{1.2-0.2}{5}=0.2$ A

Charge passed for 1 hour = 0.2× 3600 C = 720 Coulomb

Equivalent of thallium deposited = $\frac{720}{96500}$

Weight of thallium deposited = $\frac{720}{96500}\times 204 = 1.52$ g

Efficiency of thallium electrode = $\frac{0.38}{1.52}\times 100 = 25\%$

59. In the given cell

Ag | AgCl | HCl (0.1 M) | H_2 (1 atm) | Pt || Pt | H_2 (1 atm) | H^+ (c M) | KCl (1 M) | Hg_2Cl_2 | Hg

$E_{\text{cell}} = 0.1256$ V

E°= 0.2873 V for Cl^- | AgCl | Ag, and E° = 0.2415 V for Cl^- | Hg_2Cl_2 | Hg

Let E_1 and E_2 be the emf of the LHS cell and RHS cell respectively, then $E_{\text{cell}} = E_1 + E_2$

The overall cell reaction of the LHS cell is

$$\text{Ag} + \text{HCl} \longrightarrow \text{AgCl} + \frac{1}{2}\text{H}_2$$

$$\therefore\quad E_1=(E^{\text{o}}_{\text{H}^+|\text{H}_2}-E^{\text{o}}_{\text{Cl}^-\backslash\text{AgCl}|\text{Ag}})-0.059\log\frac{(P_{\text{H}_2})^{1/2}}{[\text{H}^+][\text{Cl}^-]}$$

$$=0-0.2873-0.059\log\frac{1}{(0.1)^2}=-0.4053\text{ V}$$

$E_2 = E_{\text{cell}} - E_1 = 0.1256 + 0.4053 = 0.5309$ V.

The overall cell reaction of the RHS cell is

$$\text{Hg}_2\text{Cl}_2 + \text{H}_2 \longrightarrow 2\text{Hg} + 2\text{H}^+ + 2\text{Cl}^-$$

$$\therefore E_2=(E^{\text{o}}_{\text{Cl}^-|\text{Hg}_2\text{Cl}_2|\text{Hg}}-E^{\text{o}}_{\text{H}^+|\text{H}_2})-\frac{0.059}{2}\log\frac{[\text{H}^+]^2[\text{Cl}^-]^2}{P_{\text{H}_2}}$$

$$0.5309=(0.2415-0)-\frac{0.059}{2}\log[\text{H}^+]^2;$$

On solving, $[H^+] = 1.24 \times 10^{-5}$ M.

60. The given cell is

Pt | H_2 (1 atm) | H^+ (1 M) || (M/32) $C_6H_5NH_3Cl$ | H_2 (1 atm) | Pt $E_{\text{cell}} = -0.188$ V.

The cell reactions are

$$\text{Anode:}\quad \frac{1}{2}\text{H}_2 \longrightarrow \text{H}^+ + e^-$$

$$\text{Cathode:}\quad \text{H}^+ + e^- \longrightarrow \frac{1}{2}\text{H}_2$$

$$(\text{H}^+)_c \longrightarrow (\text{H}^+)_a$$

$$\therefore\quad E_{\text{cell}}=0-0.059\log\frac{[\text{H}^+]_a}{[\text{H}^+]_c};-0.188=-0.059\log\frac{1}{[\text{H}^+]_c}$$

On solving $[H^+]_c = 6.5 \times 10^{-4}$ M

The cathode half-cell is a hydrogen electrode is which $C_6H_5\overset{+}{N}H_3$ on hydrolysis gives H^+
(Cationic hydrolysis)

$$\underset{\text{C}(1-\text{h})}{\text{C}_6\text{H}_5\overset{+}{\text{N}}\text{H}_3} + \text{H}_2\text{O} \longrightarrow \underset{\text{Ch}}{\text{C}_6\text{H}_5\text{NH}_2} + \underset{\text{Ch}}{\text{H}_3\text{O}^+}$$

$$\text{Ch} = 6.5 \times 10^{-4}$$

$$\therefore\ h = 6.5\times10^{-4}\times 32 = 2.08\times10^{-2}$$

$$K_{\text{h}}=\frac{\text{Ch}^2}{1\text{ - h}};\ \text{Ch}^2=\frac{(2.08\times10^{-2})^2}{32}=1.352\times10^{-5}\text{M}$$

61. The instability constant of

$\text{Ag(NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$ (i); $K_1 = 6.02 \times 10^{-5}$

$\therefore\quad \Delta G_1^{\text{o}} = -\text{RT}\ln 6.02\times10^{-8} = 0.426$ F

$\text{Ag}^+ + e^- \longrightarrow \text{Ag} \rightleftharpoons$ (ii); E° = 0.799 V

$\therefore\quad \Delta G_2^{\text{o}} = -F(0.799)$

Adding (i) and (ii), $\text{Ag(NH}_3)_2^+ + e^- \rightleftharpoons \text{Ag} + 2\text{NH}_3$ (iii)

The standard free energy change of (iii) is given by

$\Delta G_3^{\text{o}} = \Delta G_1^{\text{o}} + \Delta G_2^{\text{o}}$;

–FE° = 0.426 F – 0.799 F; E° = 0.373 V

Similarly, $\text{Ag(CN)}_2^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$; $K_2 = 1.995 \times 10^{-19}$

$$\Delta G_4^{\text{o}} = -\text{RT}\ln 1.995\times10^{-19} = 1.1\text{ F}$$

$$\text{Ag(CN)}_2^- + e^- \rightleftharpoons \text{Ag} + 2\text{CN}^-$$

$$\Delta G_5^{\text{o}} = \Delta G_2^{\text{o}} + \Delta G_4^{\text{o}}\ ;\ -\text{FE}° = -0.799\text{ F} + 1.1\text{ F}$$

E° = –0.301 V

62. Cell constant = $\frac{l}{a}=\frac{4}{7}\text{cm}^{-1}$

specific conductance = conductance × cell constant

$$=\frac{1}{\text{resis tan ce}}\times\frac{l}{a}=\frac{1}{245}\times\frac{4}{7}=2.332\times10^{-3}\text{mhocm}^{-1}$$

$$=\lambda_{\text{eq}}=\text{K}\times\frac{1000}{\text{N}}=\frac{2.32\times10^{-3}\times1000}{0.1}$$

$= 23.32\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$

63. **(200)** Let K_1 and K_2 be the specific conductances of the solutions *A* and *B* respectively and the constant of the cell be *l*/*A*.

∴ For solution A:

Specific conductance = conductance × cell constant

$$K_1=\frac{1}{50}\times x \qquad \text{(i)}$$

For solution B: specific conductance

$$K_2=\frac{1}{100}\times x \qquad \text{(ii)}$$

When equal volumes of *A* and *B* are mixed, both the solutions get doubly diluted; hence their individual contribution towards specific conductance of the mixture will be $\frac{K_1}{2}$ and $\frac{K_2}{2}$ respectively and the specific conductance of the mixture will be $\frac{1}{2}(K_1 + K_2)$.

$$= \frac{1}{2}\left[\frac{1}{R_1} + \frac{1}{R_2}\right]\frac{l}{A} = \frac{1}{R}\frac{l}{A} \qquad \text{(iii)}$$

$$\frac{1}{50} + \frac{1}{100} = \frac{2}{R}$$

$$\frac{3}{100} = \frac{2}{R}$$

$$R = \frac{200}{3}\Omega$$

$\therefore \quad 3R = 200$

64. Since the electrodes of the cell are just half-dipped, the effective area will be 5 sq. cm.

Cell constant $= \frac{l}{a} = \frac{1.5}{5} = 0.3 \text{ cm}^{-1}$

Specific conductance = Conductance × Cell constant

$$= \frac{1}{\text{resistance}} \times \text{cell constant}$$

$$= \frac{1}{50} \times 0.3 = \frac{3}{500} \text{ mho cm}^{-1}$$

$$\lambda_{\text{eq}} = \text{K} \times \frac{1000}{\text{N}}$$

$$= \frac{3}{500} \times \frac{1000}{0.05} = 120\Omega^{-1}\text{cm}^2\text{eq}^{-1}$$

65. Let the volume of the vessel be V cc.

Number of equivalent of NaCl $= \frac{\text{weight in grams}}{\text{equivalent weight}}$

$$= \frac{500}{58.5} = 8.547$$

$\therefore$ volume of water (cc) containing 1 equivalent of

$$\text{NaCl} = \frac{\text{V}}{8.547}$$

The specific conductance of the NaCl solution (only due to presence of Na^+ and Cl^- ions)

$$= 3.10 \times 10^{-5} - 2.56 \times 10^{-5} = 0.54 \times 10^{-5}$$

$$\therefore \quad \Lambda_{\text{NaCl}} = 0.54 \times 10^{-5} \times \frac{\text{V}}{8.547}$$

since the vessel is big, the resulting solution may be supposed to be dilute.

$$\therefore \quad \Lambda_{\text{NaCl}} = \Lambda^{o}_{\text{NaCl}} = 149.9$$

$$0.54 \times 10^{-5} \times \frac{\text{V}}{8.547} = 149.9$$

$$V = 2.37 \times 10^{8} \text{ cc.}$$

66. Cell constant $= \frac{0.50}{1.50} = \frac{1}{3} = \frac{l}{A}$

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

$$\therefore \quad \Lambda_{eq} = \frac{1}{R}\frac{\ell}{A} \times \frac{1000}{N}$$

$$97.1 = \frac{1}{R} \times \frac{1}{3} \times \frac{1000}{0.1}$$

$$\therefore \quad R = 34.328\Omega$$

$$\therefore \quad i = \frac{V}{R} = 0.1456 \text{ Amp.}$$

67. We know $\lambda_{\text{eq}} = F \times U$

$$\lambda^{o}_{\text{NH}_4\text{ClO}_4} = \lambda^{o}_{\text{NH}_4^+} + \lambda^{o}_{\text{ClO}_4^-} = \text{F} \times \text{u}^{o}_{\text{NH}_4^+} + \text{F} \times \text{u}^{o}_{\text{ClO}_4^-}$$

$$= \text{F}(\text{u}^{o}_{\text{NH}_4^+} + \text{u}^{o}_{\text{ClO}_4^-}) = 96500(6.6 \times 10^{-4} + 5.7 \times 10^{-4})$$

$$= 118.695 \text{ mho cm}^2$$

68. We know $\lambda_{\text{eq}} = F \times U$

$$u^{o}_{\text{H}^+} = \frac{\lambda^{o}_{\text{Ç}^+}}{\text{F}} = \frac{349.8}{96500} = 3.62 \times 10^{-3} \text{ cm}^2 \text{ volt}^{-1}\text{s}^{-1}$$

$$u^{o}_{\text{Na}^+} = \frac{\lambda^{o}_{\text{Na}^+}}{\text{F}} = \frac{50.11}{96500} = 5.20 \times 10^{-4} \text{ cm}^2 \text{ volt}^{-1}\text{s}^{-1}$$

Further, we know that

$$u^{o} = \frac{\text{Ionic velocity (cm/s)}}{\text{potential gradient volt/cm}}$$

$\therefore$ velocity of H^+=$3.62 \times 10^{-3} \times \frac{2}{5}$ =1.45×10^{-3} cms^{-1}

Velocity of Na^+ = $5.20 \times 10^{-4} \times \frac{2}{5}$ = 2.08×10^{-4} cms^{-1}

69. $\lambda^{o}_{\text{NH}_4\text{Cl}} = \lambda^{o}_{\text{NH}_4^+} + \lambda^{o}_{\text{Cl}^-}$

$$\therefore \quad \lambda^{o}_{\text{NH}_4^+} = \Lambda^{o}_{\text{NH}_4\text{Cl}} - \lambda^{o}_{\text{Cl}^-} = 150 - 76 = 74$$

$$\therefore \quad \lambda^{o}_{\text{NH}_4\text{OH}} = \lambda^{o}_{\text{NH}_4^+} + \lambda^{o}_{\text{OH}^-} = 74 + 198 = 272$$

Further, degree of dissociation $= \frac{\lambda_{\text{c}}}{\lambda^{\circ}} = \frac{9.6}{272} = 0.0353$

70. $\lambda^{\text{c}}_{\text{m}} = \frac{\text{K} \times 1000}{\text{M}} = \frac{5.8 \times 10^{-8} \times 1000}{55.55} = 1.044 \times 10^{-6}$

$$\alpha = \frac{\lambda^{\text{c}}_{\text{m}}}{\lambda^{\infty}_{\text{m}}} = \frac{1.044 \times 10^{-6}}{350 + 198} = \frac{1044}{548} \times 10^{-9} = 1.9 \times 10^{-9}$$

$$\begin{array}{llll} H_2O & \rightleftharpoons & H^+ \;+ & OH^- \\ C - C\alpha & & C\alpha & C\alpha \end{array}$$

$$\text{Kd} = \text{C}\alpha^2 = 55.55 \times (1.9 \times 10^{-9})^2$$

$$201.6 \times 10^{-18}$$

$$2 \times 10^{-16}$$

$$\left([\text{H}_2\text{O}] = \text{C} = \frac{1000}{18} = 55.5 \text{ mole/L}\right)$$

71. Degree of dissociation $\alpha = \frac{\Lambda_c}{\Lambda_0} = \frac{7.36}{390.7} = 0.0188$

(for CH_3COOH, 0.05 N = 0.05 M)

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

0.05

$0.05(1-\alpha) \quad 0.05\alpha \quad 0.05\alpha$

$$K_a = \frac{0.05\alpha \times 0.05\alpha}{0.05(1-\alpha)}$$

since α is very small, $\therefore \quad K_a = C\alpha^2$

$K_a = 0.05\alpha^2 = 0.05 \times (0.0188)^2 = 1.76 \times 10^{-5}$ mole/L

72. $\underset{(S)}{AgC\ell} \rightleftharpoons \underset{aq}{Ag^+} + \underset{aq}{C\ell^-}$

If the solubility of AgCl in water S moles/liter

$K_{SP} = [Ag^+][C\ell^-] = S \times S = S^2$

and $\lambda_m = \frac{K \times 1000}{M} = \frac{K \times 1000}{S}$ at saturation $M = S$

Since AgCl is sparingly soluble in water,

$\Lambda_{AgCl} = \Lambda^o_{AgCl} = 138.3$

$\therefore \quad 2.28 \times 10^{-6} \times \frac{1000}{S} = 138.3$

or $\quad S = 1.644 \times 10^{-5}$ eq./L or mole/L

$K_{sp} = S^2 = (1.644 \times 10^{-5})^{-2}$

$= 2.70 \times 10^{-10}$ (mole/L)^2

73. $2Hg(\ell) + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$

t = 0 excess 10^{-3} M – –

Equilib. excess 5×10^{-5} 4.75×10^{-4} 9.5×10^{-4}

at equilibrium $E_{cell} = 0$

$$E^o_{cell} = \frac{0.059}{2}\log\frac{4.75 \times 10^{-4} \times (9.5 \times 10^{-4})^2}{(5 \times 10^{-5})^2}$$

$$= \frac{0.059}{2}\log\frac{4.75 \times 9.5 \times 9.5}{25} \times 10^{-2}$$

$$E^o_{cell} = \frac{0.059}{2}\log 0.17 = -0.023 = \left(E^o_C - E^o_A\right)_{\text{data in SRP}}$$

$$E^o_{Fe^{3+}|Fe^{2+}} - E^o_{Hg_2^{2+}|Hg} = -0.023;\ 0.77 + 0.023 = 0.793$$

$$E^o_{Hg|Hg_2^{2+}} = -0.793V$$

74. The cell is,

$Pt\ H_{2(1atm)}|HA_2|\ |HA_1|H_{2(1atm)}\ Pt$

At L.H.S.: $E_{H/H^+} = E^\circ_{OPH/H^+} + \frac{0.059}{1} \times \log_{10}[H^+]_2$

$\because \quad -\log H^+ = pH \quad \therefore E_{H/H^+} = E^\circ_{OPH/H^+} + 0.059\ (pH)_2$ (i)

At R.H.S.: $E_{H^+/H} = E^\circ_{RPH^+/H} + \frac{0.059}{1} \times \log_{10}[H^+]_1$

$\therefore \quad E_{H^+/H} = E^\circ_{RPH^+/H} - 0.059\ (pH)_1$ (ii)

For Acid HA_1 $\quad HA_1 \rightleftharpoons H^+ + A_1^-$

$$[H^+] = C \cdot \alpha = \sqrt{K_a \cdot C}$$

Ph calculation of weak acid (Ionic equilibrium)

$\therefore \quad (pH)_1 = \frac{1}{2}pK_{a_1} - \frac{1}{2}\log_{10} C$

Similarly, $(pH)_2 = \frac{1}{2}pK_{a_2} - \frac{1}{2}\log_{10} C$ ($\because$ C are same)

$\therefore \quad E_{cell} = E_{OPH^+/H} + E_{RPH^+/H}$

$= 0.059(PH)_2 + (-0.059(PH)_1)$

From (i) and (ii)

$$= 0.059\left[\frac{1}{2}pK_{a_2} - \frac{1}{2}pK_{a_1}\right] = \frac{0.059}{2}[5-3]$$

$= \mathbf{+0.059}$

75. $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{+2}$

$$\therefore \quad K_f = 1 \times 10^{12} = \frac{[Cu(NH_3)_4]^{+2}}{[Cu^{+2}][NH_3]^4} = \frac{1.0}{x(2.0)^4}$$

$\therefore \quad x = 6.25 \times 10^{-14}$ M

Note that due to high value of K_f almost all of the Cu^{+2} ions are converted to $[Cu(NH_3)_4]^{2+}$ ion

Now $E_{cell} = E^o_{cell} + \frac{0.059}{2}\log_{10}\frac{[Cu^{2+}]}{[Zn^{+2}]}$

$$= 1.1 + \frac{0.059}{2}\log_{10}\frac{[Cu^{2+}]}{[Zn^{+2}]}$$

$$1.1 + \frac{0.059}{2}\log\frac{6.25 \times 10^{-14}}{1}$$

$1.1 - 0.3894 = 0.71V$

$E_{cell} = \mathbf{0.71\,V}$

76. $Ag \longrightarrow Ag^+ + e^- \qquad E_{RP} = 0.799$ V

$[Ag(NH_3)_2^+] + e \longrightarrow Ag + 2NH_3 \qquad E_{RP} = ?$

$[Ag(NH_3)_2^+] \rightleftharpoons Ag^+ + 2NH_3$

$$E_{cell} = E^o_{cell} + \frac{0.0591}{1}\log_{10}\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

$$0 = E^o_{cell} + \frac{0.0591}{1}\log(6 \times 10^{-8}) \Rightarrow E^o_{cell} = -0.426$$

$E^o_{cell} = E^o_C - E^o_A$

$-0.426 = E^o_C - 0.799 \Rightarrow E^o_C = 0.373$ V

77. Use $[Co(CN)_6]^{4-} \longrightarrow [Co(CN)_6]^{3-} + e$;

$E^o_{OP} = +0.83$ V

$Co^{3+} + e \longrightarrow Co^{2+}; \qquad E^o_{RP} = 1.82$ V

$[Co(CN_6)]^{4-} + Co^{3+} \rightleftharpoons Co^{2+} + [Co(CN_6)]^{3-}$

and $\quad E_{cell} = E^o_{cell} + \frac{0.059}{1}\log_{10}\frac{[Co^{3+}][Co(CN)_6^{4-}]}{[Co^{2+}][Co(CN)_6^{3-}]}$

or

$$E_{cell} = E^o_{cell} + \frac{0.059}{1}\log_{10}\frac{[Co^{3+}][Co(CN)_6^{4-}][CN^-]^6}{[Co^{2+}][Co(CN)_6^{3-}][CN^-]^6}$$

Also $6\,CN^- + Co^{2+} \rightleftharpoons [CO(CN)_6]^{4-}$

and $K_{f_1} = \dfrac{[Co(CN)_6^{4-}]}{[Co^{2+}][CN^-]^6}$

and $6\,CN^- + Co^{3+} \rightleftharpoons [CO(CN)_6]^{3-}$

and $K_{f_2} = \dfrac{[Co(CN)_6^{3-}]}{[Co^{3+}][CN^-]^6}$

$$\therefore \quad E_{cell} = E^o_{cell} + \frac{0.059}{1}\log_{10}\frac{K_{f_1}}{K_{f_2}}$$

$$0 = 0.83 + 1.82 + \frac{0.059}{1}\log_{10}\frac{K_{f_1}}{K_{f_2}}$$

(At equilibrium $E_{cell} = 0$)

$$\therefore \quad \frac{K_{f_2}}{10^{19}} = 10^{44.67} = 4.7\times10^{44}$$

$$\therefore \quad K_{f_2} = 4.7\times10^{63}$$

78. $E = E^o_{calomal} + E^o_{H_2/H^+} - \dfrac{RT}{nF}\ln\dfrac{[H^+]^2}{P_{H_2}}$

$$0.6885 = 0.28 - \frac{8.314\times313}{2\times96500}\ \ln\ \frac{[H^+]^2}{725}\times760$$

$[H^+] = 2.57\times10^{-7}$

pH = 6.6

79. For $Fe^{+3} + e^- \longrightarrow Fe^{+2}$ $E° = 0.77$

so Fe^{+3} will reduce to Fe^{+3}

Faraday of current passed

$$= \frac{1.25\times1.1\times3600}{96500} = 0.0513\text{ F}$$

gram equivalent of Fe^{+2} = gram equivalent of $KMnO_4$ required

$$0.0513 = M\times5\times\frac{25}{1000}$$

$M = 0.41$

80. **(3)** At cathode:

$Sn^{+2} + 2e^- \longrightarrow Sn$

At anode:

$X \longrightarrow X^{+n} + ne^-$

Cell reaction:

$n\,Sn^{+2} + 2X \longrightarrow 2X^{+n} + nSn$

$E° = -0.14 + 0.78 = 0.64$

$$E = E^o - \frac{0.0591}{2n}\times\log\frac{[X^{+n}]^2}{[S^{+2}]^n}$$

$$0.65 = 0.64 - \frac{0.0591}{2n}[\log 0.01 - \log(0.5)^n]$$

$$0.01 = -\frac{0.0591}{2n}[-2 + n\log 2]$$

$0.03384n = 2 - 0.3010n$

$0.6394n = 2$

$n = 3.12 \simeq 3$

81. **(A)** At cathode:

$2e^- + Cu^{+2} \longrightarrow Cu$

At anode:

$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$

Equivalent of O_2 evolved = Equivalent of Cu formed = 0.01

$$\text{Total loss in weight} = 0.01\times8 + \frac{0.01\times63.5}{2} = 0.3975$$

Weight of resulting solution = 10 – 0.03975= **9.6025 g**

(B) Equivalent of H^+ **= 0.01**

82. In beginning (Concentrate H_2SO_4 present) So

At anode:

$2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$

At cathode:

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

After some time

(When concentration of H_2SO_4 decrease)

At anode:

$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$

At cathode:

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Moles of O_2 evolved = $\dfrac{2.35}{22.4}$

During this time moles of H_2 evolved = $\dfrac{2\times2.35}{22.4}$

Volume of H_2 evolved with O_2 = $\dfrac{2\times2.35}{22.4}\times22.4$ = 4.7 L

Volume of H_2 evolved with $H_2S_2O_8$ = 9.722 – 4.7 = 5.022 L

Moles of H_2 evolved = $\dfrac{5.022}{22.4}$

Moles of $H_2S_2O_8$ formed = $\dfrac{5.022}{22.4}$

Weight of $H_2S_2O_8$ formed = $\dfrac{5.022}{22.4}\times194$ **= 43.45 g**

83. At cathode only pure copper is deposited so % of Cu = $\dfrac{22.011}{22.26}\times100$ **= 98.88%**

Since Cu is getting deposited, iron will also get reduced because its SRP value is lesser than Cu.

Charge passed

= 140 × 482.5 = 67550 Coloumb

$$= \frac{67550}{96500} = 0.7\text{ Faraday}$$

Faraday used for reduction of Cu = $\dfrac{22.011\times2}{63.5}$ = 0.69326

so Faraday used for iron = 0.7 – 69326 = 0.00674 F

$$\text{mass of iron} = \frac{0.00674\times56}{2} = 0.1887\text{ g}$$

% of Fe = $\dfrac{0.1887}{22.26}\times100$ **= 0.847%**

84. At anode:

$$Ag + Cl^- \longrightarrow AgCl + e^-$$

At cathode:

$$AgBr + e^- \longrightarrow Ag + Br^-$$

$$E = E^o_{Ag/AgCl/Cl^-} + E^o_{Br^-/AgBr/Ag} - 0.0591 \log\frac{[Br^-]}{[Cl^-]} \quad \text{(i)}$$

For reaction:

$$Ag + Cl^- \longrightarrow AgCl + e^-$$

$$Ag^+ + e^- \longrightarrow Ag$$

$$E = O = E^o_{Ag/AgCl/Cl^-} + E^o_{Ag^+/Ag} - 0.0591 \log\frac{1}{[Ag^+][Cl^-]}$$

$$E^o_{Ag/AgCl/Cl^-} = E^o_{Ag/Ag^+} - 0.0591 \log K_{sp}(AgCl) \quad \text{(ii)}$$

for reaction

$$AgBr + e^- \longrightarrow Ag + Br^-$$

$$Ag \longrightarrow Ag^+ + e^-$$

$$E = 0 = E^o_{Br^-/AgBr/Ag} + E^o_{Ag/Ag^+} - 0.0591 \log [Ag^+][Br^-]$$

$$E^o_{Br^-/AgBr/Ag} = E^o_{Ag^+/Ag} + 0.0591 \log K_{sp}(AgBr) \quad \text{(iii)}$$

From Equations (i), (ii) and (iii)

$$E = 0.0591 \log\frac{K_{sp}(AgBr)}{K_{sp}(AgCl)} - 0.0591 \log\frac{[Br^-]}{[Cl^-]}$$

$$E = 0.0591 \log\frac{3.3\times10^{-13}\times0.2}{2.8\times10^{-10}\times0.001} = -0.037\text{ V}$$

85. $2NaCl \rightleftharpoons 2Na^+ + 2Cl^-$

$2H_2O \rightleftharpoons 2H^+ + 2OH^-$

At anode:

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

At cathode:

$$2H^+ + 2e^- \longrightarrow H_2$$

Net reaction:

$$2NaCl + 2H_2O \rightleftharpoons 2OH^- + H_2 + Cl_2 + 2Na^+$$

$$W_{Cl_2} = 1000 = \frac{35.5}{96500}\times25\times\frac{62}{100}\times t$$

t = 175374.83 sec = 48.74 hr.

$$\text{Moles of }OH^- = \frac{1000}{71}\times2$$

Volume = 20 L

$$[OH^-] = \frac{2000}{71\times20} = 1.408\text{ M}$$

86. For KCl

$$\lambda_M = \frac{K\times1000}{M} = 138 = \frac{K\times1000}{0.02}$$

$$K = 2.76\times10^{-3} = \frac{1}{R}\left(\frac{l}{a}\right) = \frac{1}{85}\left(\frac{l}{a}\right)$$

$(l/a) = 0.2346$

$$\text{For } H_2O:\ K_{H_2O} = \frac{1}{9200}\times\frac{l}{a}$$

$$\text{For NaCl solution: } K_{NaCl} = \lambda_M = \frac{K_{solute}\times1000}{M}$$

$$\lambda_M = \frac{(K_{NaCl} - K_{H_2O})\times1000}{M}$$

$$126.5 = \frac{\left(\frac{1}{7600} - \frac{1}{9200}\right)\times0.2346\times1000}{M}$$

$M = 4.2438\times10^{-5}$

$$M = \frac{500}{58.5\times V} = 4.2438\times10^{-5}$$

V = 201400 L

V = **2.014 × 10^5 L**

Total volume of H_2 = **58.464 mL**

87. $$W = \frac{108\times5\times2\times3600}{96500} = 40.29$$

But since anode is 95% pure with Ag so along with silver some impurities will also come out so actual.

$$\text{Weight coming out of anode is } \frac{40.29}{0.95} = 42.41\text{ g}$$

Weight of anode now = 100 – 42.41 = **57.58 g**

88. $$\text{Moles of } H_2O_2 = \text{moles of } H_2 = \frac{100}{34}$$

$$\text{Weight of } H_2 = \frac{100}{34}\times2 = \frac{100}{17} = Z\text{ it}\times\frac{50}{100}$$

$$\frac{100}{17} = \frac{1\times i\times0.5\times3600}{96500}$$

i = **315.36 Amp.**

89. At anode: $H_2 \longrightarrow 2H^+ + 2e^-$

$E°$ = – 0.699

At cathode: $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

$E°$ = 0.28

$$E_{cell} = -0.699 + 0.28 - \frac{0.0591}{2}\log[H^+]^2[Cl^-]^2$$

$E_{cell} = -0.419 + 0.0591\text{ pH}$

(a) $E_{cell} = -0.419 + 0.0591\times5$
$= -0.1235$ V

(b) $O = -0.419 + 0.0591$ pH
pH = 7.1

(c) $E_{cell} = -0.419 + 0.0591\times7.5 = 0.2425$ is $E_{cell} > 0$ cell is spontaneous & Calomal electrode with it work as cathode i.e. positive electrode.
($E_{cell} = -0.419 + 0.0591\times7.5 = 0.2425$ $E_{cell} > 0$

90. $Ag_2S + 2e^- \rightleftharpoons 2Ag + S^{-2}$ $\quad E° = x$ ....(i)

$2Ag \rightleftharpoons 2Ag^+ + 2e^-$ $\quad E° = -0.8$

$$Ag_2S \rightleftharpoons 2Ag^+ + S^{-2} \qquad E^\circ = x - 0.8$$

$$E = x - 0.8 - \frac{0.0591}{2}\log[Ag^+]^2[S^{-2}]$$

at saturation $E = 0$
and $Q = K_{sp}$

$$0 = x - 0.8 - \frac{0.0591}{2}\log K_{sp}$$

$$x = 0.8 + \frac{0.0591}{2}\log 2\times10^{-49} = -0.639$$

so for equation (i)

$$E = E^\circ - \frac{0.0591}{2}\log[S^{-2}] \qquad ...(ii)$$

$$H_2S \rightleftharpoons 2H^+ + S^{-2} \qquad K = K_1\times K_2$$

$$1.1\times10^{-21} = \frac{[H^+]^2[S^{-2}]}{[H_2S]} = \frac{(10^{-3})^2(S^{-2})}{(0.1)}$$

$$[S^{-2}] = 1.1\times10^{-16}$$

putting this in equation (ii)

$$E = -0.639 - \frac{0.0591}{2}\log 1.1\times10^{-16} = -\mathbf{0.1674V}$$

91. $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H_1 = -56700$ J/mole ...(i)

$2H_2O \longrightarrow 2H^+ + 2OH^- \quad \Delta H_2 = 2\times19050$ ...(ii)

cell reaction:

at anode: $H_2 \longrightarrow 2H_+ + 2e^-$

at cathode: $2e^- + H_2O + \frac{1}{2}O_2 \longrightarrow 2OH^-$

net reaction: $H_2 + H_2O + \frac{1}{2}O_2 \longrightarrow 2H_+ + 2OH^-$ ...(iii)

equation (i) + (ii) = (iii)

$$\Delta G_1 + \Delta G_2 = \Delta G_3$$
$$\Delta H_1 - T\Delta S_1 + \Delta H_2 - T\Delta S_2 = -nFE$$
$$(\Delta H_1 + \Delta H_2) - T(\Delta S_1 + \Delta S_2) = -2\,FE$$
$$(\Delta H_1 + \Delta H_2) - T(\Delta S_{net}) = -2\,FE$$

$$\Delta S = nF\frac{dE}{dT} \quad \text{so}$$

(See heat of reaction in electrochemical cell)
we know

$$\Delta H = nF\left[T\left(\frac{dE}{dT}\right) - E\right]$$

$$\Delta H = -56700 + 38100 = -18600 \text{ J/mole}$$

$$T\times\left[\frac{dE}{dT}\right] = 0.001158\times298 = 0.345$$

$$\therefore \quad \frac{\Delta H}{nF} = \frac{-18600}{2\times96500} = [0.345 - E]$$

$$E = +0.09637 + 0.345 = 0.44137$$

92. λ_{eq} = Ionic mobility × 96500

$\lambda_M = \lambda_{eq}\times$ (v.f.)

For K^+ ion v.f. = 1 so

$$\lambda_{eq} = \lambda_M = 73.52$$

Ionic mobility

$$= \frac{73.52}{96500} = \frac{\text{speed}}{\text{potential gradient}}$$

$$\therefore \text{ speed } (\mu) = \frac{73.52}{96500}\times\frac{6}{10} = 0.000457 \text{ cm/sec}$$

Distance = $\mu\times t = 0.000457\times7200 = 3.29$ cm

93. moles of Tl^{+1} initially = 0.0025
moles of Co^{+3} initially = 0.005

$$\begin{array}{llll} Tl^{+1} & + \quad 2Co^{+3} & \longrightarrow 2Co^{+2} & + \quad Tl^{+3} \\ 0.0025 \text{ Mole} & 0.005 \text{ Mole} & - & - \\ x & 2x & 0.005-2x & 0.0025-x \end{array}$$

$$E^\circ\text{cell} = 1.84 - 1.25 = 0.59 = \frac{0.0591}{2}\log K_{eq}$$

$\therefore \quad K_{eq} = 10^{20}$

since K_{eq} value is very high almost all Tl^+ & Co^{+3} will convert into Tl^{+3} & Co^{+2} respectively.

$\therefore \quad 0.005 - 2x = 0.005$

$0.0025 - x = 0.0025$

$$10^{20} = \frac{(0.005)^2(0.0025)}{4x^3}$$

$x = 5.386\times10^{-10}$ mole

total volume = 50 mL = 0.05 L

$$[Co^{+3}] = \frac{2\times5.386\times10^{-10}}{0.05} = 2\times10^{-8}$$

$$[Tl^+] = 10^{-8}$$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. **(b)** For the given reaction.

$$E_{Cell} = E^o_{cell} - \frac{0.0591}{2}\log K_{eq}$$

At equilibrium, $= E_{cell} = 0$

$$\therefore \quad E^o_{cell} = \frac{0.0591}{2}\log K_{eq}$$

$$0.23 = \frac{0.0591}{2}\log K_{eq}$$

$\therefore \quad \log K_{eq} = 7.78$

$\therefore \quad K_{eq} = 6.26\times10^7$

2. **(d)** Concentration of Ag^+ in LHE = $C_1 = xM$
Concentration of Ag^+ in RHE = $C_2 = 0.1M$
For the given cell

$$E_{cell} = E^o_{cell} + \frac{0.059}{1}\log\frac{C_2}{C_1}$$

$$0.164 = \frac{0.059}{1}\log\frac{0.1}{x}$$

[since $E^o_{cell} = 0$ for concentration cell]

$$\log\frac{0.1}{x} = 2.8$$

$$\frac{0.1}{x} = 6.26\times10^{2}$$

$$x = 1.6 \times 10^{-4} = [Ag^{+}]$$

$$[CrO_4^{-2}] = \frac{1}{2}[Ag^{+}] = 0.8\times10^{-4}$$

$$K_{sp}(Ag_2CrO_4) = [Ag^{+}]^2[CrO_4^{-2}]$$

$$= 2.44 \times 10^{-12}$$

3. **(c)** Let 'E' be the emf of a cell I (With lower EMF)
According to the given value,

$$E = E^{o} - \frac{0.06}{2}\log\frac{[Zn^{+2}]}{[Cu^{+2}]} \text{ for cell-I} \quad (1)$$

$$E + 0.03 = E^{o} - \frac{0.06}{2}\log\frac{[Zn^{+2}]}{0.5} \text{ for cell-II} \quad (2)$$

Eq. (2) – Eq. (1)

$$0.03 = \frac{0.06}{2}\log\frac{0.5}{[Cu^{+2}]}$$

$$\Rightarrow \quad \log\frac{0.5}{[Cu^{+2}]} = \log 10$$

or $\quad [Cu^{+2}] = 0.05M$

4. **(b)** $In^{+2} + e^{-} \longrightarrow In^{+}, \Delta G^{0} = -1 \times F(-0.4)$
$In^{+} \longrightarrow In^{+3} + 2e^{-}\ \Delta G^{0} = -2F(0.42)$
$In^{+2} \longrightarrow In^{+3} + e^{-}$ (Oxidation)
Use $nE^{o} = n_1E_1^{o} + n_2E_2^{o}$
$-1 \times FE^{0} = 0.4F - 0.84F$

$$\therefore \quad E^{\circ}_{In^{+2}/In^{+3}} = 0.44V$$

$$\therefore \quad E^{\circ}_{In^{+3}/In^{+2}} = -0.44\,V$$

Now $E^{o}_{cell} = E^{o}_{C} - E^{o}_{A}$

$$= 0.15 - (-0.44) = 0.59V$$

At equilibrium, $E^{\circ}_{cell} = 0.59 = \frac{0.059}{1}\log K_{eq}$

$$K_{eq} = 10^{10}$$

5. **(a)** $Ksp(AgBr) = [Ag^{+}][Br^{-}] = 12 \times 10^{-14}$

$$[Ag^{+}] = [Ag^{+}]_{AgBr} + [Ag^{+}]_{AgNo_3} = x + 10^{-7}$$

$\therefore \quad (x + 10^{-7})(x) = 12 \times 10^{-14}$
On solving, $x = 3 \times 10^{-7}$
$\therefore \quad [Ag^{+}] = 3 \times 10^{-7} + 10^{-7} = 4 \times 10^{-7} \times 10^{-3}$
$= 4 \times 10^{-4}$ mole/m^3
Similarly, $[Br^{-}] = 3 \times 10^{-4}$

$$[NO_3^{-}] = 10^{-4}$$

$$K_{Ag^{+}} = \lambda c = 6\times10^{-3}\times4\times10^{-4} = 24\times10^{-7}$$

$$K_{Br^{-}} = 8\times10^{-3}\times3\times10^{-4} = 24\times10^{-7}$$

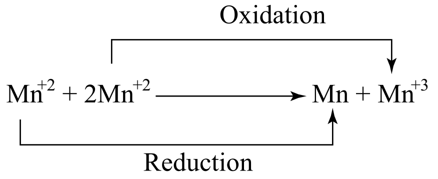
$$K_{NO_3^{-}} = 7\times10^{-3}\times10^{-4} = 7\times10^{-7}$$

Total conductivity $= K_{Ag^{+}} + K_{Br^{-}} + K_{NO_3^{-}} = 55\times10^{-7}$

6. **(d)** Higher the standard reduction potential, better is oxidising agent. Among the given $E^{o}_{MnO_4^{-}/Mn^{2+}}$ is highest, hence MnO_4^{-} is the strongest oxidising agent.

7. **(a, b) Hint:** This problem is based on characteristics of salt-bridge.
Functions of salt-bridge are
   (i) It connects the two half-cells and completes the cell circuit.
   (ii) It keeps the solutions of two half-cells and complete the cell circuit but does not participate chemically in the cell reaction.
   (iii) It maintains the diffusion of ions from one electrode to another electrode.
   (iv) A cell reaction may also occur in the absence of salt-bridge. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt-bridge. So, option (c) is incorrect.
   (v) This prevent mixing of two electrolytic solutions hence, option (d) is incorrect choice.
Hence, correct choices are (a), (b).

8. **(a)**



$$E^{\circ}_{cell} = (E^{\circ}_{A})_{OP} + (E^{\circ}_{C})_{R.P}$$

$$E^{\circ}_{Mn^{+2}/Mn^{+3}} + E^{\circ}_{Mn^{+2}/Mn} = -1.51 + [-1.18] = -2.69$$

Since $E^{o} = -Ve$
$\therefore$ Non spontaneous at standard condition.

9. **(c)** According to Debye Huckel Onasager equation,

$$\lambda_C = \lambda_{\infty} - B\sqrt{C}$$

where, λ_C = limiting equivalent conductivity at concentration C
λ_{∞} = limiting equivalent conductivity at infinite dilution
C = concentration

10. **(a)** $\quad K = 1.4$ Sm^{-1}, $R = 50\ \Omega$, $M = 0.2$

$$(K) = \frac{1}{R}\times\frac{l}{A}$$

$$\Rightarrow \quad \frac{l}{A} = 50 \times 1.4 \text{ m}^{-1}$$

For second solution, $R = 280, \frac{l}{A} = 50\times1.4 \text{ m}^{-1}$

$$K = \frac{1}{280}\times1.4\times50 = \frac{1}{4}$$

Now, molar conductivity

$$\lambda_m = \frac{K}{1000 \times M} = \frac{1/4}{1000 \times 0.5} = \frac{1}{2000}$$

$$= \mathbf{5 \times 10^{-4} S\ m^2 mol^{-1}}$$

11. (d)

Hint: When different number of electrons are involved in a redox reaction

Use $n_3E_3^o = n_1E_1^o + n_2E_2^o$

$$\therefore \quad n_3 = \frac{n_1E_1^o + n_2E_2^o}{n_3}$$

(P) $E^o_{3\ Fe^{3+}/Fe}$

Net reaction $Fe^{3+} \longrightarrow Fe$

is obtained from both given reaction

$Fe^{3+} + e^- \longrightarrow Fe^{3+}$

$n_1 = 1 \qquad E_1^o = 0.77\text{ V}$

$Fe^{2+} + 2e^- \longrightarrow Fe$

$n_2 = 2 \qquad E_2^o = -0.44\text{ V}$

$\because \quad Fe^{3+} + 3e^- \longrightarrow Fe \qquad n_3 = 3 \qquad E_3^o = ?$

$$E_3^o = \frac{n_1E_1^o + n_2E_2^o}{n_3} = \frac{0.77 + 2(-0.44)}{3}$$

$$= \frac{-0.11}{3} = -0.04\text{ V}$$

$\therefore$ P – (3)

Net reaction

$4H_2O \rightleftharpoons 4H^+ + 4OH^-$

is obtained from both given reaction

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$

$4H_2O \longrightarrow 4H^+ + 4e^-$

$$E_3^o = \frac{n_1E_1^o + n_2E_2^o}{n_3} = E_1^o + E_2^o = 1.23 + 0.40$$

$$= -0.83\text{ V}$$

$\therefore$ Q — (4)

(R) $Cu^{2+} + Cu \longrightarrow Cu^+ + Cu^+$

For thus E° of $Cu^{2+} \longrightarrow Cu^+$ is also required.

$Cu^{2+} + 2e^- \longrightarrow Cu$

$Cu \longrightarrow Cu^+ + e^-$

$Cu^{2+} + e^- \longrightarrow Cu^+$

$$E_3^o = \frac{n_1E_1^o + n_2E_2^o}{n_3}$$

$$= \frac{2 \times 0.34 + 1 \times (-0.52)}{1} = 0.16\text{ V}$$

Also,

$Cu \longrightarrow Cu^+ + e^-$

$Cu^{2+} + e^- \longrightarrow Cu^+$

$Cu^{2+} + Cu \longrightarrow Cu^+ + Cu^+$

$E^\circ = -0.52 + 0.16 = -0.36\text{ V}$

$\therefore$ (R) — (1)

(S)$Cr^{3+} \longrightarrow Cr^{2+}$

is obtained from

$Cr^{3+} + 3e^- \longrightarrow Cr$

$Cr \longrightarrow Cr^{2+} + 2e^-$

$Cr^{3+} + e^- \longrightarrow Cr^{2+}$

$$E_3^o = \frac{-0.74 \times 3 + 2 \times 0.91}{1} = -0.4\text{ V}$$

Thus, S = (2)

P — (3), Q – (4), R — (1), S – (2)

12. (b) Given, $Q = 2F$

Atomic mass of Cu = 63.5 u

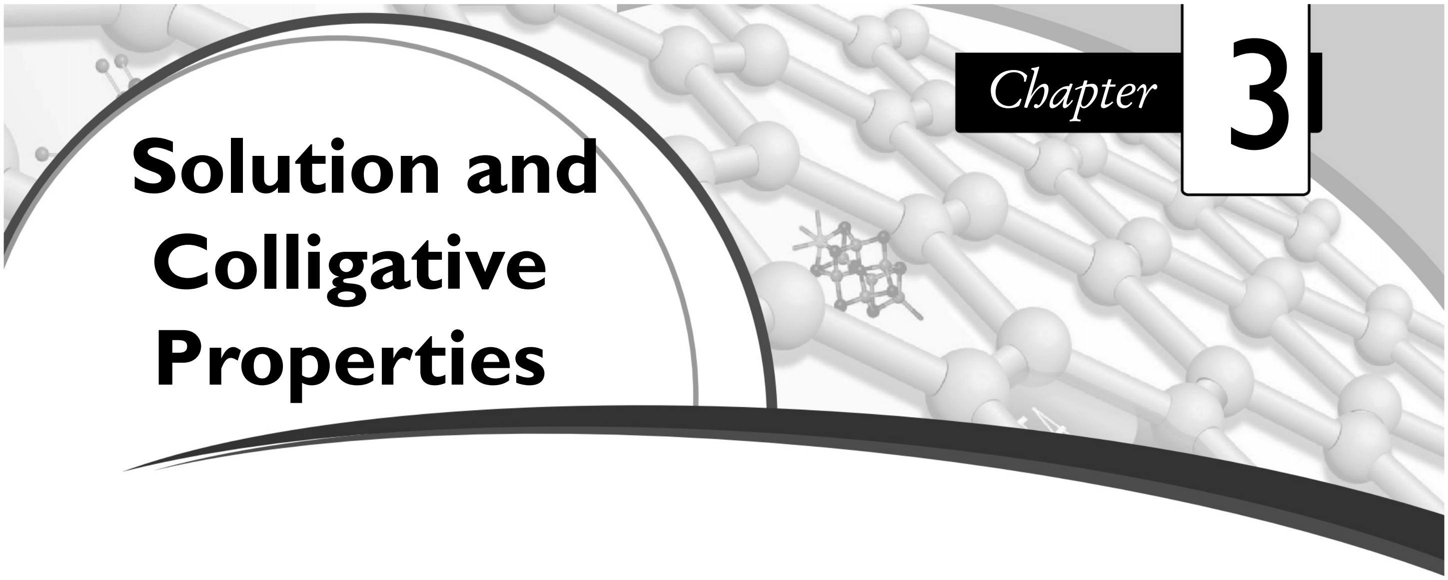
Valency of the metal $Z = 2$

We have, $CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

$$\underset{1\text{mol}}{Cu^{2+}} + \underset{\substack{2\text{mol}\\2F}}{2e^-} \longrightarrow \underset{1\text{mol}=63.5\text{g}}{Cu}$$

Alternatively,

$$W = ZQ = \frac{E}{F} \cdot 2F = 2E = \frac{2 \times 63.5}{2} = 63.5$$



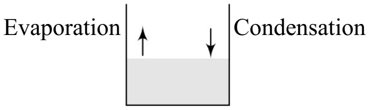
Chapter 3

Solution and Colligative Properties

Key Concepts

Solute (Solid/Liquid/Gas) + Liquid solvent $\longrightarrow$ Liquid solution (Homogeneous Mixture)

Vapour Pressure of Pure Liquid
At equilibrium
Rate of evaporation = Rate of condensation



It is the equilibrium pressure exerted by the vapours of the liquid on the liquid surface.

Factors affecting vapour pressure of pure liquid

(1) Nature of liquid
Intermolecular forces ↓ ⇒ volatility↑ or B.P. ↓ ⇒ V.P. ↑

(2) Temperature effect
Temperature ↑ → more vapour pressure ↑
Variation of Vapour Pressure with temperature is given by classius – Clapeyron's equation

$$\ln\frac{P_2}{P_1} = \frac{\Delta H\ \text{vap.}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$H_2O(l) \rightleftharpoons H_2O(g)$$

$$\partial(\Delta G) = \Delta V\,\partial P - \Delta S\,\partial T$$

At equilibrium $\Delta G = 0$

$$\Delta V = V_g - V_l \simeq V_g$$

Since $V_g >>> V_l$

$$= \frac{RT}{P}\ (\text{for 1 mole})$$

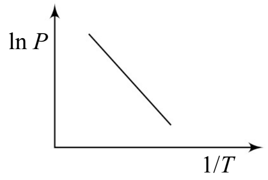
$$= \frac{nRT}{P}\ \text{for } n \text{ mole}$$

$$\Delta S = \frac{\Delta H_{\text{vap.}}}{T}$$

$$\frac{RT}{P}dP = \frac{\Delta H}{T}dT$$

$$\int_{P_1}^{P_2}\frac{dP}{P} = \frac{\Delta H}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

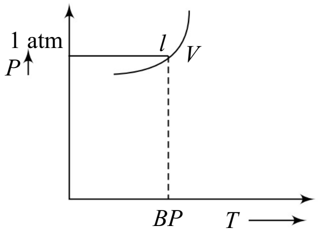
$$\ln\frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$



or $\ln P = \dfrac{-\Delta H}{RT} + C$ from indefinite integration

or $\dfrac{d}{dT}(\ln P) = \dfrac{\Delta H}{RT^2}$ **differential form** for pure liquid at a given temperature its vapour pressure is fixed it is independent of size or shape of the vessel.

Boiling Point



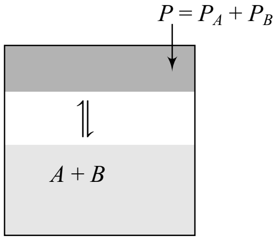
It is the temperature at which vapour pressure of liquid becomes equal to external pressure. When external pressure is 1 atm it is called normal boiling point.

⇒ It is difficult to cook food on mountains or hilly areas because boiling point decreases as external pressure is less.

⇒ It is convenient to cook the food in pressure cooker because boiling point increases as external pressure is high.

Raoult's Law

For two miscible and volatile liquids



$$P_A \propto x_A \Rightarrow P_A = P_A^o \cdot x_A$$

$$P_B \propto x_B \Rightarrow P_B = P_B^o \cdot x_B$$

at a given temperature P_A and P_B are the partial pressure of the vapours of A and B respectively.

P_A^o and P_B^o vapour pressure of pure liquid A and B respectively.

x_A and x_B mole fraction of A and B in solution or in liquid phase.

Total vapour pressure of solution

$$P = P_A + P_B$$

$$P = P_A^o x_A + P_B^o x_B \qquad \text{(i)}$$

$$P = P_A^o x_A + P_B^o (1 - x_A)$$

$$P = (P_A^o - P_B^o) x_A + P_B^o$$

If $x_A = 1 - x_B$ from (i)

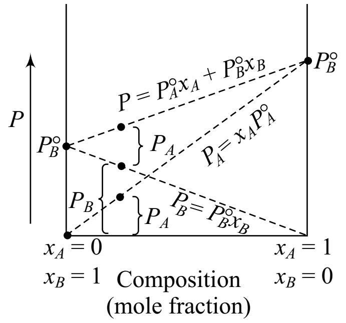
$$P = (P_B^o - P_A^o) x_B + P_A^o$$

Example, If $P = 90 + 120 x_B$ find P_A^o and P_B^o if $P_A^o = 90$ mm Hg

If $\quad x_B = 1; x_A = 0 \therefore P = P_B^o = 210$ mmHg

$\quad x_B = 0; x_A = 1 \therefore P = P_A^o = 90$ mmHg

Graphical Representation of Raoult's Law



Relationship between mole fraction in liquid phase (x_A) and mole fraction in vapour phase in distillate (y_A)

$P_A = P_A^o x_A = y_A P$ by gaseous state Dalton's law

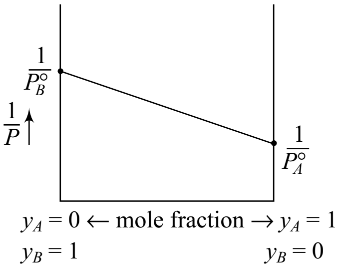
P_A = mole fraction in gas phase (y_A) × total Pressure (P)

$$P_B = P_B^o x_B = y_B P$$

TOTAL V. PRESSURE OF SOLUTION IN TERMS OF y_A

$$x_A + x_B = 1$$

$$\frac{P \cdot y_A}{P_A^o} + \frac{P \cdot y_B}{P_B^o} = 1$$

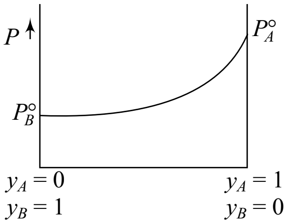


$$\frac{y_A}{P_A^o} + \frac{1 - y_A}{P_B^o} = \frac{1}{P}$$

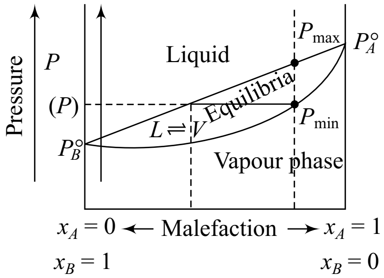
$$\frac{1}{P} = \left(\frac{1}{P_A^o} - \frac{1}{P_B^o}\right) y_A + \frac{1}{P_B^o}$$

$$P = \frac{P_A^o - P_B^o}{(P_B^o - P_A^o) y_A + P_A^o} \qquad \frac{1}{P} = \frac{(P_B^o - P_A^o) y_A + P_A^o}{P_A^o - P_B^o}$$

P vs y_A graph will be a curve definitely.



Graphical Representation of Compositions in Liquid phase, Vapour phase and Effect of Pressures



⇒ If $P_{\text{system}} > P_{\max} \Rightarrow$ only liquid phase will exist there.

⇒ If $P_{\text{system}} < P_{\max} > P_{\min} \Rightarrow L \rightleftharpoons V$ will exist.

⇒ If $P_{\text{system}} < P_{\min} \Rightarrow$ only vapour phase will exist.

Case 1

When for vapour mixture of A and B pressure is increased.

Effect:

If ($n_A = 1$ and $n_B = 1$)

Condition (a)

At $P = P_{\min} \Rightarrow$ first drop of liquid is formed, so it is called **Dew Point**.

$$y_A = \frac{1}{2} \quad y_B = \frac{1}{2}$$

Condition (b)

at $P = P_{\max.} \Rightarrow$ last bubble of vapour remains

$$x_A = \frac{1}{2} \quad x_B = \frac{1}{2}$$

Case 2

For liquid mixture of A and B pressure is decreased.

If ($n_A = 2; n_B = 1$)

Condition (a)

at $P = P_{\text{max}} \Rightarrow$ first bubble of vapour is formed, so it is called **Bubble Point.**

$$x_A = \frac{2}{3};\ x_B = \frac{1}{3}$$

Condition (b)

at $P = P_{\text{min}} \Rightarrow$ Last drop of liquid remains

$$y_A = \frac{2}{3} \quad y_B = \frac{1}{3}$$

Raoult's Law When non-volatile solute (B) is added to pure solvent (A).

Total pressure of solution P or P_S

B is non-volatile so no vapour will be there but $x_B \neq 0$. $\therefore x_A < 1$, i.e., vapour pressure will decrease.

$$P_S = P_A^{\circ} x_A + P_B^{\circ} x_B \ (P_B^{\circ} = 0)$$

$$P_S = P_A^{\circ}(1 - x_B)$$

$$P_S = P_A^{\circ} - P_A^{\circ} x_B$$

$$x_B = \frac{P_A^{\circ} - P_S}{P_A^{\circ}}$$

x_B = mole fraction of non-volatile solute

$P_A^{\circ} - P_S = \Delta P =$ Lowering in vapour pressure

$\dfrac{\Delta P}{P_A^{\circ}} =$ relative lowering in vapour pressure.

> ***Note:***
> On adding non-volatile solute vapour, pressure decreases and according to Raoult's Law, mole fraction of non-volatile solute becomes equal to relative lowering in vapour pressure.

$$\frac{P_A^{\circ} - P_S}{P_A^{\circ}} = \frac{n_B}{n_A + n_B}$$

$$\frac{P_A^{\circ}}{P_A^{\circ} - P_S} = \frac{n_A + n_B}{n_B} = \frac{n_A}{n_B} + 1$$

$$\frac{P_A^{\circ}}{P_A^{\circ} - P_S} - 1 \Rightarrow \frac{P_S}{P_A^{\circ} - P_S} = \frac{n_A}{n_B}$$

$\boxed{\dfrac{P_A^{\circ} - P_S}{P_S} = \dfrac{n_B}{n_A}}$ always correct for any solution dilute or concentrate solution.

$\dfrac{P_A^{\circ} - P_S}{P_A^{\circ}} = \dfrac{n_B}{n_A}$ for dilute solution only

Since If $n_B << n_A$

$$n_A + n_B = n_A$$

Molality $m = \dfrac{n_B}{w_A} \times 1000 = \dfrac{\text{No of moles of solute}}{\text{weight of solvent in kg}}$

$$\frac{n_B}{n_A} = \frac{n_B}{w_A} \times m_A \text{ (mol wt. of solvent)}$$

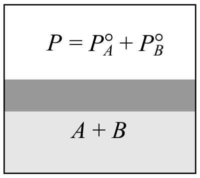
$$\Rightarrow \quad \frac{n_B}{n_A} = \frac{m}{1000} \times m_A = \frac{P_A^0 - P_S}{P_S}$$

$$\therefore \quad \frac{P_A^{\circ} - P_S}{P_S} \times \frac{1000}{m_A} = m$$

Mixture of two immiscible liquid

They will behave like two separate liquids.

$$P_A = P_A^{\circ} \quad \text{and} \quad P_B = P_B^{\circ}$$



Total vapour pressure of mixture $P = P_A^{\circ} + P_B^{\circ}$

Two immiscible liquid behave like separate pure liquids so that partial pressure will be equal to their pure form.

> ***Note:***
> As vapour pressure of the mixture is greater than both the two components in pure form, so boiling point becomes lesser than both the two components in pure form.

$$T < T_A^{\circ};\ T < T_B^{\circ}$$

$$\because P_A = P \quad \therefore \quad y_A = P_A^{\circ}; \quad P_B = P \quad \therefore\ y_B = P_B^{\circ}$$

So $\dfrac{P_A^{\circ}}{P_B^{\circ}} = \dfrac{y_A}{y_B} = \dfrac{n_A}{n_B} = \dfrac{w_A/m_A}{w_B/m_B}$

n_A, n_B are moles of A and B in vapour phase.

Ideal solutions

1. These solutions obey the Raoult's Law.

   i.e., $P_A = P_A^{\circ} x_A;\ P_B = P_B^{\circ} x_B$

   $P = P_A^{\circ} x_A + P_B^{\circ} x_B$
2. Strength of intermolecular forces remain unchanged, before and after the mixing.

   $F_{A\text{–}B} = F_{A\text{–}A} = F_{B\text{–}B}$
3. $\Delta H_{\text{mix}} = 0$ ($\because$ no changes in intermolecular forces) hence no change in interaction.
4. $\Delta V_{\text{mix}} = 0 \quad \because \quad V_f = V_A + V_B$

   $\because$ No change in intermolecular forces.
5. ΔS_{mix} = +ve (for both ideal and non-ideal solution)
6. ΔG_{mix} = –ve (has spontaneity for both ideal and non-ideal solution)

   $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$

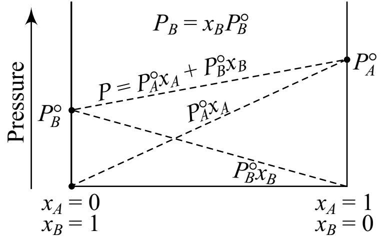
   Since $\Delta H_{\text{mix}} = 0$

   $\therefore \quad \Delta G = -T\Delta S_{\text{mix}} = -\text{ve}$

Since

$P_A = x_A P_A^\circ$

$P_B = x_B P_B^\circ$



Examples:

⇒ Benzene + Toluene

⇒ Methanol + Ethonal (Homologues)

⇒ Ethyl chloride + Ethyle bromide

⇒ Clorobenzene + Bromo benzene

⇒ Very dilute solution

Non-Ideal solution

They do not obey the Rault's law.

$$P_A \neq P_A^\circ x_A;\ P_B \neq P_B^\circ x_B;\ P \neq P_A^\circ x_A + P_B^\circ x_B$$

Non-ideal solution can be of two types:

Showing positive deviation from Rault's law.

Showing negative deviation from Rault's law.

*** Showing positive deviation from Rault's law:**

1. Volatility more compare than the ideal solution, i.e.,

   $$P_A > P_A^\circ x_A;\ P_B > P_B^\circ x_B;\ P > P_A^\circ x_A + P_B^\circ x_B .$$

2. Strength of intermolecular forces decreases
3. ΔH_{mix} = +ve (heat absorbed)
4. ΔV_{mix} = +ve, $V_f > (V_A + V_B)$ (bond formed is weak so distance between the particle increases)

Example:

Alcohol + Water

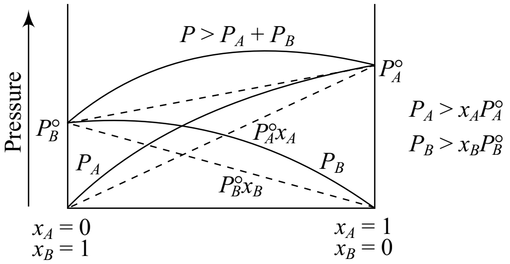
{Intermolecular H bonding comparatively weaker than pure water)

$CH_3COCH_3 + CCl_4$ or CS_2 (Interaction weaker)

↓ ↓

Polar Nature Non-Polar

Graphical Representation



Showing Negations Deviation From Raoult's Law:

1. Volatility decreases compare to the ideal solution, i.e.,

   $$P_A < P_A^\circ x_A;\ P_B < P_B^\circ x_B;\ P < P_A^\circ x_A + P_B^\circ x_B$$

2. Strength of intermolecular forces increases is

   $$F_{A-B} > F_{A-A}, F_{B-B}$$

3. ΔH_{mix} = –ve (heat releases)
4. ΔV_{mix} = –ve; $V_f < (V_A + V_B)$

Examples:

1. Acid + Water (form more stronger H bond)
2. CH_3COCH_3 + $CHCl_3$ (accetone + Chloroform)

↓ ↓ ↓

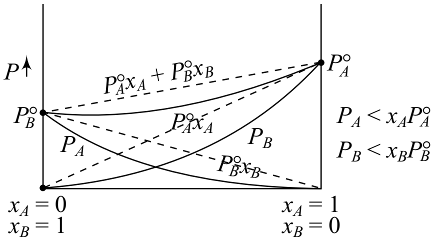
Form H-bond with chloroform due to which volatility decreases

↓es > C = 0 .... H.

Polar-polar

Van der Waal forces

Graphical Representation



Azeotropic Mixture OR Constant Boiling Mixture

These are the liquid mixtures which distill off without change in their composition.

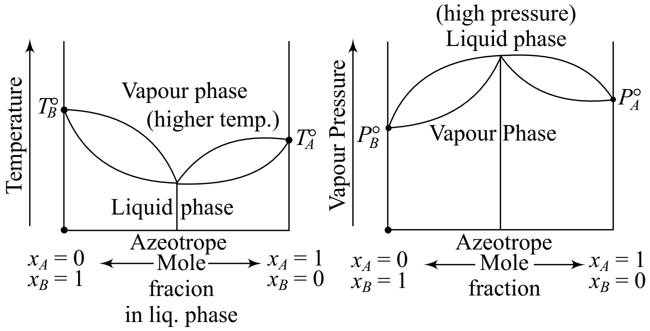
Azeotropism observed in non-ideal solution at a given pressure for the fixed composition.

At this condition separation of two liquids is not possible. Azeotropic mixtures can be of two types.

Minimum Boiling Azeotrops

1. B.P. of azeotropic mixture is less than both the two components.
2. It is formed by the solution which shows +ve deviation from R Law.

Graphical Representation



Example:

Boiling point of $C_2H_5OH + H_2O$

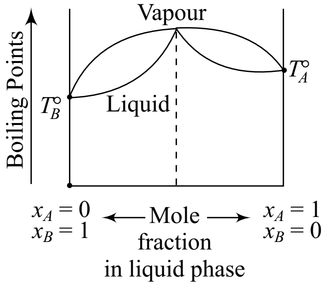
(96%) (4%) By weight

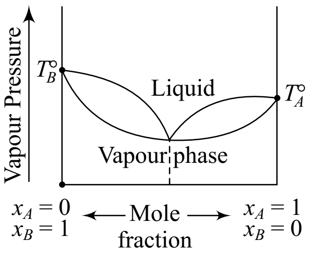
Mixture 78°C and Bolling Point of H_2O = 100°C Bolling point of ethenol = 78.6°C which is less than BP of ethanol or water.

Maximum Boiling Areotrope:

1. Bolling point of the mixture is more than both the two components.
2. It is observed in those solution which show –ve deviation.

Graphical Representation





Example:

$HNO_3 + H_2O$

(68%) (32%) by weight at 1 atm. pressure

B.P. (mixture) = 120.6°C, Which is greater than Boiling Point of water (100°C) and Boiling Point of HNO_3 (80°C)

COLLIGATIVE PROPERTIES

These are the properties of dilute solutions which depends only on the number of particles of the solute but independent of its nature.

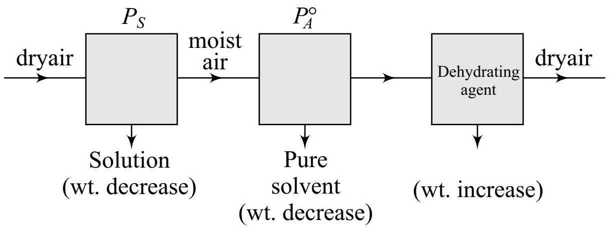
There are four colligative properties:

1. Relative lowering of vapour pressure $\dfrac{\Delta P}{P_A^o} = x_B$ (x_B = mole fraction of solute).
2. Elevation in boling point.
3. Depression in freezing point.
4. Osmotic pressure

   Osmotic pressure are mainly used to find molar mass of unknown solute.

Measurement of Relative Lowering of Vapour Pressure by Ostwald and Walker Method:

Since $P_A^o > P_S$



Decrease in mass of solution $\propto P_S$

Decrease in mass of pure solvent $\propto P_A^o - P_S$

Increase in mass of dehydrating agent = Decrease in mass of (solution + solvent) $\propto P_A^o$

$$\frac{P_A^o - P_S}{P_A^o} = \frac{\text{Decrease in mass of solvent}}{\text{Increase in mass of the dehydrating agent}}$$

$$\frac{P_A^o - P_S}{P_S} = \frac{\text{Decrease in mass of solvent}}{\text{Decrease in mass of solution}}$$

Elevation in Boiling Point:

On adding non-volatile solute vapour pressure decreases so boiling point increases. Then elevation in boiling point ΔT_b

$$\Delta T_b = T_b - T_b^o$$

T_b OR $(T_b)_s$ – boiling point of solution

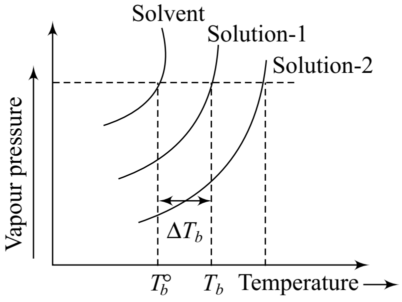
T_b^o – boiling point of pure solvent

$\Delta T_b \propto \Delta P$ Lowering is vapour pressure

$$\frac{\Delta P}{P_S} = \frac{n_B}{n_A} = \frac{m \times m_A}{1000}$$

m_A = Molarmass of solvent

m = molality



$\Delta P \propto m$

$\Delta T_b \propto m$

$\Delta T_b = K_b m$

K_b Molal elevation constant

$\Delta T_b = K_{bm}$

$$\Delta T_b = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

m_B = molarmass of solute.

Here solute is neither associating nor dissociating.

Molal elevation constant (K_b):

It is the characteristic property of the solvent.

$$K_b = \frac{R(T_b^o)^2 \times m_A}{1000 \times \Delta H_{\text{vap.}}}$$

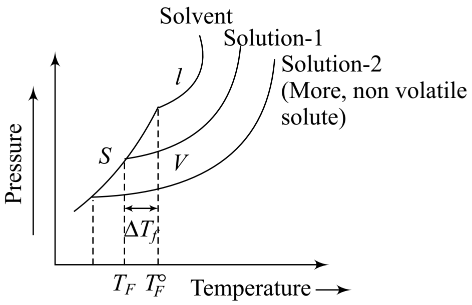
$\Delta H_{\text{vap.}}$ molar heat of vapourisation (should in per mole)

K_b for water = 0.52 K kg Mol^{-1}

Unit of K_b = K $molal^{-1}$ or K kg mol^{-1}

Depression in freezing point:

Freezing point is the temperature at which vapour pressure of solution and liquid phase becomes equal.



At Freezing Point

Liquid Solvent in Solution $\rightleftharpoons$ Solid Solvent

So, at Freezing Point only solvent solidify, so that amount of solvent remains unchanged in the solution and concentration of solution increases.

or

On adding non-volatile solute vapour pressure decreases so Freezing Point also decreases depression in Freezing Point.

$$\Delta T_F = T_F^{o} - T_F$$

T_F^{o} = Freezing Point of pure solvent

T_F = Freezing Point of solutions.

$\Delta T_F \propto \Delta P \propto m$

$\Delta T_F \propto m$

$\Delta T_F = K_F \times m$

K_F = Molal depression constant or Cryoscopic constant

$$\Delta T_F = K_F \frac{w_B \times 1000}{m_B \times w_A}$$

Molal depression constant (K_F)

It is the characteristic property of the solvent.

$$K_F = \frac{R(T_F^{o})^2 \times m_A}{1000 \times \Delta H_{\text{fusions}}}$$

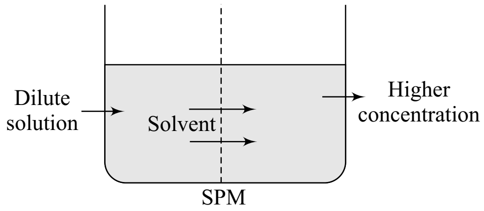
K_F for water = 1.86 K molal^{-1} or K. kg mol^{-1}

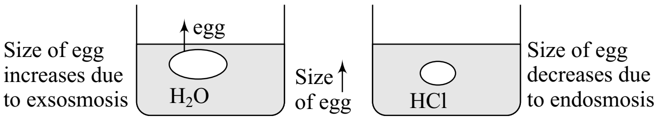
For dilute aqueous solutions molality ≃ molarity

$m \simeq M$

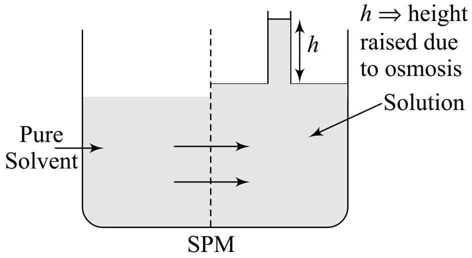
Osmosis:

It is the spontaneous phenomena in which solvent particles move from lesser concentrated solution to higher concentrated solution through a semi-permeable membrane. (SPM)





Osmotic Pressure (π):



$\pi = hdg$

It is the hydrostatic pressure developed on the solution which stops the osmosis.

It is the external pressure applied on the solution that just stops the osmosis.

1. If $P_{\text{ext}} = \pi$ no osmosis
2. If $P_{\text{ext}} < \pi$ osmosis will occur
3. If $P_{\text{ext}} > \pi$ reverse osmosis
   (Solvent particles moves in reverse direction)
   or towards dilute solution

Reverse Osmosis:

Solvent particles move in the reverse direction, i.e., from solution to the solvent.

This method is used in purification of sea water.

Vant-Hoff's Equation for Dilute Solution:

$\pi = CST$

$\pi = CRT$

π = osmotic pressure

$C = \frac{n}{V}$ [C - concentration of solution (Mol L^{-1})]

Solution constant $S = R = 0.0821$ atm L K^{-1} mol^{-1}

$$\pi = \frac{n}{V} RT$$

$\pi V = nRT$

n-moles of solute

Note:

1. For two different solution if $\pi_1 = \pi_2$ isotonic solution
2. If $\pi_1 \neq \pi_2$
   Solution with higher osmotic pressure forms hypertonic solution.
   Where solution is with lower osmotic pressure known as hypotonic solution.
   - The solvent particle moves from hypotonic to hypertonic
   - To just stop the osmosis external pressure should be applied on more concentrate solution and $P_{\text{ext.}} = \pi_2 - \pi_1$

Vant Hoff's factor (i):

$$i = \frac{\text{Number of particles of solute finally}}{\text{Number of particles of solute initially}}$$

$$= \frac{\text{Observed value of colligative properties}}{\text{Normal value of colligative properties}}$$

$$= \frac{\text{Normal molecular weight of solute}}{\text{Observed molecular weight of solute}}$$

(i) if $i > 1 \Rightarrow$ dissociation
(ii) if $i < 1 \Rightarrow$ association
(iii) if $i = 1 \Rightarrow$ neither dissociation nor association

Examples:

(i) $BaCl_2 \longrightarrow Ba^{+2} + 2Cl^-$ $\quad i = 3/1$
(ii) $K_3[Fe(CN)_6] \longrightarrow 3K^+ + [Fe(CN)_6]^-$ $\quad i = 4$
(iii) thimerisation $\Rightarrow i = 1/3$
(iv) dimerisation $\Rightarrow i = 1/2$

Relationship Between Degree of Dissociation (α) and *i*.

$$\begin{array}{lccc} & A & \rightleftharpoons & nB \\ \text{Initially} & 1 & & - \\ \text{Finally} & (1-\alpha) & & n\alpha \end{array}$$

$$i = \frac{(1-\alpha) + n\alpha}{1}$$

$$i = 1 + (n-1)\alpha$$

$$\alpha = \frac{i-1}{n-1}$$

Relationship between degree of association (α) and Vant-Huff factor (i):

$$\begin{array}{ccc} nA & \rightleftharpoons & A_n \\ 1 & & - \\ 1-\alpha & & \dfrac{\alpha}{n} \end{array}$$

$$i = \frac{1-\alpha+\dfrac{\alpha}{n}}{1} \Rightarrow i = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$$\alpha = \frac{i-1}{1-n} \times n \qquad \alpha = \frac{1-i}{n-1} \times n$$

Modified Forms of Colligative Properties:

$$\frac{\Delta P}{P_A^{\circ}} = ix_B = i \times (\text{mole fraction of solute})$$

$$\Delta T_b = iK_b m$$

$$\Delta T_f = iK_f m$$

$$\pi = iCRT$$

Isotonic Solutions:

$\pi_1 = \pi_2$ Condition for isotonic

at a given temperature T

$$i_1C_1RT = i_2C_2RT$$

$i_1C_1 = i_2C_2$ Concentration should be mole based.

1. 0.1 M glucose, 0.1 M NaCl, 0.1 M $BaCl_2$

Colligative Property $\propto i \times C$

if C.P $\uparrow \Rightarrow$ V.P of Solution decreases
C.P $\uparrow \Rightarrow$ F.P of Solution decreases
C.P $\uparrow \Rightarrow$ B.P of Solution increases
C.P $\uparrow \Rightarrow \pi$ (Osmotic pressure) increases

2. 0.1 % glucose, 0.1% urea, 0.1% sucrose. if i same then

$$\text{C.P} \propto \frac{1}{\text{Molar mass}}$$

$\therefore$ C.P$_{max}$ for urea $\therefore$ V.P. and F.P. $\Rightarrow$ minimum
BP and $\pi \Rightarrow$ maximum

Concentration Term:-

Precent Strength

$$\frac{w}{w}\% = \frac{\text{weight solute}}{\text{weight of solution}} \times 100$$

$$= \frac{w_B}{w} \times 100$$

$$\frac{w}{V}\% = \frac{\text{weight of solute (in gram)}}{\text{volume of solution (in ml)}} \times 100$$

$$\frac{w}{V}\% = \frac{w_B}{v} \times 100$$

$$\frac{v}{v}\% = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$$

$$\frac{V}{V}\% = \frac{V_B}{V} \times 100$$

weight of solution $w = (v \times d)$ of solution.

Molarity (M) No of moles of solute in one Liter Solution

$$M = \frac{n_B}{V(\text{Liter})}$$

If V in ml

$$M = \frac{n_B}{\dfrac{V(\text{ml})}{1000}} = \frac{n_B}{V\,\text{ml}} \times 1000$$

Since, $V = \dfrac{w}{d}$

$$\therefore \quad M = \frac{w_B}{m_B} \times \frac{1000}{V(\text{ml})} = \frac{w_B}{V} \times 100 \times \frac{10}{m_B} = \frac{w}{V}\% \times \frac{10}{m_B}$$

$$M = \frac{w}{w}\% \times \frac{10d}{m_B}$$

Normality N:- No of gram equivalent in 1 Liter solution.

$$N = \frac{w_B}{\text{Eq. wt.}} \times \frac{1000}{V(\text{ml})} = n_f \cdot \frac{w_B}{m_B} \times \frac{1000}{V(\text{ml})} = n_f[M]$$

$$\therefore \quad N = n_f\left[\frac{w}{w}\% \frac{10d}{m_B}\right]$$

$\therefore \quad N = n_f \left[\frac{w}{V}\%\frac{10}{m_B}\right]$

$\because \quad \text{Equivalent weight} = \frac{\text{Molarmass}}{n-\text{factor}}$

Molefraction:- ratio of number of moles of one component to the total Number of moles of solution

Mole fraction of solute $x_B = \frac{n_B}{n_A + n_B}$ for binary solution.

$$\therefore \quad x_B = \frac{n_B}{\Sigma n} \qquad \ldots(i)$$

$$x_A = \frac{n_A}{n_A + n_B} = \text{mole fraction of solvent}$$

$x_A + x_B = 1$ from (i)

$$\therefore \quad n_B = x_B \times \Sigma n$$

$$\frac{w_B}{m_B} = x_B \times \Sigma n$$

$$\therefore \quad w_B = x_B \times \Sigma n \times m_B \qquad \ldots(ii)$$

and $w_A = x_A \times \Sigma n \times m_A \qquad \ldots(iii)$

we know molality m = No of moles of solute in one kg solvent

$$\therefore \quad m = \frac{w_B}{m_B} \times \frac{1000}{w_A}$$

From (i) and (ii)

$$m = \frac{x_B \Sigma n\, m_B}{m_B} \times \frac{1000}{x_A \Sigma n\, m_A} = \frac{x_B}{x_A} \times \frac{1000}{m_A} = m$$

m_A = molar mass of solvent.

Relation between molality (m) and Molarity (M) :-

If molarity of solution (M) means M moles solute dissolve in 1000 ml solution, if density of solution d gm/ml

weight of solution = $V \times d$ = $1000 \times d$

weight of solvent = weight of solution – weight solute

$$w_A = 1000\,d - Mm_B$$

$$\therefore \quad \text{Molality } m = \frac{w_B}{m_B} \times \frac{1000}{w_A}$$

$$\boxed{m = \frac{M \times 1000}{1000d - Mm_B}}$$

Since, $n_B = \frac{w_B}{m_B} = M$ = No. of moles of solute in 1 liter solution.

Factors Affecting Solubility of Gases, in Liquid:

1. **Nature of gas and liquid:**
   In polar solvents like water polar gases are more soluble whereas, solubility of non-polar gases is lesser (like dissolves like). Gases which can be liquefied easily are comparatively more soluble in water.
2. **Temperature:**
   Gas + Liquid ⇒ Solution + heat (exothermic)
   As dissolution of gas in liquid is exothermic process. So on increasing the temperature solubility decreases.
3. **Pressure:**
   On increasing the pressure solubility of gases in liquid increases. This effect is given by Henry's Law.

Henry's Law:

⇒ At a given temperature mass of the gas dissolve in the given amount of the solvent is directly proportional to partial pressure of gas.

$$m \propto P$$

$$\frac{m}{P} = \text{constant}$$

⇒ At constant temperature, mole fraction of the gas dissolve in liquid is directly proportional to partial pressure of the gas.

$$x_g \propto P$$

$P = K_H x_g$ $\quad K_H$: Henry constant

Unit → Pressure units.

Value of K_H depends on temperature and nature of gas and liquid.

$P = K_H \frac{n_g}{n_g + n_l}$ $\quad n_g$ – moles of gas dissolved

n_l - moles of the liquid

but

$$n_g << n_l$$

$$\Rightarrow \quad n_g + n_l \simeq n_l$$

$P = K_H \frac{n_g}{n_l}$ use this

According to Henry's law, at a constant temperature volume of gas dissolve in the given amount of solvent is independent of the pressure.

Applying ideal gas equation for dissolved gas,

$$PV = nRT$$

$$PV = \frac{\text{Mass}}{\text{Mwt}} RT$$

$$V = \left(\frac{M}{P}\right)\frac{RT}{\text{Mwt}}$$

$$V = \text{Constant}$$

Limitations of Henry' Law

1. Solubility of gases in liquid should not be too much.
2. Henry' law is applicable at high temperature and low pressure concentration.

Solved Examples

1. If 0.4 g of NaOH is present in 40 mL of solution. What is the molarity and normality [M.wt. of NaOH = 40]

Sol. We know that

Given $w_B = 0.4$ gram

$V = 40$ ml

$m_B = 40$

$$\therefore \quad M = \frac{w_B}{m_B} \times \frac{1000}{V(\text{ml})}$$

$$= \frac{0.4}{40} \times \frac{1000}{40} = 0.25 \text{ M}$$

$$N = n_f \times M$$
$$= 1 \times 0.25$$
$$= 0.25 \text{ N}$$

2. The normality of 1.5M H_3PO_4 is

Sol. Basicity of H_3PO_4 is 3

We know that $\text{N} = n_f \times M$

$$\text{N} = 1.5 \times 3 = 4.5$$

3. How much volume of 10 M HCl should be diluted with water to prepare 2.00 L of 5M HCl?

Sol. In dilution the following equation is applicable:

$$M_1V_1 = M_2V_2$$

10M HCl = 5M HCl

$$10 \times V_1 = 5 \times 2.00$$

$$V_1 = \frac{5 \times 2.00}{10} = 1.00 \text{ L}$$

4. Find out the weight of H_2SO_4 in 150 mL, $\frac{N}{7}$ H_2SO_4.

Sol. $$N = \frac{\text{Weight in gram}}{\text{Equivalent weight} \times \text{Volume}}$$

Weight in gram = Equivalent weight $\times N \times$ volume

$$= 49 \times \frac{1}{7} \times \frac{150}{1000} = \frac{21}{20} = 1.05 \text{ g}$$

5. Find out the molarity of 1 L of 93% H_2SO_4 and its density is 1.84.

Sol. Molatrity

$$M = \frac{\text{w}}{\text{w}}\% \times \frac{10d}{m_B} = \frac{93 \times 1.84 \times 10}{98}$$

$$= 78.68 \text{ M}$$

6. A 100 cm^3 solution is prepared by dissolving 2 g of NaOH in water. Calculate the normality of the solution.

Sol. $$N = \frac{w_B}{\text{Equivalent weight}} \times \frac{1000}{V(\text{ml})}$$

$$= \frac{2.0}{40} \times \frac{1000}{100} = \frac{N}{2}$$

7. Find the percentage by weight and weight fraction of aspirin in the solution prepared by dissolving 3.65 g of aspirin in 25.08 g of water.

Sol. Weight of solution = 3.65 + 25.08 = 28.73 g

$$\text{Weight fraction} = \frac{3.65}{28.73} = 0.127$$

Weight percent = 0.127 × 100 = 12.7%

8. A solution was prepared by adding 125 cm^3 of isopropyl alcohol to water until the volume of the solution was 175 cm^3. Find the volume fraction and volume percent of isopropyl alcohol in the solution.

Sol. Volume of solute = 125 cm^3

Volume of solution = 175 cm^3

$$\therefore \text{ volume fraction} = \frac{125}{175} = 0.714$$

$$\text{and volume percent} = \frac{125}{175} \times 100 = 71.4\%$$

9. The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. Calculate the molarity and normality of the solution.

Sol. $$M = \frac{w}{w}\% \times \frac{10d}{m_B}$$

$$= \frac{13 \times 10 \times 1.09}{98}$$

$$= 1.445 \text{ M}$$

10. Vapour pressure of solution containing 3 and 1 mol respectively of x and y is 550 mm at the same temperature another solution (containing 4 and 1 mol x and y respectively). The vapour pressure becomes 560 mm at this temperature calculate vapour pressure of x and y in pure form.

Sol. $x_x = \frac{3}{4}$ $\quad x_y = \frac{1}{4}$ $\quad P = 550$

$y_x = \frac{4}{5}$ $\quad x_y = \frac{1}{5}$ $\quad P = 560$

$$P = x_xP_x^o + x_yP_y^o$$

$$550 = \frac{3}{4}P_x^o + \frac{1}{4}P_y^o$$

$$560 = \frac{4}{5}P_x^o + \frac{1}{5}P_y^o$$

$$2200 = 3P_x^o + P_y^o$$

$$2800 = 4P_x^o + P_y^o$$

$$\underline{- \quad - \quad -}$$

$$-600 = -P_x^o$$

$$2200 = 1800 + P_y^o$$

$P_x^o = 600$ $\quad P_y^o = 400$

11. Two liquids A and B are miscible over the whole range of composition obeying the Raoults law at 350 K. The vapour pressure of pure A is 24 KP_a and B is 12 KP_a.

A mixture of 60% A and 40% B is distilled at this temperature. A small amount of the distillate is collected and read distill at 350 K. What is the composition of second distillate.

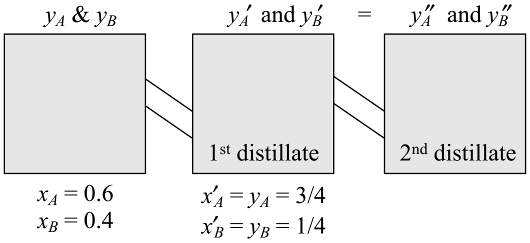
Sol. $P_A^o = 24\,\text{KP}_a \quad P_B^o = 12\,\text{KP}_a$

$$x_A = \frac{60}{60+40} \qquad x_B = \frac{40}{60+40}$$

$$= \frac{60}{100} \qquad = \frac{40}{100}$$

$$\frac{24\text{K}}{0.6} = P_A^o \qquad P_B^o = \frac{12\text{K}}{0.4}$$

$$40\text{K} = P_A^o \qquad P_B^o = 30\,\text{K}$$



$$y_A = \frac{P_A^o x_A}{P} = \frac{24 \times 0.6}{24 \times 0.6 + 12 \times 0.4} = \frac{3}{4}$$

$$y_B = \frac{1}{4}$$

$$x''_A = y'_A = \frac{24 \times \frac{3}{4}}{24 \times \frac{3}{4} + 12 \times \frac{1}{4}} = \frac{6}{7}$$

$$x''_B = \frac{1}{7}$$

12. A liquid mixture of A and B is composed of 1 mol of A and 1 and of B. If the pressure over the mixture at 300 K is reduced, at what pressure does the first bubble of vapour is formed. What is the composition of first bubble of vapour formed. If the pressure is reduced further. At what pressure does last drop of liquid disappear. What is the composition of last drop of liquid given.

P_A^o = 150 torr and P_B^o = 600 torr

Sol. (a) $P = \dfrac{P_A^o - P_B^o}{(P_B^o - P_A^o)\,y_A^o + y_B^o}$

$$x_A = x_B = \frac{1}{2}$$

$$P = P_A^o x_B + P_B^o x_B \qquad 150 \times \frac{1}{2} + 600 \times \frac{1}{2}$$

$$= 375 \text{ torr} \qquad 75 + 300 \Rightarrow 375$$

(b) Composition of vapour phase is required.

$$\text{So} \quad \frac{P_A^o x_A}{P} = y_A \Rightarrow \frac{150 \times 1/2}{375} = \frac{1}{5}$$

$$\therefore \quad y_B^o = \frac{4}{5}$$

(c) $y_A = y_B = \dfrac{1}{2}$

$$\frac{1}{P} = \left(\frac{1}{P_A^o} - \frac{1}{P_B^o}\right) y_A + \frac{1}{P_B^o}$$

$$\therefore \quad P = 240 \text{ torr}$$

(d) $x_A = \dfrac{4}{5} \quad x_B = \dfrac{1}{5}$ i.e., liquid phase composition is asked.

$$x_A = \frac{P y_A}{P_A^o} = \frac{240 \times 1/2}{150} = \frac{4}{5}$$

13. What mass of non-volatile solute is to be dissolved in 100 g of water to decrease the vapour pressure of water by 25%.

Sol. $\dfrac{\Delta P}{P_S} = \dfrac{n_B}{n_A}$

$$\boxed{\frac{P_A^o - P_S}{P_S} = \frac{n_B}{n_A}} = \frac{25}{75} = \frac{w_B \times 18}{60 \times 100}$$

$$\frac{25 \times 60 \times 100}{75 \times 18} = w_B$$

$$\frac{10}{9} \times 100 = w_B$$

$$111 \text{ g} = \text{w}_\text{B}$$

14. 1000 g of 0.6 molal sucrose solution in water cooled to –3.2°C. What weight of ice would be separated out at this temperature. Molar mass of sucrose = 342.

Sol. Weight of ice = Weight of H_2O initially – Weight of H_2O finally.

1000 g H_2O have 0.6 mol sucrose.

$\text{w}_{\text{sol.}}$ = 1000 + 0.6 × 342 = 1205.2 g

Moles of sucrose in 1000 g solution = $\dfrac{0.6}{1205.2} \times 1000$ = 0.5

w_{H_2O} initially = 1000 – 0.5 × 342 = 829 g

$$\Delta T_f = 3.2 = \frac{1.86 \times 0.5 \times 1000}{W_{H_2O}\text{finally}}$$

$$(w_{H_2O})_{\text{finally}} = 290.6$$

Weight of ice = 829 – 290.6 = 538.4 g

15. Calculate the osmotic pressure of solution containing 0.4% urea and 3.42% sucrose at 27°C.

Sol. Molecular Mass urea = 60

Molecular Mass sucrose = 342

We know π = CRT

$$= \frac{n}{V} RT$$

$$\pi = \pi_1 + \pi_2 = \left(\frac{w}{V}\%\frac{10}{m_B}\right)RT_{\text{urea}} + \left(\frac{w}{V}\%\frac{10}{m_B}\right)RT_{\text{sucrose}}$$

$$= \left(\frac{0.4 \times 10}{60} + \frac{3.42 \times 10}{342}\right)0.082 \times 300$$

$\pi = 4.1$ atm

16. 100 mL aq. solution of glucose with osmotic pressure 1.2 atm at 25°C is mixed with 300 mL of aqueous solution of urea at 2.4 atm, at 25°C. Calculate the osmotic pressure of the mixture.

Sol. Must U = 60 Must 60 = Constant temperature

$\pi_1 = 1.2$; $T_1 = 298$

$\pi_2 = 2.4$; $T_2 = 298$

At constant temperature

$$\pi_{\text{mix}} = \frac{\pi_1 V_1 + \pi_2 V_2}{V_1 + V_2}$$

$$= \frac{1.2 \times 100 + 2.4 \times 300}{400}$$

$$= \frac{1.2 + (2.4 \times 3)}{4}$$

$$= \frac{1.2(1+6)}{4}$$

$$\frac{8.4}{4} \Rightarrow 2.1 \text{ atm}$$

17. The Van' hoff factor for 0.1 M barium nitrate solution is 2.74. What is the degree of dissociation?

$i = 2.74$ C = 0.1 M $\text{Ba(NO}_3)_2 \rightarrow \underbrace{\text{Ba}^{+2} + 2\text{NO}_3^-}_{\therefore n = 3}$

Sol. $\alpha = \dfrac{i-1}{n-1} = \dfrac{2.74-1}{3-1} \Rightarrow \dfrac{1.74}{2} \Rightarrow 0.87$

18. The vapour pressure of 0.1 M solution of urea at 20°C is 0.311 mm less than that of water and vapour pressure of 0.1 M KCl solution is 0.574 mm less than that of water. Calculate the apparent degree of dissociation of KCl at this dilution.

Sol. For urea

$$\frac{\Delta P}{P_A^{\circ}} = i\,x_B$$

$$\frac{0.311}{P_A^{\circ}} = (i = 1)x_B \qquad (1)$$

$\Rightarrow$ since equal molal

For KCl

$$\frac{0.574}{P_A^{\circ}} = i\,x_B \qquad (2)$$

$$\frac{(2)}{(1)} = \frac{0.574}{0.311} = i = 1.845$$

$i = 1 + (n-1)\alpha$

$1.845 - 1 = \alpha$

$0.845 = \alpha$

$\alpha = 84.5\%$

19. A substance x Mwt = 94 associates in water to form dimer. A solution of 1.25 g of x in 50 g of water lower the freezing point by 0.3°C calculate degree of association of x. $K_f = 1.86$.

Sol. $\Delta T_f = iK_f m$

$$0.3 = i\frac{1.86 \times 1.25 \times 1000}{94 \times 50}$$

$$i = \frac{0.3 \times 94 \times 50}{1.86 \times 1.25 \times 1000}$$

$$i = 0.6$$

$$i = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$$0.6 = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$$0.6 = 1 + \left(\frac{-1}{2}\right)\alpha$$

$$0.6 = 1 - \frac{1}{2}\alpha$$

$$\frac{1}{2}\alpha = 0.4$$

$$\alpha = 0.8 = 80\%$$

20. At 20°C and 0.02 atm pressure. Calculate the solubility of oxygen in 1 L of water. Given K_H for oxygen is 4.6×10^4 atm.

Sol. $K_H = 4.6 \times 10^4$

$P = 0.02$

$T = 293$ K

$$P = K_H \times \frac{n_g}{n_l}$$

$$0.02 = 4.6 \times 10^4 \times \frac{n_g}{n_l}$$

$$\frac{0.02 \times n_l}{4.6 \times 10^4} = n_g$$

n_l = No. of moles of water in one liter

$$= \frac{1000}{18} = 55.55$$

$$\therefore \quad n_g = \frac{0.02 \times 55.5}{4.6 \times 10^4}$$

$$\left(\frac{0.02 \times 55.5}{4.6 \times 10^4}\right) \times 32 = \text{mass of O}_2 \text{ per litre}$$

7.7×10^{-3} g/L

21. 1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mole Octane (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution.

Sol. Total mole = 1 + 4 = 5

Mole fraction of heptane = $x_A = 1/5$

Mole fraction of octane = $x_B = 4/5$

$$P_S = x_A P_A^{o} + x_B P_B^{o}$$
$$= \frac{1}{5}\times 92 + \frac{4}{5}\times 31$$
$$= 43.2 \text{ mm of Hg.}$$

22. At 88°C benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88°C at 1 atm pressure, benzene – toluene form an ideal solution.

Sol. $P_S = 760$ torr, because solution boils at 88°C.
Now 760 = 900 × mole fraction of C_6H_6 + 360 × [1 – mole fraction of C_6H_6]
$\therefore\ 760 = 900a + 360 - 360a$
$a = 0.74$ where 'a' is mole fraction C_6H_6.

23. The vapour pressure of benzene at 90°C is 1020 torr. A solution of 5 g of a solute in 58.5 g benzene has vapour pressure 990 torr. What is the molecular weight of the solute?

Sol. $$\frac{P^0 - P_S}{P_S} = \frac{n_B}{n_A} = \frac{w_B}{m_B}\times\frac{m_A}{w_A}$$

$$\frac{1020-990}{990} = \frac{5\times 78}{m_B\times 58.5}$$

$m_B = 220$

24. Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

Sol. According to Raoult's law,

$$\frac{\Delta P}{P^{o}} = x_B = \frac{n_B}{n_A + n_B}$$

or $$\Delta P = \frac{n_B}{n_A}\times P^{o}$$

Given: $n_B = \frac{50}{342} = 0.146$; $n_A = \frac{500}{18} = 27.78$ and $P^{o} = 23.8$ mm Hg

Substituting the values in the above equation,

$$\Delta P = \frac{0.146}{0.146 + 27.78}\times 23.8 = 0.124 \text{ mm Hg}$$

25. 0.15 g of a substance dissolved in 15 g of solvent boiled at a temperature higher by 0.216°C than that of the pure solvent. What is the molecular weight of the substance. [K_b for solvent = 2.16°C]

Sol. Given: $K_b = 2.16°C$
$w_B = 0.15$ g
$\Delta T_b = 0.216°C$
$w_A = 15$ g
$\Delta T_b = \text{molality}\times K_b$

$$\Delta T_b = \frac{w}{m\times W}\times 1000\times K_b$$

$$0.216 = \frac{0.15}{m_B\times 15}\times 1000\times 2.16$$

$$m_B = \frac{0.15\times 1000\times 2.16}{0.216\times 15} = 100$$

26. The rise in boiling point of a solution containing 1.8 g glucose in 100 g of a solvent is 0.1°C. The molal elevation constant of the liquid is

Sol. $\Delta T_b = K_b\times m$

$$\Delta T_b = K_b\times\frac{w_B}{m_B\times w_A}\times 1000$$

$$\therefore\quad K_b = \frac{\Delta T_b\times m_B\times w_A}{1000\times w_B}$$

$\Delta T_b = 0.1°C$
$m_B = 180$
$w_A = 100$
$w_B = 1.8$

$$K_b = \frac{180\times 0.1\times 100}{1000\times 1.8} = 1.0$$

27. If freezing point of a solution prepared from 1.25 g of a non-electrolyte and 20 g of water is 271.9 K, the molar mass of the solute will be

Sol. Given = $T_f = 271.9$ K
$w_B = 1.25$ g $\quad w_A = 20$ g $\quad K_f = 1.86$
$\Delta T_f = T^0 - T_f$
$= 273 - 271.9$
$\Delta T_f = 1.1$
$\Delta T_f = \text{molality}\times K_f$

$$\Delta T_f = \frac{w_B}{m_B\times w_A}\times 1000\times K_f$$

$$m_B = \frac{w_B\times 1000\times K_f}{\Delta T_f\times w_A}$$

$$m_B = \frac{1.25\times 1000\times 1.86}{1.1\times 20}$$

$m_B = 105.68$

28. Molal depression constant for water is 1.86°C. What is the freezing point of a 0.05 molal solution of a non-electrolyte in water?

Sol. $\Delta T_f = \text{molality}\times K_f$
$= 0.05\times 1.86 = 0.093°C$
$T_f = T^{o} - 0.093 = 0 - 0.093$
$T_f = -0.093$ = Freezing point of solution

29. A cane sugar solution has an osmotic pressure of 2.46 atm at 300 K. What is the strength of the solution?

Sol. $\pi V = nST$

or $$\pi = \frac{n}{V}\text{ST} = \text{CST}$$

or $$C = \frac{\pi}{\text{ST}} = \frac{2.46}{300 \times 0.0821} = 0.1\,\text{M}$$

30. A solution containing 8.6 g urea in 1 L was found to be isotonic with 0.5% (wt./vol.) solution of an organic, non-volatile solute. What is the molecular weight of organic solute?

Sol. Solutions are isotonic

so $\pi_1 = \pi_2$

$$\frac{n_1}{V_1}ST = \frac{n_2}{V_2}ST \quad \{S \text{ and } T \text{ are constant}\}$$

so, $$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$

or $$\left(\frac{w_1}{m_1 \times V_1}\right)_{\text{urea}} = \left(\frac{w_2}{m_2 \times V_2}\right)_{\text{organic}}$$

or $$\frac{8.6}{60 \times 1000} = \frac{0.5}{m_2 \times 100}$$

$m_2 = 34.89$

31. A very dilute saturated solution of a sparingly soluble salt A_3B_4 has a vapour pressure of 20 mm of Hg at temperature T, while pure water exerts a pressure of 20.0126 mm Hg at the same temperature. Calculate the solubility product constant of A_3B_4 at the same temperature.

Sol. $P_s = 20 \quad P° = 20.0126$

$$\frac{P° - P_s}{P_s} = \frac{0.0126}{20} = \frac{n_B}{n_A} = \frac{w_B}{m_B} \times \frac{m_A}{w_A}$$

$$\frac{\text{moles of solute}}{\text{moles of H}_2\text{O}} = 0.00063$$

1 mole H_2O = 18 g = 18 mL

18 mL solution = 0.00063 mole

1 L solution = $\frac{0.00063}{18} \times 1000$ = 0.035 mole/L

Let solubility of salt A_3B_4 is S then

$7S = 0.035$

$S = 0.005$ mole/L

$K_{\text{sp}} = 3^3 \times 4^4 \times (\text{S})^7 = 27 \times 256 \times (0.005)^7$

$K_{\text{sp}} = 5.4 \times 10^{-13}$

32. A 5% solution of anhydrous $CaCl_2$ at 0°C developed 15 atm osmotic pressure. What is the degree of dissociation of $CaCl_2$?

Sol. $\pi = \text{i}CST$

$$15 = i\left[\frac{w}{V}\%\frac{10}{m_B}\right]ST$$

$$= i \times \left[\frac{5 \times 10}{111}\right] \times .0821 \times 273$$

$i = 1.4857$

and $$\alpha = \frac{i-1}{n-1} = \frac{1.487-1}{3-1}$$

here $n = 3$

$\alpha = 0.2433$ or 24.33%

33. A solution containing 30 g of a non-volatile solute in exactly 90 g water has a vapour pressure of 21.85 mm Hg at 25°C. Further 18 g of water is then added to the solution. The resulting solution has vapour pressure of 22.15 mm Hg at 25°C. Calculate (a) molar mass of the solute, and (b) vapour pressure of water at 25°C.

Sol. $$\frac{P^0 - 21.85}{21.85} = \frac{30 \times 18}{90 \times m_B} \quad \text{for I case......I} \qquad \text{(i)}$$

Now weight of solvent = 90 +18 =108 g

$$\frac{P^0 - 22.15}{22.15} = \frac{30 \times 18}{108 \times \text{m}} \quad \text{for II case.......II} \qquad \text{(ii)}$$

∴ By eq. (i) $P°m_B - 21.85\, m_B = 21.85 \times 6 = 131.1$

By eq. (ii) $P°m_B - 22.15\, m_B = 22.15 \times 5 = 110.75$

$0.30\, m_B = 20.35$

∴ $$m_B = \frac{20.35}{0.30} = 67.83$$

On substituting in Eq. (i),

$$\frac{P^0 - 21.85}{21.85} = \frac{30 \times 18}{90 \times 67.83}$$

∴ $P° = 23.78$ mm

34. The freezing point of ether was lowered by 0.60°C on dissolving 2.0 g of phenol in 100 g of ether. Calculate the molar mass of phenol and comment on the result. Given: K_f (ether) = 5.12 K kg mol^{-1}.

Sol. $$\Delta T_f = K_f \cdot m = K_f \frac{w_B}{m_B} \times \frac{1000}{w_A}$$

$$0.6 = 5.12 \times \frac{2}{m_B} \times \frac{1000}{100}$$

$$m_B = \frac{5.12 \times 2 \times 10}{0.6} = 170.6$$

= observed molar mass

Actual molar mass of phenol C_6H_5OH

72 + 6 + 16 = 94

It means phenol dimerise in solution.

35. To 500 cm^3 of water 3.0×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression of freezing point? K_f and density of water are 1.86 K kg mol^{-1} and 0.997 g cm^{-3}, respectively?

Sol. $\Delta T = K_f \times \text{molality} \times (1 + \alpha)$

For acetic acid: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$\begin{array}{ccc} 1 & 0 & 0 \\ 1-\alpha & \alpha & \alpha \end{array}$$

Given, $\alpha = 0.23$; Also,

$$\text{molality } (m) = \frac{\text{Mole of acetic acid}}{\text{Weight of water in kg}}$$

$$= \frac{3 \times 10^{-3} \times 10^3}{60 \times \dfrac{500 \times 0.997}{10^3}} = 0.10$$

$\Delta T = K_f \times \text{molality}\ (1 + \alpha)$

$\Delta T = 1.86 \times 0.1 \times 1.23 = 0.229$

36. A 0.01 m aqueous solution of $K_3[Fe(CN)_6]$ freezes at –0.062°C. What is the apparent percentage of dissociation? [K_f for water = 1.86]

Sol. $\Delta T_f = i\,K_f m \qquad 0.062 = i \times 1.86 \times 0.01$

$i = 3.33 \qquad \text{and} \qquad \alpha = \dfrac{i-1}{n-1}$

$\alpha \Rightarrow \dfrac{3.33-1}{4-1} \qquad \alpha \Rightarrow 0.777 \qquad \therefore \quad 77.77\%$

37. A solution containing 0.011 kg of barium nitrate in 0.1 kg of water boils at 100.46°C. Calculate the degree of ionisation of the salt. K_b (water) = 0.52 K kg mol^{-1}.

Sol. $\Delta T_b = i\,K_b m \qquad 0.46 = i \times 0.52 \times \dfrac{0.011 \times 10^{-3}}{0.1 \times 261}$

$i = 2.098 \qquad \alpha = \dfrac{i-1}{n-1}$

$\Rightarrow \quad \dfrac{2.098-1}{3-1} \qquad \alpha \Rightarrow 0.55$

38. At 300 K, two solutions of glucose in water of concentration 0.01 M and 0.001 M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure?

Sol.

For 0.01 M solution,	For 0.001 M solution,
$n_1/V_1 = 0.01$	$n_1/V_2 = 0.001$
$T = 300$ K	$T = 300$ K
$\pi_1 V_1 = n_1 S T_1$	$\pi_2 V_2 = n_2 S T_2$
$\therefore \quad \pi_1 = 0.01 \times 0.0821 \times 300$	$\therefore \quad \pi_2 = 0.001 \times 0.0821 \times 300$
$= 0.2463$ atm	$= 0.02463$ atm

The movement of solvent particles occurs from dilute to concentrate solution, i.e., 0.001 M to 0.01 M solution. Thus, pressure should be applied on concentrated solution, i.e., on 0.01 M solution to prevent osmosis. Also, magnitude of external pressure = 0.2463 – 0.0246 = 0.2217 atm pressure on 0.01 M solution.

39. At 10°C, the osmotic pressure of urea solution is 500 mmHg. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mmHg. Determine extent of dilution.

Sol. For initial solution,

$\because \quad \pi = \dfrac{500}{760}\,\text{atm},\ T = 283 \text{ K}$

$$\frac{500}{760} \times V_1 = n \times S \times 283 \qquad \text{(i)}$$

After dilution, let volume becomes V_2 and temperature is raised to 25°C, i.e., 298 K

$\pi = \dfrac{105.3}{760}\,\text{atm}$

$$\frac{105.3}{760} \times V_2 = n \times S \times 298 \qquad \text{(ii)}$$

$\therefore$ by Eqs. (i) and (ii), we get

$$\frac{V_1}{V_2} = \frac{283}{298} \times \frac{105.3}{500} \qquad \frac{V_1}{V_2} = \frac{1}{5}$$

$\therefore \quad V_2 = 5V_1$

i.e., solution was diluted five times.

40. A 0.1 M solution of potassium ferrocyanide is 46% dissociated at 18°C. What will be its osmotic pressure?

Sol. $\pi = i\,\text{CST} \qquad \alpha = \dfrac{i-1}{n-1}$

$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{-4}$

$\therefore \qquad n = 5$

$0.46 = \dfrac{i-1}{5-1} \qquad i = 2.84$

$\pi = 2.84 \times 0.1 \times 0.082 \times 291$

$\pi = 6.785$ atm

41. A 1 L solution is prepared by dissolving some solid lead-nitrate in water. The solution was found to boil at 100.15°C. To the resulting solution 0.2 mole NaCl was added. The resulting solution was found to freeze at –0.83°C. Determine solubility product of $PbCl_2$. Given K_b= 0.5 and K_f= 1.86. Assume molality to be equal to molarity in all cases.

Sol. $Pb[NO_3]_2 \rightarrow Pb^{+2} + 2NO_3^-$

$\because$ Strong electrolyte completely ionise.

$\therefore \quad n = 3$

$\Delta T_b = iK_b m$

$0.15 = 3 \times 0.5 \times m \qquad \Rightarrow \quad m = 0.1$

$$\begin{array}{lccccccc} \text{Now,} & Pb(NO_3)_2 & + & 2NaCl & \longrightarrow & PbCl_2 & + & 2NaNO_3 \\ & 0.1 & & 0.2 & & — & & — \\ & — & & — & & 0.1 & & 0.2 \end{array}$$

Now, this solution contains two salts

$NaNO_3$ strong Electrolyte $\therefore$ Completely ionise and $PbCl_2$ partially ionise

$$\underset{\text{Solid}}{PbCl_2} \longrightarrow \underset{\text{(aq)}}{PbCl_2} \longrightarrow \underset{\text{S}}{Pb^{+2}} + \underset{\text{2S}}{2Cl^-}$$

$0.446 = 0.4 + 3S$

$S = 1.54 \times 10^{-2}$

$\therefore \quad K_{SP} = [Pb^{+2}]\,[Cl^-]^2$

$= 4S^3 = 1.46 \times 10^{-5}$

42. A protein has been isolated as sodium salt with their molecular formula Na_xP (this notation means that xNa$^+$ ions are associated with a negatively charged protein P^{-x}). A solution of this salt was prepared by dissolving 0.25 g of this sodium salt of protein in 10 g of water and ebulliscopic analysis revealed that solution boils at temperature 5.93×10^{-3} °C higher than the normal boiling point of pure water. K_b of water 0.52 kg mol^{-1}. Also elemental analysis revealed that the salt contain 1% sodium metal by weight. Deduce molecular formula and determine molecular weight of acidic form of protein H_xP.

Sol. $\Delta T_b = i \times K_b \times m$ Molar mass of $Na_xP = M$

$$5.93 \times 10^{-3} = \frac{(x+1) \times 0.52 \times 0.25 \times 1000}{M \times 10}$$

$$\frac{(x+1)}{M} = 4.56 \times 10^{-4} \tag{i}$$

$$\frac{M}{100} = 23x \tag{ii}$$

$\therefore$ $M = 2300\,x$

$\therefore$ $x + 1 = 2300x \times 4.56 \times 10^{-4}$

$x + 1 = 1.0488x$

$x = 20.34 \simeq 20$

From Eqs. (i) and (ii)

Formula of protein = $H_{20}P$

$M = 2300 \times 20 - 20 \times 23 + 20 = 45560$ amu

43. The vapour pressure of two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 mole of (A) is mixed with 12 mole of (B). However, as soon as (B) is added, (A) starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 min, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation, and ideal behaviour for the final solution.

Sol. $A + B \longrightarrow A_n + B$

$P_S = P_T = P_M$ = Vapour pressure of solution.

$$P_M = P_A^{o} x_A + P_B^{o} x_B$$

Let a mole of A are left due to polymerisation after 100 min.

$$P_M = 300\left(\frac{a}{12+a}\right) + 500\left(\frac{12}{12+a}\right) \tag{i}$$

$$K = \frac{2.303}{100}\log\frac{10}{a} \tag{ii}$$

in 2nd Case

After 100 minute solute is added and final vapour pressure is 400 mm Hg, i.e., $P_s = 400$

$$\frac{P_M - 400}{400} = \frac{0.525}{(a+12)} \tag{iii}$$

from Eqs. (i) and (iii) $a = 9.9$

Putting this in eq. (ii) $K = \dfrac{2.303}{100}\log\dfrac{10}{9.9} = 1.0 \times 10^{-4}$

44. Two beakers A and B present in a closed vessel. Beaker A contains 152.4 g aqueous solution of urea, containing 12 g of urea. Beaker B contains 196.2 g glucose solution, containing 18 g of glucose. Both solutions allowed to attain the equilibrium. Determine weight % of glucose in its solution at equilibrium:

Sol. Beaker A:

wt. of water = (152.4 – 12) gram

= 140.4 gram

Mole fraction of urea

$$= \frac{\frac{12}{60}}{\frac{12}{60} + \frac{140.4}{18}} = \frac{0.2}{0.2 + 7.8} = 0.025$$

Beaker B:

wt. of water = 196.2 – 18

= 178.2 gram

Mole fraction of glucose $= \dfrac{\frac{18}{180}}{\frac{18}{180} + \frac{178.2}{18}} \Rightarrow 0.01$

Mole fraction of glucose is less so vapour pressure above the glucose solution will be higher than the pressure above urea solution, so some H_2O molecules will transfer from glucose to urea side in order to make the solutions of equal mole fraction to attain equilibrium. Let x mole of H_2O transferred

$$\frac{0.2}{0.2 + 7.8 + x} = \frac{0.1}{0.1 + 9.9 - x} \Rightarrow x = 4$$

now mass of glucose solution = 196.2 – 18 × 4 = 124.2

weight % of glucose $= \dfrac{18}{124.2} \times 100 \times 100 \Rightarrow 14.49\ \%$

45. The addition of 3 g of substance to 100 g CCl_4 (M = 154 g mol^{-1}) raises the boiling point of CCl_4 by 0.60°C of K_b (CCl_4) is 5.03 kg mol^{-1} K. Calculate

(a) the freezing point depression.

(b) the relative lowering of vapour pressure.

(c) the osmotic pressure at 298 K.

(d) the molar mass of the substance.

Given: $K_f(CCl_4)$ = 31.8 kg mol^{-1} K and r (density) of solution = 1.64 g/cm^3.

Sol. (a) $\dfrac{\Delta T_f}{\Delta T_b} = \dfrac{K_f}{K_b} = \Delta T_f = \dfrac{0.6 \times 31.8}{5.03} = 3.793°\text{C}$

(b) Relative lowering of vapour pressure

$$= \frac{n}{n+N} = \frac{\frac{3}{251.5}}{\frac{3}{251.5} + \frac{100}{154}} = 0.018$$

(c) $\pi = CRT = \frac{n}{V}RT$

$$n = \frac{3}{251.5} = 0.012$$

$$V = \frac{103}{1.64} = 62.8 \text{ mL}$$

$$\pi = \frac{0.012}{0.0628} \times 0.0821 \times 298 = 4.65 \text{ atm}$$

(d) $0.6 = \frac{5.03 \times 3 \times 1000}{m_B \times 100} \Rightarrow m_B = 251.5$

46. If 20 mL of ethanol (density = 0.7893 g/mL) is mixed with 40 mL water (density = 0.9971 g/mL) at 25°C, the final solution has density of 0.9571 g/mL. Calculate the percentage change in total volume of mixing. Also calculate the molality of alcohol in the final solution.

Sol. $C_2H_5OH \longrightarrow V_1 = 20 \text{ mL}, d_1 = 0.7893 \text{ g/mL}$

$$m_1 = 15.786 \text{ g} = w_B$$

$H_2O \rightarrow V_2 = 40 \text{ mL}, d_2 = 0.9971 \text{ g/mL}$

$$m_2 = 39.884 \text{ g} = w_A$$

Total mass = 55.65 g

$$d_{\text{sol.}} = 0.9571 \text{ g/mL}$$

$$V_{\text{sol.}} = 58.14 \text{ mL} = \frac{\text{Total mass of solution}}{\text{density of solution}}$$

$$\% \text{ change} = \frac{60 - 58.14}{60} \times 100 = 3.1\%$$

$$m = \frac{w_B}{m_B} \times \frac{1000}{w_A} = \frac{15.766 \times 1000}{46 \times 39.884} = 8.6$$

47. Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C is given by P (mm Hg) = 179 X_B + 92, where X_B is the mole fraction of C_6H_6. A solution is prepared by mixing 936 g benzene and 736 g toluene and if the vapours over this solution are removed and condensed into liquid and again brought to the temperature of 50°C, what would be mole fraction of C_6H_6 in the vapour state?

Sol. $P = 179X_B + 92$

$P_B = 271, P_T = 92$

$$P_B^o = 271, P_T^o = 92$$

$$n_B = \frac{936}{78} = 12, n_T = \frac{736}{92} = 8$$

$$X_B = \frac{12}{20} = 0.6, X_T = 0.4$$

$$P_T = 271 \times 0.6 + 92 \times 0.4 = 199.4$$

$$Y_B = \frac{271 \times 0.6}{199.4} = 0.815$$

$$Y_T = 0.185$$

On further condensation

$$X_B = 0.815, X_T = 0.185$$

$$P_T = 271 \times 0.815 + 92 \times 0.185 = 237.844$$

$$Y_B = \frac{271 \times 0.815}{237.844} = 0.9286$$

48. The vapour pressure of a certain liquid is given by the equation:

$\text{Log}_{10}P = 3.54595 - \frac{313.7}{T} + 1.40655 \log_{10}T$ where P is the vapour pressure in mm and T = Kelvin Temperature. Determine the molar latent heat of vaporisation as a function of temperature. Calculate its value at 80 K.

Sol. $\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}$ ...(i)

$$\log P = 3.54595 - \frac{313.7}{T} + 1.40655 \log T$$

$$\ln P = 3.54595 \times 2.303 - \frac{313.7}{T} \times 2.303 + 1.40655 \ln T$$

$$\frac{d \ln P}{dT} = \frac{313.7 \times 2.303}{T^2} + \frac{1.40655}{T} \quad \text{...(ii)}$$

Comparing Eqs. (i) and (ii)

$$\Delta H = R[313.7 \times 2.303 + 1.40655\ T]$$

at $T = 80$ K

$$\Delta H = 1659.9 \text{ Cal.}$$

Exercise

LEVEL I

1. If P_A^0 is the vapour pressure of a pure liquid A and the mole fraction of A in the mixture of two liquids A and B is x, the partial vapour pressure of A is

(a) $(1-x)P_A^0$ (b) xP_A^0

(c) $\frac{x}{(1-x)}P_A^0$ (d) $\frac{(1-x)}{x}P_A^0$

2. In a mixture of A and B if the mole fraction of the component A in vapour phase is x_1 and mole fraction of component A in liquid mixture is x_2 (P_A^0 = vapour pressure of pure A; P_B^0 = vapour pressure of pure B), then total vapour pressure of the liquid mixture is

(a) $\frac{P_A^0 x_2}{x_1}$ (b) $\frac{P_A^0 x_1}{x_2}$ (c) $\frac{P_B^0 x_1}{x_2}$ (d) $\frac{P_B^0 x_2}{x_1}$

3. At 40°C, the vapour pressure in torr of methanol and ethanol solution is $P = 119x + 135$, where x is the mol. fraction of methanol. Hence
(a) vapour pressure of pure methanol is 119 torr.
(b) vapour pressure of pure ethanol is 135 torr.
(c) vapour pressure of equimolar mixture of each is 127 mm.
(d) mixture is completely immiscible.

4. A solution that obeys Raoult's law is
(a) non-ideal (b) colloid
(c) ideal (d) saturated

5. In a mixture A and B components show negative deviation as
(a) $\Delta V_{\text{mix}} = +\text{ve}$
(b) $\Delta H_{\text{mix}} = -\text{ve}$
(c) A–B interaction is weaker than A–A and B–B interaction.
(d) None of the above.

6. 100 mL of liquid A was mixed with 25 mL of liquid B to give a non-ideal solution of A–B mixture. The volume of this mixture would be
(a) 75 mL
(b) Either less or more than 125 mL.
(c) Close to 125 mL but not exceeding 125 mL.
(d) Just more than 125 mL.

7. Which of the following liquid pairs shows a positive deviation from Raoult's law?
(a) Water-nitric acid
(b) Benzene-methanol
(c) Water-hydrochloric acid
(d) Acetone-chloroform

8. Liquids A and B form an ideal solution.
(a) The enthalpy of mixing is zero.
(b) The entropy of mixing is zero.
(c) The free energy of mixing is zero.
(d) The free energy as well as the entropy of mixing are each zero.

9. Which of the following solution (in H_2O) has the highest boiling point elevation?
(a) 0.2 m urea (b) 0.1 m $K_4[Fe(CN)_6]$
(c) 0.2 m K_2SO_4 (d) 0.3 m Glucose

10. When mango is placed in dilute aqueous solution of hydrochloric acid, it
(a) shrinks (b) swells
(c) brusts (d) Nothing happens

11. If 32 g of an unknown molecule (assumed to be unionised in solution) dissolved in 200 g of H_2O of, then elevation in boiling point is found to be 1.04°C . Find out the molar mass of the unknown molecule (given K_b for $H_2O = 0.52$ kg mol^{-1})
(a) 160 g/mole (b) 80 g/mole
(c) 40 g/mole (d) 320 g/mole

12. Arrange the following compounds in order of decreasing the depression in freezing point of aqueous solution.
(i) Acetic acid
(ii) Trichloroacetic acid
(iii) Trifluoroacetic acid
(a) i > ii > iii (b) ii > iii > i
(c) iii > i > ii (d) iii > ii > i

13. During depression of freezing point in a solution, which of the following are in equilibrium?
(a) liquid solvent, solid solvent
(b) liquid solvent, solid solute
(c) liquid solute, solid solute
(d) liquid solute, solid solvent

14. Nitrobenzene freezes at 278.98°C. 0.25 molal solution of a solute in nitrobenzene causes freezing point depression of 2°C. K_f for nitrobenzene is
(a) 2 K m^{-1} (b) 4 K m^{-1}
(c) 8 K m^{-1} (d) 12 K m^{-1}

15. 0.15 g of a substance dissolved in 15 g of a solvent is boiled at a temperature higher by 0.216°C than that of the pure solvent. Find out the molecular weight of the substance. (K_f for solvent is 2.16 k.kg. m^{-1}).
(a) 1.01 (b) 10.1 (c) 100 (d) 10.0

16. The freezing point of equimolal aqueous solution will be highest for
(a) $C_6H_5NH_3Cl$ (aniline hydrochloride)
(b) $Ca(NO_3)_2$
(c) $La(NO_3)_3$
(d) $C_6H_{12}O_6$ (glucose)

17. When mercuric iodide is added to the aqueous solution of potassium iodide, the
(a) freezing point is raised.
(b) freezing point is lowered.
(c) freezing point does not change.
(d) boiling point does not change.

18. Which of the following is not a colligative property?
(a) Osmotic pressure
(b) Elevation in B.P.
(c) Vapour pressure
(d) Depression in freezing point

19. Arrange the following in order of decreasing solubility in H_2O.
Phenol (i), Toluene (ii), Chloroform (iii)
(a) (i) > (ii) > (iii) (b) (iii) > (ii) > (i)
(c) (i) > (iii) > (ii) (d) (iii) > (i) > (ii)

20. A X molal solution of a compound in benzene has mole fraction of solute equal to 0.2. The value of X is
(a) 14 (b) 3.2 (c) 1.4 (d) 2.0

21. What will be the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN?
(a) 2.848% (b) 1.424%
(c) 14.24% (d) 28.48%

22. The vapour pressure of a solvent decreased by 10 mm Hg when a non-volatile solute was added to the sol-

vent. The mole fraction of solute in solution is 0.2. What would be mole fraction of the the solvent if decrease in vapour pressure is 20 mm of Hg?
(a) 0.8 (b) 0.6 (c) 0.4 (d) 0.2

23. What is the mole fraction of toluene in vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.400?
(P_B^o = 119 torr and P_T^o = 37.0 torr)
(a) 0.0237 (b) 0.337 (c) 0.437 (d) 0.237

24. At a given temperature, total vapour pressure in torr of a mixture of volatile components *A* and *B* is given by $P_{\text{Total}} = 120 - 75X_B$ hence, vapour pressure of pure *A* and *B* respectively (in torr) are
(a) 120, 75 (b) 120, 195
(c) 120, 45 (d) 75, 45

25. Liquids *A* and *B* form an ideal solution and the former has stronger intermolecular forces. If X_A and X'_A are the mole fractions of A in the solution and vapour phase in equilibrium, then
(a) $\frac{X'_A}{X_A} = 1$ (b) $\frac{X'_A}{X_A} > 1$
(c) $\frac{X'_A}{X_A} < 1$ (d) $X'_A + X_A = 1$

26. What will be the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%?
(a) 10 g (b) 4 g (c) 2 g (d) 16 g

27. Vapour pressure of water at 293 K is 17.535 mm Hg. What will be the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water?
(a) 17.44 mm Hg (b) 174.4 mm Hg
(c) 34.88 mm Hg (d) 8.72 mm Hg

28. The modal elevation constant is the ratio of the elevation in B.P. to
(a) molarity
(b) molality
(c) mole fraction of solute
(d) mole fraction of solvent

29. The boiling point of an aqueous solution of a non-volatile solute is 100.15°C. What is the freezing point of an aqueous solution obtained by diluting the above solution with an equal volume of water? The values of K_b and K_f for water are 0.512°C and 1.86°C molality^{-1}.
(a) –0.544°C (b) –0.512°C
(c) –0.272°C (d) –1.86°C

30. Which of the following 0.1 M aqueous solution will have the lowest freezing point?
(a) Potassium sulphate (b) Sodium chloride
(c) Urea (d) Glucose

31. What will be the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 L of water at 25°C, assuming that it is completely dissociated?
(a) 5.27×10^{-3} atm (b) 52.7×10^{-3} atm
(c) 26.3×10^{-3} atm (d) 2.63×10^{-3} atm

32. The values of observed and calculated molecular weights of silver nitrate are 92.64 and 170 respectively. The degrees of dissociation of silver nitrate is
(a) 60% (b) 83.5% (c) 46.7% (d) 60.23%

33. For a dilute solution, Raoult's law states that
(a) the lowering of vapour pressure is equal to the mole fraction of the solute.
(b) the relative lowering of vapour pressure is equal to the mole fraction of the solute.
(c) the relative lowering of vapour pressure is proportional to the amount of the solute in solution.
(d) the vapour pressure of the solution is equal to the mole fraction of the solvent.

34. Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and naphthalene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. What will be the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of naphthalene?
(a) 0.0675 (b) 0.675 (c) 0.35 (d) 0.5

35. Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure (in torr) of benzene, at 20°C for a solution containing 78 g of benzene and 46 g of toulene, is
(a) 50 (b) 25 (c) 37.5 (d) 53.5

36. The vapour pressure of pure liquid *A* is 0.80 atm. On mixing a non-volatile *B* to *A*, its vapour pressure becomes 0.6 atm. The mole fraction of B in the solution is
(a) 0.150 (b) 0.25 (c) 0.50 (d) 0.75

37. 100 g of liquid *A* (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid *B* (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 torr. What will be the vapour pressure of pure liquid A and its vapour pressure in the solution respectively if the total vapour pressure of the solution is 475 torr?
(a) 28.7 torr and 32 torr (b) 280.7 torr and 32 torr
(c) 28.7 torr and 3.2 torr (d) 280.7 torr and 3.2 torr

38. 3.0 molal NaOH solution has a density of 1.110 g/mL. The molarity of the solution is
(a) 2.9732 (b) 3.05
(c) 3.64 (d) 3.0504

39. When 5.0 g of $BaCl_2$ is dissolved in water to have 10^6 g of solution. The concentration of solution is
(a) 2.5 ppm (b) 5 ppm
(c) 5M (d) 5 g L^{-1}

40. At a certain hill station pure water boils at 99.725°C. If K_b for water is 0.513°C kg mol^{-1}, the boiling point of 0.69 m solution of urea will be
(a) 100.079°C (b) 103°C
(c) 100. 359°C (d) unpredictable

41. The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is
(a) –1.86°C (b) –3.72°C
(c) +1.86°C (d) +3.72°C

42. 10 g of solute with molecular mass 100 g mol^{-1} is dissolved in 100 g solvent to show 0.3°C elevation in boiling point. The value of molal ebullioscopic constant will be

(a) 10 (b) 3
(c) 0.3 (d) unpredictable

43. If the observed and theoretical molecular mass of NaCl is found to be 31.80 and 58.50, then the degree of dissociation of NaCl is

(a) 83.96% (b) 8.39%
(c) 90% (d) 100%

44. The substance *A* when dissolved in solvent *B* shows the molecular mass corresponding to A_3. The Vant Hoffs factor will be

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

45. A 5% solution of cane sugar is isotonic with 0.877 % of *X*. The molecular weight of substance *X* is

(a) 59.98 (b) 119.96 (c) 95.58 (d) 126.98

46. The osmotic pressure of equimolar solutions of urea, $BaCI_2$ and $AlCI_3$ will be in which order?

(a) $AlCl_3 > BaCl_2 >$ Urea
(b) $BaCl_2 > AlCl_3 >$ Urea
(c) Urea $> BaCl_2 > AlCl_3$
(d) $BaCl_2 >$ Urea $> AlCl_3$

47. A certain substance 'A' tetramerises in water to the extent of 80%. A solution of 2.5 g of *A* in 100 g of water lowers the freezing point by 0.3°C. The molar mass of *A* is

(a) 122 (b) 31 (c) 244 (d) 62

48. Which of the following solutions will exhibit highest boiling point?

(a) 0.01 M Na_2SO_4 (b) 0.01 M KNO_3
(c) 0.015 M urea (d) 0.015 M glucose

49. What is the osmotic pressure of 12% solution of can sugar (mol. wt. 342) at 17°C?

(a) 8.35 atm (b) 9.35 atm
(c) 5.36 atm (d) 7.35 atm

50. Mixture of volatile components *A* and *B* has total vapour pressure (in torr):

$P = 254 - 119x_A$, where x_A is mole fraction of A in mixture.

Hence P_A^o and P_B^o are (in torr)

(a) 254, 119 (b) 119, 254
(c) 135, 254 (d) 154, 119

LEVEL II

1. A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. What will be the mass percentage of the solute and solvent resulting solution?

(a) 23% and 77% (b) 12.5% and 87.5%
(c) 33.6% and 66.4% (d) 50% and 50%

2. 0.2 molal acid HX is 20% ionised in solution. $K_f = 1.86$ K molality^{-1} the freezing point of the solution is

(a) –0.45°C (b) –0.90°C
(c) –0.31°C (d) –0.53°C

3. How much the amount of $CaCl_2$ ($i = 2.47$) dissolved in 2.5 L of water such that its osmotic pressure is 0.75 atm at 27°C?

(a) 0.3 mole (b) 0.03 mole
(c) 3 mole (d) 0.003 mole

4. Boiling point of pure H_2O is 373.15 K. If 32.5 g of KCN is dissolved in 100 mL of H_2O, what will be the boiling point of solution? (Given K_b for H_2O = 0.52 K. kg mol^{-1} and molar mass of KCN= 65 g/mole)

(a) 105.28°C (b) 100.52°C
(c) 373.67 K (d) 373.75 K

5. The freezing point of a solution of acetic acid (mole fraction is 0.02) in benzene is 277.4 K. Acetic acid exists partly as a dimer $2A \rightleftharpoons A_2$. Determine the equilibrium constant for dimerisation. Freezing point of benzene is 278.4 K and (K_f for benzene is 5).

(a) 3.39 kg mol^{-1} (b) 33.9 kg mol^{-1}
(c) 1.68 kg mol^{-1} (d) 16.8 kg mol^{-1}

6. Which one of the following pairs of solution can we expect to be isotonic at the same temperature?

(a) 0.1 M urea and 0.1 M NaCl
(b) 0.1 M urea and 0.2 M $MgCl_2$
(c) 0.1 M NaCl and 0.1 M Na_2SO_4
(d) 0.1M $Ca(NO_3)_2$ and 0.1 M Na_2SO_4

7. The osmotic pressure of a 5% aqueous solution of cane sugar at 150°C is (Mol. Wt. of cane sugar = 342)

(a) 4 atm (b) 3.4 atm
(c) 5.07 atm (d) 2.45 atm

8. If the solution of mercuric cyanide of strength 3 g/L has an osmotic pressure 0.3092×10^5 Nm^{-2} at 298 K, what is the apparent molecular weight and degree of dissociation of $Hg(CN)_2$ respectively? (Hg = 200.61, C = 12, N = 14)

(a) 240.2, 2.45% (b) 480.4, 2.45%
(c) 480.4, 24.5% (d) 240.2, 24.5%

9. Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1}?

(a) 1.623 M (b) 16.23 M
(c) 162.3 M (d) 0.1623 M

10. Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively, what will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?

(a) 7.308 kPa (b) 73.08 kPa
(c) 730.8 kPa (d) 7308 kPa

11. The vapour pressure of water is 12.3 k pa at 300 K. What will be the vapour pressure of 1 molal solution of a non-volatile solute in it?

(a) 24.16 k pa (b) 1.208 k pa
(c) 2.416 k pa (d) 12.08 k pa

12. The boiling point elevation constant for toluene is 3.32 K kg mol^{-1}, the normal boiling point of toluene is 110.7°C. The enthalpy of vaporisation of toluene would by nearly
(a) 17.0 k $Jmol^{-1}$ (b) 34.0 kJ mol^{-1}
(c) 51.0 kJ mol^{-1} (d) 68.0 kJ mol^{-1}

13. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. What will be the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K?
(a) 273.15 K (b) 279.07 K
(c) 269.07 K (d) 293.07 K

14. At 300 K 36 g of glucose present in a litre of its solution has osmotic pressure of 4.98 bar. lf the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?
(a) 0.061 M (b) 0.61 M
(c) 0.0061 M (d) 6.1 M

15. The ratio of the value of any colligative property for KCl solution to that for sugar is nearly ____ times
(a) 1 (b) 0.5 (c) 2 (d) 2.5

16. When 0.6 g of urea dissolved in 100 g of water, the water will boil at (K_b for water = 0.52 kJ. mol^{-1} and normal boiling point of water = 100°C):
(a) 373.052 K (b) 273.52 K
(c) 372.48 K (d) 273.052 K

17. A solution prepared by dissolving a 2.50 g sample of an unknown compound dissolved in 34.0 g of benzene, C_6H_6 boils at 1.38°C higher than pure benzene. Which expression gives the molar mass of the unknown compound?
Compound K_b
C_6H_6 2.53°C.m^{-1}

(a) $2.53 \times \dfrac{2.50}{1.38}$

(b) $1.38 \times \dfrac{34.0}{2.53} \times 2.50$

(c) $2.50 \times 10^3 \times \dfrac{2.53}{34.0} \times \dfrac{1}{1.38}$

(d) $2.50 \times 10^3 \times \dfrac{1.38}{34.0} \times 2.53$

18. When 1.20 g of sulphur is melted with 15.00 g of naphthalene, the solution freezes at 77.2° C. What is the molar mass of this from of sulphur. Data for Napthalene Melting point, m.p 80°C Freezing point, depression constant, $K_f = 6.80$°C m^{-1}
(a) 180 g mol^{-1} (b) 194 g mol^{-1}
(c) 260 g mol^{-1} (d) 450 g mol^{-1}

19. 12.2 g benzoic acid (M = 122) in 100 g H_2O has elevation of boiling point of 0.27°C, $K_b = 0.54$ K kg/mole. If there is 100% dimerisation, the number of molecules of benzoic acid in associated state is
(a) 1 (b) $N_A/20$ (c) 2 (d) 0.1 N_A

20. 1.0 molal aqueous solution of an electrolyte X_3Y_2 is 25% ionised. The boiling point of the solution is (K_b for $H_2O = 0.52$ K kg/mol):
(a) 375.5 K (b) 374.04 K
(c) 377.12 K (d) 373.25 K

21. The molal boiling point constant of water is 0.573°C kg $mole^{-1}$. When 0.1 mole of glucose is dissolved in 1000 g of water, the solution boils under atmospheric pressure at
(a) 100.513°C (b) 100.0573°C
(c) 100.256°C (d) 101.025°C

22. The boiling point of an aqueous solution of a non-volatile solute is 100.15°C. What is the freezing point of an aqueous solution obtained by diluting the above solution with an equal volume of water. The values of K_b and K_f for water are 0.512 and 1.86°C mol^{-1}:
(a) –0.544°C (b) –0.512°C
(c) –0.272°C (d) –1.86°C

23. An aqueous solution of acetone, CH_3COCH_3, is 10% acetone by weight. What is the mole percentage of acetone in this solution:
(a) 3.332% (b) 5.000%
(c) 10.00% (d) 11.11%

24. The freezing point of an aqueous solution of a non-electrolyte is –0.14°C. The molality of this solution is [$K_f(H_2O) = 1.86$ K kg mol^{-1}]:
(a) 1.86 m (b) 1.00 m (c) 0.15 m (d) 0.075 m

25. Dry air was passed successively through a solution of 5 g of a solute in 180 g of water and then through pure water. The loss in weight of solution was 2.5 g and that of pure solvent 0.04 g. The molecular weight of the solute is
(a) 31.25 (b) 3.125
(c) 312.5 (d) None of these

LEVEL III

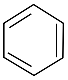
1. Match the columns:

	Column I		Column II
(a)	CH_3COOH in H_2O	(p)	Neither association nor dissociation
(b)	CH_3COOH in benzene	(q)	When a non-volatile solute is added.
(c)	Polymer in water	(r)	Molecular mass observed greater than molecular mass actual.
(d)	Vapour pressure of a liquid decreases	(s)	$\Delta T_{b(\text{obs})} > \Delta T_{b(\text{calc.})}$
		(t)	van't Hoff factor, $i > 1$

2. Match the columns:

Column I		Column II	
(a)	Azeotropes	(p)	Molality
(b)	A mixture of $CHCl_3$ and benzene shows	(q)	Intermolecular attraction negative deviation from ideal behaviour.
(c)	The ratio of observed molecular mass to theoretical molecular mass	(r)	van't Hoff factor
(d)	The number of moles of solute dissolved in 1000 g of solvent	(s)	Solutions with same composition in vapour and liquid phase.
		(t)	Constant boiling mixtures.

3. Match the columns:

Column I			Column II
(a)	$CCl_4 + CHCl_3$	(p)	Raoult's law
(b)	 + H_2O	(q)	Nearly ideal solution
(c)	$P_A \propto x_A$	(r)	Non-ideal solution with –ve deviation
(d)	$CHCl_3$ + acetone	(s)	Non-ideal solution with +ve deviation
		(t)	Hydrogen bonding

4. Match the columns:

ΔH_f = Molar heat of fusion of ice; L_f = Latent heat of fusion of ice (g^{-1})

ΔH_v = Molar heat of vaporisation of water; L_v = Latent heat of vaporisation of water (g^{-1})

Column I			Column II
(a)	Molal depression constant of water	(p)	$\dfrac{18 \times 373 \times 373 \times R}{1000\,\Delta H_v}$
(b)	Molal elevation constant of water	(q)	$\dfrac{373 \times 373 \times R}{1000\,L_v}$
(c)	ΔT_f of solution containing 9.0 g of glucose in 50 g of water	(r)	$\dfrac{18 \times 273 \times 273 \times R}{1000 \Delta H_f}$
(d)	ΔT_b of solution containing 3.0 g of urea in 50 g of water	(s)	$\dfrac{273 \times 273 \times R}{1000 L_f}$
		(t)	K_f

Comprehension I

According to Raoult's law (which is applicable for a mixture of volatile liquids) the partial vapour pressure of a liquid is directly proportional to the mole fraction of that component. Further assuming ideal behaviour for vapours and applying Dalton's law we can write different equations as follows:

$$P_A = P_A^o x_A, \qquad P_B = P_B^o x_B$$

$$P_{\text{Total}} = P_A + P_B = P_A^o x_A + P_B^o x_B = P_B^o + (P_A^o - P_B^o)x_A$$

Further mole fraction of a component in vapour phase is equal to the ratio of partial vapour pressure to total vapour pressure of mixture.

The vapour pressure of two pure liquids A and B which form an ideal solution are 300 and 500 torr respectively at temperature T. A mixture of the vapours of A and B for which the mol fraction of A is 0.25 is slowly compressed at temperature T.

5. The total pressure when first drop of condensate is formed will be
(a) 428 torr (b) 400 torr
(c) 388 torr (d) 358 torr

6. The pressure when only the last bubble of vapour remains will be
(a) 350 torr (b) 375 torr
(c) 525 torr (d) 450 torr

7. The mole fraction of B in the last bubble of vapour will be
(a) 0.16 (b) 0.84 (c) 0.20 (d) 0.80

Comprehension II

A solution of sucrose (molar mass = 342) has been prepared by dissolving 68.4 g of sucrose in one kg of water. K_f for water is 1.86 K kg mol^{-1} and vapour pressure of water at 298 K is 0.024 atm.

8. The vapour pressure of the solution at 298 K will be
(a) 0.230 atm (b) 0.235 atm
(c) 0.236 atm (d) 0.0235 atm

9. The osmotic pressure of the solution at 298 K will be
(a) 4.29 atm (b) 4.49 atm
(c) 4.69 atm (d) 4.89 atm

10. The freezing point of the solution will be
(a) –0.684°C (b) –0.342°C
(c) –0.372°C (d) –0.186°C

Comprehension III

A system of greater disorder of molecules is more probable. The disorder of molecules is reflected by the entropy of the system. A liquid vaporises to form a more disordered gas. When a solute is present, there is additional contribution to the entropy of the liquid due to increased randomness. As the entropy of solution is higher then that of pure liquid, there is weaker tendency of it to form the gas. Thus, a solute (non volatile) lowers the vapour pressure of a liquid, and hence a higher boiling point of the solution.

Similarly, the greater randomness of the solution opposes the tendency to freeze. In consequence, a lower temperature must be reached for achieving the equilibrium between the solid (frozen solvent) and the solution.

Elevation of boiling point (ΔT_b) and depression of freezing point (ΔT_f) of a solution are the colligative properties which depend only on the concentration of particles of the solute, not their identity. For dilute solutions, ΔT_b and ΔT_f are proportional to the molality of the solute in the solution.

$$\Delta T_b = K_b m \; K_b = \text{Ebulliscopic cons tan } t = \frac{RT_b^{o^2} M}{1000\,\Delta H_{\text{vap}}}$$

and $\Delta T_f = K_f m$;

$$K_f = \text{Cryoscopic constant} = \frac{RT_f^{o^2} M}{1000\,\Delta H_{\text{fus}}}$$

(M = molecular mass of the solvent)

The values of K_b and K_f do depend on the properties of the solvent. For liquids, $\frac{\Delta H_{\text{vap}}}{T_b^{\text{o}}}$ is almost constant. For solutes undergoing change of molecular state is solution (ionisation or association), the observed ΔT values differ from the calculated ones using the above relations. In such situations, the relationships are modified as $\Delta T_b = iK_b m$; $\Delta T_f = iKf_m$ where i = Van't-Hoff factor, greater than unity for ionisation and smaller than unity for association of the solute molecules in solutions.

11. Depression of freezing point of which of the following solutions does represent the cryoscopic constant of water?
   (a) 6% by mass of urea in aqueous solution.
   (b) 100 g of aqueous solution containing 18 g of glucose.
   (c) 59 g of aqueous solution containing 9 g of glucose.
   (d) 1 M KCl solution in water.

12. Dissolution of a non-volatile solute into a liquid leads to the?
   (a) Decrease of entropy.
   (b) Increase in tendency of the liquid to freeze.
   (c) Increases in tendency to pass into the vapour phase.
   (d) Decrease in tendency of the liquid to freeze.

13. To aqueous solution of NaI, increasing amounts of solid HgI_2 is added. The vapor pressure of the solution
   (a) decreases to a constant value
   (b) increases to a constant value
   (c) increases first and then decreases
   (d) remains constant because HgI_2 is sparingly soluble in water

Assertion and Reasoning Code

(a) Statement 1, is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1
(b) Statement 1 is True, Statement 2 is True; Statement 2, is NOT a correct explanation for Statement 1
(c) Statement 1 is True, Statement 2, is False
(d) Statement 1 is False, Statement 2 is True

14. **Statement 1:** If a solution is heated such that keeping rest of all things unchanged, volume is changed, then it also brings changes to colligative properties related with it.
Statement 2: The molarity of solution changes on changing the volume of solution for same amount of solute.

15. **Statement 1:** The vapour pressure of a liquid is the equilibrium pressure of liquid-vapour equilibrium at the given temperature.
Statement 2: The ratio of the lowering of vapour pressure of a solvent upon dissolution of a non-volatile solute, to the vapour pressure of pure solvent increases with temperature.

16. **Statement 1:** Reverse osmosis is used to purify saline water.
Statement 2: Solvent molecules pass from concentrated to dilute solution through semipermeable membrane if high pressure is applied on solution.

17. **Statement 1:** The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution because
Statement 2: Elevation of boiling point is directly proportional to the number of species present in the solution.

18. **Statement 1:** Gases always tend to be less soluble in liquids as the temperature is raised.
Statement 2: Vapour pressure of liquids increase with increase in temperature.

19. **Statement 1:** Azeotropic mixtures are formed only by non-ideal solutions.
Statement 2: Boiling point of an azeotrope is either higher than both the components or lower than both the components.

20. **Statement 1:** The vapour pressure of 0.1 M sugar solution is more than 0.1 M KCl solution because
Statement 2: Lowering of vapour pressure is directly proportional to the number of species present in the solution.

21. **Statement 1:** One molar solution is always more concentrated than one molal solution because
Statement 2: The amount of solvent in 1 M and 1 m aqueous solution is not equal.

22. **Statement 1:** Out of various colligative properties, osmotic pressure is used for determination of molecular masses of polymers because
Statement 2: Polymer solutions do not possess constant boiling point or freezing point.

23. **Statement 1:** If a liquid solute more volatile than the solvent is added to the solvent, then the vapour pressure may increase i.e., $P_s > P^{\text{o}}$ because
Statement 2: In the presence of a more volatile liquid solute, only solute will form the vapours and solvent will not.

24. **Statement 1:** van't Hoff factor is equal to unity if the elecrolytic solute undergoes 100% dissociation because

Statement 2: van't Hoff factor for sucrose solution is unity.

Multiple Correct Type

25. When a solute is added to a pure solvent, the
- (a) vapour pressure of the solution becomes lower than that of the pure solvent.
- (b) rate of evaporation of the pure solvent is reduced.
- (c) solute does not affect the rate of condensation.
- (d) rate of evaporation of the solution is equal to the rate of condensation of the solution at a lower vapour pressure than that in the case of the pure solvent.

26. Which is/are correct statement(s)?
- (a) When mixture is less volatile, there is positive deviation from Raoult's law.
- (b) When mixture is more volatile, there is negative deviation from Raoult's law.
- (c) When mixture is less volatile, there is negative deviation from Raoult's law.
- (d) When mixture is more volatile, there is positive devation from Raoult's law.

27. According to Raoult's law, the relative decrease in the solvent vapour pressure over the solution is equal to
- (a) the mole fraction of the solvent.
- (b) the mole fraction of the solute if solute does not undergo association or dissociation.
- (c) the number of moles of the solute.
- (d) *i* times the mole fraction of the solute which undergoes dissociation or association in the solvent (*i* = van't Hoff factor).

28. Which of the following statements are correct for a binary solution which shows negative deviation from Raoult's law?
- (a) The negative deviation from linearity diminishes and tends to zero as the concentration of the solution component approaches unity.
- (b) When solutions form, their volumes are smaller than the sum of the volumes of their components.
- (c) Heat is released during the formation of the solution.
- (d) Heat is absorbed during the formation of the solution.

29. In the depression of freezing point experiment, it is found that the
- (a) vapour pressure of the solution is less than that of pure solvent.
- (b) vapour pressure of the solution is more than that of pure solvent.
- (c) only solute molecules solidify at the freezing point.
- (d) only solvent molecules solidify at the freezing point.

30. The colligative properties of a solution are
- (a) $\propto$ molality
- (b) $\propto \dfrac{1}{\text{molecular mass of the solute}}$
- (c) Proportional to each other.
- (d) Independent of the nature of the solute, i.e., electrolyte or non-electrolyte.

31. Identify the correct statements.
- (a) The solution formed by mixing equal volumes of 0.1 M urea and 0.1 M glucose will have the same osmotic pressure.
- (b) 0.1 M $K_4[Fe(CN)_6]$ and 0.1 M $Al_2(SO_4)_3$ are isotonic solutions.
- (c) For association of a solute in a solution, $i > 1$.
- (d) The ratio of van't Hoff factors for 0.2 M glucose and 0.1 M sucrose is 2: 1.

32. 1 mole benzene $(P^0_{\text{benzene}} = 42 \text{ mm})$ and 2 mole toluene $(P^0_{\text{toulene}} = 36 \text{ mm})$ will have
- (a) total vapour pressure 38 mm
- (b) mole fraction of vapours of benzene above liquid mixture is 7/19.
- (c) positive deviation from Raoult's law.
- (d) negative deviation from Raoult's law.

33. A binary liquid (AB) shows positive deviation from Raoult's law when
- (a) $p_A > p^0_A X^{\text{liq}}_A$ and $p_A > p^0_B X^{\text{liq}}_B$
- (b) Intermolecular forces: A-A, B-B > A-B
- (c) $\Delta V_{\text{mix}} > 0$
- (d) $\Delta H_{\text{mix}} > 0$

34. The azeotropic solutions of two miscible liquids
- (a) can be separated by simple distillation.
- (b) may show positive or negative deviation from Raoult' law.
- (c) are supersaturated solutions.
- (d) behave like a single component and boil at a constant temperature.

35. If P^0 and P_s are the vapour pressures of the solvent and its solution respectively and N_1 and N_2 are the mole fractions of the solvent and solute respectively, then
- (a) $P_S = P^0 N_2$
- (b) $P^0 - P_S = P^0 N_2$
- (c) $P_S = P^0 N_1$
- (d) $(P^0 - P_S)/P_S = N_1/(N_1 + N_2)$

36. Which of the following form ideal solution?
- (a) C_6H_5Cl and C_6H_5Br (b) C_6H_6 and $C_6H_5CH_3$
- (c) Hexane and Heptane (d) Ethanol + Cyclohexane

37. At constant temperature, the osmotic pressure of a solution is
- (a) directly proportional to the concentration.
- (b) inversely proportional to the molecular weight of the solute.

(c) directly proportional to the square of the concentration.
(d) directly proportional to the square root of the concentration.

38. Ideal solution is formed when its components
(a) have zero heat of mixing.
(b) have zero volume change.
(c) obey Raoult's law.
(d) can be converted into gases.

39. In the depression of freezing point experiment, it is found that
(a) the vapour pressure of the solution is less than that of pure solvent.
(b) Freezing point of 1 m sucrose solution greater than 1 m NaCl solution at same temperature.
(c) only solute molecules solidify at the freezing point.
(d) only solvent molecules solidify at the freezing point.

Integer and Subjective Question

40. At 20°C, the osmotic pressure of urea solution is 400 mm. The solution is diluted and the temperature is raised to 35°C, when the osmotic pressure is found to be 105.3 mm. Find $\frac{V_{\text{final}}}{V_{\text{initial}}}$

41. An aqueous solution containing 5% by weight of urea and 10% by weight of glucose. What will be the ΔT_f of solution? K_f' for H_2O is 1.86° mol^{-1} kg?

42. A certain mass of a substance when dissolved in 100 g C_6H_6 lowers the freezing point by 1.28°C. The same mass of solute dissoved in 100 g of water lowers the freezing point by 1.40°C. If the substance has normal molecular weight in benzene and is completely dissocated in water, into how many ions does it dissociate in water? K_f of H_2O and C_6H_6 are 1.86 and 5.12 K mol^{-1} respectively.

43. A complex is represented as $COCl_3 . xNH_3$. Its 0.1 molal solution in aqueous solution shows $\Delta T_f = 0.558°$. K_f for H_2O is 1.86 K molality^{-1}. Assuming 100% ionisation of complex and coordination number of Co as six, find the value of x.

44. A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.89g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. If the freezing temperature of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing depression constant of benzene in nearest integer?

45. The molal freezing point depression constant for benzene (C_6H_6) is 4.90 K kg mol^{-1}. Selenium exists as a polymer of the type Se_x. When 3.26 g of selenium is dissolved in 226 g of benzene, the observed freezing point is 0.112°C lower than that of pure benzene. Deduce the value of x. (Atomic mass of Se = 78.8 g mol^{-1}).

46. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molar mass of the solid substance in nearest integer?

47. Addition of 0.643 g of a compound to 50 mL of benzene (density: 0.879 g mL^{-1}) lower the freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K kg mol^{-1}, calculate the molar mass of the compound in nearest integer.

48. The vapour pressure of two pure liquids A and B, that form an ideal solution are 100 and 900 mm Hg respectively at temperature T. This liquid solution of A and B is composed of 1 mole of A and 1 mole of B. What will be the pressure, in mm Hg when 1 mole of mixture has been vaporised?

49. Mixture of two liquids A and B is placed in cylinder containing piston. Piston is pulled out isothermally so that volume of liquid decreases but that of vapour increases. When negligibly small amount of liquid was remaining, the mole fraction of A in vapour is 0.4. Given $P°_A = 0.4$ atm and $P°_B = 1.2$ atm at the experimental temperature. Calculate the total pressure at which the liquid has almost evaporated. (Assume ideal behaviour)

50. 1.5 g of monobasic acid when dissolved in 150 g of water lowers the freezing point by 0.165°C. 0.5 g of the same acid when titrated, after dissolution in water, requires 37.5 mL of N/10 alkali. Calculate the degree of dissociation of the acid (K_f for water = 1.86° C mol^{-1}).

51. The molar volume of liquid benzene (density = 0.877 g mL^{-1}) increase by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density = 0.867 g mL^{-1}) increases by a factor of 7720 at 20°C solution has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.

52. Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of carbon disulphide assuming 84% dimerisation of the acid. The boiling point and K_b of CS_2 are 46.2°C and 2.3 K kg mol^{-1}, respectively.

53. At 25°C, 1 mol of A having a vapour pressure of 100 torr and 1 mol of B having a vapour pressure of 300 torr were mixed. The vapour at equilibrium is removed, condensed and the condensate is heated back to 25°C. The vapour now formed are again removed, recondensed and analysed. What is the mole fraction of A in this condensate?

54. 30 mL of CH_3OH ($d = 0.7980$ g cm^{-3}) and 70 mL of H_2O ($d = 0.9984$ g cm^{-3}) are mixed at 25°C to form a solution of density 0.9575 g cm^{-3}. Calculate the freezing point of the solution. $K_f(H_2O)$ is 1.86 kg mol^{-1} K. Also calculate its molarity.

55. When the mixture of two immiscible liquids (water and nitrobenzene) boils at 372 K and the vapour pressure at this temperature are 97.7 kPa (H_2O) and 3.6 kPa ($C_6H_5NO_2$). Calculate the weight % of nitrobenzene in the vapour.

56. The molar volume of liquid benzene (density = 0.877 g mL^{-1}) increases by a factor of 2750 as it vaporises at 20°C while in equilibrium with liquid benzene. At 27°C when a non-volatile solute (that does not dissociate) is dissolved in 54.6 cm^3 of benzene vapour pressure of this solution, is found to be 98.88 mm Hg. Calculate the freezing point of the solution.

Given: Enthalpy of vaporization of benzene (l) = 394.57 J/g.

Molal depression constant for benzene = 5.12 K kg. mol^{-1}.

Freezing point of benzene = 278.5 K.

57. An ideal solution was prepared by dissolving some amount of cane sugar (non-volatile) in 0.9 moles of water. The solution was then cooled just below its freezing temperature (271 K), where some ice get separated out. The remaining aqueous solution registered a vapour pressure of 700 torr at 373 K. Calculate the mass of ice separated out, if the molar heat of fusion of water is 96 kJ.

58. The freezing point depression of a 0.109 M aqueous solution of formic acid is –0.21°C. Calculate the equilibrium constant for the reaction,

$HCOOH\ (aq) \rightleftharpoons H^+\ (aq) + HCOO^{\ominus}\ (aq)$

K_f for water = 1.86 kg mol^{-1} K

59. 10 g of NH_4Cl (mol. weight = 53.5) when dissolved in 1000 g of water lowered the freezing point by 0.637°C. Calculate the degree of hydrolysis of the salt if its degree of dissociation is 0.75. The molal depression constant of water is 1.86 kg mol^{-1} K.

60. The freezing point of 0.02 mol fraction solution of acetic acid (A) in benzene (B) is 277.4 K. Acetic acid exists partly as a dimer 2A = A_2. Calculate equilibrium constant for the dimerisation. Freezing point of benzene is 278.4 K and its heat of fusion ΔH_f is 10.042 kJ mol^{-1}.

61. Tritium, T (an isotope of H) combines with fluorine to form weak acid TF, which ionises to give T^+. Tritium is radioactive and is a β-emitter. A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at –0.372°C. If 600 mL of freshly prepared solution were allowed to stand for 24.8 years, calculate (i) ionisation constant of TF. (ii) Number of β-particles emitted.

(Given: K_f for water = 1.86 kg mol K^{-1}, $t_{1/2}$ for tritium = 12.4 years.)

62. The freezing point of an aqueous saturated solution of I_2 is –0.0024°C. More than this can dissolve in a KI solution because of the following equilibrium:

$$I_{2(aq)} + I^-_{aq} \rightleftarrows I^-_{3\,(aq)}$$

0.1 M KI solution dissolves 12.5 g/L of I_2. Calculate the equilibrium constant K_c for the above equilibrium. Also calculate the freezing point of the resulting solution. Assume molarity to be equal to molality and also assume that conc. of I_2 in all saturated solutions is same. [K_f for water = 1.86 K kg mol^{-1}].

63. Two solutions of non-volatile solutes A and B are prepared. The molar mass ratio, $\frac{M_A}{M_B} = \frac{1}{3}$. Both are prepared as 5% solutions by weight in water. Calculate the ratio of the freezing point depressions, $\frac{(\Delta T_f)_A}{(\Delta T_f)_B}$ of the solutions. If the two solutions are mixed to prepared two new solutions, S_1 and S_2, the mixing ratio being 2:3 and 3:2 by volume for S_1 and S_2 respectively what would be the ratio $\frac{(\Delta T_f)_{S_1}}{(\Delta T_f)_{S_2}}$?

64. The vapour pressures of two pure liquids A and B that form an ideal solution are 300 and 800 torr, respectively, at temperature T. A mixture of the vapours of A and B for which the mole-fraction of A is 0.25 is slowly compressed at temperature T. Calculate

(a) the composition of the first drop of the condensate.
(b) the total pressure when this drop is formed.
(c) the composition of the solution whose normal boiling points is T.
(d) the pressure when only the last bubble of vapour remains.
(e) composition of the last bubble.

65. At solution containing 12.5 g of non-electrolyte substance in 175 gram of water gave boiling point elevation of 0.70 K. Calculate the molar mass of the substance. Molal elevation constant (K_b) for water 0.52 K kg mol^{-1}.

66. What weight of the non-volatile solute, urea ($NH_2 - CO - NH_2$) need to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

67. Ethylene dibromide ($C_2H_4Br_2$) and 1,2-dibromo propane ($C_3H_6Br_2$) form a series of ideal solution over the whole range of composition. At 85°C, the vapour pressures of these pure liquids are 173 mm Hg and 127 mm Hg respectively.

(a) If 10 g of ethylene dibromide is dissolved in 80 g of 1, 2-dibromo propane. Calculate the partial pressures of each components and the total pressure of the solution at 85°C.
(b) Calculate the composition of the vapour in equilibrium with the above solution and express as mole fraction of ethylene dibromide.
(c) What would be the mole fraction of 1,2-dirbomo propane in solution at 85°C equilibriated with 50:50 mole mixture in the vapour?

68. A dilute solution contains m mol of solute A in 1 kg of a solvent with molal elevation constant K_b. The solute dimerises in solution as $2A \rightleftharpoons A_2$. Show that equilibrium constant for the dimer formation is

$$K = \frac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$$

Where ΔT_b is the elevation of the boiling point for the given solution. Assume molarity = molality.

69. Distribution coefficient of an organic acid between water and benzene is 4.1 in favour of C_6H_6. If 5 g of acid is distributed in between 50 mL of benzene and 100 mL of water, calculate the concentration of acid in two solvents.

70. Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquids are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure, in bar, of a mixture of 25g of heptane and 35 g of octane?

71. The freezing point depression of 0.001 m $K_x[Fe(CN)_6]$ is 7.10×10^{-3} K. Determine the value of x. Given, K_f = 1.86 K kg mol^{-1} for water.

72. The composition of vapour over a binary ideal solution is determined by the composition of the liquid. If x_A and y_A are the mole fractions of A in the liquid and vapour, respectively find the value of x_A for which ($y_A - x_A$) has maximum. What is the value of the pressure at this composition?

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution, containing 7.0 g of the salt per 100 g water at 100°C is 70 per cent. If the vapour pressure of water at 100°C is 760 mm, calculate vapour pressure of the solution. **[IIT-JEE, 1991]**

2. Addition of 0.643 g of a compound to 50 mL of benzene (density 0.879 g/mL) lowers the freezing point from 5.51°C to 5.03°C. If K'_f for benzene is 5.12 k m^{-1}. Calculate the molecular weight of the compound. **[IIT-JEE, 1992]**

3. A solution of non-volatile solute in water freezes at –0.30°C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298 K. **[IIT-JEE, 1998]**

4. To 500 cm^3 of water, 3×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg mol^{-1} and 0.997 g cm^{-3} respectively. **[IIT-JEE, 2000]**

5. 1.22 g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17°C, while that in the benzene increases by 0.13°C; k_b for acetone and benzene is 1.7 K kg mol^{-1} and 2.6 K kg mol^{-1}. Find molecular weight of benzoic acid in two cases and justify your answer. **[IIT-JEE, 2004]**

6. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take K_b = 0.76 K kg mol^{-1}). **[IIT-JEE, 2012]**

(a) 724 (b) 740 (c) 736 (d) 718

7. Consider separate solution of 0.500 M C_2H_5OH (aq), 0.100 M $Mg_3(PO_4)_2$ (aq), 0.250 M KBr (aq) and 0.125 M Na_3PO_4 (aq) at 25°C. Which statement is true about these solution, assuming all salts to be strong electrolytes? **[2014 Main]**

(a) They all have the same osmotic pressure.
(b) 0.100 M $Mg_3(PO_4)_2$ (aq) has the highest osmotic pressure.
(c) 0.125 M Na_3PO_4 (aq) has the highest osmotic pressure.
(d) 0.500 M C_2H_5OH (aq) has the highest osmotic pressure.

8. The vapour pressure of acetone at 20°C is 185 torr. **[2015 Main]**

When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 Torr. The molar mass of the substance is

(a) 32 (b) 64 (c) 128 (d) 488

Answer Key

LEVEL I

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

LEVEL II

1. (c) 2. (a) 3. (b) 4. (a) 5. (a) 6. (d) 7. (c) 8. (a) 9. (b) 10. (b)
11. (d) 12. (b) 13. (c) 14. (a) 15. (c) 16. (a) 17. (c) 18. (b) 19. (b) 20. (b)
21. (b) 22. (c) 23. (a) 24. (d) 25. (a)

LEVEL III

1. (A) → s, t; (B) → r; (C) → p; (D) → q 2. (A) → s, t; (B) → q; (C) → r; (D) → p
3. (A) → p, q; (B) → s, t; (C) → p, q; (D) → r 4. (A) → r, t; (B) → p; (C) → r, s, t; (D) → p, q
5. (a) 6. (d) 7. (b) 8. (d) 9. (d) 10. (c) 11. (c) 12. (d) 13. (b) 14. (b)
15. (c) 16. (a) 17. (a) 18. (b) 19. (b) 20. (a) 21. (d) 22. (c) 23. (c) 24. (d)
25. (a, b, c, d) 26. (c, d) 27. (b, d) 28. (a, b, c) 29. (a, d) 30. (a, b, c)
31. (a, b) 32. (a, b) 33. (a, b, c, d) 34. (b, d) 35. (b, c) 36. (a, b, c) 37. (a, b)
38. (a, b, c) 39. (a,b,d) 40. (4) 41. (3) 42. (3) 43. (5) 44. (5) 45. (8)
46. (65) 47. (156) 48. (300) 49. (0.66 atm) 50. (18.27%) 51. (0.732) 52. (46.31°C)
53. (0.1 and 0.9) 54. (–19.91°C, 7.63 M) 55. (20.11%) 56. (277.51 K)
57. (12.54 gram) 58. (1.44×10^{-4}) 59. ($h = 0.109$) 60. (3.225)
61. ($K_a = 7.3 \times 10^{-3}$, 3.7×10^{22} β-particle) 62. (707.2 and 272.62 K) 63. 9/11
64. (a) $X_A = 0.47$ (b) 565 torr (c) $X_A = 0.08$ (d) 675 torr (e) $X_A'' = 0.11$ 65. (53) 66. (111.118 gram) and (18.52 m)
67. (a) $P_A = 20.42$ mm Hg; $P_B = 112.04$ mm Hg (b) 0.154 (c) 0.5 and 0.5 68. Derivation
69. 67.22 gram/litre and 16.39 gram/litre 70. (73.08 kPa) 71. (3) 72. $\sqrt{P_A^{o} P_B^{o}}$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (746.24 mmHg) 2. (156.06) 3. (23.44 mmHg) 4. (0.229) 5. (122 and 244) 6. (a)
7. (a) 8. (b)

Hints and Solutions

LEVEL I

1. **(b)** $P_A = x P_A^{o}$
2. **(a)** Mole fraction of A in vapour

$$= \frac{P_A}{P_{\text{total}}} = \frac{P_A^0 x_2}{P} = x_1 = y_A$$

$$\therefore \quad P_{\text{total}} = P_s = \frac{P_A x_2}{x_1}$$

3. **(b)** $P_T = P_A + P_B$, for pure ethanol, $x = 0$

$\therefore \quad P^0_{\text{ethanol}} = (119 \times 0 + 135)$ torr

$\therefore$ vapour pressure of pure ethanol = 135 torr

4. **(c)** Ideal solution obey Roult's law.
5. **(b)** For a non-ideal solution with negative deviation,

$\Delta H_{\text{mix}} = -\text{ve}$
$\Delta V_{\text{mix}} = -\text{ve}$

6. **(b)** Either less than or more than 125 mL because $\Delta V_{\text{mixing}} = 0$ for ideal solution.
7. **(b)** mixture of polar CH_3OH and non polar benzene show +ve deviation.
8. **(a)** For an ideal solution $\Delta H_{\text{mix}} = 0$; $\Delta S_{\text{mix}} > 0$; $\Delta G_{\text{mix}} < 0$.
9. **(c)** $\Delta T_b \propto i \times m$: Higher the value of $i \times m$. more will be ΔT_b order of ΔT_b $b > c > d > a$.
10. **(a)** The H^+ ion concentration in the medium is lower than that of H^+ concentration present in the mango juice, therefore osmotic pressure inside the mango is higher than that of aqueous hydrochloric acid. Therefore, H_2O will be passes out from the mango into aqueous hydrochloric acid. Therefore mango shrinks,
11. **(b)** $\Delta T_b = iK_b \cdot m = iK_b \dfrac{w_B}{m_B} \times \dfrac{1000}{w_A}$

$\because \quad i = 1$

$$\therefore \quad \Delta T_b = \frac{1 \times 0.52 \times 32 \times 1000}{m_B \times 200} = 1.04$$

$\therefore \quad m_B = 80$ g/mole

12. **(d)** 'i' value of $CF_3COOH > CCl_3COOH > CH_3COOH$ Since, $i \propto$ acidic strength

13. **(a)** On freezing a solution, only solvent freeze, but not solute.

14. **(c)** $K_f = \frac{\Delta T_f}{m} = \frac{2}{0.25} = 8\text{ Km}^{-1}$

15. **(c)** $\Delta T_f = \frac{1000 \times K_f \times w_B}{w_A \times m_B} \Rightarrow 0.216 = \frac{1000 \times 2.16 \times 0.15}{15 \times m_B}$

$\therefore\ m_B = 100$

16. **(d)** Higher the value of '*i*' less will be freezing point.

17. **(a)** $2KI + HgI_2 \rightarrow K_2[HgI_4]$

18. **(c)** Relative lowering of vapour pressure is a colligative property.

19. **(c)** Solubility of phenol > chloroform > toluene due to H-bonding.

20. **(b)** $m = \frac{x_B \times 1000}{(1 - x_B) \times m_A} = \frac{0.2 \times 1000}{0.8 \times 78} = 3.2$

21. **(b)** Mass percentage of solute

$$= \frac{\text{Weight of solute} \times 100}{\text{Weight of [solute + solvent]}}$$

Mass percentage of aspirin in acetonitrile

$$= \frac{6.5}{(450 + 6.5)} \times 100 = 1.424\%$$

22. **(b)** $\frac{\Delta p}{P^o} = \frac{10}{P^o} = 0.2 \Rightarrow P^o = 50$

$$\frac{\Delta P}{P^o} = \frac{20}{P^o} = 0.4$$

$\therefore\ x_{\text{solvent}} = 0.6$

23. **(d)** Total pressure of the solution is given by

$$P_{\text{Total}} = X_B P^o_B + X_T P^o_T$$

$$= 0.4 \times 119 + 0.6 \times 37 = 47.6 + 22.2$$

$$= 69.8 \text{ torr}$$

Applying Dalton's law for mole fraction in vapour phase

$$y_B = \frac{P_B}{P_{\text{Total}}} = \frac{47.6}{62.4} = 0.763$$

$$y_T = 1 - 0.763 = 0.237$$

24. **(c)** Given $P_{\text{Total}} = 120 - 75\, x_B$

$$P = x_A P^0_A + x_B P^0_B$$

For pure A, $X_B = 0$; $P^o_A = 120$ torr

For pure B, $X_B = 1$; $P^o_B = 120 - (75 \times 1) = 45$ torr

25. **(c)** $x'_A = \frac{P_A}{P_S} = \frac{P^o_A x_A}{P_S} \Rightarrow \frac{x'_A}{x_A} = \frac{P^o_A}{P} < 1$

(Since the liquid A is less volatile, $P^o_A < P_S$)

26. **(a)** $\frac{\Delta P}{P_S} = \frac{n_B}{n_A} = \frac{w_B}{m_B} \times \frac{m_A}{w_A}$

$$\Rightarrow \quad \frac{20}{80} = \frac{w_B}{40} \times \frac{114}{114}$$

$$w_B = 10 \text{ gram.}$$

27. **(a)** $\frac{P_0 - P_S}{P_0} = \frac{17.5 - P_S}{17.5} = \frac{n_B}{n_B + n_A} = \frac{25/180}{\frac{25}{180} + \frac{450}{18}}$

Relative lowering of vapour pressure

$$\frac{P^o - P_{\text{solution}}}{P^o} = x_{\text{solute}};$$

$$\frac{17.535 - P_s}{17.535} = \frac{\frac{25}{180}}{\frac{450}{18} + \frac{25}{180}} \approx \frac{\frac{25}{180}}{\frac{450}{18}};$$

$\therefore\ P_s = 17.44$ mm Hg

28. **(b)** $K_b = \frac{\Delta T_b}{m}$

Since, $\Delta T_b = K_b \cdot m$

29. **(c)** $\Delta T_b = K_b \cdot m$ and $\Delta T_f = K_f \cdot m$

$\Delta T_b = 0.15°\text{C}$; $0.15 = K_b \times m$

On diluting the above solution with equal volume of water molality becomes approximately half.

$$\frac{\Delta T_f}{\Delta T_b} = \frac{K_f}{K_b} \times \frac{1}{2}; \frac{\Delta T_1}{0.15} = \frac{1.86}{0.512} \times \frac{1}{2}; \Delta T_f = 0.272°\text{C}$$

30. **(a)** $\Delta T_f = i \times K_f \times m$; i value of K_2SO_4 is maximum, so the freezing point is least.

31. **(a)** π = iCST; $K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$; Van't Hoff Factor, $i = 3$

$\because$ osmotic Pressure, $\pi = i\frac{n}{V}RT$;

$$\pi = 3 \times \frac{25 \times 10^{-3}}{174 \times 2.0} \times 0.0821 \times 298;\ \pi = 5.27 \times 10^{-3} \text{ atm}$$

32. **(b)** $i = \frac{\text{Observed molecular weight}}{\text{Calculated molecular weight}}$;

$$i \text{ for } AgNO_3 = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}} = 1 + \alpha$$

$$\alpha = \frac{170}{92.64} - 1 = 0.835 = 83.5\%$$

33. **(b)** Roult's Law states that the relative lowering of vapour pressure is equal to mole fraction of solute.

34. **(b)** $P_T = x_A P^0_A + x_B P^0_B$

$$y_A = \frac{P_A}{P_T} \text{ or } y_B = \frac{P_B}{P_T}$$

35. **(a)** $\frac{P_0 - P_S}{P_0} = \frac{n_A}{n_A + n_B}$

$$n_A + n_B = \frac{78}{78} + \frac{46}{92} = 1 + 0.5$$

$$P_B = P^o_B \times \frac{1}{1.5} = 75 \times 0.66 = 50$$

36. (d) $\frac{P_0 - P_S}{P_0} = x_B$

$$= \frac{0.8 - 0.6}{0.8} = \frac{0.2}{0.8} = 0.25$$

37. (b) $P = x_A P_A^0 + x_B P_B^0$

$$P_T = P_A + P_B = P_A^0 x_A + P_B^0 x_B = P_B^0(1 - x_A)$$

$$x_A = \frac{\frac{100}{140}}{\frac{1000}{180} + \frac{100}{140}} = 0.11$$

∴ $4.75 = P_A^0 \times 0.11 + 500(1 - 0.11)$

$$P_A^0 = \frac{31.0}{0.11} = 280.7 \text{ torr}$$

$$P_A = P_A^0 \times x_A = 280.7 \times 0.11 = 32 \text{ torr}$$

38. (a) $m = \frac{M \times 1000}{d \times 1000 - M \times \text{Molar mass of solute}}$

$$3 = \frac{M \times 1000}{1110 - M \times 40}$$

$3330 - 120M = M \times 1000$

$3330 = M(1120)$ ∴ $M = \frac{3330}{1120}$

$M = 2.97$

39 (b) The concentration of solution (ppm)

$$= \frac{\text{Weight of solute}}{\text{Weight of solvent}} \times 10^6 = \frac{5}{10^6} \times 10^6 = 5 \text{ ppm}$$

40. (a) $\Delta T_b = m \times K_b$

$\Delta T_b = 0.69 \times 0.513°\text{C}$

$\Delta T_b = 0.69 \times 0.513°\text{C}$

$T_{\text{solution}} - T_{\text{solvent}} = 0.3597$

$T_{\text{solution}} - 99.725°\text{C} = 0.3597$

$T_{\text{solution}} = 100.0789°\text{C}$

41. (b) $\Delta T_f = i \times m \times K_f$ $[\text{NaCl} = \text{Na}^+ + \text{Cl}^-]$

$\Delta T_f = 2 \times 1 \times 1 \times 1.86$ Since, $i = 2$

$\Delta T_f = 3.72$

$T_{\text{solvent}} - T_{\text{solution}} = 3.72$

$0° - T_{\text{solution}} = 3.72$

$T_{\text{solution}} = -3.72°\text{C}$

42. (c) $\Delta T_b = m \times K_b$

$$0.3 = \frac{10 \times 1000}{100 \times 100} \times K_b$$

$K_b = 0.3$

43. (a) $\alpha = \frac{M_T - M_0}{M_0} = \frac{58.50 - 31.80}{31.80} = 0.8396 = 83.96\%$

44. (d) $3\text{A} \longrightarrow \text{A}_3$

$1 - \alpha \qquad \alpha/3$

$i = 1 - \alpha + \alpha/3 \qquad \alpha = 100\%$

$= 1 - 1 + \frac{1}{3} = \frac{1}{3}$

45. (a) 5% solution means 100 mL solution contain 5 g cane sugar.

0.877% means 100 mL solution contain 0.877 g X isotonic solution $C_1 = C_2$

$\pi_1 = \pi_2$

∴ $C_1ST = C_2ST$

$C_1 = C_2$

$$\frac{5}{342 \times 100} = \frac{0.877}{\text{M wt.} \times 100}$$

$$\text{Mwt} = \frac{0.877}{5} \times 342 = 59.98$$

46. (a) Osmotic pressure ∝ Colligative properties

OP = iCRT

AlCl_3 (i = 4), BaCl_2 (i = 3), Urea (i = 1)

47. (d) $\alpha = \frac{1 - i}{1 - \frac{1}{n}} = \left(\frac{1 - i}{1 - n}\right)n$

$$0.8 = \frac{1 - i}{1 - \frac{1}{n}}; i = 0.4$$

$\Delta T = iK_f \times m$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$m_B = 62$

48. (a) $\Delta T = i \times K_b \times m$

$i \times m$ of Na_2SO_4 is highest, hence its boiling point will also be highest

Na_2SO_4 $\quad i \times m = 3 \times 0.01 = 0.03$

KNO_3 $\quad i \times m = 2 \times 0.01 = 0.02$

Urea $\quad i \times m = 1 \times 0.015 = 0.015$

Glucose $\quad i \times m = 1 \times 0.015 = 0.015$

49. (a) $\pi = \frac{n}{V} ST$

$$= \frac{12}{342} \times \frac{1}{0.1} \times 0.0821 \times 290$$

$= 8.35$ atm

50. (c) When $x_A = 0$, $x_B = 1$

∴ $P = P_B^{\text{o}}$

∴ $P_B^{\text{o}} = 254$,

when $x_A = 1$, $x_B = 0$

∴ $P_A^{\text{o}} = P = 254 - 119 = 135$

LEVEL II

1. **(c)** Weight of solute in 300 g solution $= \frac{300 \times 25}{100} = 75$ g

Weight of solute in 400 g solution $= \frac{400 \times 40}{100} = 160$ g

$\therefore$ Total weight of solute in resultant solution = 75 + 160 = 235 g

Total weight of solution = 300 + 400 = 700 g

Mass percentage of solute in resulting solution

$= \frac{235}{700} \times 100 = 33.6\%$

Mass percentage of solvent in resulting solution

$= (100 - 33.6)\% = 66.4\%$

2. **(a)** $\Delta T_f = i \times K_f \times m$

$0 - T_f = (1 + 0.2) \times 1.86 \times 0.2 = 0.4464$

$\therefore \quad T_f = -0.4464°\text{C}$

3. **(b)** $\pi = i$CST; Osmotic Pressure; $\pi = i$CRT

or $\quad \pi = i\frac{n}{V}RT$

$\therefore \quad 0.75 = \frac{n}{2.5} \times 0.0821 \times 300 \times 2.47$

$n = \frac{0.75 \times 2.5}{0.0821 \times 300 \times 2.47}; \quad \therefore \quad n = 0.03$ mole

4. **(a)** $\Delta T_b = iK_b \frac{\text{w}_\text{B}}{\text{m}_\text{B}} \times \frac{1000}{\text{w}_\text{A}}$

$= 2 \times 0.52 \times \frac{32.5}{64} \times \frac{1000}{100}$

$\Delta T_b = 5.28$

$\therefore \quad T_f = 100 + 5.28 = 105.28°\text{C}$

5. **(a)** Let acetic acid = A; Benzene = B

Assume, α part of A forms dimer

$2A \rightleftharpoons$	A_2	
1	0	Initially moles
$1 - \alpha$	$\alpha/2$	Moles after dimer is formed

$\therefore \quad i = \frac{(1-\alpha) + \alpha/2}{1} = 1 - \alpha/2$

Molecular fraction of $A = x_A = 0.02$;
= mole fraction of solute

Molecular fraction of $B = x_B = 0.98$
= mole fraction of solvent

Molality of A in $B = \frac{0.02}{78} \times \frac{1000}{0.98}$
$= 0.262$ mol kg^{-1} of Benzene

Since, $\Delta T_f = K_f \times i \times$ molality

$278.4 - 277.4 = 5 \times i\ 0.262$ or, $1 = 5 \times i \times 0.262$

$i = \frac{1}{5 \times 0.262} = 0.763$; $1 - \alpha/2 = 0.763 \Rightarrow \alpha = 0.48$

Hence the molality of A after dimer is formed = $(1 - \alpha)$ × Initial molality = (1 – 0.48) × initial molality = 0.52 × 0.262

Molality of A_2 after dimer is formed = $\frac{\alpha}{2}$ × molality = $\frac{0.48}{2} = 0.24 \times 0.26 = 0.06288$

The equilibrium constant

$$K_{\text{eq}} = \frac{[A_2]}{[A]^2} = \frac{0.06288}{(0.13624)^2} = 3.39 \text{ kg mol}^{-1}$$

$\therefore \quad m_A = 100$

6. **(d)** Number of ions in solution of NaCl = 2

$MgCl_2 = 3$; Urea = 1; $Na_2SO_4 = 3$; $Ca(NO_3)_2 = 3$

$\therefore \quad iC = 3 \times 0.1 = 0.3$ for both $Ca(NO_3)_2$ and Na_2SO_4

7. **(c)** $\pi = CRT = \frac{n}{V}RT$

$$= \left(\frac{w}{V}\% \times \frac{10}{m_B}\right) \times RT$$

$$= 5 \times \frac{10}{342} \times 0.0821 \times [150 + 273]$$

$= 5.07$ atm

8. **(a)** Let the apparent molecular weight = m_o

Osmotic pressure = $\pi = \frac{n}{V} \times \text{RT} = \frac{w}{m_\text{o}} \times \frac{1}{V} \times RT$

or $\quad 0.3092 \times 10^5 = \frac{3 \times 10^{-3}}{m_o} \times \frac{1}{10^{-3}} m^3 \times 8.314 \times 298$

$\therefore \quad m_o = 240.2 \times 10^{-3}$ kg $\quad = 240.2$ gram/mole

Since,

$$i = \frac{\text{Number of particles after dissociation}}{\text{Number of particles before dissociation}}$$

$$= \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$

$\therefore \quad Hg(CN)_2 \rightleftharpoons Hg^{++} + 2CN^-$

$\quad 1 - \alpha \qquad \alpha \qquad 2\alpha$

$\therefore$ Number of particles after dissociation

$= (1 - \alpha) + \alpha + 2\alpha = 1 + 2\alpha$

$\therefore \quad i = \frac{1 + 2\alpha}{1} = \frac{252.61 \times 10^{-3}}{240.2 \times 10^{-3}}$;

$\alpha = 0.02457$ or 2.4567%

9. **(b)** Given $\frac{w}{w}\% = 68\%$

$m_B = 63$ and $d = 1.504$ gmL^{-1}

$$M = \frac{w}{w}\% \frac{10d}{m_B} = \frac{68 \times 10 \times 1.504}{63} = 16.23 \text{ M}$$

10. **(b)** $P = x_A P_A^\text{o} + x_B P_B^\text{o}$

$$P^{\circ}_{\text{Heptane}} = 105.2 \text{ kPa}$$

$$P^{\circ}_{\text{Octane}} = 46.8 \text{ kPa}$$

$$P_S = 105.2 \times \left(\frac{\frac{26}{100}}{\frac{26}{100} + \frac{35}{114}} \right) + 46.8 \times \left(\frac{\frac{35}{114}}{\frac{26}{100} + \frac{35}{114}} \right)$$

$$= 73.08 \text{ kPA}$$

11. **(d)** $\dfrac{P^{\circ}_A - P_S}{P_S} \times \dfrac{1000}{m_A} = m$

$$\frac{12.3 - P_S}{P_S} \times \frac{1000}{18} = 1$$

$$1018 \times P_S = 12300$$

$$\therefore \quad P_S = \frac{12300}{1018} = 12.082 \text{ KPa}$$

12. **(b)** $K_b = \dfrac{RT_b^2 \times m_A}{1000 \times \Delta H_V}$

$$\because \quad \Delta H_V = \frac{R(T_b^{\circ})^2 m_A}{1000 \times K_b}$$

$$= 33919 \text{ J} \approx 34 \text{ KJ}$$

13. **(c)** Let the mass of solution = 100 g

$$(\Delta T_f)_1 = K_f m_1 \Rightarrow K_f = \frac{(\Delta T_f)_1}{m_1} = \frac{273 - 271}{\frac{5}{342} \times \frac{1000}{95}}$$

For glucose $(\Delta T_f)_2 = K_f m_2$ and $(T_f)_2 = T_f^0 - \Delta T_f$

$$273.15 - T_f = K_f \times m_2$$

$$= \frac{273 - 271}{\frac{5}{342} \times \frac{1000}{95}} \times \frac{5}{180} \times \frac{1000}{95}$$

$$T_{f(\text{glucose})} = 269.07 \text{ K}$$

14. **(a)** $\pi = \text{CRT}$

We know that

$$\pi_1 V_1 = C_1 R T_1 \quad \text{and} \quad \pi_2 V_2 = C_2 R T_2$$

Since, $(V_1 = V_2, T_1 = T_2)$

$$\therefore \quad \frac{\pi_1}{C_1} = \frac{\pi_2}{C_2}$$

$$\therefore \quad C_2 = \frac{\pi_2 C_1}{\pi_1} = \frac{1.52 \times 36}{4.98 \times 180} = 0.061 \text{ M}$$

15. **(c)** $\dfrac{(\text{C.P})_1}{(\text{C.P})_2} = \dfrac{i_1}{i_2}; \; i_{\text{KCl}} = \dfrac{\text{Exp. colligative property}}{\text{Normal colligative property}}$

$$= \frac{\text{Number of particle furnished by KCl}}{\text{Number of particles before dissociation}} = 2$$

For an ideal solution of sugar $i_{\text{sugar}} = 1$

16. **(a)** $\Delta T_b = T_b - T_b^{\circ} = \dfrac{1000 K_b w_B}{m_B w_A} = \dfrac{1000 \times 0.52 \times 0.6}{60 \times 100}$

$$T_b - 373 = 0.052 \qquad T_b = 373.052$$

17. **(c)** $m_B = \dfrac{1000 \times K_b \times w_2}{\Delta T_b w_1} \qquad m_B = \dfrac{1000 \times 2.53 \times 2.5}{1.38 \times 34}$

18. **(b)** $\Delta T_f = \dfrac{1000 \, K_f w_B}{m_B w_A}$

$$m_B = \frac{1000 \times 6.8 \times 1.2}{2.8 \times 15} \qquad \therefore \quad m_B = 194.2 \text{ g/mole}$$

19. **(b)** $\Delta T_b = i \times \dfrac{1000 K_b w_B}{m_B w_A} \qquad i = \dfrac{0.27 \times 122 \times 100}{1000 \times 0.54 \times 12.2}$

$$i = 0.5 \qquad i = 1 - \alpha + \frac{\alpha}{n}$$

$$\text{No. of moles} = \frac{\text{weight}}{\text{Molar mass}} = \frac{12.2}{122} = 0.1 \text{ mole}$$

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

$$0.1 \qquad 0$$

$$0 \qquad \frac{0.1}{2} \text{mole}$$

$$\frac{0.1}{2} \text{mole} = \frac{0.1}{2} N_A = \frac{N_A}{20}$$

20. **(b)**

$$\begin{array}{ll} & 1 - \alpha \qquad 3\alpha \qquad 2\alpha \\ \Delta T_b = i \, K_b m & x_3y_2 \longrightarrow 3x^{+2} + 2y^{+3} \\ i = 1 - \alpha + 3\alpha + 2\alpha & i = 0.75 + 1.25 \\ i = 2 & T_b - T_b^{\circ} = 2 \times 1 \times 0.52 \\ T_b = 373 + 1.04 & T_b = 374.04 \end{array}$$

21. **(b)**

$$\begin{array}{ll} \Delta T_b = K_b m & T_b - T_b^{\circ} = 0.573 \times 0.1 \\ T_b = 373.0573 \text{ K} & \end{array}$$

22. **(c)**

$$\begin{array}{ll} \Delta T_b = K_b m & 0.15 = 0.512 \times m \\ m = 0.292 & \Delta T_f = K_f m' \\ m' = m/2 & T_f - T_f^{\circ} = 1.86 \times \dfrac{0.292}{2} \\ T_f = -0.27°\text{C} & \end{array}$$

23. **(a)** Acetone = 10 gm Water = 90 gm

$$\text{mole \% of acetone} = \frac{10/58}{10/58 + 90/18} \times 100 = 3.33\%$$

24. **(d)** $\Delta T_f = K_f m \qquad m = \dfrac{0.14}{1.86} = 0.075 \text{ molal}$

25. **(a)** $\dfrac{P^{\circ} - P_S}{P_S} = \dfrac{\text{Loss in weight of solvent}}{\text{Loss in weight of solution}}$ (i)

$$\frac{P^{\circ} - P_S}{P_S} = \frac{w_B}{m_B} \times \frac{m_A}{w_A} \qquad \text{(ii)}$$

from eq. (i) and (ii)

$$\frac{0.04}{2.5} = \frac{5 \times 18}{180 \times m_B}$$

$$m_B = 31.25$$

LEVEL III

1. **(A - s, t), (B - r), (C - p), (D - q)**
   1. CH_3COOH in H_2O undergoes dissociation.
   2. CH_3COOH in C_6H_6 undergoes dimerisation
   3. Polymer in water undergoes neither association nor dissociation.
2. **(A – s, t) (B – q) (C – r) (D – p)**
   (a) Azeotropes or constant boiling mixtures with equal composition in both vapour phase and liquid phase.
   (b) $CHCl_3$ in benzene shows negative deviation because of increase in molecular interactions.
   (c) $i = \dfrac{\text{Observed molecular mass}}{\text{Theoritical molecular mass}}$
   (d) $m = \dfrac{\text{Weight of solute}}{\text{Molar mass of solute}} \times \dfrac{1000}{\text{Weight of solvent}}$
3. **(A - p,q), (B - s,t), (C -p, q), (D - r)**
   (a) CCl_4 and $CHCl_3$ are similar in structure and possess similar interaction so they are nearly ideal solution and obeys Roult's law.
   (b) C_6H_6 in H_2O, weakness the hydrogen bonding in H_2O and exhibit positive deviation.
   (c) In ideal solution, $P_A \propto X_A$
   (d) For non-ideal solution with negative deviation $P < x_A P_A^o$
4. **(A - r,t), (B - p), (C - r, s, t), (D - p,q)**

(Match the Column)

(a) $K_f = \dfrac{RT_f^{o^2}}{1000L_f} = \dfrac{RT_f^{o^2} m_A}{1000\Delta H_f}$;

T_f^o (water) = 273 K, $m_A = 18$

(b) $K_f = \dfrac{RT_f^{o^2}}{1000L_f} = \dfrac{RT_f^{o^2} m_A}{1000\Delta H_f}$;

T_f^o (water) = 373 K, $m_A = 18$

(c) $\Delta T_f = K_f \times m = K_f \times \dfrac{9 \times 1000}{180 \times 50} = K_f$

(d) $\Delta T_b = K_b \times m = K_b \times \dfrac{3 \times 1000}{60 \times 50} = K_b$

5. **(a)** $P = x_A P_A^o + x_B P_B^o$

   $y_A = \dfrac{P_A}{P_T},\ y_B = 1 - y_A$

6. **(d)** $P = x_A P_A^o + x_B P_B^o$

   $= 300 \times 0.25 + 500 \times 0.75 = 450$ torr

   $y_A = \dfrac{P_A}{P_T},\ y_B = 1 - y_A$

7. **(b)** $P = x_A P_A^o + x_B P_B^o$

   $y_A = \dfrac{P_A}{P_T},\ y_B = 1 - y_A$

8. **(d)** $\dfrac{P^o - P_S}{P_S} \times \dfrac{1000}{m_A} = m = \dfrac{w_B}{m_B} \times \dfrac{1000}{w_A}$

   $\dfrac{0.024 - P_S}{P_S} \times \dfrac{1000}{18} = \dfrac{68.4}{342} \times \dfrac{1000}{1000}$

   $P_S = 0.0239$ atm

9. **(d)** $\pi = \text{CST}\ ;\ \pi = \text{C} \times \text{R} \times \text{T};$

   $= \dfrac{\dfrac{68.4}{342}}{1\text{L}} \times 0.0821 \times 298;\ \pi = 4.89$ atm

10. **(c)** $\Delta T_f = i \times K_f \times m;\ T_f^0 - T_f = i \times K_f \times m$

    $0 - T_f = 1 \times 11.86 \text{ k kg mol}^{-1} \times \dfrac{\dfrac{68.4}{342}}{1}$ mol/kg

    $= 0.372°C$

    $T_f = –0.372°C$

11. **(c)** $\Delta T_f = K_f.m$ for a solution with $m = 1$, $\Delta T_f = K_f$
    Cryoscopic constant $K_f = \Delta T_f$ of solution having unit molality of normal solutes (means $i = 1$)
    Molality of glucose solution in $m = \dfrac{9 \times 1000}{(59 - 9) \times 180} = 1$
12. **(d)** Since the solution has greater entropy (disorder) than the pure liquid, so former has lesser tendency to freeze, i.e., the temperature has to be lowered to freeze the solution. It has lesser tendency to pass into the vapour phase.
13. **(b)** $2Na^+_{(aq)} + 2I^-_{(aq)} + HgI_{2(s)} \longrightarrow 2Na^+_{(aq)} + HgI^{2-}_{4(aq)}$
    The number of mole particles decreases from 4 = ($2Na^+$ + $2i^-$) to 3 = ($2Na^+$ + HgI_4^{2-}). Hence, the colligative property will decrease or, the vapour pressure will increase to a constant value until NaI is completely consumed
14. **(b)** On heating a solution, volume decreases and molarity increases. Therefore, colligative property also changes
15. **(c)** $\ln\dfrac{P_2}{P_1} = \dfrac{\Delta H}{R} \times \left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$
16. **(a)** In the process of reverse osmosis, solvent flows from concentrated side to dilute side of the so saline water can be purified.
17. **(a)** $\Delta T_b = iK_b \cdot m$
    i for urea < KCl
18. **(b)** Follow Henry's Law
19. **(b)** Azeotropes the boiling point of solution is either lower (+ve deviation to R-Law) or higher (–ve deviation to R-Law) than that pure components.

20. **(a)** $\frac{\Delta P}{P^{\text{o}}} = i \times x_A$

i for KCl > urea

21. **(d)** $M = \frac{n_{\text{solute}}}{V_{(\text{solution})}}; m = \frac{n_{\text{solute}}}{W_{(\text{solvent})}}$

22. **(c)** Since molecular weight of polymers is very high, ΔT_f and ΔT_b will be very small so that accurate values cannot be obtained. But osmotic pressure of polymer solution can be measured accurately.

23. **(c)** Vapours formed above a solution in composed of both volatile solute and solvent.

24. **(d)** For 100% ionisation, i is equal to number of ions produced from one mole of solute. e.g., For 100% ionisation of NaCl, $i = 2$

25. **(a, b, c, d)** When a non-volatile solute is added to a pure solvent, the solution vapour pressure is less than that of pure solvent.

26. **(c, d)** If a mixture is less volatile then the solution exhibits negative deviation and if the mixture is more volatile then the solution exhibits positive deviation from Roult's Law.

27. **(b, d)** $\frac{P_0 - P_s}{P_0} = X_{\text{solute}}$

28. **(a, b, c)** For a solution with negative deviation, $\Delta H_{\text{mix}} < 0$; $\Delta V_{\text{mix}} < 0$.

29. **(a, d)** When a non-volatile solute is added to a pure solvent to form a solution vapour pressure of solution decreased compared to that of a solution. At freezing point, only solvent freezes in a solution.

30. **(a, b, c)** Colligative property ∝ molality

$$\propto \frac{1}{\text{Molecular mass}}$$

31. **(a, b)**

1. For both urea and glucose $i = 1$
2. For both $K_4[Fe(CN)_6]$ and $Al_2(SO_4)_3$, $i = 1 + 4\alpha$
3. For association of a solute in a solution $i < 1$
4. Glucose and sucrose do not undergo either association or dissociation

32. **(a, b)** $P_T = P^{\text{o}}_{\text{benzero}} x_{\text{benzene}} + P^{\text{o}}_{\text{toulene}} X_{\text{toulene}}$

$$y_{\text{benzene}} = \frac{P_{\text{benzene}}}{P_T} = \frac{14}{38} = \frac{7}{19}$$

$$P_T = 42 \times \frac{1}{3} + 36 \times \frac{2}{3} = 38 \text{ mm}$$

33. **(a, b, c, d)** In case of non-ideal solution with positive deviation from Roult's law.

1. $P_s > x_A P_A^0 + x_B P_B^0$
2. $\Delta H_{\text{mix}} > 0$
3. $\Delta V_{\text{mix}} > 0$
4. A-A and B-B later actions are more than of A-B interaction

34. **(b, d)** In azeotrofric mixture, both components will boil at same temperature.

35. **(b, c)** $\frac{P^{\text{o}} - P_S}{P^{\text{o}}} = 1 - x_{\text{solvent}}$

$$P^{\text{o}} - P^{\text{o}} x_{\text{solvent}} = P^{\text{o}} - P_S$$

$$-P^{\text{o}} x_{\text{solvent}} = -P_S$$

$$\therefore \quad \frac{P_S}{P^{\text{o}}} = x_{\text{solvent}} = N_1$$

$$\therefore \quad P_S = P^{\text{o}} N_1$$

$$\frac{P^{\text{o}} - P_S}{P^{\text{o}}} = x_{\text{solute}} = N_2$$

$$\therefore \quad P^{\text{o}} - P_S = P^{\text{o}} N_2$$

36. **(a, b, c)** Components with similar molecular structure and similar molecular interaction will form an ideal solution.

e.g. C_6H_5Cl and C_6H_5Br, C_6H_6 and $C_6H_5CH_3$;

37. **(a, b)** $\pi = \text{iCST}$

38. **(a, b, c)** Ideal solution: Obeys Roult's law

$$\Delta H_{\text{mix}} = \Delta V_{\text{mix}} = 0$$

39. **(a, b, d)** When a non-volatile solute is added to a pure solvent to form a solution vapour pressure of solution decreased compared to that of a solution. At freezing point, only solvent freezes in a solution $\Delta T_f = iK_f m$.

40. **(4)** $\pi_1 = C_1 ST$; $\pi_2 = C_2 ST$; $\frac{\pi_1}{\pi_2} = \frac{C_1}{C_2}$

For initial solution, $\pi = \frac{400}{760}$ atm, $T = 293$ K

$$\frac{400}{760} \times V_1 = n \times S \times 293 \qquad \text{(i)}$$

After dilution, let volume becomes V_2 and temperature is raised to 35°C, i.e., 308 K. $\pi = \frac{105.3}{760}$ atm

$$\frac{105.3}{760} \times V_2 = n \times S \times 308 \qquad \text{(ii)}$$

By Eqs. (i) and (ii) we get $\frac{V_1}{V_2} = \frac{293}{308} \times \frac{105.3}{400}$

$$\frac{V_1}{V_2} = \frac{1}{4}$$

$$V_2 = 4V_1$$

i.e., solution was diluted to four times.

41. **(3)** $\Delta T_f = (1.86)[(n_{\text{area}} + n_{\text{glucose}})10]$

∵ solution has 5% by weight urea and 10% by weight glucose

$$\because \quad \text{\% by weight} = \frac{\text{Weight of solute}}{\text{Weight of solution}} \times 100$$

∴ Weight of water = 85 g; Weight of urea = 5 g; Weight of glucose = 10 g

$$\Delta T_f = \Delta T_{\text{urea}} + \Delta T_{\text{Glucose}}$$

$$\Delta T = \frac{1000 \times 1.86 \times 5}{60 \times 85} + \frac{1000 \times 1.86 \times 10}{180 \times 85} = 3.04$$

42. **(3)** We know,

$$\because \quad \Delta T_f = \frac{1000 K_f \times w_B}{m_B \times w_A}$$

In C_6H_6: $1.28 = \dfrac{1000 \times 5.12 \times w}{m_N \times 100}$ (i)

In H_2O: $1.40 = \dfrac{1000 \times 1.86 \times \text{w}}{m_{\text{exp}} \times 100}$ (ii)

(Since given that solute behaves as normal in C_6H_6 and dissociates in water.) By Eqs. (i) and (ii)

$$\frac{m_N}{m_{\text{exp}}} = \frac{1.40}{1.28} \times \frac{5.12}{1.86} = 3.01$$

Since, $i = \dfrac{m_n(\text{Normal molar mass})}{m_{\text{exp.}}(\text{experimental molar mass})}$

$$i = 3.01 \approx 3.0$$

43. **(5)** $\Delta T_f = i \times K_f \times m$

$$\begin{array}{ccc} CoCl_3.\,xNH_3 \longrightarrow & CoCl.\,xNH_3 + & nCl^- \\ 1 & 3-n & 0 \\ 1-\alpha & \alpha & n\alpha \end{array}$$

Let n ions of Cl^- are attached with Co. through primary valencies which undergo dissociation. All the NH_3 molecules are attached through secondary valencies. (NH_3 behave as neutral ligand)

$\Delta T_f = (1 - \alpha + \alpha + n\alpha) \times K_f \times$ molality

$0.558 = (1 - 1 + 1 + n) \times 1.86 \times 1 \quad (\because \alpha = 1)$

$\therefore \quad n = 2$

Thus complex is $[CoCl.xNH_3].Cl_2$.

Since coordination number of Co is six, thus $x + 1 = 6$ or $x = 5$.

44. **(5)** $\dfrac{P^o - P_S}{P_S} \times \dfrac{1000}{m_A} = m = \dfrac{\Delta T_f}{K_f}$

$$\therefore \quad m = \frac{100 - 98.88}{98.88} \times \frac{1000}{78} = 0.1452$$

now $K_f = \dfrac{\Delta T_f}{m} = \dfrac{0.73}{0.1452} = 5.027$

$$\therefore \quad m = \frac{100 - 98.88}{98.88} \times \frac{1000}{78} = 0.1452$$

45. **(8)** Given $K_f = 4.9$

$w_B = 3.26 \qquad w_A = 226$

$\Delta T_f = 0.112°C \qquad m_B = x \times 78.8$

$$\Delta T_f = K_f \times \frac{w_B}{m_B} \times \frac{1000}{w_A}$$

$$0.112 = \frac{4.9 \times 3.26}{x \times 78.8} \times \frac{1000}{226}$$

46. Given that,

$P° = 640$ mm, $P_s = 600$ mm,

$w_B = 2.175$ g, $w_A = 39.0$ g, $m_B = 78$

$$\because \quad \frac{P^o - P_s}{P_s} = \frac{w_B}{m_B} \times \frac{m_A}{w_A}$$

$$\therefore \quad \frac{640 - 600}{600} = \frac{2.175 \times 78}{m_B \times 59}$$

$\therefore \quad m = 65.25$

47. Given

$w_B = 0.643$ gram, $K_f = 5.12\ \text{Kmol}^{-1}$ kg

$\Delta T_f = 5.51 - 5.03 = 0.48$

w_A = wt. of benzene $= V \times d = 50 \times 0.879$ g

$$\therefore \quad 0.48 = \frac{1000 \times 5.12 \times 0.643}{m_B \times 50 \times 0.879}$$

$$= \Delta T_f = K_f \times \frac{w_B}{m_B} \times \frac{1000}{w_A}$$

$\therefore \quad m_B = 156.06$

48. Let n_B mole of B present in 1 mole of mixture that has been vaporised.

Thus, $y_B = n_B$

$x_B = 1 - n_B$

$P = P_A°x_A + P_B°x_B = P_A° + x_B(P_B° - P_A°)$

$$x_B = \frac{P - P_A^o}{P_B^o - P_A^o} = 1 - n_B$$

$$y_B = \frac{P_B^o x_B}{P} \Rightarrow n_B = \frac{P_B^o(1 - n_B)}{P}$$

$$n_B P = P_B^o - n_B P_B^o \qquad \text{(i)}$$

$$n_B = \frac{P_B^o}{P_B^o + P} \qquad \text{(ii)}$$

From Eqs. (i) and (ii)

$$1 - \frac{P_B^o}{P_B^o + P} = \frac{P - P_A^o}{P_B^o - P_A^o} \Rightarrow \frac{P}{P_B^o + P} = \frac{P - P_A^o}{P_B^o - P_A^o}$$

On solving

$$P = \sqrt{P_A^o\ P_B^o} = \sqrt{100 \times 900} \Rightarrow 300 \text{ mm Hg}$$

49. $P_T = P_A^o x_A + P_B^o x_B = P_A^o x_A + P_B^o\ (1 - x_A)$

$$P_T = P_B^o + x_A = (P_A^o - P_B^o)$$

$$y_A = \frac{P_A^o x_A}{P_T} = \frac{P_A^o x_A}{P_B^o + x_A(P_A^o - P_B^o)}$$

$$0.4 = \frac{0.4 x_A}{1.2 - 0.8 x_A}$$

$$1.2 = 1.8 \times x_A$$

$$x_A = \frac{2}{3}$$

so $\quad x_B = \dfrac{1}{3}$

$$P_T = 0.4 \times \frac{2}{3} + 1.2 \times \frac{1}{3} = \frac{2}{3} = 0.66 \text{ atm}$$

50. $\dfrac{0.5}{m_B} = 3.75 \times 10^{-3} \Rightarrow m_B = 133.33$

$$0.165 = (1 + \alpha) \times \frac{1.86 \times 1.5 \times 1000}{133.33 \times 150}$$

$1 + \alpha = 1.1827$

$\alpha = 0.1827 = 18.27\%$

51. $V_B = \dfrac{78}{0.877} \times 2750 \text{ mL} = 244.583 \text{ L}$

$$V_T = \frac{92}{0.867} \times 7720 \text{ mL} = 819.192 \text{ L}$$

$$P_B = \frac{1 \times 0.0821 \times 293 \times 760}{244.583} = 74.74 \text{ torr}$$

$$P_T = \frac{1 \times 0.0821 \times 293 \times 760}{819.192} = 22.317$$

$46 = 74.74\, x_B + 23.317(1 - x_B)$

$52.423 x_B = 23.683$

$x_B = 0.451$

$$y_B = \frac{P_B^{\circ} \times x_B}{P_T} = \frac{74.74 \times 0.451}{46} = 0.732$$

52. $i = 1 - \dfrac{\alpha}{2} = 1 - \dfrac{0.84}{2} = 0.48$

$$\Delta T_b = \frac{0.48 \times 2.3 \times 0.61 \times 1000}{122 \times 50} = 0.1104$$

$T_b = 46.2 + 0.1104 = 46.31°\text{C}$

53. $P_A^{\circ} = 100,\ P_B^{\circ} = 300,\ x_A = x_B = \dfrac{1}{2}$

$$P_T = 100 \times \frac{1}{2} + 300 \times \frac{1}{2} = 200 \text{ torr}$$

$$y_A = \frac{100 \times \frac{1}{2}}{200} = \frac{1}{4}$$

On condensation $x'_A = \dfrac{1}{4},\ x'_B = \dfrac{3}{4}$

$$P'_T = 100 \times \frac{1}{4} + 300 \times \frac{3}{4} = 250$$

$$y'_A = \frac{25}{250} = 0.1$$

On further condensation

$x''_A = 0.1$

$x''_B = 0.9$ means composition of 2nd distillate

54. $CH_3OH \rightarrow V_1 = 30 \text{ mL},\ d_1 = 0.798 \text{ g/mL}$

$m_1 = 23.94 \text{ g}$ = mass of CH_3OH

$H_2O \rightarrow V_2 = 70 \text{ mL},\ d_2 = 0.9984 \text{ g/mL}$

$m_2 = 69.888 \text{ g}$ = mass of water

$m_T = 93.828 \text{ g}$ = Total mass of solution

$d_{\text{solution}} = 0.9575 \text{ g/mL}$

$V_{\text{solution}} = 98 \text{ mL}$

$$\Delta T_f = \frac{1.86 \times 23.94 \times 1000}{32 \times 69.888} = \mathbf{19.91}$$

$T_f = -19.91°\text{C}$

$$M = \frac{23.94}{32 \times 0.98} = \mathbf{7.63\ M}$$

55. $\dfrac{\text{wt of Nitrobenzene}}{\text{wt of Nitrobenzene} + \text{wt of water}} \times 100$

$$= \frac{3.6 \times 123}{3.6 \times 123 + 97.7 \times 18} \times 100$$

$= 20.11\%$

56. At 20°C:

For $C_6H_6 \rightarrow V = \dfrac{78}{0.877} \times 2750 \text{ mL}$

$PV = 1 \times 0.0821 \times 293$

$P = 74.74 \text{ mm Hg}$

If vapour pressure of benzene at 27°C is P_1 then

$$\ln\frac{P_1}{P} = \frac{\Delta H_V}{R}\left[\frac{1}{T} - \frac{1}{T_1}\right]$$

$$\ln\frac{P_1}{74.74} = \frac{394.57 \times 78}{8.314}\left[\frac{1}{293} - \frac{1}{300}\right]$$

$P_1 = 100.364 \text{ mm Hg}$

$$m = \frac{P^{\circ} - P_s}{P_s} \times \frac{1000}{m_A}$$

$$m = \frac{100.364 - 98.88}{98.88} \times \frac{1000}{78} = 0.1924$$

$\Delta T_f = K_f \times m = 5.12 \times 0.1924 = 0.985°\text{C}$

$T_f = 278.5 - 0.985 = 277.51 \text{ K}$

57. Initial moles of $H_2O = 0.9$

$\Delta H_f = 6 \text{ kJ}$

$$K_f = \frac{RT_f^2 M}{1000 \Delta H_f} = \frac{8.314 \times (273)^2 \times 18}{1000 \times 6000} = 1.86$$

$\Delta T_f = K_f \times \text{m}$

$$m = \frac{2}{1.86} = 1.075$$

so in 1000 g $H_2O \rightarrow$ 1.075 mole solute

in 1 g $H_2O \rightarrow \dfrac{1.075}{1000}$ mole solute

in 0.9×18 g $H_2O \rightarrow \dfrac{1.075}{1000} \times 0.9 \times 18$ mole solute

Mole of solute $(n_B) = 0.0174.15$

$$\frac{P^{\circ} - P_s}{P_s} = \frac{n_B}{n_A} \Rightarrow \frac{760 - 700}{700} = 0.0857$$

Moles of H_2O $(n_A) = \dfrac{0.017415}{0.0857} = 0.2032$

Moles of Ice separate out $= 0.9 - 0.2032 = 0.6968$

Mass of Ice separate out $= 0.6968 \times 18 = 12.54$ g

58. $\Delta T_f = (1 + \alpha)\, K_f \times \text{m}$

$0.21 = (1 + \alpha) \times 1.86 \times 0.109$

$1 + \alpha = 1.0358$

$\alpha = 0.0358$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.109(0.0358)^2}{1-0.0358} = 1.44 \times 10^{-4}$$

59. $NH_4Cl \longrightarrow NH_4^+ + Cl^-$, $NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$

$C \qquad\qquad\qquad\qquad\qquad C\alpha$

$C - C\alpha \qquad C\alpha \qquad C\alpha \qquad C\alpha - C\alpha h \qquad C\alpha h \qquad C\alpha h$

$$i = \frac{C - C\alpha + C\alpha + C\alpha - C\alpha h + C\alpha h + C\alpha h}{C}$$

$= (1 + \alpha + \alpha h)$

$\Delta T_f = i \times K_f \times \mathrm{m}$

$$0.637 = \frac{(1+\alpha+\alpha h)\times 1.86 \times 10}{53.5}$$

$1 + \alpha + \alpha h = 1.832$ and

since $\alpha = 0.75$, $h = 0.109$

60. $$K_f = \frac{8.314 \times (278.4)^2 \times 78}{1000 \times 10042} = 5$$

$$m = \frac{0.02 \times 1000}{0.98 \times 78} = 0.2614$$

$\Delta T_f = i \times K_f \times m$

$$i = 1 - \frac{\alpha}{2} = 0.7643$$

$\alpha = 0.4713$

$2A \rightleftharpoons A_2$

C

$C - C\alpha \qquad C\alpha/2$

$$K_{\text{eq}} = \frac{C\alpha/2}{(C - C\alpha)^2} = \frac{\alpha}{2C(1-\alpha)^2}$$

$$K_{\text{eq}} = \frac{0.4713}{2 \times 0.2614(1-0.4713)^2} = \mathbf{3.225}$$

61. $TF \longrightarrow T^+ + F^-$

$C - C\alpha \qquad C\alpha \qquad C\alpha$

$$i = \frac{C - C\alpha + C\alpha + C\alpha}{C} = 1 + \alpha$$

for dilute solution $C = M = m$ (molality)

$\therefore \quad \Delta T_f = iK_f \cdot m = iK_f \cdot C$

$P^T = 1.5 \Rightarrow [T^+] = 0.0316 = C\alpha$ (i)

$0.372 = 1.86 \times C(1 + \alpha)$

$C + C\alpha = 0.2$ (ii)

from Eqs. (i) and (ii)

$C = 0.1684$, $\alpha = 0.1876$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.1684(0.1876)^2}{(1-0.1876)} = \mathbf{7.3 \times 10^{-3}}$$

In 600 mL solution [TF] = $C - C\alpha = 0.1368$ mole/L

So moles = $0.1368 \times 0.6 = 0.08208$

Since, $24.8y = 2t_{1/2}$

Moles left after 24.8 years = $\dfrac{0.08208}{4} = 0.02052$

Moles disintegrated

$= 0.08208 - 0.02052 = 0.06156$

Moles of β-particle emitted = 0.06156

Number of β-particle emitted = $0.06156 \times 6.023 \times 10^{23}$

$= 3.7 \times 10^{22}$

62. 272.6256 K

$$K_c = \frac{[I_3^-]}{[I_2][I^-]}$$

$\Delta T_f = i \times K_f \times M (M = m)$

$\Delta T_r = K_f m$

$$m = \frac{0.0024}{1.86} = 0.0013 \text{ mole/kg}$$

$I_{2(aq)} \quad + \quad I^-_{(aq)} \quad \rightleftharpoons \quad I_3^-(aq)$

$0.0492 \qquad 0.1 \qquad 0$ Initial

$(0.0492 - x) \qquad (0.1x) \qquad x$ Equilibrium

Now, $0.0492 - x = 0.0013$, because of conc. of I_2 in all saturated solutions is same

$x = 0.0479$

$$K_c = \frac{[I_3^-]}{[I_2][I^-]}$$

$$K_c = \frac{(0.0479)}{(0.0013)(0.0521)}$$

$K_c = 707.2 \quad I_3^- + I_2 + I^- + K^+$

$\Delta T_f = 1.86(0.0479 + 0.0013 + 0.0521 + 0.1)$

$\therefore$ freezing point of the resulting solution = 272.6256 K

63. 9/11

$$\frac{(\Delta T_f)_1}{(\Delta T_f)_2} = \frac{M_2}{M_1}$$

$$(\Delta T_f) = K_f \times \frac{5}{95M_A} \times 1000;$$

$$(\Delta T_f) = K_r \times \frac{5}{95M_B} \times 1000$$

$$\therefore \quad \frac{(\Delta T_f)_A}{(\Delta T_f)_B} = \frac{M_B}{M_A} = \frac{3}{1}$$

Further for solution S_1, molality

$$= \left[\frac{5 \times 1000}{95M_A}\right] \times \frac{2}{5} + \left[\frac{5 \times 1000}{95M_B}\right] \times \frac{3}{5}$$

For solution S_2, molality

$$= \left[\frac{5 \times 1000}{95M_A}\right] \times \frac{3}{5} + \left[\frac{5 \times 1000}{95M_B}\right] \times \frac{2}{5}$$

$$\frac{(\Delta T_f)_{S_1}}{(\Delta T_f)_{S_2}} = \frac{\text{molality of } S_1}{\text{molality of } S_2}$$

$$= \left[\frac{2}{M_A} + \frac{3}{M_B}\right] \Big/ \left[\frac{3}{M_A} + \frac{2}{M_B}\right]$$

$$\frac{2 + 3\dfrac{M_A}{M_B}}{3 + 3\dfrac{M_A}{M_B}} = \frac{2 + 3 \times \dfrac{1}{3}}{3 + 2 \times \dfrac{1}{3}} = \frac{3}{3\frac{2}{3}} = \frac{9}{11}$$

64. (a) $X_A = 0.47$ (b) 565 torr (c) $X_A = 0.08$ (d) 675 torr (e) $X_A'' = 0.11$

$$x'_A = \frac{x_A p_A^{o}}{p} \quad \text{and} \quad x'_B = \frac{x_B p_B^{o}}{p}$$

$$\frac{x_A}{x_B} = \frac{p_A^{o} \times x_A}{p_B^{o}(1 - x_A)}$$

Given

$P_A^0 = 300$ torr, $P_B^0 = 800$ torr

$X'_A = 0.25, \quad X'_B = 1 - 0.25 = 0.75$

(a) By the condensation of only one drop, we can assume that composition of the vapour remains the same

$$X'_A = \frac{P_A^0 X_A}{P} \text{ and } X'_B = \frac{P_B^0 X_B}{P}$$

or $\dfrac{X'_A}{X'_B} = \dfrac{P_A^0 X_A}{P_B^0 (1 - X_A)}$

Putting various known values, we get

$X_A = 0.47$ and $X_B = 0.53$

(b) $P = 300 \times 0.47 + 800 \times 0.53 = 565$ torr

(c) $760 = 300\,X_A + 800\,X_B$

$X_A = 0.08$ and $X_B = 0.92$

(d) When only the last bubble of vapour remains, we can assume composition of vapour is now the composition of the condensate.

Hence, $P = 0.25 \times 300 + 0.75 \times 800 = 675$ torr

(e) Composition of the last bubble;

$$X''_A = \frac{P_A^{o} X_A}{P} = \frac{0.25 \times 300}{675} = 0.11$$

$$X''_B = 0.89$$

65. $\Delta T_b = K_b \times \dfrac{w_B}{m_B} \times \dfrac{1000}{w_A}$

$$\therefore \quad m_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

According to available data

Mass of solute (w_B) = 12.5 g

Mass of water (w_A) = 1.75 g

Molal elevation constant (K_b) = 0.52 K kg mol^{-1}

Elevation in boiling point temperature (ΔT_b) = 0.70 K

$$\therefore \quad m_B = \frac{(0.052\,K \text{ kg mol}^{-1}) \times (12.5\text{ g}) \times 1000}{(0.70\text{ K}) \times (175\text{ g})}$$

$$= 53 \text{ g mol}^{-1}$$

66. $\dfrac{P^0 - P_s}{P_0} = \dfrac{w_B}{m_B} \times \dfrac{m_A}{w_A}$

$$\Rightarrow \quad \frac{P^{o} - P^{o} \times \frac{75}{100}}{P^{o} \times \frac{75}{100}} = \frac{w}{60} \times \frac{18}{100}$$

$$\Rightarrow \quad \frac{0.25}{0.75} = \frac{w_B}{60} \times \frac{18}{100} \therefore w_B = 111.118$$

$$\therefore \text{ molality} = \frac{111.11}{60} \times \frac{1000}{100} = 18.52$$

67. (a) $P_A = 20.42$ mm Hg, $P_B = 112.014$ mm Hg

(b) $y_A = 0.154$

(c) $y_A = 0.5$

We know $\quad P_T = x_A P_A^0 + x_B P_B^0$

$$x_A = \frac{n_A}{n_A + n_B}, \; x_B = 1 - x_A$$

$$y_A = \frac{P_A}{P_T}, \; y_B = 1 - y_A$$

Let $C_2H_4Br_2 = A$, $m_A = 24 + 4 + 160$, where m_A = molecular weight of A

m_B = molecular weight of B and B is $C_3H_6Br_2 = m_B = 36 + 6 + 160 = 202$ Moles of A,

$$n_A = \frac{w_A}{m_A} = \frac{10}{188} = 0.053 \text{ Moles of } B,$$

$$n_B = \frac{w_B}{m_B} = \frac{80}{202} = 0.396$$

$$\therefore \quad x_B = \frac{n_B}{n_A + n_B} = \frac{0.396}{0.053 + 0.396} = \mathbf{0.882}$$

$\therefore \quad x_A + x_B = 1$

$\therefore \quad x_A = 1 - 0.882 = \mathbf{0.118}$

(a) We know, total pressure

$P_T = P_A + P_B$ Where P_A, P_B are partial pressures of A and B respectively.

$= P_A^0 \cdot x_A + P_B^0 \cdot x_B$, where P_A^0, P_B^0 are partial pressures of pure component of A and B.

$P_T = 173 \times 0.118 + 127 \times 0.882 = 20.42 + 112.014 = 132.43$ mm Hg

Here partial pressure of A, P_A = **20.42 mm Hg**

Here partial pressure of B, P_B = **112.014 mm Hg.**

(b) Mole fraction of ethylene dibromide in the vapour

$$y_A = \frac{\text{Partical Pressure of } A}{\text{Total pressure}} = \frac{20.42}{132.43} = \mathbf{0.154}$$

(c) In vapour phase $n_A : n_B = 50{:}50$ y_A = **0.5**, y_B = **0.5**

$$= \frac{n_B}{n_A + m_B}$$

68.

$$\begin{array}{lcll} 2A & \rightleftharpoons & A_2 & \\ m & & 0 & \text{initially} \\ (m - m\alpha) & & \dfrac{m\alpha}{2} & \text{after dimerisation} \\ m(1 - \alpha) & & \dfrac{m\alpha}{2} & \end{array}$$

where α is the degree of dimerisation and m is molality which is also molarity (given for dilute solution)). Hence due to dimerisation, final molality = m

$$m(1-\alpha)+\frac{m\alpha}{2} = m\left(1-\frac{\alpha}{2}\right)$$

$$i = 1+(n-1)\alpha$$

$$i=1+\left(\frac{1}{2}-1\right)\alpha$$

$$=\left(1-\frac{\alpha}{2}\right)$$

$$\Delta T_b = K_b\times m\times i = K_b\times m\left(1-\frac{\alpha}{2}\right)$$

$$\therefore \quad \alpha=\frac{2(K_bm-\Delta T_b)}{K_bm}$$

Equilibrium constant K for the dimer formation is

$$K=\frac{[A_2]}{[A]^2}=\frac{\frac{m\alpha}{2}}{m^2(1-\alpha)^2}=\frac{\alpha}{2m(1-\alpha)^2}\text{ from Eq. (i)}$$

$$K=2\left[\frac{K_bm-\Delta T_b}{K_bm}\right]\Big/2\text{m}\left[1-\frac{2(K_bm-\Delta T_b)}{K_bm}\right]^2$$

$$K=\frac{K_b(K_bm-\Delta T_b)}{(K_bm-2K_bm+2\Delta T_b)^2}$$

$$K=\frac{K_b(K_bm-\Delta T_b)}{(2\Delta T_b-K_bm)^2}\quad\text{Proved}$$

69. Let the amount of organic acid in

C_6H_6 layer = a g

Volume of C_6H_6 = 50 mL

$\therefore$ concentration of acid in $C_6H_6 = \frac{a}{50}$ g mL^{-1}

Since total amount of acid = 5 g

$\therefore$ amount of acid in H_2O layer = $(5-a)$ g

and volume of H_2O = 100 mL

$\therefore$ Concentration of acid in $H_2O = \left(\frac{5-a}{100}\right)\frac{\text{g}}{\text{mL}}$

$$\text{Now, } K=\frac{\text{Concentration of acid in } C_6H_6}{\text{Concentration of acid in } H_2O}$$

$$=\frac{a}{50}\times\frac{100}{(5-a)}$$

$$\therefore \quad 4.1=\frac{a}{50}\times\frac{100}{(5-a)}$$

or $a = 3.361$ g.

$\therefore$ Amount of acid in 50 mL

C_6H_6 = 3.361 g

$$\therefore \text{ acid concentration in } C_6H_6=\frac{3.361}{50}\times 1000$$

$$= 67.22 \text{ g/L}$$

Also, amount of acid in 100 mL $H_2O = 5-a = 5-3.361$

$= 1.639$ g.

$$\therefore \text{ acid concentration in } H_2O=\frac{1.639}{100}\times 1000$$

$$= 16.39 \text{ g/L}$$

70. (a) Heptane C_7H_{16} $\quad m_A = 100$

(b) Octane C_8H_{18} $\quad m_B = 114$

$$n_A=\frac{w_A}{m_A}=\frac{25}{100}=0.25\,;\ n_B=\frac{35}{114}=0.3$$

$$x_A=\frac{0.25}{0.25+0.30}=0.45\ x_B=\frac{0.3}{0.25+0.30}=0.55$$

$$=0.45$$

$$P=P_A^0x_A+P_B^0x_B$$

$$=105.2\times0.45+46.8\times0.55$$

$$=47.34+25.74=73.08\text{ kPa}$$

71. $\Delta T_f = i\times K_f\times m$

$7.10\times10^{-3} = i\times1.86\times0.001$

$i = 3.817$

$$\alpha=\frac{i-1}{n-1}$$

$$\alpha=\frac{3.817-1}{(x+1)-1}$$

$x = 2.817 \approx 3$

$\therefore$ molecular formula of the compound is $K_3[Fe(CN)_6]$.

72. Since

$$y_A=\frac{x_AP_A^{\circ}}{P_B^{\circ}+(P_A^{\circ}-P_B^{\circ})x_A}$$

Subtracting x_A from both the sides, we get

$$y_A-x_A=\frac{x_AP_A^{\circ}}{P_B^{\circ}+(P_A^{\circ}-P_B^{\circ})x_A}-x_A$$

Differentiating this with respect to x_A, we get

$$\frac{d(y_A-x_A)}{dx_A}=\frac{P_A^{\circ}}{P_A^{\circ}+(P_A^{\circ}-P_B^{\circ})x_A}-\frac{x_AP_A^{\circ}(P_A^{\circ}-P_B^{\circ})}{\{P_B^{\circ}+(P_A^{\circ}-P_B^{\circ})x_A\}^2}-1$$

The value of x_A at which $y_A - x_A$ has a maximum value can be obtained by setting the above differential equal to zero. Thus, we have

$$\frac{P_A^{\circ}}{P_A^{\circ}+(P_A^{\circ}-P_B^{\circ})x_A}-\frac{x_AP_A^{\circ}\left(P_A^{\circ}-P_B^{\circ}\right)}{\{P_B^{\circ}+(P_A^{\circ}-P_B^{\circ})x_A\}^2}-1$$

Solving for x_A, we get $x_A=\dfrac{\sqrt{P_A^{\circ}P_B^{\circ}}-P_B^{\circ}}{P_A^{\circ}-P_B^{\circ}}$

The value of P at this composition is

or $\quad P=x_AP_A^{\circ}+x_BP_B^{\circ}$

$$P=P_B^{\circ}+(P_A^{\circ}-P_B^{\circ})x_A$$

or $\quad P=P_B^{\circ}+(P_A^{\circ}-P_B^{\circ})\left(\dfrac{\sqrt{P_A^{\circ}P_B^{\circ}}-P_B^{\circ}}{P_A^{\circ}-P_B^{\circ}}\right)$

or $\quad P=\sqrt{P_A^{\circ}P_B^{\circ}}$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1.

$$\begin{array}{lccc} & Ca(NO_3)_2 \rightleftharpoons & Ca^{2+} + & 2NO_3^- \\ \text{Before dissociation} & 1 & 0 & 0 \\ \text{After dissociation} & 1-\alpha & \alpha & 2\alpha \end{array}$$

$\therefore$ total mole at equilibrium $= (1 + 2\alpha)$ $(\because \alpha = 0.7)$

$= (1 + 2 \times 0.7) = 2.4$

For $Ca(NO_3)_2$:

$$\frac{P^o - P_S}{P_S} = i\frac{n_B}{n_A}$$

$$\frac{760 - P_S}{P_S} = 2.4 \times \frac{7}{164} \times \frac{18}{100} = 0.01844$$

$$P_S = \frac{760}{1.01844} = 746.24 \text{ mm Hg}$$

2. Given $w_B = 0.643$ gram, $K_f = 5.12$ Kmol^{-1} kg

$\Delta T_f = 5.51 - 5.03 = 0.48$

w_A = Weight of benzene $= V \times d = 50 \times 0.879$ g

$$\therefore \quad 0.48 = \frac{1000 \times 5.12 \times 0.643}{m_B \times 50 \times 0.879}$$

$$= \Delta T_f = K_f \times \frac{w_B}{m_B} \times \frac{1000}{w_A}$$

$\therefore \quad m_B = 156.06$

3. $\Delta T_f = K_f \times m$

$$\therefore \quad m = \frac{\Delta T_f}{K_f} = \frac{P^o - P_S}{P_S} \times \frac{1000}{m_A}$$

$$\frac{0.30}{1.86} = \frac{23.51 - P_S}{P_S} \times \frac{1000}{18}$$

$$1002.9 P_S = 23510$$

$\therefore \quad P_S = 23.44$ mmHg

4. $\Delta T_f = i \times K_f \times M,\ i = (1 + \alpha)$

$\Delta T_f = K_f \times$ molality $\times (1 + \alpha)$

$$\begin{array}{lccc} \text{For acetic acid:} & CH_3COOH \rightleftharpoons & CH_3COO^- & + H^+ \\ & C & 0 & 0 \\ & (1-\alpha) & C\alpha & C\alpha \end{array}$$

Given, $\alpha = 0.23$;

$$\text{Also, molality} = \frac{\text{Mole of acetic acid}}{\text{Weight of water in kg}}$$

$$= \frac{3 \times 10^{-3} \times 10^3}{60 \times \dfrac{500 \times 0.997}{10^3}}$$

$C = 0.10$

$\Delta T_f = K_f \times$ molality $(1 + \alpha)$

$\Delta T_f = 1.86 \times 0.1 \times 1.23$

$= 0.229$

5. Since, $\Delta T_b = K_b \dfrac{w_B}{m_B} \times \dfrac{1000}{w_A}$

$$\therefore \quad m_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

For acetone solution:

$$m_B = \frac{1000 \times 1.7 \times 1000}{0.17 \times 100} = 122$$

For benzene solution:

$$m_B = \frac{1000 \times 2.6 \times 1.22 \times 1000}{0.13 \times 100} = 244$$

Molecular weight of C_6H_5COOH is 122 and thus it is evident that benzoic acid remains as normal molecular species in acetone but shows 100% dimerisation in C_6H_6, i.e., in C_6H_6 it exists as $(C_6H_5COOH)_2$.

6. (a) $\Delta T_b = K_b \dfrac{w_B}{m_B} \times \dfrac{1000}{w_A}$

$$\frac{w_B}{m_B} = n_B = \frac{\Delta T_b \times w_A}{K_b \times 1000}$$

$$= \frac{2 \times 100}{0.76 \times 1000} = \frac{5}{19}$$

[For very dilute solution $(n_A + n_B = n_A)$]

$$\frac{P^o - P_S}{P^o} = x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A} = \frac{w_B}{m_B} \times \frac{m_A}{w_A}$$

$$\frac{760 - P_S}{760} = \frac{5}{19} \times \frac{18}{100}$$

$$\frac{760 - P_S}{760} = \frac{9}{190}$$

$$760 - P_S = 36$$

$$P_S = 760 - 36 = 724 \text{ mmHg}$$

7. (a) Given Salts are completely ionise

Since, colligative properties $\propto i \times M$

and $i \times M$ for $C_2H_5OH = 1 \times 0.5 = 0.5$

For $Mg_3(PO_4)_2 = 5 \times 0.1 = 0.5$

For $KBr = 2 \times 0.25 = 0.5$

For $Na_3PO_4 = 4 \times 0.125 = 0.5$

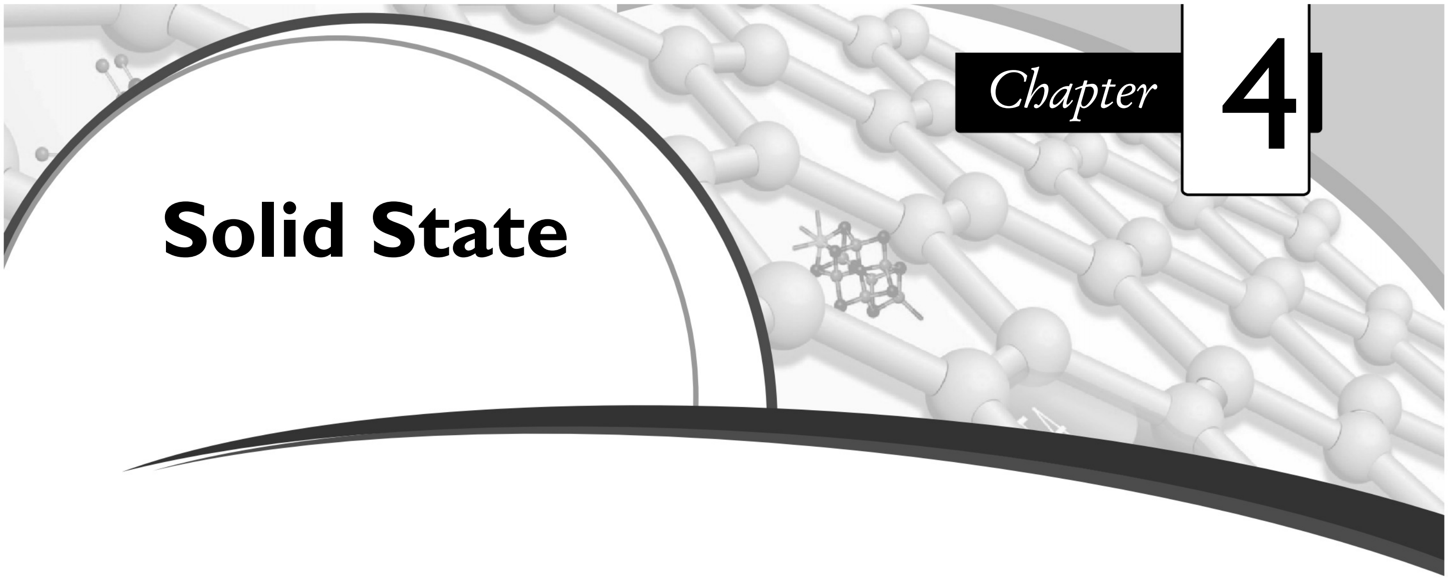
$\therefore$ all have same osmotic pressure because $(i \times M$ same) $\pi = [i \times M]RT$

8. (b) $\dfrac{P^o - P_s}{P_s} = \dfrac{w_B}{m_B} \times \dfrac{m_A}{w_A}$

$$\frac{185 - 183}{183} = \frac{1.2}{m_B} \times \frac{58}{100}$$

$$\frac{1}{183} = \frac{1.2 \times 58}{m_B \times 100}$$

$$m_B = 63.68$$



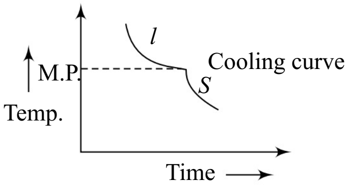
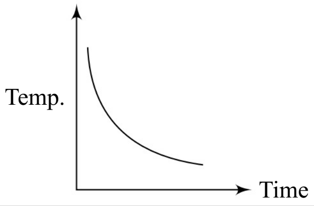
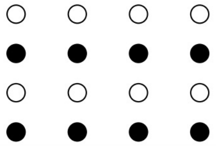
Chapter 4

Solid State

Key Concepts

Classification of Solids

1. Crystalline
2. Amorphous

	Crystalline		Amorphous
1.	In these solids, constituent particles are arranged in fixed pattern.	1.	Constituent particles are arranged randomly.
2.	Having sharp melting point  	2.	No sharp melting point. They melt over a range. 
3.	These are anisotropic in nature (different physical properties in the different direction). 	3.	These are isotropic in nature (having similar physical properties in different direction).
4.	These are called true solid. For example, NaCl, diamond, i.e., quartz.	4.	These are called pseudo-solids or super cooled liquids. For example, rubber, glass, plastic.

Classification of crystalline solids

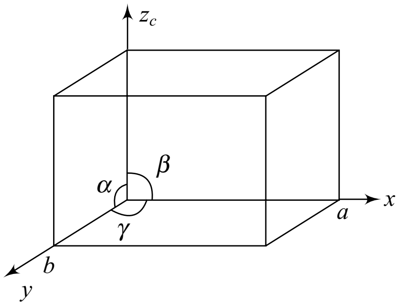
Based on the type of binding forces among the constituent particles they are classified into four types.

Type of Solid	Constituent particles	Binding forces	Examples
1. Molecular solid	Molecules	Van der waals force and hydrogen bonding	Solid Ar, dry ice
2. Ionic solid	Ions, i.e., cations and anions	Electrovalent bond or ionic bond	NaCl, ZnS
3. Covalent solid	Atoms or molecules	Covalent bond	Diamond, quartz, SiC
4. Metallic solids	Metal atoms and free valance electron	Metallic bond	Cu, Zn, Fe

UNIT CELL

It is the smallest repeating unit in the crystal lattice.

Geometry of the unit cell depends on the intercept made on the 3 crystallographic axis, i.e., a, b, c and angle between these, i.e., α, β, γ.



if, $a = b = c$ and $\alpha = \beta = \chi$
cubic unit cell

Crystal System

Seven crystal systems are possible.

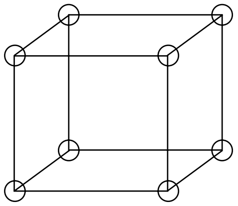
Crystal System	Bravais lattice	Unit cell Parameters	
		Inter-cepts	Crystal Angles
1. Cubic	P, F, B	$a = b = c$	$\alpha = \beta = \gamma = 90°$
2. Orthorhombic	P, F, B, E	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
3. Rhombohedral	P	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
4. Monoclinic	P, E	$a \neq b \neq c$	$\alpha = \gamma = 90\ \beta \neq 90°$
5. Triclinic	P	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
6. Tetragonal	P, B	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
7. Hexagonal	P	$a = b \neq c$	$\alpha = \beta = 90°\ \gamma = 120$

Types of Unit Cells

These are of four types.

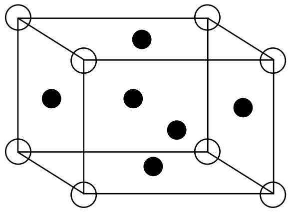
1. Simple or Primitive (P)

One atom is present on each corner of the cell.



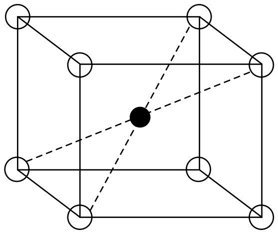
2. Face Centered (F)

Atom is present on each corner as well as on each face centre.



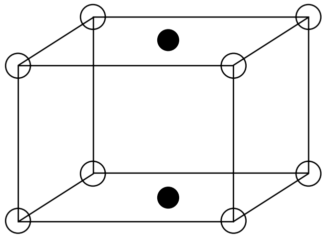
3. Body Centered (B)

Atom is present on each corner as well as at body centre.



4. End Centered or Base Centered (E)

Atom is present on each corner as well as at only one set of opposite face centre.



> ***Note:***
> 1. There are 14 Bravais Lattice.
> 2. In cubic system, there are only three types of unit cell, i.e., simple, face centred and body centered.

Calculation of Effective Number of Atoms (Z) in Unit Cell.

Position	No. of position in unit cell	Fraction or atom in unit cell
1. Body centered	1	1 {Fully enclosed}
2. Face centered	6	1/2
3. Edge center	12	1/4
4. Corner	8	1/8
5. Body diagonal	4	1

For example,

1. Simple Cubic

$$z = \frac{1}{8} \times 8 = 1$$

2. Face-centered cubic (FCC)

$$Z=\frac{1}{8}\times 8+\frac{1}{2}\times 6=4$$

3. Body-centered cubic (BCC)

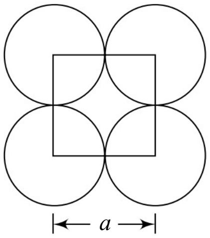
$$z=8\times\frac{1}{8}+1\times 1=2$$

Analysis of Cubic System

1. Atomic Radius (r)

It is half of the distance between the two nearest neighbour atom.

(a) Simple Cubic



$$2r=a$$

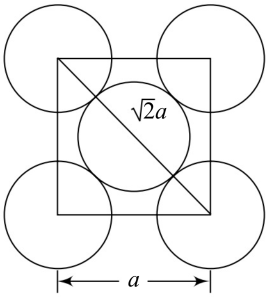
$$r=a/2$$

Atom touch each other along the edge length.

(b) Face Centered Cubic

$$a\sqrt{2}=4r$$

$$r=\frac{a}{2\sqrt{2}}$$

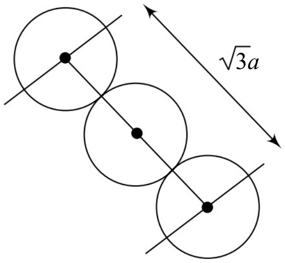


Atoms touch each other along the face diagonal.

(c) Body Centred Cubic

$$\sqrt{3}a=4r$$

$$r=\frac{\sqrt{3}a}{4}$$



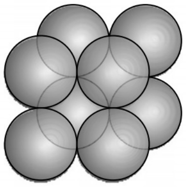
Atoms touch each other along the body diagonal.

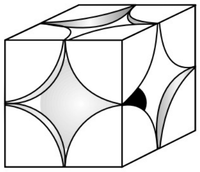
PACKING FRACTION (P.F.)

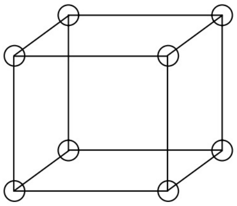
$$\text{P.F.}=\frac{\text{Volume occupied by the spheres}}{\text{Volume of the unit cell}}$$

$$\text{P.F.}=\frac{\pi\times\frac{4}{3}\pi r^3}{\text{Volume of unit cell}}$$

(a) Simple Cubic





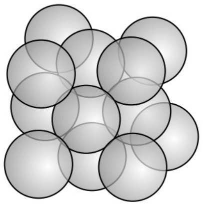


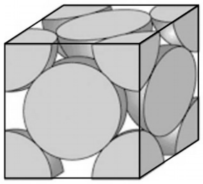
$$\text{P.F.}=\frac{\frac{4}{3}\pi r^3\times 1}{a^3}=\frac{4/3\pi r^3\times 1}{2\times 2\times 2\times r^3}$$

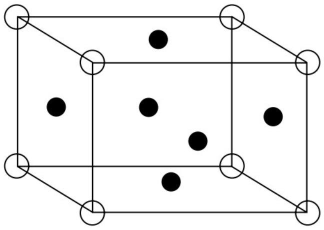
$$=\frac{\pi}{6}=0.52\%$$

52% packed; 48% voids.

(b) Face Centered Cubic



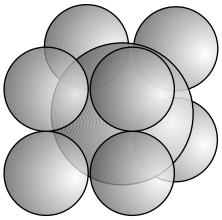


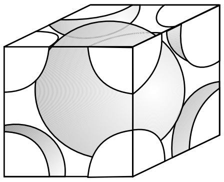


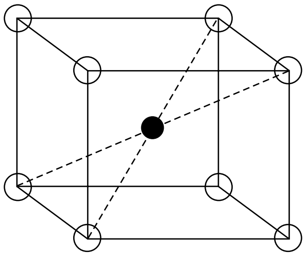
$$\text{P.F.}=\frac{\frac{4}{3}\pi r^3\times 4}{a^3}=\frac{4/3\pi r^3\times 4}{(2\sqrt{2}r)^3}=\frac{\pi}{3\sqrt{2}}=0.74$$

i.e., 74% packed; 26% voids.

(c) Body Centred Cubic







$$\text{P.F.} = \frac{\frac{4}{3}\pi r^3 \times 2}{a^3} = \frac{\frac{4}{3}\pi r^3 \times 2}{(4r/\sqrt{3})^3} = \frac{\sqrt{3}\pi}{8} = 68\%$$

60% packed; voids are 32%.

3. Density of the Unit Cell

$$d = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{\text{Total mass}}{\text{Total volume}}$$

$$= \frac{Z \times \text{Atomic mass or M mass}}{N_A \cdot a^3} \text{g/cm}^3$$

1 Å = 10^{-9} cm 1 nm = 10^{-7} cm

1 Pm = 10^{-10} cm

Coordination Number (CN)

It is the number of nearest neighbour atom for the given atom in the crystal lattice.

(a) Simple Cubic
CN = 6 (1 atom is surrounded by 6 atoms)

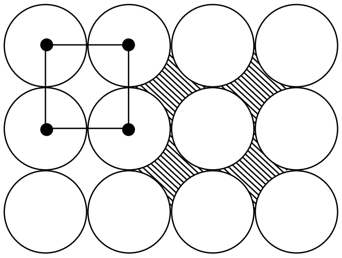
(b) fcc
CN = 12

(c) bcc
CN = 8

4. Packing in Two Dimension

First layer of the spheres can be formed in 2 ways: square lattice and hexagonal lattice.

(a) Square lattice

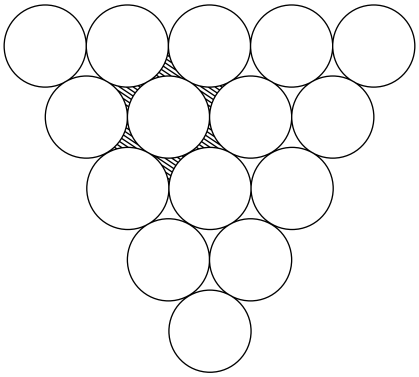


⇒ In this packing, each row of spheres is identical.

⇒ Each sphere is surrounded by four voids.

⇒ All the voids can be occupied by the second layer sphere.

(b) Hexagonal Lattice

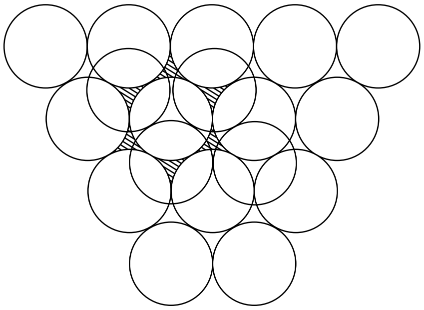


⇒ This is more closely packed compare to the square lattice.

⇒ Alternate rows of spheres are identical.

⇒ Each sphere is surrounded by 6 voids and out of these only three alternate voids can be occupied by the second layer sphere.

5. Closed Packing in 3-D



Based on the arrangement of third layer sphere packing in 3-D. This can be of two types:

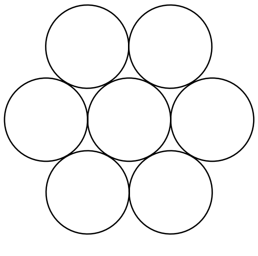
(a) Hexagonal closed packing (hcp)

(b) Cubic closed packing (ccp)

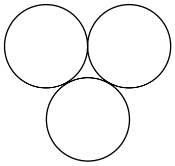
Hexagonal Closed Packing

1. Here third layer sphere is kept on the newly formed void in the second layer, so that first and third become identical. Hence it is also called ABAB......... type packing.

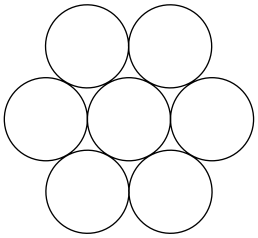
(A)



(B)

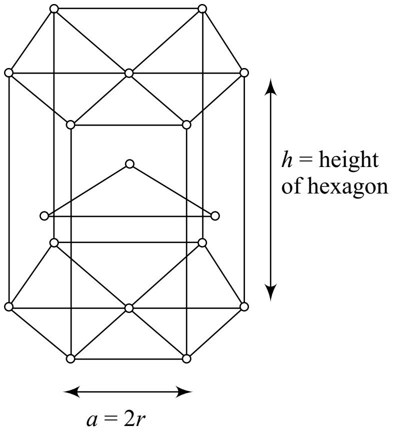


(A)



Coordination number of each sphere is 12.

Packing efficiency 74%



Effective number of atoms in unit cell (Z)

$$= \left[1\times\frac{1}{2}+6\times\frac{1}{6}\right]\times 2+3\times 1=6$$

$$\therefore \quad Z=6$$

Volume of hexagonal unit cell = $6\times\frac{\sqrt{3}}{4}a^2\times h$

Since $\frac{\frac{h}{2}}{a}=\frac{\sqrt{2}}{\sqrt{3}}$

$$\therefore \quad h=4r\frac{\sqrt{2}}{\sqrt{3}}$$

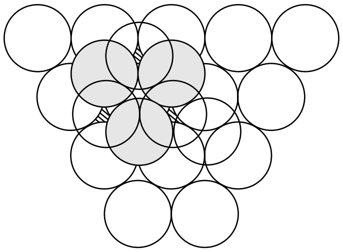
and $\quad V=6\times\frac{\sqrt{3}}{4}\times(2r)^2\times 4r\frac{\sqrt{2}}{\sqrt{3}}=24\sqrt{2}r^3$

$\therefore$ packing Fraction

$$=\frac{6\times 4/3\pi r^3}{24\sqrt{2}r^3}=\frac{\pi}{3\sqrt{2}}=0.74$$

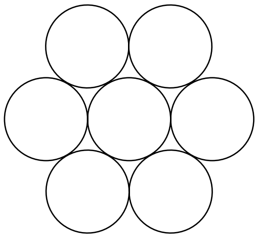
(b) Cubic Closed Packing (ccp) or Face Centered Cubic (fcc)

Second layer colour change.

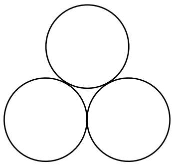


1. In this packing, third layer spheres are kept on the old voids. So that first and fourth layer become identical. Hence it is called as ABC ABC .... type packing.

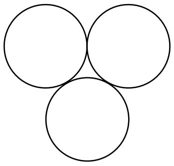
(a)



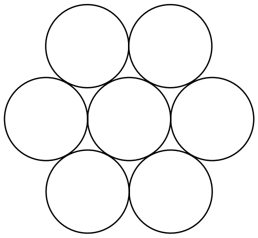
(b)



(c)



(a)

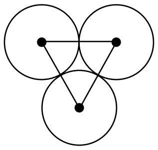


C.N. = 12

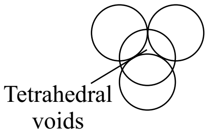
Packing Efficiency = 74%

VOIDS OR INTERSTITIAL HOLES

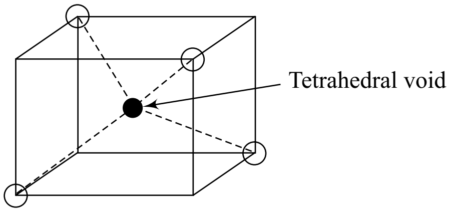
1. **Triangular Void**
   Triangular void is enclosed between the three spheres on joining their centres an equilateral triangle is formed.



2. **Tetrahedral Void**
   When a sphere kept on the triangular void is enclosed between the 4 spheres. So that on joining their centres a regular tetrahedron is formed.



$$\frac{r_{\text{Void}}}{R_{\text{Sphere}}} = 0.225$$



Tetrahedral Void

$$R + r = \frac{\sqrt{3}}{2}a \qquad \text{(i)}$$

$$2R = a\sqrt{2} \qquad \text{(ii)}$$

$$\therefore \quad \frac{r}{R} = 0.225$$

Number of tetrahedral voids = 2 × effective number of atoms

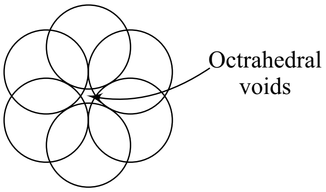
Position of tetrahedral void = 2 at each body diagonal

See Li$_2$O Crystal

→ O^{--} ion in face centred cubic

→ Li$^+$ ion in each tetrahedral void

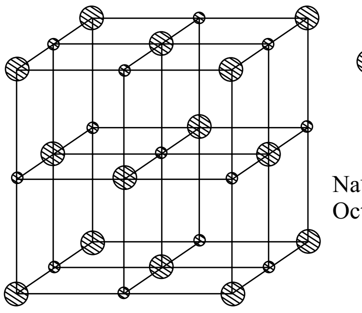
3. Octahedral Void



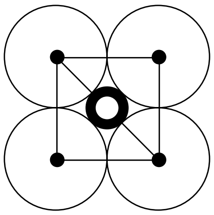
This void is formed by the overlapping of two triangular voids in different layers. So that void is enclosed between the 6 spheres on joining their centres regular octahedron is formed.

Number of octahedral voids = Effective number of atoms

In fcc unit cell, octahedral void are produced at edge centre and body centre.



$$\frac{r_{\text{void}}}{R_{\text{sphere}}} = 0.414$$



$$R + r = \frac{a\sqrt{2}}{2} \qquad (1)$$

$$2R = a \qquad (2)$$

From (1) and (2)

$$\frac{r}{R} = 0.414$$

⇒ **In hcp and fcc there exist only tetrahedral and octahedral voids.**

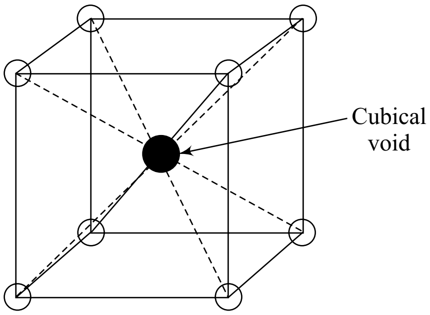
4. Cubical Void

This void is formed in the square closed packing at the body centre of a cube when atom is present on each corner.

$$\frac{r}{R} = 0.414$$

$$R + r = \frac{\sqrt{3}a}{2} \qquad (1)$$

$$2R = r \qquad (2)$$



$$(1)/(2) \quad \frac{r}{R} = 0.732$$

Order of size of void

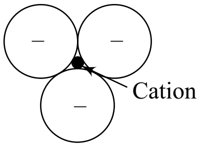
Cubical > Octahedral > Tetrahedral > Triangular

Radius Ratio in Ionic Compounds

$$\frac{r^+}{r^-} = \frac{\text{Radius of cation}}{\text{Radius of anion}}$$

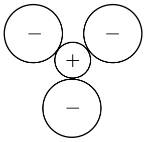
Radius ratio determines the coordination number and shape in ionic compound.

If $\frac{r^+}{r^-} \uparrow \Rightarrow CN \uparrow$

1. 

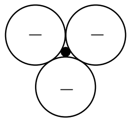
$r_{\text{cation}} = r_{\text{void}}$

Stable for coordination number = 3

2. 

$r_{\text{cation}} > r_{\text{void}}$

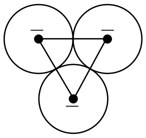
C.N.↑ here. So stable for higher C.N.

3. 

$r_{\text{cation}} < r_{\text{void}}$

This system does not exist because of anion-anion repulsion.
No close packing is possible.

Limiting radius ratio for close packing



$$\cos 30° = \frac{r^-}{r^+ + r^-}$$

$$\frac{r^+}{r^-} = 0.155$$

S.No.	Radius ratio	C.N.	Shape
1.	< 0.155	2	Linear
2.	[0.155 to 0.225)	3	Triagonal planner
3.	[0.225 to 0.414)	4	Tetrahedral
4.	[0.414 to 0.732)	6	Octahedral
5.	[0.732 to 1)	8	bcc

Packing in ionic Compound

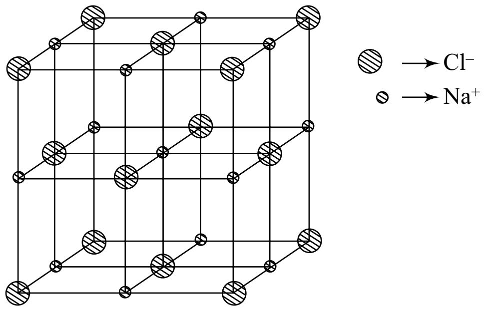
- AB type
- AB_2 types or A_2B type

AB type

Here C.N. of both cations and anion are equal. AB-type solids can be of three types.

1. NaCl type or Rock salt type
2. CsCl type
3. ZnS type or Zinc blend type

1. NaCl or Rock Salt Type



(a) Cl^- is present at each corner and on each face centre whereas Na^+ is present on edge center and body center or vice versa.

(b) Cl^- is present in fcc lattice while Na^+ occupy all the octahedral holes.

(c) C.N of both Na^+ and Cl^- is 6. So it is called 6: 6 coordination.

(d) Number of NaCl formulae unit/unit cell

$$Na^+ = 12 \times \frac{1}{4} + 1 \times 1 = 4$$

$$Cl^- = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$Z = 4$ means 4 NaCl per unit cell

(e) $2(r^+ + r^-) = a$ a = edge length

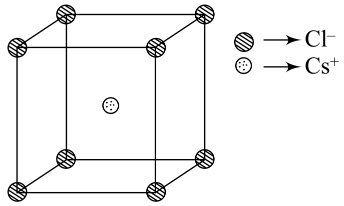
$4r^- = a\sqrt{2}$ only for ideal crystal, i.e., anion-anion contact.

(f) Packing fraction = $\frac{\text{Actual volume occupied}}{\text{Volume of unit cell}}$

$$\text{P.F.} = \frac{4 \times \frac{4}{3}\pi(r^+)^3 + 4 \times \frac{4}{3}\pi(r^-)^3}{(2\sqrt{2}r^-)^3}$$

$$= \frac{\pi}{3\sqrt{2}}\left[\left(\frac{r^+}{r^-}\right)^3 + 1\right]\left[\text{here } \frac{r^+}{r^-} = 0.414\right]$$

2. CsCl Type



(a) Cl^- is present on each corner while Cs^+ is present at the body center of the cube or vice versa.

(b) Cs^+ is present in the cubical void.

(c) (Number of both Cl^- and Cs^+ is 8 so it is also called 8 : 8 coordination.

(d) $Cl^- = 8 \times \frac{1}{8} = 1$ $Cs^+ = 1 \times 1 = 1$

CsCl unit/unit cell, i.e., $Z = 1$

(e) $2(r^+ + r^-) = \sqrt{3}a$

$2r^- = a$ only for ideal crystal.

(f) Packing fraction

$$\text{P.F.} = \frac{1 \times \frac{4}{3}\pi(r^+)^3 + 1 \times \frac{4}{3}\pi(r^-)^3}{(2r^-)^3}$$

$$= \frac{\pi}{6}\left[\left[\left(\frac{r^+}{r^-}\right)^3\right] + 1\right]$$

$$\frac{r^+}{r^-} = 0.732$$

3. ZnS type OR Zinc blends type

(a) S^{2-} are present in fcc lattice while Zn^{+2} occupy $\frac{1}{2}$ of the tetrahedral voids.

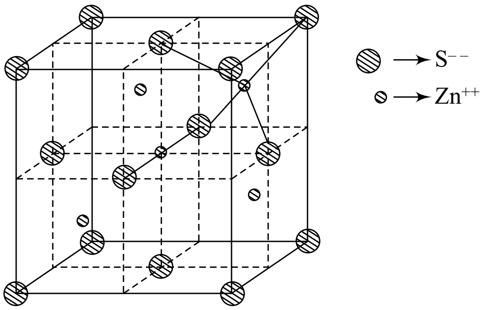
(b) CN of both Zn^{+2} and S^{--} ion is 4, so it is called 4: 4 coordination.

(c) Number of ZnS units per unit cell = 4

$$S^{-2} = 4(\text{fcc})$$

$$Zn^{+2} = 8 \times \frac{1}{2} = 4$$

(d) $(r^+ + r^-) = \dfrac{\sqrt{3}\cdot\frac{a}{2}}{2} = \dfrac{\sqrt{3}a}{4}$



$4r^- = a\sqrt{2}$ only for ideal crystal.

(e) Packing fraction

$$\text{P.F.} = \frac{4 \times \frac{4}{3}\pi(r^+)^3 + \frac{4}{3} \times 4 \times \pi(r^-)^3}{(2\sqrt{2}r^-)^3}$$

$$= \frac{\pi}{3\sqrt{2}}\left[\left(\frac{r^+}{r^-}\right)^3 + 1\right]$$

here $\left(\frac{r^+}{r^-} = 0.225\right)$

AB_2 Type or A_2B type

1. AB_2 type on CaF_2 type or fluorite structure.
2. Ca^{+2} is present in fcc lattice whereas F^- occupy all the tetrahedral holes.
3. CN of Ca^{+2} is 8 while that of F^- is 4. So, it is called 8: 4 coordination.
4. Number of CaF_2 units/unit cell (Z) = 4

$$(r^+ + r^-) = \frac{\sqrt{3}a}{4}$$

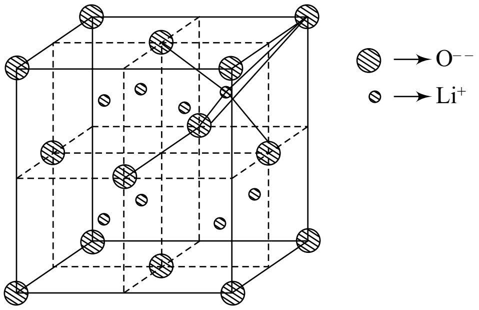
5. For ideal crystal $4r^+ = a\sqrt{2}$ Lattice will be cation.
6. Packing fraction

$$= \frac{4 \times \frac{4}{3}\pi(r^+)^3 + 8 \times \frac{4}{3}\pi(r^-)^3}{(2\sqrt{2}r^+)^3}$$

$$= \frac{\pi}{3\sqrt{2}}\left[1 + 2\left(\frac{r^-}{r^+}\right)^3\right]\left(\text{here } \frac{r^-}{r^+} = 0.225\right)$$

A_2B type or Ant fluoride Structure: for example, Li_2O

1. Anion forms the fcc lattice and cations occupy all the tetrahedral voids.
2. C.N. of cation is 4 whereas that of anion is 8. So it is called 4: 8 coordination.



3. No. of A_2B units per unit cell i.e. Z = 4 for ideal crystal

$$\frac{r^+}{r^-} = 0.225$$

Defect or Imperfection in Solids

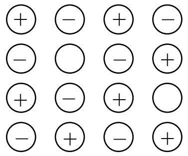
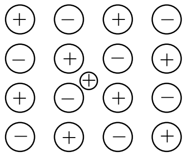
Electronic defect	Atomic defect or point defect
(due to excitation and	(it is due to dislocation of
removal of e^- from the atom)	atom from its regular site)

Atomics defect can be of three types:

1. Stoichiometeric defect
2. Non-stoichiometric defect
3. Impurity defect

Because of atomic defects there is no change in electrical neutrality.

1. Stiochiometric Defect: This can be of two types

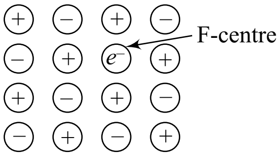
(A)	Shottky defect 	(b)	Frenkel defect 
(1)	Equal number of cations and anions are missing from their lattice sites.	(1)	Cation is missing from its regular lattice site by occupying the void in the crystal.
(2)	Density will decrease.	(2)	No change in density.
(3)	This defect is observed in the ionic solids having similar sizes of cation and anion, i.e., having high CN.	(3)	This defect is observed in ionic solids having dissimilar sizes of cation and anion, i.e. having the low coordination number.

2. Non-Stiochiometric Defect: This can be of two types:

(a) Excess of cation

It can happen in two ways:

⇒ When anion is missing from its lattice site and e^- in entrapped in place of it called F-centre (forbe means colour)

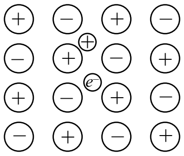


For example, NaCl LiCl KCl

NaCl	LiCl	KCl
↓	↓	↓
Yellow	Pink	Violet

Presence of F-centre ↑ the conductivity and impart the color to the crystal.

⇒ When extra cation and extra e^- are entrapped into the voids of the crystal.

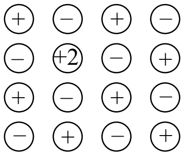


For example, ZnO (white colour)

but when use heat yellow colour

$$ZnO \longrightarrow Zn^{+2} + \frac{1}{2}O_2\uparrow + 2e^-$$

(b) Deficiency of cations



This defect is observed in the compounds of transition metal, because they can show the variable oxidation state.

Density will decrease.

For example, wustite $Fe_{0.94}O$

Cationic vacancy is 6%. Here some Fe^{+3} is there.

3. Impurity Defect

When any foreign or external atom occupies the lattice site in the crystal, it is called impurity defect.

Example 1 Formation of P type of N type semiconductors by adding the impurities in the pure semiconductor lattice. Bi and Ge.

Example 2 Impurity of $SrCl_2$ in NaCl.

P type impurity due to presence of IIIA (Al), element N type impurity due to presence of element of VA(As)

Properties of Solids

Electrical Properties of Solids

Solids are classified into following classes depending on the extent of conducting nature:

S. No.	Solids	Conductivity
1.	Metals	$10^8 \Omega^{-1}$ cm^{-1}
2.	Insulators	$10^{-12} \Omega^{-1}$ cm^{-1}
3.	Semiconductors	10^{-5} to $10^6 \Omega^{-1}$cm^{-1}

Metals oxides and sulphites have metallic to insulator behaviour at different temperatures.

Magnetic Properties of Solids

1. **Paramagnetic:** These substance are weakly attracted by magnetic field. These substances possess permanent magnetic dipoles due to the presence of unpaired electrons. For example, TiO_2, CuO, O_2, etc.
2. **Ferromagnetic:** These substances are strongly attracted by magnetic field. These substances possess more unpaired electrons than ordinary paramagnetic substances. For example, Fe, Co, Ni, etc.
3. **Anti-ferromagnetic:** This arises when net dipole alignment is zero due to equal and opposite alignment, MnO, MnO_2, Cr_2O_3, etc.
4. **Ferrimagnetic:** This arises when there is net dipole moment non-zero. For example, Fe_3O_4, ferrities.
5. **Diamagnetic:** The substances which are feebly repelled by the magnetic fields. These substances have all their electrons paired, For example, V_2O_5, NaCl, C_6H_6, etc.

Dielectric Properties of solids

1. **Piezoelecticity:** It is electricity which is produced by applying mechanical stress on solid crystal, e. g., $PbZrO_3$ (lead zirconate)
2. **Pyro-electricity:** It is electricity which is produced by heating solid crystal.
3. **Ferro-electricity:** Sometimes in a piezo-electric crystal, the dipoles are polarised even when no electricity flows through them. When electric field is applied to them, the direction of polarisation changes. This is called ferro-electricity.

   For example, Sodium potassium tartarate.
4. **Anti ferroelctricity:** When dipoles of a crystal align in such a way that they do not have any net dipole moment, the phenomenon is called antiferroelectricity. For example, $PbZrO_3$.

Bragg's Equation: The structure of crystal is determined by X–ray analysis.

$$n\lambda = 2d \sin\theta$$

where, d = diffraction order [1, 2, 3, …]

λ = wavelength of incident X–ray

θ = angle of diffraction

Solved Examples

1. A solid has a cubic structure in which *x* atoms are located at the corner of cube and *y* atoms are at cube center and *O* atoms are at edge centres. What is the formula of the compound?

Sol. $x = 8 \times \frac{1}{8} = 1$

$y = 1 \times 1 = 1$

$O = 12 \times \frac{1}{4} = 3$

XYO_3

2. Potassium crystallises in a bcc lattice. What is the number of unit cells in 3.9 g of K. Atomic weight of K = 39.

Sol. (Number of atoms) K = $\frac{3.9}{39} \times \text{NA} = \frac{\text{NA}}{10}$

in bcc = $Z = 2$

2 atom = 1 unit cell

Number of unit cell = $\frac{1}{2}$ Number of atoms

i.e.,

$\therefore$ Number of unit cells = $\frac{\text{NA}}{20}$

3. Calculate the number of atoms in a cubic-based unit cell having one atom on each corner and 2 atoms on or each body diagonal.

Sol. Number of corner = 8 Number of body diagonal = 4 in each cubic crystal

Number of atoms present at corner = $8 \times \frac{1}{8} = 1$

Number of atoms present body diagonal = $4 \times 2 = 8$

$\therefore \quad z = 9$

4. Silver crystallises in is fcc unit cell. Density of silver is 10.8 g/cm^3. Calculate the edge length of the unit cell in Picometers.

Sol. $d = \frac{z \times \text{Atomic Mass}}{N_A \times a^3}$

$$a^3 = \frac{4 \times 108}{6.023 \times 10^{23} \times 10.8}$$

$$= \frac{4}{6} \times 10^{-22}$$

$$a^3 = 0.66 \times 10^{-22}$$

$$= 6.6 \times 10^{-21}$$

$$= 10^{-7} (6.6)^{1/3} \text{ cm}$$

$$\approx 400 \text{ pm}$$

5. In a compound oxide ions have ccp arrangement, cations A are present in $\frac{1}{8}$ of the tetrahedral voids and cations B occupy $\frac{1}{2}$ of the octahedral voids. What is the formulae of the compound?

Sol. Oxides ions are forming the lattice reference

$\therefore$ Number of oxide ion = 4 (CCP)

$\therefore$ Tetrahedral void = $2 \times 4 = 8$

and Number of A atom = $\frac{1}{8} \times 8 = 1$

Number of octahedral void = 4

$\therefore$ Number of B atom = $\frac{1}{2} \times 4 = 1$

$\therefore$ molecular formula AB_2O_4

6. What is the simplest formula of a solid whose unit cell has the atom *A* at each corner, the atom *B* at each face centre and a *C* atom at the body centre?

(a) A_2BC (b) AB_2C (c) AB_3C (d) ABC_2

Sol. An atom at the corner of a cube is shared among 8 unit cells. As there are 8 corners in a cube, number of corner atom (A) per unit cell = $8 \times \frac{1}{8} = 1$.

Face-centred atom in a cube is shared by two unit cells. As there are 6 faces in a cube, number of face-centred atoms (B) per unit cell = $6 \times \frac{1}{2} = 3$.

An atom in the body of the cube is not shared by other cells.

$\therefore$ Number of atoms (C) at the body centre per unit cell = 1.

hence, the formula of the solid is AB_3C.

7. Analysis show that nickel oxide consist of nickel ion with 96% ions having d^8 configuration and 4% having d^7 configuration. Which amongst the following best represents the formula of the oxide.

(a) $Ni_{1.02}O_{1.00}$ (b) $Ni_{0.96}O_{1.00}$

(c) $Ni_{0.98}O_{0.98}$ (d) $Ni_{0.98}O_{1.00}$

Sol. **(d)** $d^8 \rightarrow Ni^{+2}$ $\quad d^7 \rightarrow Ni^{+3}$

Total charge of nickel

$(0.96 \times 2) + (0.04 \times 3) = 2.04$

Number of O^{-2} ion = $\frac{2.04}{2} = 1.02$

Formula of solid = $NiO_{1.02} = Ni_{0.98}O_{1.00}$

8. Ferric oxide crystallises in a hexagonal close packed array of oxide ions with two out of every three. Octahedral holes occupied by ferric ions. The formula of the ferric oxide is

(a) FeO (b) Fe_3O_4

(c) Fe_2O_3 (d) None of these

Sol. Suppose the number of oxide ions (O^{2-}) in the packing = *N*.

Number of octahedral voids = N

As 2/3rd of the octahedral voids are occupied by ferric ions, therefore, number of ferric ions present

$$= \frac{2}{3} \times N = \frac{2N}{3}$$

Therefore, ratio of Fe^{3+}: $O^{2-} = \frac{2N}{3} : N = 2 : 3$

Hence, the formula of ferric oxide is Fe_2O_3.

9. Iron crystallises in a body centred cubic structure. The radius of Fe atom (if edge length of unit cell is 286 pm) is.

(a) 120.9 pm (b) 123.8 pm
(c) 23.8 pm (d) 223.8 pm

Sol. Edge length, $a = 286$ pm

For BCC, radius of atom, $r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 286$

$$= \frac{1.732 \times 286}{4} = 123.8 \text{ pm}$$

10. The limiting radius ratio of the complex $[Ni(CN)_4]^{2-}$ is

(a) 0.225 – 0.414 (b) 0.414 – 0.732
(c) 0.155 – 0.225 (d) None

Sol. **(b)** The complex $[Ni(CN)_4]^{-2}$ is square planar Since Since CN^- strong field ligand ∴ hybridisation dsp^2. So, it has limiting radius ratio as octahedral structure, i.e., 0.414 – 0.732.

11. In closest packing of A type of atoms (radius, r_A), the radius of atom B that can be fitted into octahedral void is

(a) $0.155\, r_A$ (b) $0.125\, r_A$
(c) $0.414\, r_A$ (d) $0.732\, r_A$

Sol. **(c)** For octahedral void

$$\frac{r_B}{r_A} = 0.414$$

or $r_B = 0.414\, r_A$.

12. Copper crystallises into a *fcc* lattice with edge length 3.61×10^{-8} cm. The calculated density is

(a) 8.97 g/cc (b) 10.9 g/cc
(c) 5.45 g/cc (d) 6.02 g/cc

Sol. $d = \frac{Z \times \text{atomic mass}}{a^3 \times N_A}$

For fcc lattice of copper, $Z = 4$

Atomic mass of copper, = 63.5 g mol^{-1}

$$d = \frac{4 \times 63.5 \text{ g mol}^{-1}}{(3.61 \times 10^{-8} \text{cm})^3 \times (6.022 \times 10^{23} \text{mol}^{-1})}$$

$$= 8.97 \text{ g cm}^{-3}$$

13. The number of unit cells in 58.5 g of NaCl is approximately

(a) 6×10^{20} (b) 1.5×10^{23}
(c) 6×10^{23} (d) 0.5×10^{24}

Sol. **(b)** Molar mass of NaCl = 23 + 35.5 = 58.5 g

∴ moles of Na^+ = moles of Cl^- = Moles of NaCl = $\frac{58.5}{58.5} = 1$

In a unit cell of NaCl ⇒

Number of Na^+ ion = 4

Number of Cl^- ion = 4

∴ Total Number unit cell = $\frac{1}{4}$ × Number of NaCl

Total number of unit cell $\frac{1}{4} \times N_A = \frac{6.02 \times 10^{23}}{4} = 1.5 \times 10^{23}$

14. In fluorite structure (CaF_2)

(a) Ca^{++} ions are ccp and F^- ions are present in all the tetrahedral voids.
(b) Ca^{++} ions are ccp and ions are present in all the octahedral voids.
(c) Ca^{++} ions are ccp and ions are present in all the octahedral voids and half of ions are.
(d) F^- ions are in *fcc* and Ca^{++} are present in all the tetrahedral voids.

Sol. **(a)** Ca^{2+} ions are ccp and F^- ions are present in the tetrahedral voids. So, the number of Ca^{2+} ions is 4 and number of F^- ions is 8.So, the formula of the calcium fluoride Ca_4F_8 or, the simplest formula of calcium fluoride is CaF_2.

Exercise

LEVEL I

1. A cubic solid is made up of two elements A and B. Atoms B are at the corners of the cube and A at the body centre. What is the formula of compound?

(a) AB (b) AB_2 (c) A_2B (d) None

2. A compound alloy of gold and copper crystallises in a cubic lattice in which gold occupy that lattice point at corners of the cube and copper atom occupy the centres of each of the cube faces. What is the formula of this compound?

(a) $AuCu_6$ (b) AuCu
(c) $AuCu_3$ (d) None of these

3. KF crystallises in the NaCl type structure. If the radius of K^+ ions 132 pm and that of F^- ion is 135 pm, what is the closet K–K distance?

(a) Cannot say (b) 534 pm
(c) 755 pm (d) 378 pm

4. AgCl has the same structure as that of NaOH. The edge length of unit cell of AgCl is found to be 555 pm and

the density of AgCl is 5.561 g cm^{-3}. Find the percentage of sites that are unoccupied.
(a) 0.24% (b) 2.4% (c) 24% (d) None

5. The effective radius of the iron atom is 1.42 Å. It has fcc structure. Calculate its density (Fe = 56 amu).
(a) 2.87 g/cm^3 (b) 11.48 g/cm^3
(c) 1.435 g/cm^3 (d) 5.74 g/cm^3

6. The density of CaF_2 (fluorite structure) is 3.18 g/cm^3. The length of the side of the unit cell is
(a) 253 pm (b) 344 pm (c) 546 pm (d) 273 pm

7. If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is
(a) CA (b) CA_2 (c) C_2A_3 (d) C_3A_2

8. A solid is formed and it has three types of atoms X, Y, Z. X forms a FCC lattice with Y atoms occupying all the tetrahedral voids and Z atoms occupying half the octrahedral voids. The formula of the solid is
(a) X_2Y_4Z (b) XY_2Z_4 (c) X_4Y_2Z (d) X_4YZ_2

9. A compound XY crystallises in BCC lattice with unit cell edge length of 480 pm. If the radius of Y^- is 225 pm, then the radius of X^+ is:
(a) 127.5 pm (b) 190.68 pm
(c) 225 pm (d) 255 pm

10. An ionic compound AB has ZnS type structure. If the radius A^+ is 22.5 pm, then the ideal radius of B^- would be
(a) 54.35 pm (b) 100 pm.
(c) 145.16 pm (d) None of these

11. NH_4Cl crystallises in a body centred cubic type lattice with a unit cell edge length of 387 pm. The distance between the oppositely charged ions in the lattice is
(a) 335.1 pm (b) 83.77 pm
(c) 274.46 pm (d) 137.23 pm

12. A cubic solid is made by atoms A forming close pack arrangement, B occupying one/fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound?
(a) $A_4B_4C_2$ (b) $A_4B_2C_4$
(c) A_4BC (d) $A_4B_2C_2$

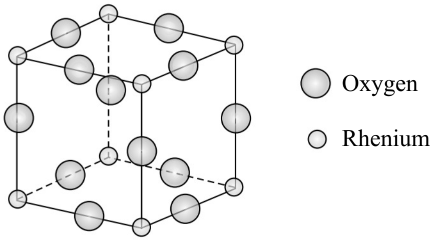
13. An element crystallises into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its body diagonals. If the volume of this unit cell is 24×10^{-24} cm^3 and density of element is 7.2 g cm^{-3}, calculate the number of atoms present in 200 g of element.
(a) 1.1513×10^{24} (b) 3.472×10^{24}
(c) 10.416×10^{24} (d) None of these

14. Xenon crystallises in the face centred cubic lattice and the edge of the unit cell is 620 pm. What is the next nearest neighbour distance?
(a) 738.5 pm (b) 620 pm
(c) 438.5 pm (d) 310 pm

15. An element crystallises in a structure having fcc unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains 5×10^{24} atoms.
(a) 5 m/cm^3 (b) 30 g/cm^3
(c) 10 g/cm^3 (d) 20 g/cm^3

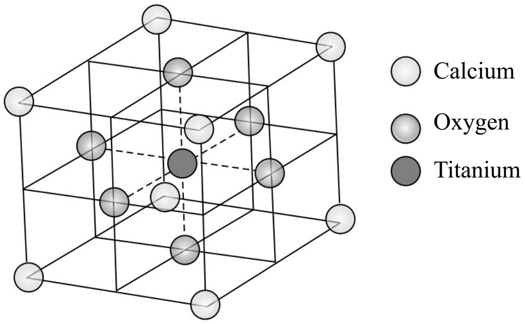
16. If the length of the body diagonal for CsCl which crystallises into a cubic structure with Cl^- ions at the corners and Cs^+ ions at the centre of the unit cells is 7 Å and the radius of the Cs^+ ion is 1.69 Å. What is the radii for Cl^- ion?
(a) 1.81 Å (b) 5.31 Å (c) 3.62 Å (d) None

17. Which of the following formulas is consistent with the unit cell of the rhenium oxide compound shown below?



(a) Re_2O_6 (b) Re_2O_3 (c) ReO_6 (d) ReO

18. The figure below shows a unit cell of the mineral Perovskite (the titanium atom is at the centre of the cube). Which of the following is a correct chemical formula for this mineral?



(a) Ca_8TiO_6 (b) CaTiO
(c) Ca_2TiO_3 (d) $CaTiO_3$

19. An atomic solid has hexagonal arrangement of unit cell with height of hexagonal (in close packed arrangement) as "*h*". The radius of atom in terms of height is
(a) $4\sqrt{\frac{2}{3}}h$ (b) $\frac{h}{4}\sqrt{\frac{2}{3}}$ (c) $\frac{h}{4}\sqrt{\frac{3}{2}}$ (d) $\frac{h}{4}\sqrt{\frac{3}{2}}$

20. What is the formula of a compound of niobium and nitrogen that crystallises in a hexagonal closest packed array of nitrogen atoms with niobium atoms in half of the tetrahedral holes?
(a) Nb_4N (b) Nb_2N (c) NbN (d) NbN_2

21. Select the incorrect statement for CsCl crystal.
(a) Coordination number for Cs^+ and Cl^- is 6

(b) $\frac{r_{Cs^+}}{r_{Cl^-}} = 0.732$

(c) The structure changes to NaCl at 760 K

(d) Cl^- ions are present at cubic sites

22. The radius of an atom of an element is 80 pm. If it crystallises as a body centred cubic lattice, what is the edge of its unit cell?

(a) 140 pm (b) 184.7 pm
(c) 209.2 pm (d) 147.5 pm

23. A solid XY has NaCl structure. If radius of X^+ is 100 pm. What is the radius of Y^- ion?

(a) 120 pm (b) 136.6 to 241.6 pm
(c) 136.6 pm (d) 241.6 pm

24. A solid is made of two elements P and Q. Atoms P are in CCP arrangement and atoms Q occupy all the octahedral voids and half of the tetrahedral voids, then the simplest formula of the compound is

(a) PQ_2 (b) P_2Q (c) PQ (d) P_2Q_2

25. Fraction of total volume occupied by atoms in a simple cubic cell is

(a) $\frac{\pi}{2}$ (b) $\frac{\sqrt{3}\pi}{8}$ (c) $\frac{\sqrt{2}\pi}{6}$ (d) $\frac{\pi}{6}$

26. The number of atoms in 100 g of an fcc crystal with density $d = 10$ g/cm^3 and cell edges as 200 pm is equal to

(a) 3×10^{25} (b) 5×10^{24}
(c) 1×10^{25} (d) 5.96×10^{-3}

27. The correct statement regarding defects in solids is

(a) Frenkal defect is favoured by a very small difference in the size of cation and anion.
(b) Frenkal defect is not a dislocation defect.
(c) trapping of e^- in lattice leads to the formation of F–centre.
(d) Schottky defects have no effect on the physical properties of solid.

28. 'C' represent the height of the hcp unit cell and 'a' represent edge length of the hexagonal surface of the hcp unit cell. What is the value of C/a?

(a) $\sqrt{\frac{2}{3}}$ (b) $\sqrt{\frac{8}{3}}$ (c) $\sqrt{\frac{32}{3}}$ (d) $\sqrt{\frac{3}{2}}$

29. Antifluorite structure is derived from fluorite structure by

(a) heating fluorite crystal lattice.
(b) subjecting fluorite structure to high pressure.
(c) interchanging the positions of positive and negative ions in the lattice.
(d) introducing the impurities to the lattice.

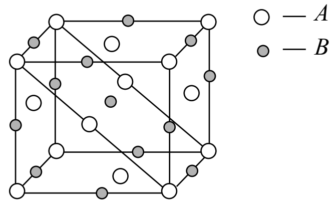
30. The anions (A) form hexagonal closest packing and the cations (C) occupy only 2/3 of octahedral holes. The simplest formula of the ionic compound is

(a) CA (b) C_3A_2 (c) C_4A_3 (d) C_2A_3

31. At what angles for the first order diffraction, spacing between two planes respectively are λ and $\frac{\lambda}{2}$?

(a) 0°, 90° (b) 90°, 0° (c) 30°, 90° (d) 90°, 30°

32. A crystal is made of particles A and B. A forms fcc packing and B occupies all the octahedral voids. If all the particles along the plane as shown in figure are removed, then, the formula of the crystal would be



(a) AB (b) A_5B_7 (c) A_7B_5 (d) A_2B_3

33. The number of atoms on HCP unit cell is

(a) 4 (b) 6 (c) 12 (d) 17

34. The volume of HCP unit cell is

(a) $24\sqrt{2}r^3$ (b) $16\sqrt{2}r^3$
(c) $12\sqrt{2}r^3$ (d) $\frac{64r^3}{3\sqrt{3}}$

35. In a ccp lattice of X and Y, X atoms are present at the corners while Y atoms are at face centres. Then the formula of the compound would be if one of the X atoms from a corner is replaced by Z atoms (also monovalent)?

(a) $X_7Y_{24}Z_2$ (b) $X_7Y_{24}Z$
(c) $X_{24}Y_7Z$ (d) $XY_{24}Z$

36. The density of solid argon (Ar = 40 g/mol) is 1.68 g/mL at 40 K. If the argon atom is assumed to be a sphere of radius = 1.50×10^{-8} cm, what % of solid Ar is apparently empty space?

(a) 35.64 (b) 64.36
(c) 74% (d) None of these

37. A body centered cubic lattice is made up of hollow spheres of B. Spheres of solid A are present in hollow spheres of B. Radius A is half of radius of B. What is the ratio of total volume of spheres of B unoccupied by A in a unit cell and volume of unit cell?

(a) $\frac{7\sqrt{3}\pi}{64}$ (b) $\frac{7\sqrt{3}\pi}{128}$
(c) $\frac{7\pi}{24}$ (d) $\frac{7\pi}{64\sqrt{3}}$

38. A compound formed by elements A and B crystallises in a cubic structure where A atoms are at the corners of a cube and B atoms are at the face centre. The formula of the compound is

(a) AB_3 (b) AB_2
(c) AB_4 (d) None of these

39. A binary solid has rocksalt structure. The edge length is 400 pm and the radius of cation is 75 pm, the radius of anion is

(a) 100 pm (b) 125 pm
(c) 250 pm (d) 325 pm

40. Total volume of all atoms present in face centred cubic unit cell of metal is (r = edge length)

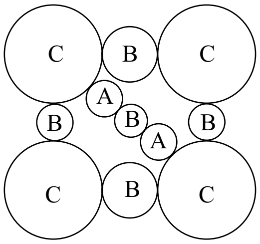
(a) $\frac{\pi r^3}{3\sqrt{2}}$ (b) $\frac{24}{3}\pi r^3$ (c) $\frac{12}{3}\pi r^3$ (d) $\frac{16}{3}\pi r^3$

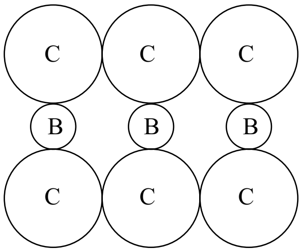
LEVEL II

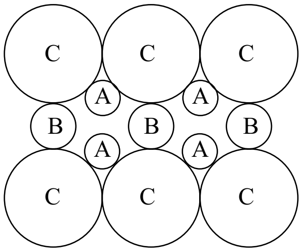
1. Niobium crystallises in a body centred cubic structure. If density is 8.55 g cm^{-3}. The atomic radius of niobium, (given that its atomic mass is 93 u) is

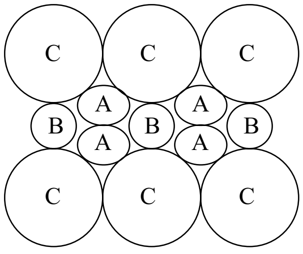
(a) 49.8 pm (b) 150.1 pm
(c) 143.1 Å (d) 143.1 pm

2. In a hypothetical solid C atoms are found to form cubical close packed lattice. A atoms occupy all tetrahedral voids and B atoms occupy all octahedral voids. A and B atoms are of appropriate size, so that there is no distortion in ccp lattice of C atoms. Now if a plane as shown in the following figure is cut. Then the cross section of this plane will look like.

(a)


(b)


(c)


(d)


3. In a cubic packed structure of mixed oxides, the lattice is made up of oxide ions, one fifth of tetrahedral voids are occupied by divalent (X^{++}) ions, while one-half of the octahedral voids are occupied by trivalent ions (Y^{3+}), then the formula of the oxide is

(a) XY_2O_4 (b) X_2YO_4 (c) $X_4Y_5O_{10}$ (d) $X_5Y_4O_{10}$

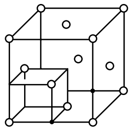
4. Xenon crystallises in face centre cubic lattice and the edge of the unit cell is 620 pm, then the radius of xenon-atom is

(a) 438.5 pm (b) 219.20 pm
(c) 536.94 pm (d) 265.5 pm

5. Calculate the ionic radius of a Cs$^+$ion assuming the cell edge length for CsCl is 0.4123 nm and that the ionic radius of a Cl$^-$ ion is 0.181 nm.

(a) 0.176 nm (b) 0.231 nm
(c) 0.358 nm (d) 0.116 nm

6. An alloy of two metals Q and R has a cubic structure. The unit cell maybe described as cubic close packed with respect to metal atoms Q. The R atoms are in the body centres of alternate minicubes made by partitioning the main cube into 8 equal parts as shown in the diagram.



On the basis of above description, identify the incorrect conclusion.

(a) The number of nearest neighbours of R is 4.
(b) The radius of R atom is less than that of Q atoms.
(c) The angle made by the line connecting any R atom with two of its nearest neighbours (Q atoms) is 109°28′.
(d) The number of nearest neighbours of Q is 8.

7. X^+Y^- crystallises in a bcc lattice in which the radius of $X^+ = 0.4A$. If all the X^+ ions are removed and another cation z^+ is inserted, what should be the maximum radius of the cation z^+ to crystallise in a fcc lattice with y^-?

(a) 0.548 Å (b) 0.010 Å
(c) 0.400 Å (d) 0.226 Å

8. When heated at 916°C , iron changes its bcc crystalline form to fcc. The ratio of density of the crystal before heating and after heating is

(a) 1.069 (b) 0.918 (c) 0.725 (d) 1.23

9. A metal M crystallised in both fcc lattice and in bcc lattice. If the densities of these forms are in 2:1 ratio the corresponding cubic edges are in the ratio

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

10. A metal of atomic mass = 75 forms a cubic lattice of edge length 5 Å and density 2 g cm^{-3}. Calculate the radius of the atom (given Avogadro's number, $N_A = 6 \times 10^{23}$.)

(a) 261.5 pm (b) 523 pm
(c) 145 pm (d) 130.5 pm

11. Ionic compound AB has NaCl type of structure. The radius of A^+ ion is 41.4 pm. If the radius of A^+ ion decreases and becomes equal to 30 pm, then in what type of structure would AB crystallise and what would be coordination number of A^+ ion?

(a) ZnS-4 (b) CsCl-8
(c) MgO-6 (d) BeO-8

12. A metal crystallises into a lattice containing a sequence of layers of *ABC ABC*. If the radius of metal atoms is 174 pm, then the distance between the two successive layers (i.e., *A* and *B*) is
(a) 348 pm (b) 174 pm
(c) 284. 2 pm (d) 492. 2 pm

13. A metallic element exists in simple cubic structure. Each edge of the unit cell is 3 Å. The density of metal is 10 g cm^{-3}. How many unit cells will be there in 16.2 g of the metal?
(a) 6×10^{22} (b) 16×10^{31}
(c) 2.8×10^{23} (d) 4.2×10^{21}

14. The percentage vacant space in one layer of square packing of spheres touching each other having 4 spheres is
(a) $\frac{3}{8}\pi \times 100$ (b) $\left(100 - \frac{\pi}{6}\right)100$
(c) $\frac{3}{8}\pi$ (d) $100 - \frac{\pi}{6} \times 100$

15. In a face centered cubic cell, the atom at the face centre is supposed to touch adjacent corner atoms. In this cubic close packing of identical atoms, some vacant space is left in the crystal. The layers are arranged parallel to the body diagonal. Copper metal crystallises in fcc with an edge length of 3.61 Å. Calculate the size of largest atom which could fit into the interstices of copper lattice without distorting it is nearly
(a) 0.212 Å (b) 0.421 Å
(c) 0.525 Å (d) 0.640 Å

16. The height of a hcp unit cell is 5.715 Å. What is the volume of the unit cell in $(Å)^3$?
(a) 91 (b) 182 (c) 273 (d) 82.5

17. A crystal is made up of particles *X*, *Y* and *Z*. *X* forms fcc packing, *Y* occupies all octahedral voids of *X* and *Z* occupies all tetrahedral voids of *X*. If all the particles along one body diagonal are removed, then the formula of crystal would be
(a) XYZ_2 (b) X_2YZ_2 (c) $X_8Y_4Z_5$ (d) $X_5Y_4Z_8$

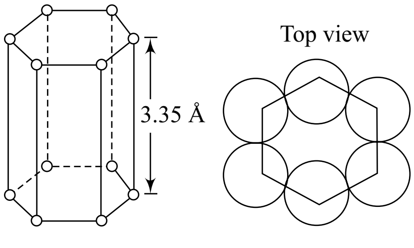
18. KCl crystallises in the same type of latice as does NaCl. Given that $\frac{r_{Na^+}}{r_{Cl^-}} = 0.55$ and $\frac{r_{K^+}}{r_{Cl^-}} = 0.74$. Calculate the ratio of the side of the unit cell for KCl to that of NaCl.
(a) 1.123 (b) 0.891 (c) 1.414 (d) 0.414

19. In cubic ZnS, the radii of the Zn and S atoms are 0.83 Å and 1.74 Å respectively. What is the edge length of the unit cell of ZnS?
(a) 2.57 Å (b) 3.64 Å (c) 2.97 Å (d) 5.935 Å

20. An elemental crystal has a density of 8570 kg/m^3. The packing efficiency is 0.68. The closest distance of approach between neighbouring atom is 2.86 Å. What is the mass of one atom approximately?
(a) 29 amu (b) 39 amu (c) 63 amu (d) 93 amu

21. X-ray analysis Mn–Si alloy with 75% by atoms of Mn and 25% by atoms of Si, showed that the unit cell is cubic and lattice parameter is 2.86 Å. The density of alloy = 6850 kg/m^3. How many number of atoms are present in the unit cell?
Mn: 55 and Si: 28
(a) 2 (b) 4 (c) 6 (d) 8

22. Regarding graphite the following information is available:



The density of graphite = 2.25 g/cm^3. What is C–C bond distance in graphite?
(a) 1.68 Å (b) 1.545 Å
(c) 2.852 Å (d) 1.426 Å

23. A CCP of *n* spheres of radius *r*, *n* spheres of radius 0.414*r* and 2*n* spheres of radius 0.225*r* are introduced in the octahedral and tetrahedral void respectively. Therefore packing fraction of the lattice.
(a) 0.74 (b) 0.81 (c) 0.68 (d) 0.79

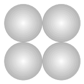
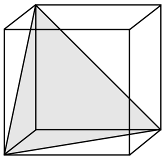
24. What is the diameter of the largest sphere that will fit in the void at the centre of the cube edge of a bcc crystal of edge length *a*?
(a) 0.134*a* (b) 0.76*a*
(c) 0.05548*a* (d) 0.098*a*

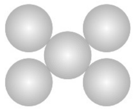
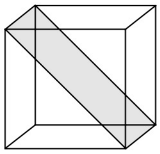
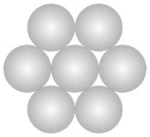
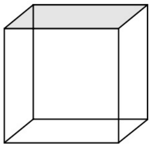
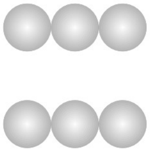
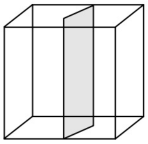
LEVEL III

1. Match the columns:

Column I (Crystal System)		**Column II (Possible unit cells)**	
(A)	Cubic	(P)	Simple or primitive
(B)	Tetragonal	(Q)	Body Centred
(C)	Orthorhombic	(R)	Face Centred
(D)	Monoclinic	(S)	End Centred

2. Match the columns:

Column I (Arrangement of the atoms/ions)			**Column II (Planes in fcc lattice)**
(A)		(P)	

(B)		(Q)	
(C)		(R)	
(D)		(S)	

3. Match the columns:

Column I		Column II	
(A)	ZnS crystal	(P)	fcc
(B)	CaF_2 crystal	(Q)	hcp
(C)	NaCl crystal	(R)	Distance between closest particles is $\frac{\sqrt{3}}{4}a$
(D)	Diamond crystal	(S)	Only one type of voids are occupied

4. Match the columns:

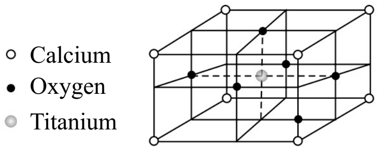
Column I		Column II	
(A)	Schottky defect	(P)	In NaCl defect produced by heating NaCl in $SrCl_2$
(B)	Frenkel defect	(Q)	Defect produced by heating NaCl.
(C)	F-centres	(R)	NaCl
(D)	Metal deficiency	(S)	AgCl

5. Match the columns:

Column I		Column II	
(A)	Cubic close packing	(P)	Empty space = 48%
(B)	Body centred cubic	(Q)	Empty space = 26%
(C)	Hexagonal close packing	(R)	Coordination number = 12
(D)	Simple cubic	(S)	Coordination number = 8

Passage 1 (Q. No. 6 to Q. No. 8)

Perovskite, a mineral containing calcium, oxygen and titanium crystallises in the given unit cell.



6. Total number of atom present in a unit cell is
(a) 3 (b) 4 (c) 5 (d) 6

7. The oxidation number of titanium in the perovskite is
(a) 5 (b) 4 (c) 3 (d) 2

8. If oxygen atom is removed from alternate position then the formula of perovskite is
(a) CaTiO (b) $CaTi_2O$
(c) $CaTiO_2$ (d) Ca_3Ti_2O

Passage 2 (Q. No. 9)

There are solids which are difficult to prepare in the stoichiometric composition, e.g., pure FeO is difficult to obtain and normally we get a composition of $Fe_{0.95}O$ but it may range from $Fe_{0.93}O$ to $Fe_{0.96}O$. Zinc oxide loses oxygen reversibly at high temperatures and turns yellow in colour. The excess metal is accommodated interstitially, giving rise to electrons trapped in the neighbourhood. One of the common methods of introducing defects in ionic solids is by adding impurity ions having different charge than host ions.

9. $Fe_{0.95}O$ can be due to presence of iron in +2 and +3 oxidation numbers. Then iron present in +3 oxidation state will be
(a) 15% (b) 13.5% (c) 10.5% (d) 8.85%

Assertion/Reason

(a) Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
(b) Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion.
(c) Assertion is correct but Reason is incorrect.
(d) Both Assertion and Reason are incorrect.

10. **Assertion:** As $\frac{r_+}{r_-}$ increase coordination number is also increases because

Reason: When $\frac{r_+}{r_-} = 1$ the C No. tend to 12.

11. **Assertion:** The square close packing is not possible in closest packing but hexagonal close packing is possible in the closest packing.
Reason: In the closest packing three spheres of same radius are mutually touching each other.

12. **Assertion:** There is a large difference between the melting points of NaF and MgO.
Reason: Cations and anions are both the salts are isoelectronic.

13. **Assertion:** In NaCl structure, Na^+ ions occupy octahedral holes and Cl^- ions occupy ccp.
Reason: The distance of the nearest neighbours in NaCl structure is a/2 where a is the edge length of the cube.

Multiple Answer Type Questions

14. The ionic radii of Cs^+ and Cl^- are 0.165 nm and 0.181 nm respectively. Their atomic weights are 133 and 35.5. Then,
(a) The lattice parameter is 0.4 nm
(b) Inter ionic distance is 0.4nm.
(c) The density of Cs Cl is 4.37×10^3 kg/m^3.
(d) The Cs Cl structure has a bcc structure

15. The data given below is used to find the type of cubic lattice to which the crystal belong.

	Ag	Al	Cu	Na
a (pm)	407.7	405	361	424
ρ (g cm^{-3})	10.5	2.7	8.92	1.002
At. mass (gm)	108	27	63.5	23

Which of the above crystallizes in FCC unit cell
(a) Ag (b) Al (c) Cu (d) Na

16. The coordination number of FCC structure for metals is 12, since
(a) each atom touches 4 others in same layer, 3 in layer above and 3 in layer below.
(b) each atom touches 4 others in same layer, 4 in layer above and 4 in layer below.
(c) each atom touches 6 others in same layer, 3 in layer above and 3 in layer below.
(d) each atom touches 3 others in same layer, 6 in layer above and 6 in layer below.

17. Which of the following is/are true?
(a) Piezoelectricity is due to net dipole moment.
(b) Some electric current is produced on heating polar crystals, this is pyroelectricity.
(c) Ferro-electricity is due to alignment of dipole in the same direction.
(d) Ferri-electricity is due to the alignment of dipole in the same direction.

18. Which of the following is/are correct?
(a) Crystalline solids are anisotropic.
(b) Amorphous solids are isotropic.
(c) Crystalline solids have sharp melting points.
(d) Amorphous solids also have sharp melting points.

Integer and Subjective

19. KF has NaCl structure. What is the distance between K^+ and F^- in KF, if the density is 2.48 g cm^{-3}?

20. The density of CaO is 3.35 g/cm^3. The oxide crystallises in one of the cubic systems with an edge of 4.80 Å. How many Ca^{++} ions and O^{-2} ions belong to each unit cell, and which type of cubic system is present?

21. Silver has a cubic unit cell with a cell edge of 408 pm. Its density is 10.6 g cm^{-3}. How many atoms of silver are there in the unit cell?

22. A compound AB has a rock salt-type structure with A:B = 1:1. The formula weight of AB is 6.023 y amu and the closest $A - B$ distance is $y^{1/3}$ nm. Calculate the density of lattice.

23. At room temperature, sodium crystallises in a body-centered cubic lattice with $a = 4.24$ Å. Calculate theoretical density of sodium (Atomic weight of Na = 23).

24. Copper has the fcc crystal structure. Assuming an atomic radius of 130 pm for copper atom (Cu = 63.54):
(a) What is the length of unit cell of Cu?
(b) What is the volume of the unit cell?
(c) How many atoms belong to the unit cell?
(d) Find the density of Cu.

25. Compute the percentage void space per unit volume of unit cell in zinc sulphide structure.

26. In a close packed structure of mixed oxides, the lattice is composed of oxide ions, one eighth of tetrahedral voids are occupied by divalent cations while one half of octahedral voids are occupied by trivalent cations. What is the formula of the oxide?

27. A compound formed by elements A and B crystallises in cubic structure where A atoms are at the corners of a cube and B atoms are at the face centre. What is the formula of the compound?

28. NH_4Cl crystallises in a body centred cubic lattice, with a unit cell distance of 387 pm. Calculate (a) the distance between the oppositely charged ions in the lattice, and (b) the radius of the NH_4^+ ion if the radius of the Cl^- ion is 181 pm.

29. Iron occurs as bcc as well as fcc unit cell. If the effective radius of an atom of iron is 124 pm, compute the density of iron in both these structures.

30. A solid $A^+ B^-$ has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius of the cation? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal $A^+ B^-$? Give reason for your answer.

31. Calculate the void space in a primitive unit cell and also the fraction of the total volume occupied.

32. The density of solid argon is 1.65 g/mL at –233°C. If the argon atom is assumed to be sphere of radius 1.54×10^{-8} cm, what percentage of solid argon has apparently empty space? (Atomic weight of Ar = 40).

33. An element crystallises as body centred cubic lattice. Its density is 7.12 g cm^{-3} and the length of the side of the unit cell is 2.88 Å. Calculate the number of atoms present in 288 g of the element.

34. An ionic solid $A^+ B^-$ crystallises as a body centred cubic structure. The distance between cation and anion in the lattice is 338 pm. Calculate the edge length of the unit cell.

35. The edges length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2 g/cc then find the radius of metal atom ($N_A = 6 \times 10^{23}$). Give the answer in pm.

36. In face centred cubic (fcc) crystal lattice, edge length is 400 pm. Find the diameter of greatest sphere which can be fit into the interstitial void without distortion of lattice.

37. A metal crystallises into two cubic phases, face centrered cubic (fcc) and body centred cubic (bcc), whose unit cell lengths are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of fcc and bcc.

38. The density of mercury is 13.6 g/mL. Calculate volume of mercury atom assuming that each atom is occupying a cube of edge length equal to the diameter of mercury atom.

39. An element (atomic mass = 60) having face centred cubic crystal has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell (Avogadro constant, $N_A = 6.02 \times 10^{23}\ mol^{-1}$)

40. The density of KBr is 2.75 g cm^{-3}. The length of the edge of the unit cell is 654 pm. Find number of KBr in one unit cell.

41. An element crystallises in a structure having fcc unit cell of an edge 200 pm. Calculate its density, if 200 g of this element contains 24×10^{23} atoms.

42. An element crystallises into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its diagonals. If volume of this unit cell is $24 \times 10^{-24}\ cm^3$ and density of the element is 7.2 g cm^{-3}. Calculate the number of atoms present in 200 g of the element.

43. Element *A* is every element of FCC, atom *B* is present at every octahedral void, atom *C* is present at 25% of tetrahedral void. Find out the possible molecular formula of the compound?

44. Thallium chloride, TiCl (240 g mol^{-1}) crystallises in either a simple cubic lattice or a face centered cubic lattice Cl^- ions with Ti^+ ions in the holes. If the density of the solid is 9.00 g cm^{-3} and edge of the unit cell is 3.85×10^{-8} cm, what is the unit geometry ?

45. A crystal of lead (II) sulphide has NaCl structure. In this crystal the shortest distance between Pb^{+2} ion and S^{2-} ions is 297 pm. What is the volume of unit cell.

46. The length of the side of the unit cell is 412 pm and Cl^- ion has a radius of 181 pm. Calculate the radius of Cs^+ ion.

47. If the radius of Mg^{2+} ion, Cs^+ ion, O^{2-} ion, S^{2-} ion and Cl^- ion are 0.65 Å, 1.69 Å, 1.40 Å, 1.84 Å, and 1.81Å respectively. Calculate the coordination numbers of the cations in the crystals of MgS, MgO and CsCl.

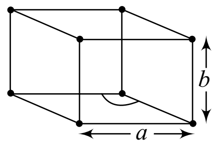
48. Formula mass of NaCl is 58.45 g mol^{-1} and density of its pure form is 2.167 g cm^{-3}. The average distance between adjacent sodium and chloride ions in the crystal is 2.814×10^{-8} cm. Calculate Avogadros constant.

49. An element *A* (Atomic weight = 100) having bcc structure has unit cell edge length 400 pm. Calculate the density of *A* and number of unit cells and number of atoms in 10 g of *A*.

50. A unit cell of sodium chloride has four formula units. The edge of length of the unit cell is 0.564 nm. What is the density of sodium chloride?

51. The composition of a sample of wustite is $Fe_{0.93}O_{1.0}$. What percentage of iron is present in the form of Fe(II)?

52. If NaCl is dopped with 10^{-3} mol % $SrCl_2$, what is the number of cation vacancies?



53. Ice crystallises in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants were *a* = 4.53Å, and *b* = 7.60Å (see figure). How many molecules are contained in a given unit cell? [density (ice) = 0.92 g/cm^3]

54. A compound formed by elements *X* and *Y*. Crystallises in a cubic structure, where *X* is at corners of the cube and *Y* is at six face centres. What is the formula of the compound? If side length is 5 Å, estimate the density of the solid assuming atomic weight of *X* and *Y* as 60 and 90 respectively.

55. The element chromium exists as a bcc lattice whose unit cell edge is 2.88 Å. The density of chromium is 7.20 g/cc. How many atom does 52.0 g of chromium contain?

56. The edge length of the unit cell of MCl (NaCl like structure; fcc) is 6.28 Å. Assuming anion-cation contact along the cell edge, calculate the radius of the M^+ ion. (r_{Cl^-} = 1.8173 Å).

57. A cubic unit cell contains manganese ions at the corners and fluoride ions at the centre of each edge.
(a) What is the empirical formula?
(b) What is the C.N. of the Mn ion?
(c) Calculate the edge length of the unit cell if the radius of a Mn ions is 0.65 Å and that of F^- ion is 1.36 Å.
(d) Calculate the density of the compound (Mn = 55, F = 19).

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. The number of atoms per unit cell in bcc and fcc is respectively **[AIEEE, 2002]**
(a) 8, 10 (b) 2, 4 (c) 1, 2 (d) 1, 3

2. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g? **[AIEEE, 2003]**
(a) 1.28×10^{21} unit cells
(b) 1.71×10^{21} unit cells
(c) 2.57×10^{21} unit cells
(d) 5.14×10^{21} unit cells

3. (i) *AB* crystallises in a rock salt structure with *A*:*B* = 1:1. The shortest distance between *A* and *B* is $Y^{1/3}$ nm. The formula mass of *AB* is 6.023 *Y* amu where *Y* is any arbitrary constant. Find the density in kg m^{-3}.

(ii) If measured density is 20 kg m^{-3}. Identify the type of point defect. **[JEE, 2004]**

4. What type of crystal defect is indicated in the diagram below? **[AIEEE, 2004]**

Na^+	Cl^-	Na^+	Cl^-	Na^+	Cl^-
Cl^-		Cl^-	Na^+		Na^+
Na^+	Cl^-	Cl^-	Na^+	Cl^-	
Cl^-	Na^+	Cl^-	Na^+	Na^+	

(a) Frenkel defect
(b) Schottky defect
(c) Interstitial defect
(d) Frenkel and Schottky defects

5. The edge length of unit cell of a metals having atomic weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2 g/cc then find the radius of metal atom ($N_A = 6 \times 10^{23}$). Give the answer in pm. **[JEE, 2006]**

6. Total volume of atoms present in a face centred cubic unit cell of a metal is (r is atomic radius) **[AIEEE, 2006]**

(a) $\frac{24}{3}\pi r^3$ (b) $\frac{12}{3}\pi r^3$ (c) $\frac{16}{3}\pi r^3$ (d) $\frac{20}{3}\pi r^3$

7. In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be **[AIEEE, 2008]**

(a) X_4Y_3 (b) X_2Y_3 (c) X_2Y (d) X_3Y_4

Paragraph for Question No. 8 to 9

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched between them. A space-filling model of this structure, called hexagonal close-packed (hcp), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

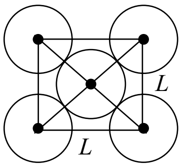
8. The volume of this hcp unit cell is **[JEE, 2008]**

(a) $24\sqrt{2}r^3$ (b) $16\sqrt{2}r^3$
(c) $12\sqrt{2}r^3$ (d) $\frac{64}{3\sqrt{3}}r^3$

9. The empty space in this hcp unit cell is **[JEE, 2008]**

(a) 74% (b) 47.6 % (c) 32% (d) 26%

10. The packing efficiency of the two-dimensional square unit cell shown below is **[JEE, 2010]**

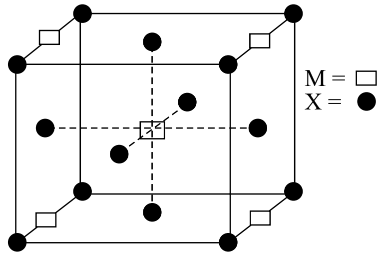


(a) 39.27% (b) 68.02% (c) 74.05% (d) 78.54%

11. Copper crystallises in fcc lattice with a unit cell edge of 361 pm. The radius of copper atom is **[AIEEE, 2011]**

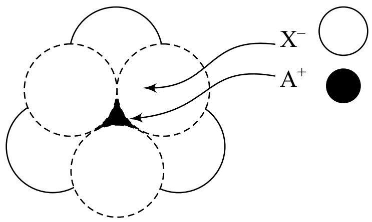
(a) 181 pm (b) 108 pm (c) 128 pm (d) 157 pm

12. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is **[JEE, 2012]**



(a) MX (b) MX_2 (c) M_2X (d) M_5X_{14}

13. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is **[2013 Adv.]**



(a) 104 pm (b) 125 pm (c) 183 pm (d) 57 pm

14. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be **[2013, Main]**

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

15. Which of the following exists as covalent crystals in the solid state? **[2013, Main]**

(a) Iodine (b) Silicon
(c) Sulphur (d) Phosphorus

16. CsCl crystallises in body centred cubic lattice. If 'a' its edge length, then which of the following expressions is correct? **[2014, Main]**

(a) $r_{Cs^+} + r_{Cl^-} = 3a$ (b) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$

(c) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$ (d) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$

17. Sodium metal crystallises in a body centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately **[2015, Main]**

(a) 1.86 Å (b) 3.22 Å
(c) 5.72 Å (d) 0.93 Å

Answer Key

LEVEL I

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

LEVEL II

1. (d) 2. (c) 3. (c) 4. (b) 5. (a) 6. (d) 7. (d) 8. (b) 9. (d) 10. (a)
11. (a) 12. (c) 13. (a) 14. (d) 15. (c) 16. (b) 17. (d) 18. (a) 19. (d) 20. (d)
21. (a) 22. (d) 23. (b) 24. (a)

LEVEL III

1. (A) → P, Q, R, (B) → P, Q; (C) → P, Q, R, S; (D) → P, S 2. (A) → S; (B) → R; (C) → P; (D) → Q
3. (A) → P, Q, R, S; (B) → P, R, S; (C) → P, S; (D) → P, R, S 4. (A) → R; (B) → S; (C) → Q; (D) → P
5. (A) → Q, R; (B) → S; (C) → Q, R; (D) → P
6. (c) 7. (b) 8. (a) 9. (c) 10. (b) 11. (a) 12. (b) 13. (a) 14. (a, c, d)
15. (a, c) 16. (b, c) 17. (a, b, c) 18. (a, b, c) 19. (269 pm) 20. (fcc)
21. (4) 22. (5.0 kg m^{-3}) 23. (1.002 g cm^{-3}) 24. (a) [367.64] (b) [4.94×10^{-23} cm^3] (c) 4 (d) 8.54 g cm^{-3}
25. (25.16%) 26. (AB_2O_4) 27. (AB_3) 28. (a) [335.15 pm] (b) [154.15 pm]
29. (7.886 g/cc in bcc and 8.89 g/cc in fcc) 30. (103.4 pm and cannot slipped) 31. (0.48 and 0.52)
32. (62%) 33. (3.386×10^{24}) 34. (390.3 pm) 35. (216.5 pm) 36. (117.2 pm) 37. (1.259)
38. (2.44×10^{-23} cc) 39. (4×10^{-8} cm) 40. (4) 41. (41.7 g/cc) 42. (3.472×10^{24})
43. ($A_2 B_2C$) 44. (scc) 45. (2.096×10^{-22} cc) 46. (175.8 pm) 47. (4, 6, 8)
48. (6.05×10^{23}) 49. (5.188 g/cc, 3.0115×10^{24}, 6.022×10^{22}) 50. (2.169 g/cc) 51. (15.053%)
52. (6.023×10^{18}) 53. (4) 54. (XY_3, 4.38 g/cc) 55. (6.05×10^{23}) 56. (1.3227 Å)
57. (a - MnF_3, b - 6, c - 4.02 Å d - 1)

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (b) 2. (c) 3. (i) 5 kg/m^3 (ii) non stoichiometric defect 4. (b) 5. (216.5 nm) 6. (c)
7. (a) 8. (a) 9. (d) 10. (d) 11. (c) 12. (b) 13. (a) 14. (b) 15. (b) 16. (c)
17. (a)

Hints and Solutions

LEVEL I

1. (a) $B = 8 \times \frac{1}{8} = 1$ $A = 1 \times 1$

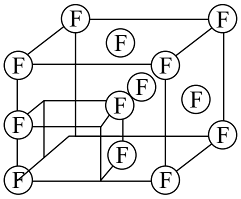
$\therefore$ $MF = AB$

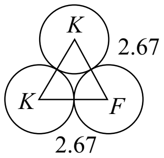
2. (c) $Au = 8 \times \frac{1}{8} = 1$

$Cu = 6 \times \frac{1}{2} = 3$

$\therefore$ formula $AuCu_3$

3. **(d)**





$\Rightarrow \quad a = \sqrt{2}$

(distance) $\Rightarrow 267\sqrt{2}$ $\Rightarrow 377.6$ pm

4. **(a)** $d = \dfrac{z \times \text{Molar mass}}{N_\text{A} \times a^3}$

$$a^3 = V = \frac{4 \times 143.5}{6.023 \times 10^{23} \times 5.561}$$

$$V = 17.137 \times 10^{-23} = \frac{170.954 \times 10^{-24} \times 100}{17.137 \times 10^{-23}}$$

% occupied = $\dfrac{(5.55 \times 10^{-8})^3}{\text{Volume}} \times 100 = 99.75$

% unoccupied $\Rightarrow 0.245$

5. **(d)** For fcc

Use $d = \dfrac{Z \times M}{N_\text{A} \times a^3} = \dfrac{\text{total mass}}{\text{Total volume}}$

6. **(b)** $d = 3.18 = \dfrac{4 \times \left[\dfrac{40 + 2 \times 19}{6.023 \times 10^{23}}\right]}{(a \times 10^{-10})^3} \Rightarrow a = 344$ pm

7. **(c)** $A = 6$ $\qquad C = 6 \times \dfrac{2}{3} = 4$

$A_6C_4 \quad \Rightarrow \quad A_3C_2$ or C_2A_3

8. **(a)** $X = 4$

$Y = 8 \qquad Z = 4 \times \dfrac{1}{2} = 2$

$\therefore$ formula $X_4Y_8Z_2$ OR X_2Y_4Z

9. **(b)** $a = 480$ pm

$$a\sqrt{3} = 2r_{x^+} + 2r_{y^-}$$

$$480 \cdot \sqrt{3} = 2r_{x^+} + 2 \times 225 \Rightarrow r_{x^+} = 190.68 \text{ pm}$$

10. **(b)** $\dfrac{r_{A^{+1}}}{r_{B^{-1}}} = 0.225 = \dfrac{22.5}{r_{B^-}}$

$r_{B^{-1}} = 100$ pm

11. **(a)** $a = 387$ pm

$$d_{\text{NH}_4^+\text{-Cl}^-} = \frac{a\sqrt{3}}{2} = 335.1 \text{ pm}$$

12. **(d)** $A = 4$ $\qquad B = 8 \times \dfrac{1}{4} = 2$

$C = 4 \times \dfrac{1}{2}$ $\qquad \therefore$ formula $A_4B_2C_2$

13. **(b)** $Z = 8 \times \dfrac{1}{8} + 2 = 3$

$$7.2 = \frac{[3 \times M]}{6.023 \times 10^{23} \times 24 \times 10^{-24}}$$

$\Rightarrow$ Number of atoms in 200 g = $\left(\dfrac{200}{M} \times N_A\right)$

$= 3.472 \times 10^{24}$ atoms

14. **(b)** $a = 620$ pm

r_1 = nearest neighbour = $\dfrac{a}{\sqrt{2}}$

r_2 = next nearest neighbours = $a = 620$

15. **(d)** $\dfrac{200}{M} \times N_A = 5 \times 10^{24} \cdot \dfrac{M}{N_A} = \left(\dfrac{200}{5 \times 10^{24}}\right)$

$$d = \frac{4 \times \dfrac{M}{N_A}}{(200 \times 10^{-10})^3} = 20 \text{ g cm}^3$$

16. **(a)** $a\sqrt{3} = 2r_{\text{Cs}^+} + 2r_{\text{Cl}^-} \cdot r_{\text{Cl}^-} = 1.81$ Å

17. **(a)** Effective number of Rhenium = $\dfrac{1}{8} \times 8 = 1$

Effective number of oxygen = $12 \times \dfrac{1}{4} = 3$

$\therefore$ formula = ReO_3 or Re_2O_6

18. **(d)** Effective number of Ca = $8 \times \dfrac{1}{8} = 1$

Effective number of Ti = 1 × 1 = 1

Effective number of O = $6 \times \dfrac{1}{2} = 3$

$\therefore$ formula = CaTiO_3

19. **(d)** **For hexagon $a = 2r$**

$$\frac{h/2}{a} = \sqrt{\frac{2}{3}} \Rightarrow \frac{h}{4r} = \sqrt{\frac{2}{3}}$$

$$\therefore \quad r = \frac{h}{4}\sqrt{\frac{3}{2}}$$

Volume of hexagonal = $24\sqrt{2}\,r^3$

Cross-section area of hexagonal = $6 \times \dfrac{\sqrt{3}}{4} \times 4r^2$

$= 6\sqrt{3}r^2$

Volume = Height × Area = $24\sqrt{2}\,r^3$

20. **(c)** Effective number of N = 6

Effective number of Nb = $6 \times 2 \times \dfrac{1}{2} = 6$

$\therefore$ formula = Nb_6N_6

or = NbN

21. **(a)** The Coordination Number of CsCl is 8

22. **(b)** For bcc edge length (a) = $\dfrac{4}{\sqrt{3}}r$

$= \dfrac{4}{1.732} \times 80$

$= 184.7$ pm

23. **(b)** For NaCl like structure. The radius ratio should be (Since C.N = 6)

$\Rightarrow$ 0.414 to 0.732

$$\frac{r^+}{r^-} = \frac{100}{r^-_{\max}} = 0.414\,,\ \frac{100}{r^-_{\min.}} = 0.732$$

$$\therefore \quad r^-_{\max} = \frac{100}{0.414} = 241.6 \text{ pm}$$

$$\therefore \quad r^-_{\min} = \frac{100}{0.732} = 136.6 \text{ pm}$$

24. **(a)** Since, P atoms are forming the lattice reference ∴ No. of P atom 4(ccp) and 4 atoms (Q) from the half of the tetrahedral void contributes one unit cell. So, formula of solid is P_4Q_8 so, the simplest formula of the solid is PQ_2.

25. **(d)** In simple cubic arrangement, number of atoms = 1, $a = 2r$

$$\therefore \text{ packing fraction} = \frac{\text{Volume occupied by one atom}}{\text{Volume of unit cell}}$$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

26. **(b)** $M = \dfrac{d \times a^3 \times N_A}{Z}$

$$= \frac{10 \times (200 \times 10^{-3})^3 \times (6.02 \times 10^{23})}{4}$$

$= 12.04$ g

$$\text{Number of atoms in 100 g} = \frac{6.02 \times 10^{23}}{12.04} \times 100$$

$$= 5 \times 10^{24}$$

27. **(c)** It is the characteristic fact.

28. In hcp unit cell

$$\mathbf{h} = C = 4r\sqrt{\frac{2}{3}}$$

$$a = 2r$$

$$\therefore \quad \frac{C}{a} = 2\sqrt{\frac{2}{3}} = \sqrt{\frac{8}{3}}$$

29. Since the C.N. of fluorite and antifluorite structure are same, hence by interchanging the positions of cation and anions lattice can be interchanged.

30. Since, A forming the lattice reference.

The number of C in one unit cell $= \dfrac{2}{3} \times 6 = 4$

∴ m.f is $C_4A_6 \equiv C_2A_3$

31. $n \times \lambda = 2d \sin\theta$

In first case, $1 \times \lambda = 2\lambda \sin\theta$

or $\quad \sin\theta = \dfrac{1}{2} = \sin 30^\circ$

or $\quad \theta = 30^\circ$

In second case, $1 \times \lambda = 2 \times \dfrac{\lambda}{2} \times \sin\theta$

or $\quad \sin\theta = 1 = \sin 90^\circ$

or $\quad \theta = 90^\circ$

32. **(a)** $A_{\frac{4}{8}+\frac{4}{2}}\ B_{4-1-\frac{2}{4}}$

$A_{2.5}\,B_{2.5}$ or $\boxed{AB}$

33. **(a)** Total number of atoms in 1 hcp unit cell $= \dfrac{12}{6} + \dfrac{2}{2} + \dfrac{3}{1}$

[(12 corner, 2 face centered, 3 body centers)] = 2 + 1 + 3 = 6

34. **(a)** $\dfrac{h}{2} = \sqrt{4r^2 - \dfrac{4r^2}{3}} = \sqrt{\dfrac{12r^2 - 4r^2}{3}} = 4r\sqrt{\dfrac{2}{3}}$

Area of base = area of 6 equilateral Δ^{le}

$$= 6 \times \frac{\sqrt{3}}{4}(2r)^2$$

∴ volume = area of base × height = $24\sqrt{2}r^3$

35. **(b)** $X_{\frac{7}{8}}\,Y_3\,Z_{\frac{1}{8}} \Rightarrow \therefore X_7Y_{24}Z$

36. **(b)** Volume of all atoms in 1.68 gm Argon

$$= \frac{1.68}{40} \times \mathrm{N_A} \times \frac{4}{3} \times \pi \times (1.5 \times 10^{-8})^3 = 0.3564$$

Volume of solid argon = 1 cm^3 = Volume of unit cell

% empty space = (1 – 0.3564) × 100 = 64.36

37. **(d)** Number of atoms of B in unit cell = 2

Total volume of B unoccupied by A

In a unit cell $= 2 \times \dfrac{4}{3}(R^3 - r^3) \times \pi = \dfrac{7\pi R^3}{3}$

Volume of unit cell $= a^3 = \dfrac{64}{3\sqrt{3}}R^3$

For bcc $\sqrt{3}a = 4R$

$$\therefore \quad \rho_{\text{ratio}} = \frac{7\pi R^3/3}{\frac{64}{3\sqrt{3}}R^3} = \frac{7\pi}{64\sqrt{3}}$$

38. **(a)** Number of atoms of ‘A’ in a unit cell $\dfrac{1}{8} \times 8 = 1$

Number of atoms of ‘B’ in a unit cell $\dfrac{1}{2} \times 6 = 3$

∴ formula of the compound = AB_3

39. **(d)** $a = 2[r^+ + r^-] = 400$

$2r^+ = 400 - 2 \times 75$

$2r^+ = 250$

∴ $\quad r^+ = 125$

40. **(a)** $a\sqrt{2} = 4r$

$$\therefore \quad r = \frac{a\sqrt{2}}{4} = \frac{a}{2\sqrt{2}}$$

∴ Total volume of 4 atoms $= 4 \times \dfrac{4}{3}\pi r^3$

$$= 4 \times \frac{4}{3}\pi\left[\frac{a}{2\sqrt{2}}\right]^3 = \frac{\pi a^3}{3\sqrt{2}}$$ but in question symbol of edge length given r

$\therefore$ Total volume $= \dfrac{\pi r^3}{3\sqrt{2}}$

LEVEL II

1. $$a^3 = \frac{M \times Z}{d \times N_A \times 10^{-30}}\,\text{pm}^3$$

$$= \frac{93\text{ g mol}^{-1} \times 2}{8.55\text{ g cm}^{-3} \times 6.02 \times 10^{23}\text{ mol}^{-1} \times 10^{-30}}\,\text{pm}^3$$

$a^3 = 3.61 \times 10^7 = 36.1 \times 10^6\ \text{pm}^3$

$a = (36.1)^{1/3} \times 10^2\ \text{pm} = 3.304 \times 10^2\ \text{pm} = 330.4\ \text{pm}$

For body centred cubic,

$$r = \frac{\sqrt{3}}{4}a = 0.433a = 0.433 \times 330.4\ \text{pm} = 143.1\ \text{pm.}$$

2. (c) Atoms occupying at tetrahedral holes and octahedral holes do not touch with each other if touches distortion in ccp seen.

3. (c) In CCP anions oxide ion are forming the lattice reference and cations occupied voids. In ccp there are two tetrahedral voids and one octahedral hole.

For one oxygen atom there are two tetrahedral holes and one octahedral hole.

Since one fifth of the tetrahedral voids are occupied by divalent cations (X^{2+}).

$\therefore$ number of divalent cations in tetrahedral voids $= 2 \times \dfrac{1}{5}$

Since half of the octahedral voids are occupied by trivalent cations (Y^{3+})

$\therefore$ number of trivalent cations $= 1 \times \dfrac{1}{2}$

So the formula of the compound is $X_{2/5}Y_{1/2}O$ or $X_4Y_5O_{10}$

4. (b) For fcc lattice

$4r = \sqrt{2}a$ where $a = 620$ pm

$$r = \frac{1}{2\sqrt{2}} \times a$$

$$\frac{1}{2\sqrt{2}} \times 620\ \text{m} = 219.20\ \text{pm}$$

5. (a) Cs Cl has bcc structure and for it

$$r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{\sqrt{3} \times a}{2} = \frac{\sqrt{3} \times 0.4123}{2}$$

$$= \frac{0.7141}{2} = 0.3571\ \text{nm}$$

$$r_{\text{Cs}^+} = 0.3571 - 0.181 = 0.176\ \text{nm}$$

6. (d) It is a typical zinc blende (ZnS) structure

Q atoms are cubic close packed, R atoms are situated in alternate tetrahedral voids.

$\angle QRQ = 109°28$ (tetrahedral)

Coordination number

With respect to $Q = 4$

With respect to $R = 4$

7. (d) For a bcc lattice

$$\frac{x^+}{y^-} = 0.732 \Rightarrow y^- = \frac{0.4}{0.732} = 0.546\ \text{Å}$$

Now for fcc lattice $\dfrac{z^+}{y^-} = 0.414$

$\Rightarrow \quad z^+ = 0.544 \times 0.414 = 0.226\ \text{Å}$

8. (b) $$d_1 = \frac{2 \times 56}{\left(\frac{4r}{\sqrt{3}}\right)^3 \times N_A \times 10^{-30}}\,\text{g/cc}$$

$$d_2 = \frac{4 \times 56}{(2\sqrt{2} \cdot r)^3 \times N_A \times 10^{-30}}\,\text{g/cc}$$

$$\frac{d_1}{d_2} = 0.918$$

9. (d) $$d \propto \frac{Z}{a^3} \therefore \frac{d_{\text{FCC}}}{d_{\text{BCC}}} = \left(\frac{Z_{\text{FCC}}}{Z_{\text{BCC}}}\right)\left(\frac{a_{\text{BCC}}}{a_{\text{FCC}}}\right)^3$$

$$\Rightarrow \quad \frac{2}{1} = \frac{4}{2}\left[\frac{a_{\text{BCC}}}{a_{\text{FCC}}}\right]^3 \Rightarrow 1:1$$

10. (a) $$d = \frac{Z \times M}{N_A \times a^3}$$

$$Z = \frac{d \times N_A \times a^3}{M} = \frac{2 \times 6 \times 10^{23} \times 5 \times 5 \times 5 \times 10^{-24}}{75}$$

$= 20 \times 10^{-1} = 2$

Therefore, the cubic lattice will be body centered.

For bcc lattice: $\sqrt{3}a = 4r$

$\therefore \quad r = \dfrac{\sqrt{3}}{4}a$, since $a = 5$ Å $= 5 \times 10^2$ pm

$$= \frac{1.732 \times 5 \times 10^2}{4} = 2.165 \times 10^2 = 216.5\ \text{pm}$$

11. (a) $r_A = r_{\text{Na}^+}, r_B = r_{\text{Cl}^-}$

(i) $\dfrac{r_A}{r_B} = 0.414$ is the ideal radius ratio for NaCl structure.

(ii) $$r_B = \frac{r_A}{0.414} = \frac{41.4}{0.414}\text{pm} = 100\text{pm}\,\frac{r'_{A^+}}{r_{B^-}} = \frac{30}{100} = 0.3$$

Radius ratio is in 0.225 – 0.414 range which is for tetrahedral. It crystallises in ZnS type of structure. Coordination number of A^+ ion changes from 6 (in NaCl) to 4 (in ZnS) type of structure

12. **(c)** ABCABC… pattern gives rise to face centred cubic lattice. The layers (ABCA) are present perpendicular to the body diagonal of the unit cell.

∴ the distance between two successive layers = $\left(\frac{\text{Length of body diagonal}}{3}\right)$ and $a = 2\sqrt{2}r$

for FCC or CCP

$$= \frac{\sqrt{3}a}{3} = \frac{\sqrt{3}}{3}2\sqrt{2}r = 2r\sqrt{\frac{2}{3}}$$

13. **(a)** 1 unit cell volume (a^3) = 27×10^{-24} cm^3

1 cm^3 volume contains = $\frac{10^{24}}{27}$ unit cells

density given 10 g/ml

10 g of metal of 1 ml of metal contains $\frac{10^{24}}{27}$ unit cells

∴ 16.2 g metal contains

$$= \frac{16.2}{10} \times \frac{10^{24}}{27} = 6 \times 10^{22} \text{ (unit cell)}$$

14. **(d)** Volume of cuboid box = $4R \times 4R \times 2R = 32R^3$

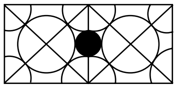
Volume of 4 sphere = $\frac{16}{3}\pi R^3$

$$\text{P.F.} = \frac{\text{Volume occupied by spheres}}{\text{Total volume}} = \frac{\frac{16}{3}\pi R^3}{32R^3} = \frac{\pi}{6}$$

Percentage vacant space = $100\left(1 - \frac{\pi}{6}\right)$

15. **(c)** $4r = \sqrt{2}$ a $\quad r = \frac{3.61}{2\sqrt{2}} = 1.28$ Å

We have to find the radius of dark circle in the figure.



$$\text{Radius} = \frac{3.61 - 2.56}{2} = 0.525 \text{ Å}$$

16. **(b)** The height of the hcp unit cell = $4\sqrt{\frac{2}{3}} \times r = 5.715$

$$\therefore \quad r = \frac{5.715 \times \sqrt{3}}{\sqrt{2} \times 4} = 1.75 \text{ Å}$$

The base area of the unit cell = $6\sqrt{3}\, r^2$

The volume of the unit cell = Base area × Height

$$= 24\sqrt{2}\, r^3 = 181.8 \text{ Å}^3$$

17. **(d)** When all particles along one body diagonal are removed, $2X$ particle from corner are removed, one Y particle is removed and $2Z$ particle is removed.

$$X \text{ particle} = \frac{1}{8} \times 6 + \frac{1}{2} \times 6 = \frac{15}{4}$$

(Y particle = 3, Z particle = 6)

$$\therefore \quad X_{\frac{15}{4}}Y_3Z_6 = X_5Y_4Z_3$$

18. **(a)** $\frac{r_{Na^+}}{r_{Cl^-}} = 0.55, \frac{r_{K^+}}{r_{Cl^-}} = 0.74$

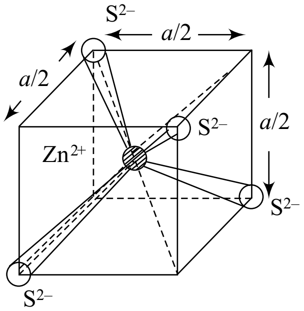
$$\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 1.55 \text{ ...(1)},$$

$$\frac{r_{K^+}}{r_{Cl^-}} + 1 = 1.74 \text{ ...(2)}$$

Dividing (ii) by (i)

$$\frac{1.74}{1.55} = \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} \times \frac{r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = 1.123$$

19. **(d)**



Let edge length of the unit cell = a

$$\sqrt{3} \times \frac{a}{2} \times \frac{1}{2} = r_{Zn^{2+}} + r_{S^{2-}}$$

$$\text{or} \quad \sqrt{3}\frac{a}{4} = 0.83 + 1.74 = 2.57$$

$$\text{or} \quad a = 2.57 \times \frac{4}{\sqrt{3}} = 5.935 \text{ Å}$$

20. **(d)** The packing efficiency = 0.68, means the given lattice is bcc.

The closest distance of approach = $2r$

$$2r = 2.86 \text{ Å} = \frac{\sqrt{3}a}{2} \quad \text{or} \quad a = \frac{2 \times 2.86}{\sqrt{3}} = 3.30 \text{ Å}$$

Let atomic weight of the element = M

$$\therefore \quad \frac{2 \times M}{6 \times 10^{23} \times (3.3)^3 \times 10^{-24}} = 8.57$$

$$M = 8.57 \times 3 \times (3.3)^3 \times 0.1 = 92.39 \simeq 93$$

21. **(a)** Let total number of atoms present in the unit cell = n

∴ number of Mn atoms = $\frac{3}{4}n$; number of Si atoms = $\frac{n}{4}$

$$\therefore \quad \frac{\left(\frac{3}{4}n \times 55 + \frac{n}{4} \times 28\right)}{6 \times 10^{23} \times (2.86)^3 \times 10^{-24}} = 6.85$$

$$\text{or} \quad \frac{n[41.25 + 7]}{6 \times 23.39 \times 0.1} = 6.85$$

$$\text{or} \quad n = \frac{6.85 \times 6 \times 2.339}{48.25} = 1.99 \simeq 2$$

22. **(d)** Let C–C bond distance in graphite is a Å

∴ surface area = $6\times\frac{\sqrt{3}}{4}\times a^2$

$$= 6\times\frac{\sqrt{3}}{4}\times a^2\times 10^{-16}\text{ cm}^2$$

∴ volume of the unit cell

$$= 6\times\frac{\sqrt{3}}{4}\times a^2\times 10^{-16}\times 3.35\times 10^{-8}\text{ cm}^3$$

∴ mass of the unit cell

$$= 6\times\frac{\sqrt{3}}{4}\times 3.35\times a^2\times 2.25\times 10^{-24}\text{ g.}$$

$$\therefore \quad 6\times\frac{\sqrt{3}}{4}\times 3.35\times 2.25\times 10^{-24}\times a^2$$

$$= 12\times\frac{10}{6}\times 10^{-24}\times 2$$

$$\therefore \quad a^2 = \frac{10}{3}\times 4\ \frac{1\times 2}{\sqrt{3}\times 3.35\times 2.25} = 2.04265$$

or $a = 1.429$ Å

23. **(b)** CCP means $Z = 4$ and $a = 2\sqrt{2}r$

$$\text{P.F.} = \frac{4\times\frac{4}{3}\pi r^3 + 4\times\frac{4}{3}\pi\times(0.414r)^3 + 8\times\frac{4}{3}\pi\times(0.225r)^3}{(2\sqrt{2}r)^3}$$

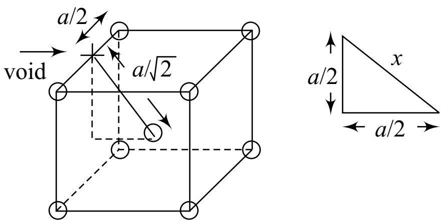
$$\text{P.F.} = \frac{4\times\frac{4}{3}\pi r^3[1+(0.414)^3+2\times(0.225)^3]}{16\sqrt{2}r^3}$$

$$\text{P.F.} = \frac{\pi}{3\sqrt{2}}[1+(0.414)^3+2\times(0.225)^3$$

$$= \frac{\pi}{3\sqrt{2}}(1 + 0.070958 + 0.022781)$$

or P.F. = $0.8096 \simeq 0.81$

24. **(a)**



$$x = \sqrt{\frac{a^2}{4}+\frac{a^2}{4}} = \sqrt{\frac{a^2}{2}} = \frac{a}{\sqrt{2}}$$

The atom present in the void will touch the atom at the corner at first

$$\therefore \quad r_x + r = a/2; \quad 4r = \sqrt{3}a \quad \text{or} \quad r = \frac{\sqrt{3}a}{4}$$

$$\therefore \quad r_x = \frac{a}{2} - \frac{\sqrt{3}a}{4} = \frac{2a}{4} - \frac{\sqrt{3}a}{4} = \frac{a}{4}(2-\sqrt{3})$$

$$= 0.067a$$

$$\therefore \quad 2r_x = 2\times 0.067a = 0.134a.$$

LEVEL III

1. (A) → P, Q, R, (B) → P, Q; (C) → P, Q, R, S; (D) → P, S
2. (A) → S; (B) → R; (C) → P; (D) → Q
3. (A) → P, Q, R, S; (B) → P, R, S; (C) → P, S; (D) → P, R, S
4. (A) → R; (B) → S; (C) → Q; (D) → P
5. (A) → Q, R; (B) → S; (C) → Q, R; (D) → P

Cubic close packing is fcc both ccp and hcp have a packing fraction = 0.74. They both have a coordination number of 12.

Passage 1

6. **(c)** Number of Ca atoms = $8\times\frac{1}{8}=1$

Number of O–atoms = $6\times\frac{1}{2}=3$

Number of Ti–atoms = 1 × 1 = 1

Total number of atoms = 5

7. **(b)** $CaTiO_3$

$2 + x - 6 = 0$

$x = 4$

8. **(a)** If no O–atom is removed from alternate position (face)

Number of O–atom remain = $\frac{1}{2}\times 2 = 1$

Hence formula of perovskite is CaTiO.

Comprehension Type-2

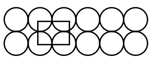
9. **(c)** Let iron present in +3 oxidation state is x, then

$3x + 2(0.95 - x) = 2,\ x = 0.1$

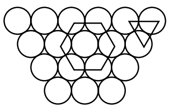
% of Fe in +3 oxidation state = $\frac{0.1}{0.95}\times 100 = 10.5\%$

10. **(b)** As cation size increase more number of anion can attached with it hence C. No increase.

11. **(a)**



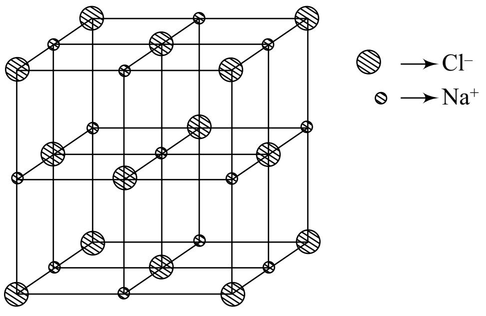
Square close packing
Not possible in closest
packing



Hexagonal close packing and
triangular close packing are
possible

12. **(b)** In MgO electrostatic attraction between Mg^{2+} and O^{2-} is much greater than the electrostatic attraction between Na^+ and F^-.

13. **(b)** NaCl or Rock Salt Type



1. Cl^- is present at each corner and on each face centre whereas Na^+ is present on edge center and body center or vice versa.
2. Cl^- is present in FCC lattice while Na^+ occupy all the octahedral holes.

   $2(r^+ + r^-) = a$ = edge length

   $4r^- = a\sqrt{2}$ Only for ideal crystal, i.e. anion-anion contact.

14. **(a, c, d)** Cs Cl packed in bcc unit cell

$r^+ = 0.165$ nm, $r^- = 0.181$ nm

$$\sqrt{3}a = 2r^+ + 2r^-$$

$$a = \frac{(2 \times 0.165) + (2 \times 0.181)}{\sqrt{3}} = 0.399526 = 0.4 \text{ nm}$$

$$\text{Density} = \frac{Z \times M_{(\text{kg})}}{N_A \times a^3_{(\text{meter})}} = \frac{1 \times 168.5 \times 10^{-3}}{6.02 \times 10^{23} \times (0.4 \times 10^{-9})^3}$$

$$= 437 \times 10^{-26} \times 10^{27} = 4.37 \times 10^3 \text{ kg/m}^3$$

15. **(a, b, c)**

$$Z_{\text{Ag}} = \frac{d \cdot a^3 N_A}{M} = \frac{10.5 \times (4.07 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{108} = 4$$

$$Z_{\text{Al}} = \frac{(4.05 \times 10^{-8})^3 \times 2.7 \times 6.023 \times 10^{23}}{27} = 4$$

$$Z_{\text{cu}} = \frac{(3.61 \times 10^{-8})^3 \times 8.92 \times 6.023 \times 10^{23}}{63.5} = 4$$

Hence all crystallises in FCC unit cell.

16. **(b, c)**

See HCP Diagram and FCC diagram in theory.

17. **(a, b, c)**

See dielectric properties of solid in theory.

18. **(a, b, c)**

See Classification of solid in theory.

19. Due to NaCl type structure, $Z = 4$

$$\therefore \quad d = \frac{Z \times M}{a^3 N_A}$$

$$\therefore \quad a^3 = \frac{Z \times M}{d \times N_A} = \frac{4 \times 58}{2.48 \times 6.02 \times 10^{23}}$$

$$a = 5.3762 \times 10^{-8} \text{cm}$$

$$\therefore \quad 2(r^+ + r^-) = a$$

$$\therefore \quad (r^+ + r^-) = \frac{a}{2}$$

$= 2.688 \times 10^{-8}$ cm = 269 pm

20. (ans :- fcc)

From equation

d(density) = 3.35 gm/cm^3

$$d = \frac{Z \times M}{a^3 \times N_A} = \frac{Z \times 56}{(4.8 \times 10^{-8})^3 \times 6 \times 10^{23}}$$

$\therefore \quad Z = 4$

So, cubic system is fcc type.

21. Length of the edge of unit cell = 408 pm

Volume of unit cell = (408 pm)^3 = 67.92×10^{-24} cm^3

Mass of unit cell = Density × Volume

$= 10.6 \text{ g cm}^{-3} \times 67.92 \times 10^{-24} \text{ cm}^3 = 7.20 \times 10^{-24}\text{g}$

Mass of unit cell = Number of atoms in unit cell × Mass of each atom

Now, mass of each atom

$$= \frac{\text{Atomic mass}}{\text{Avogadro number}} = \frac{108}{6.023 \times 10^{23}} = 1.79 \times 10^{-22}\text{g}$$

Let the unit cell contain 'Z' atoms, so that

Mass of unit cell = $Z \times 1.79 \times 10^{-22} = 7.20 \times 10^{-22}$

$$Z = \frac{7.20 \times 10^{-22}}{1.79 \times 10^{-22}} = 4.02$$

∴ number of atoms present in a unit cell = 4

22. AB has rock salt (A:B::1:1) structure, i.e., fcc structure ($n = 4$) and formula weight of BB is 6.023 y amu having closest distance $A - B$ y$^{1/3}$ nm. Therefore edge length of unit cell = $2(A^+ + B^-) = 2 \times y^{1/}3 \times 10^{-9}$ m

$$\therefore \quad \text{Density of } AB = \frac{Z \times M}{N_A \times a^3}$$

$$= \frac{4 \times 6.023 \times y \times 10^{-3}}{6.023 \times 10^{23} \times (2y^{1/3} \times 10^{-9})^3}$$

(molecular weight in kg)

$= 5.0 \text{ kg m}^{-3}$

23. The total number of atoms per unit cell = $8 \times \frac{1}{2} + 1 = 2$

$$\text{Density} = \frac{Z \times M}{N_A \times a^3} = \frac{2 \times 23}{6.023 \times 10^{23} \times (4.24 \times 10^{-8})^3}$$

$= 1.002$ g cm^{-3} approx. 1g/cc

24. As we know $d = \dfrac{Z \times M}{N_A \times a^3}$,

(a) For fcc structure $4r = \sqrt{2}a$, $a = 2\sqrt{2}\ r$

$= 2\sqrt{2} \times 130$ pm = 367.64 pm

(b) Volume of unit cell = a^3 $(3.67 \times 10^{-8} \text{ cm})^3$

$= 4.94 \times 10^{-23}$ cm^3

(c) $Z = 4$

(d) density = 8.54 g/cm^3

25. Given data show ZnS type crystal

$$\therefore \quad PF = \frac{\pi}{3\sqrt{2}}\left[\left(\frac{r^+}{r^-}\right)^3 + 1\right]$$

$$= \frac{3.14}{3\sqrt{2}}[(0.225)^3 + 1] \quad \text{Since } \frac{r^+}{r^-} = 0.225$$

$$= \frac{3.14 \times 1.0114}{3 \times 1.414} = 0.7486$$

% of void = 100 – 74.86 = 25.16%

26. Since oxide ion forming the lattice reference

$\therefore$ Number of oxide ion = 4

Number of tetrahedral voids in lattice = 2 × 4 = 8

Number of divalent cation (A) = $\frac{1}{8} \times 8 = 1$

Number of octahedral voids in lattice = 1 × 4 = 4

Number of trivalent cations (B) = $\frac{1}{2} \times 4 = 2$

$\therefore$ Formula = AB_2O_4

27. *A* atom are eight corners of the cube.

Therefore, the number of *A* atoms in the unit cell = 8 × 1/8 = 1

B atoms are at the face centre of six faces = 6 × 1/2 = 3

The formula is AB_3.

28. **(a)** In a body centred cubic lattice, oppositely charged ions touch each other along the body-diagonal of the cube. So, we can write,

$$2r^+ + 2r^- = \sqrt{3}a$$

$$r^+ + r^- = \frac{\sqrt{3}}{2}a = \frac{\sqrt{3}}{2}\ (387\text{ pm}) = 335.15\text{ pm}$$

Now, since $r^- = 181$ pm

We have, $r^+ = (335.15 - 181)$ pm = 154.15 pm

29. In a body centred unit cell, atoms touch each other along the body-diagonal.

Hence, $4r = \sqrt{3}a$

$$a = \frac{4}{\sqrt{3}}r = \frac{4}{\sqrt{3}}\ (124\text{ pm}) = 286.4\text{ pm}$$

for bcc lattice, $Z = 2$, Hence,

$$r = \frac{ZM}{a^3N_A} = \frac{2 \times 55.8}{(286.4 \times 10^{-12})^3 \times 6.023 \times 10^{23}}$$

$$= 7.887 \times 10^6 \text{ g}^{-3} = 7.886 \text{ g/cc}$$

In a face centred unit cell, atoms touch each other along the face diagonals.

Hence, $4r = \sqrt{2}a$

$$a = \frac{4}{\sqrt{2}}\ r = (124\text{ pm}) = 350.7\text{ pm}$$

For fcc lattice, $Z = 4$, hence,

$$= 8.89 \times 106\text{ g m}^{-3} = 8.89\text{ g cm}^{-3}$$

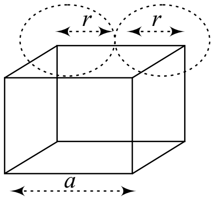
30. As A^+B^- has NaCl structure, A^+ ions will be present in the octahedral voids. Ideal radius of the cation will be equal to the radius of the octahedral void because in that case it will touch the anions and the arrangement will be closely packed. Hence,

Radius of the octahedral void = $r_{A^+} = 0.414 \times r_{B^-}$ = 0.414 × 250 = 103.4 pm

Radius of the tetrahedral site = $0.225 \times r_{B^-}$ = 0.225 × 250 pm = 56.25 pm

As the radius of the cation C^+ (180 pm) is larger than the size of the tetrahedral site, it cannot be slipped into it.

31. $a = 2r$ Volume of the cube = $a^3 = (2r)^3 = 8r^3$



$$\text{Packing fraction} = \frac{\text{Volume of one atom}}{\text{Volume of the cube}}$$

$$= \frac{\left(\frac{4}{3}\pi r^3\right)}{8r^3} = \frac{\pi}{6} = 0.52$$

$\therefore$ void fraction = 1 – 0.52 = 0.48 $\quad\therefore$ Void space = 48%

32. Volume of one atom of Ar = $\frac{4}{3}\pi r^3$

Also, number of atoms in 1.65 g = $\frac{1.65}{40} \times 6.023 \times 10^{23}$

$\therefore$ total volume of all atoms of Ar in solid state

$$= \frac{4}{3}\pi r^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$$= \frac{4}{3} \times \frac{22}{7} \times (1.54 \times 10^{-8})^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$$= 0.380 \text{ cm}^3$$

Volume of solid argon = 1 cm^3

$$\therefore \%\text{ empty space} = \frac{[1 - 0.380]}{1} \times 100 = 62\%$$

33. Volume of unit cell = a^3 = (2.88 Å)^3 = $(2.88 \times 10^{-8}\text{ cm})^3$ = 23.887×10^{-24} cm^3

Volume of 288 g of the element

$$= \frac{\text{Mass}}{\text{Density}} = \frac{288\text{ g}}{7.12\text{ g cm}^{-3}} = 40.499\text{ cm}^3$$

Number of unit cells in the given volume of the element

$$= \frac{\text{Volume of the element}}{\text{Volume of the unit cell}} = \frac{40.449}{23.887 \times 10^{-24}}$$

$$= 1.693 \times 10^{24}$$

$\because$ each unit cell of bcc lattice contains 2 atoms

$\therefore$ number of atoms in 288 g of element

= Number of unit cells × number of atoms per unit cell

= $1.693 \times 10^{24} \times 2 = 3.386 \times 10^{24}$

34. In a body centred cubic unit cell, the distance between the cation and anion $(r^+ + r^-)$ is related to the edge length (a) by

$$r^+ + r^- = \sqrt{3} \times \frac{a}{2}$$

$$\therefore \quad a = \frac{2}{\sqrt{3}}(r^+ + r^-)$$

It is given that $(r^+ + r^-) = 338$ pm

$$\therefore \quad a = \frac{2}{\sqrt{3}} \times 338 \text{ pm} = \frac{676}{1.732} = 390.3 \text{ pm}$$

35. Edge length of unit cell = 5×10^{-8} cm
Density = 2.0 g/cc, molecular mass = 75
N_A = Avogadro number = 6×10^{23}

$$d = \frac{Z \times M}{a^3 \times N_A} = 2.0 = \frac{Z \times 75}{(5 \times 10^{-8})^3 \times 6.0 \times 10^{23}}$$

$$Z = 2 \times \frac{125 \times 10^{-24} \times 6.0 \times 10^{23}}{75} = 2$$

Hence, it is a body centred cubic structure

$$r = \frac{\sqrt{3}}{4} \times a = \frac{\sqrt{3}}{4} \times 5\text{Å} = 2.165 \text{ Å} = 216.5 \text{ pm}$$

36. For a face centred cubic crystal

$$a\sqrt{2} = 4r, \ r = \text{radius of sphere}$$

$$r = \frac{\sqrt{2}}{4} a = \frac{a}{2\sqrt{2}}$$

$$= \frac{400 \times \sqrt{2}}{4} = 100 \times 1.414$$

$$= 141.4 \text{ pm.}$$

For an octahedral void
$a = 2(r + R)$
Diameter of sphere = $2R = a - 2r = 400 - 2 \times 141.4$
Diameter = $2R = 400 - 282.8 = 117.2$ pm

37. Length of edge of fcc = 3.5 Å, noumber of atoms in fcc $(Z_1) = 4$
length of edge of bcc = 3.0 Å, number of atoms in bcc $(Z_2) = 2$

Density of $fcc = d_{fcc} = \dfrac{Z_1 \times M}{V_1 \times N_A}$, N_A = Avogadro number

Atomic weight of metal = M, $V_1 = (3.5 \times 10^{-8})^3 = a_1^3$

$$d_{fcc} = \frac{4 \times M}{(3.5 \times 10^{-8})^3 \times N_A} \qquad \text{(i)}$$

$V_2 = (3.0 \times 10^{-8})^3$ volume of bcc unit cell

$$d_{bcc} = \frac{2 \times M}{(3 \times 10^{-8})^3 \times N_A} \qquad \text{(ii)}$$

Divide Eq. (i) by (ii)

$$\frac{d_{fcc}}{d_{bcc}} = \frac{4 \times M}{(3.5 \times 10^{-8})^3 \times N_A} \times \frac{(3 \times 10^{-8})^3 \times N_A}{2 \times M}$$

$$\frac{d_{fcc}}{d_{bcc}} = \frac{4 \times 27}{2 \times (3.5)^3} = 1.259$$

38. $d = 13.6$ g/mL
Atomic mass of Hg = 200 = M

1 g atomic weight of Hg = 200 g = weight of 6.023×10^{23} atoms

Number of atoms present in 1 g of Hg = $\dfrac{6.023 \times 10^{23}}{200}$
= 3.0115×10^{21}

Volume of 1 atom of Hg or unit cell = $\dfrac{1 \text{ g of Hg}}{\text{Number of atoms} \times \text{density}}$

$$= \frac{1}{13.6 \times 3.0115 \times 10^{21}} = 2.44 \times 10^{-23} \text{cm}^3$$

39. Since element has fcc structure hence there are 4 atoms in a unit cell (or $Z = 4$), Atomic mass is 60 (or $M = 60$), $N_A = 6.02 \times 10^{23}$ and $d = 6.23$ g cm^{-3}.

$$\because \quad d = \frac{Z \times M}{a^3 \times N_A} \quad \therefore \ a^3 = \frac{Z \times M}{d \times N_A}$$

$$= \frac{(4)\,(60 \text{ g mol}^{-1})}{(6.23 \text{ g cm}^{-3})(6.02 \times 10^{23} \text{mol}^{-1})}$$

$$= \frac{240 \times 10^{-23}}{37.5046} = 6.4 \times 10^{-23} \text{cm}^3$$

$$a^3 = 64 \times 10^{-24} \text{ cm}^3$$

$$\therefore \quad a = 4 \times 10^{-8} \text{ cm}$$

40. Length of the edge of the unit cell
$a = 654$ pm $= 6.54 \times 10^{-8}$ cm
$\therefore$ volume (V) of the unit cell = $(6.54 \times 10^{-8} \text{ cm})^3$
Molecular mass of KBr = 39 + 80 = 119 g mol^{-1}
Density of KBr = 2.75 g cm^{-3}

$$\because \quad d = \frac{Z \times M}{a^3 \times N_A} \quad \therefore \ Z = \frac{d \times a^3 \times N_A}{M}$$

$$= \frac{(2.75 \text{ g cm}^{-3})(6.54 \times 10^{-8} \text{cm})^3 (6.023 \times 10^{23} \text{ mol}^{-1})}{119 \text{ g mol}^{-1}}$$

$$= \frac{2.75 \times (6.54)^3 \times (6.023)(10^{-1})}{119} = 4$$

41. Use $d = \dfrac{Z \times M}{a^3 \times N_A} = \dfrac{\text{Total Mass}}{\text{Total volume}}$

42. $a^3 = 24 \times 10^{-24}$ cm^3 and $d = 7.2$ g cm^{-3}
Mass of the element (M) = 200 g
Number of the atoms (Z) per unit cell
= $(1/8) \times 8 + 1 \times 2 = 3$ atom

$$\because \quad d = \frac{Z \times M}{a^3 \times N} = \frac{\text{Total Mass}}{\text{Total volume}}$$

$$N = \frac{(3)\,(200 \text{ g})}{(24 \times 10^{-24} \text{cm}^3)(7.2 \text{ g cm}^{-3})}$$

$$N = 3.472 \times 10^{24} \text{atoms}$$

43. Atom A is every element of fcc = 4 atoms of A
Atom B is present at every octahedral void = 4 atoms of B
Atom C is present at 25% of tetrahedral void = $8 \times \dfrac{25}{100}$
= 2 atoms of C

So, the possible molecular formula is $A_4B_4C_2 = A_2B_2C$.

44. (Ans:- scc)

$$d = \frac{Z \times M}{a^3 N_A}$$

$$\therefore \quad Z = \frac{da^3 N_A}{M}$$

$$= \frac{9.00 \times (3.85 \times 10^{-8})^3 \times 6.02 \times 10^{23}}{240}$$

$$= 1.3 (= 1) \text{ being whole number}$$

Thus simple cubic lattice.

45. $r_{\mathrm{Pb}^{+2}} + r_{\mathrm{S}^{-2}} = 297$ pm

$a = 2 \times 297 \text{ pm} = 5.94 \times 10^{-8}$ cm

$V = a^3 = 2.096 \times 10^{-22}$ cm^3

46. $a\sqrt{3} = 2r_{\mathrm{Cl}^-} + 2r_{\mathrm{CS}^+}$

$412\sqrt{3} = 2 \times 181 + 2r_{\mathrm{CS}^+}$

$r_{\mathrm{CS}^+} = 175.8$ pm

47.

S.No.	Radius ratio	C.N.	Shape
1.	< 0.155	2	Linear
2.	[0.155 to 0.225)	3	triagonal planner.
3.	[0.225 to 0.414)	4	Tetrahedral
4.	[0.414 to 0.732)	6	Octahedral
5.	[0.732 to 1)	8	BCC

$$\mathrm{MgS} \Rightarrow \frac{r_{\mathrm{Mg}^{+2}}}{r_{\mathrm{S}^{-2}}} = \frac{0.65}{1.84} = 0.35$$

CN = 4

$$\mathrm{MgO} \Rightarrow \frac{r_{\mathrm{Mg}^{+2}}}{r_{\mathrm{O}^{-2}}} = \frac{0.65}{1.40} = 0.464$$

CN = 6

$$\mathrm{CsCl} \Rightarrow \frac{r_{\mathrm{Cs}^{+}}}{r_{\mathrm{Cl}^{-}}} = \frac{1.69}{1.81} = 0.933$$

CN = 8

48. $d = \dfrac{Z \times M}{a^3 N_A}$

$$\therefore \quad N_A = \frac{Z \times M}{a^3 \times d}$$

$$= \frac{4 \times 58.45}{(2 \times 2.184 \times 10^{-8})^3 \times 2.167}$$

$$= 6.05 \times 10^{23} \,\mathrm{mol}^{-1}$$

49. No. of atoms $= \dfrac{10}{100} \times N_A = 0.1\, N_A$

$$d = \frac{\left(2 \times \dfrac{10}{N_A}\right)}{(400 \times 10^{-10})} = 5.188 \text{ g/cm}^3$$

$$V_{\text{Total}} = \left(\frac{10}{5.188}\right) = 1.9275 \text{ cm}^3$$

$$\Rightarrow \quad \text{Number of unit cells} = \frac{1.9275}{(400 \times 10^{-10})}$$

$= 3.0115 \times 10^{22}$ unit cells

50. $d = \dfrac{4 \times \left(\dfrac{58.5}{N_A}\right)}{(0.564 \times 10^{-7})^3} = 2.16 \text{ gm/cm}^3$

51. $\mathrm{Fe_{0.93}O}$

$\Rightarrow \quad x \times 3 + y \times 2 = 2$ (i)

$x + y = 0.93$ (ii)

$$\% \, \mathrm{Fe}^{+2} = \frac{y}{0.93} \times 100 = 15.053\%$$

52. Since one Sr^{+2} can replace two Na$^+$ So each doping will create vacancy so total vacancy per mole

$$= 6.023 \times 10^{23} \times \frac{10^{-3}}{100} = 6.023 \times 10^{18}$$

53. $V = \left[a^2 \dfrac{\sqrt{3}}{4} \times 2\right] \times b$

$$d = \frac{Z \times \dfrac{M}{N_A}}{\mathrm{V}} = \frac{Z \times \dfrac{18}{6.023 \times 10^{23}}}{\left[\dfrac{\sqrt{3}}{2} \times (4.53)^3 \times (10^{-8})^2 \times (7.6 \times 10^{-8})\right]}$$

$Z = 4$

54.

$$\begin{array}{cc} x & y \\ 8 \times \dfrac{1}{8} & 6 \times \dfrac{1}{2} \Rightarrow \mathrm{XY_3} \end{array}$$

$$d = \frac{\text{Mass of unit cell}}{a^3} = \frac{\dfrac{1 \times [60 + 3 \times 90]}{6.023 \times 10^{23}}}{(5 \times 10^{-8} \text{ cm})^3}$$

$= 4.38$ gm/cm^3

55. Density $d = \dfrac{Z \times M}{a^3 N_A}$

$$= \frac{7.2 \times 6.02 \times 10^{23} \times (2.88 \times 10^{-8})^3}{2} = 51.77 \text{ g mol}^{-1}$$

$$\therefore \quad 52.0 \text{ g} = \frac{52.0}{51.77} \text{mol} = \frac{52 N_A}{51.77} = 6.05 \times 10^{23} \text{atoms}$$

56. For fcc structure,

Edge length $r(\mathrm{M}^+) + r(\mathrm{Cl}^-) = \dfrac{a}{2}$

$$r(\mathrm{M}^+) + r(\mathrm{Cl}^-) = \frac{6.28}{2} = 3.14 \text{ Å}$$

$r(\mathrm{M}^+) = 3.14 - 1.8173 = 1.3227$ Å

57. (a) Number of Mn atoms at corners $= 8 \times \dfrac{1}{8} = 1$

Number of F atoms at faces $= \dfrac{6}{2} = 3$

Empirical formula = MnF_3

(b) C.N. = 6 structure being fcc type

(c) $a = 2(r_+ + r_-) = 2(0.65 + 1.36) = 4.02$ Å

(d) Total atoms in the unit cell = 4 [one Mn and three F]

∴ $z = 1$

$$d = \frac{Z \times M}{a^3 N_A} = 2.86 \text{ g/cm}^3$$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. **(b)** Number of per atom unit cell in bcc and fcc are 2 and 4 respectively.
2. **(c)** One unit cell of NaCl contains 4 NaCl units which has

$$\text{Mass} = \frac{4 \times 58.5}{6.02 \times 10^{23}} \text{ g}$$

∴ number of unit cells in

$$1\text{g} = \frac{6.02 \times 10^{23}}{4 \times 58.5} = 2.57 \times 10^{21}$$

3. (i) $d = \dfrac{Z \times M}{a^3 \times N_A}$

$$a = 2Y^{1/3} \times 10^{-9} \text{ m}$$

$$M = 6.023\, Y = \frac{6.023}{1000} Y \text{kg.} = 6.023 \times 10^{-3}\, Y \text{kg}$$

$$d = \frac{4 \times 6.023 \times 10^{-3} \times \text{Y}}{6.023 \times 10^{23} \times (2Y^{1/3} \times 10^{-9})^3}$$

$$= \frac{4 \times 6.023 \times 10 \times \text{Y}}{6.023 \times 8 \times \text{Y}}$$

$$d = 5 \text{kg/m}^3$$

(ii) Observed density is higher – non-stoichiometric defect.

4. **(b)** As equal number of Na^+ and Cl^- ions are missing from their lattice site so it is Schottky defect.
5. $d = \dfrac{Z \times M}{a^3 \times N_A}$

$$2 = \frac{Z \times 75}{(5 \times 10^{-8})^3 \times 6 \times 10^{23}} \Rightarrow Z = 2 \text{(bcc)}$$

For bcc: $r = \dfrac{\sqrt{3}}{4} \times a = \dfrac{\sqrt{3}}{4} \times 5$

$r = 216.5$ nm

6. **(c)** Total number of atoms in fcc = $Z = 4$

Assuming atom to be spherical, its volume = $\dfrac{4}{3}\pi r^3$

Total volume of all atoms present in fcc

$$= \frac{4 \times 4\pi r^3}{3} = \frac{16}{3}\pi r^3$$

7. **(a)** Since element Y form lattice reference

∴ Number of Y atom in one unit cell = 4

Number of tetrahedral voids = 2 × 4 = 8

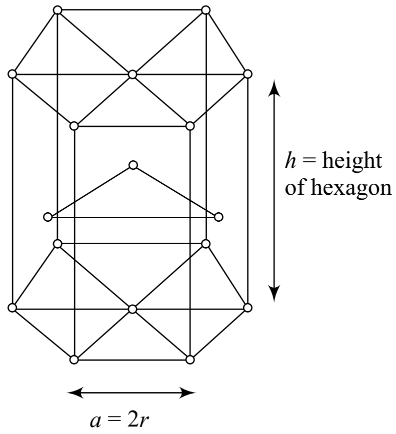
∴ Number of X atom per unit cell

$$= \frac{2}{3} \times 8 = \frac{16}{3}$$

∴ Formula = $X_{\frac{16}{3}} Y_{\frac{4}{1}} = X_{16}Y_{12} = X_4Y_3$

Paragraph for Question No. 8 to 9

8. **(a)**



Effective no. of atoms in unit cell (Z)

$$= \left[1 \times \frac{1}{2} + 6 \times \frac{1}{6}\right] \times 2 + 3 \times 1 = 6$$

∴ $Z = 6$

Total atoms = 6

Volume of hexagonal unit cell = $6 \times \dfrac{\sqrt{3}}{4} a^3 \times h$

Since $\dfrac{\frac{h}{2}}{a} = \dfrac{\sqrt{2}}{\sqrt{3}}$

∴ $h = 4r\dfrac{\sqrt{2}}{\sqrt{3}}$

and $V = 6 \times \dfrac{\sqrt{3}}{4} \times (2r)^2 \times 4r\dfrac{\sqrt{2}}{\sqrt{3}} = 24\sqrt{2}\, r^3$

9. **(d)** ∴ Packing fraction

$$= \frac{6 \times 4/3\pi r^3}{24\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = 0.74.$$

Vacant space = 100 – 74 = 26%

10. **(d)** Diagonal = $4r = \sqrt{2} \times L$

$$L = \frac{4r}{\sqrt{2}}$$

Area = $L^2 = 8r^2$

Number of spheres = $1 + 4 \times \dfrac{1}{4} = 2$

Area of each = πr^2

Packing fraction = $\dfrac{2 \times \pi r^2}{8r^2} = \dfrac{\pi}{4} = 0.785$

11. **(c)** For fcc:

$$\sqrt{2}a = 4r$$

$$r = \frac{\sqrt{2}}{4} \times 361 = 127.6$$

12. **(b)** Number of $M = \frac{1}{4} \times 4 + 1 = 2$

Number of $X = \frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 4$

$$M_2X_4 = MX_2$$

14. **(a)** Given arrangement represents octahedral void and for this

$$\frac{r_+(\text{cation})}{r_-(\text{anion})} = 0.414$$

$$\frac{r(A^+)}{r(X^-)} = 0.414$$

$$r(A^+) = 0.414 \times r(X^-) = 0.414 \times 250 \text{ pm}$$
$$= 103.5 \text{ pm} = 104 \text{ pm}$$

14. **(b)** From the valency of M^{2+} and M^{3+}, it is clear that three M^{2+} ions will be replaced by two M^{+3} causing a loss of one M^{3+} ion. Total loss of them from one molecule of MO = 1 – 0.98 = 0.02

Total M^{3+} present in one molecule of

MO = 2 × 0.02 = 0.04

∴ total M^{2+} and M^{3+} = 0.98

Thus, % of $M^{3+} = \frac{0.04 \times 100}{0.98} = 4.08\%$

OR

$$2x + (0.98 - x) \times 3 = 1 \times 2$$

$$\% \text{ of } M^{+3} = \frac{0.98 - x}{0.98} \times 100 = 4.08\%$$

15. **(b)** Silicon exists as covalent crystal in solid state. (Network like structure, as seen in diamond.)

16. **(c)** In CsCl, Cl^- lies at corners of simple cube and Cs^+ at the body centre. Hence, along the body diagonal, Cs^+ and Cl^- touch each other so

$$2(r_{Cs^+} + r_{Cl^-}) = \sqrt{3}a$$

Hence, ∴ $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$

17. **(a)** For bcc unit cell, $\sqrt{3}a = 4r$

$$r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 4.29 \text{ Å} = 1.86 \text{ Å}$$

Chapter 5

Surface Chemistry

Key Concepts

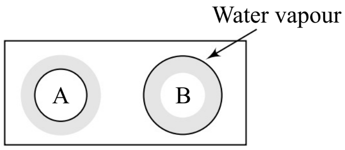
Surface chemistry is the branch of chemistry that deals with the properties and processes occurring at the surface or interface that is the boundary separating two bulk phases.

ADSORPTION

The phenomenon of attracting and retaining the particles of a substance on the surface of a solid or a liquid resulting in a higher concentration at the surface rather than the bulk is known as adsorption.

- → The substance of the surface of which the process of adsorption takes place is known as adsorbent (s/*l*).
- → The substance which is gating adsorbed on the surface is known as adsorbate (s/*l*/g).
- → The removal of adsorbate from the surface of adsorbent is known as desorption.
- → The adsorption of gases on the surface of a metal is known as occlusion.

Adsorption	Absorption
→ In the process of adsorption the concentration of the substances increases only at the surface of adsorbent.	→ In the process of absorption the concentration of the substances is uniformly distributed throughout the bulk of the solid or liquid.
→ It is a surface phenomenon.	→ It is a bulk phenomenon.
→ The rate of adsorption decreases with time.	→ The rate of absorption is uniform through out the process.
For example, NH_3 on charcoal	For example, NH_3 in water



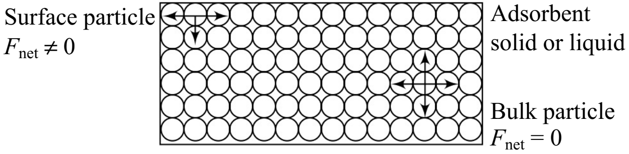
A ⇒ Silica Gel (Adsorption)
B ⇒ Anhydrous $CaCl_2$ (Absorption)

If the process of adsorption and absorption both occur simultaneously then the process is known as sorption.

For example, Chalk dipped in Ink.

Mechanism of Adsorption

The particles present in the bulk and at the surface of a substance are under different conditions. The forces acting on the bulk particles are mutually balanced as they are surrounded by the same type of particles from all sides but the particles on the surface have unbalanced or residual attractive forces as they are not surrounded by same type of particle from all sides as a result they have a tendency to attract and retain the particles of other substance on their surface.



Thermodynamic approach for Adsorption
ΔH adsorption = –ve [Due to decrease in surface energy]
ΔS adsorption = –ve [Due to decrease in degree of movement]

As we know,

$$\Delta G = \Delta H - T\Delta S$$
$$= -\Delta H + T\Delta S$$
$$\therefore \quad \Delta G_{\text{adsorption}} = -\Delta H + T\Delta S$$

(i) At low temperature

$\Delta H > T\Delta S$

$\therefore \quad \Delta G = -\text{ve}$

Adsorption is spontaneous

(ii) At high Temperature

$\Delta H < T\Delta S$

$\Delta G = +\text{ve}$

Adsorption is non-spontaneous

(iii) When $T = \dfrac{\Delta H}{\Delta S}$

then $T\Delta S = \Delta H$

$\therefore \Delta G = 0$

Hence, equilibrium is attained in between adsorption and desorption.

$$\text{Adsorbate + Adsorbent} \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Adsorbed}$$

Types of Adsorption

1. **Physical Adsorption** → Also called physisorption.
   → When the particle of adsorbate are held to the surface of adsorbent by the weak Van der Waal forces. Then, the process is called physical adsorption.
2. **Chemical Adsorption** → Also called Chemisorption.
   → When the particles of the adsorbate held to the surface of adsorbent due to the formation of strong chemical bonds then, the process is called chemical adsorption.
   → The bond may be covalent or ionic and it requires activation energy. Hence, it is also known as activated adsorption.

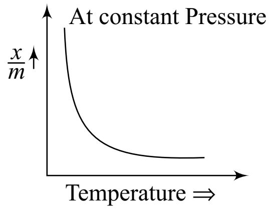
Physical Adsorption	Chemical Adsorption
→ Not specific in nature	→ Specific
→ Activation energy is not required	→ Activation energy is required
→ It arises due to weak Van der Waal forces	→ It arises due to formation of strong chemical bonds
→ Heat of adsorption is low, i.e., from –20 to –40 kJ mol^{-1}	→ Heat of adsorption is high, i.e., from –80 to –240 kJ mol^{-1}
→ Reversible in nature	→ Generally irreversible in nature
→ Multi layer of adsorbate are formed on the surface of adsorbent	→ Mono layer is formed on the surface of adsorbent
→ Low temperature is favourable for adsorption and extent of adsorption decreases with the increase in temperature	→ Favourable at high temperature and extent of adsorption decreases with increase in temperature

Note: I
The process of physical adsorption occuring at a low temperature can be converted to chemical adsorption at a higher temperature.

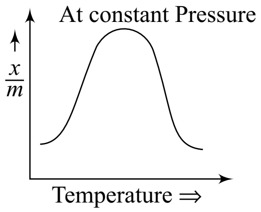
For example, adsorption of Hydrogen on the surface of Ni to form metal hydride.

FACTORS EFFECTING ADSORPTION

1. **Surface Area of Adsorbent**
   Surface area ∝ Extent of Adsorption
2. **Nature of Adsorbate**
   (i) In chemical adsorption, the particles of the adsorbate adsorb on the surface of adsorbent only if they are able to make chemical bonds.
   For example, Oxygen is adsorbed on the surface of metals to form metal oxides.
   For example, Hydrogen is adsorbed on the surface of transition metals to form metal hydrides.
   (ii) In physical adsorption critical temperature (Tc)
   Tc ∝ Ease of Liquification ∝ Extent of Adsorption
   For example, H_2 N_2 CO CH_4 CO_2 HCl NH_3 SO_2
   If Tc increases, Ease of liquification increases Extent of adsorption increases.
3. **Effect of Temperature**
   ⇒ **Extent of Adsorption** → $\left(\dfrac{x}{m}\right)$
   It is defined as the mass of adsorbate adsorbed per unit mass of adsorbent.
   x ⇒ Mass of adsorbate
   m ⇒ Mass of adsorbent



(A) Physisorption



(B) Chemisorption

→ These curves are called adsorption of isobars.
(A) ⇒ The extent of physical adsorption decreases with increase of temperature because the strength of Van der Waal forces decreases with increase in temperature and also as the process is exothermic.
(B) ⇒ The extent of chemical adsorption firstly increases with temperature because it requires activation energy for the bond formation and after that on increasing the temperature the extent of chemical adsorption decreases because the process is exothermic.

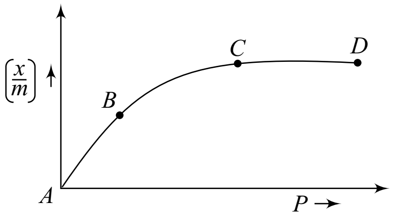
4. **Effect of Pressure**
   The variation in extent of adsorption with change in pressure at constant temperature can be explained with the help of some graphs called adsorption isotherms.

(A) Freundlich adsorption isotherm: For physisorption

→ He explained the variation in adsorption due the change in pressure graphically and mathematically as follows.

→ Adsorbate – Gas

→ Adsorbent – Solid



Case-I At low pressure (A → B)

$$\frac{x}{m} \propto P$$

Case-II At high pressure (C → D)

$$\frac{x}{m} \propto P^{\circ}$$

Case-III At intermediate pressure (B → C)

$$\frac{x}{m} \propto P^{1/n} \text{ [where } n = 1 \text{ to } \infty]$$

The resultant condition $\frac{x}{m} = KP^{1/n}$

At low $P \Rightarrow n = 1$

At high $P \Rightarrow n = \infty$

At intermediate $P \Rightarrow 1 < n < \infty$

$\therefore$ the value of $(1/n)$ ranges from 0 to 1.

Here $x \Rightarrow$ Mass of adsorbate

$m \Rightarrow$ Mass of adsorbent

$P \Rightarrow$ Pressure of adsorbate gas

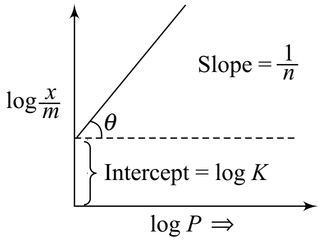
K and $n \Rightarrow$ Constants that depends on the nature of adsorbate and adsorbent.

Note: 1

For adsorption of solute in the solution, the expression for Freundlich adsorption isotherm can be given as:

$\frac{x}{m} = KC^{1/n}$ where, $C \Rightarrow$ Concentration of solution.

Logarithmic form of Freundlich adsorption Isotherm



As we know

$$\frac{x}{m} = KP^{1/n}$$

Taking log on both sides

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log P$$

(B) Langmuir Adsorption Isotherm: For chemical adsorption

Postulate–1 He postulated that, the particles of adsorbate can only form a single layer in depth on the surface of adsorbent.

Postulate–2 There is no interaction in between the adjacent adsorbed particles.

Postulate–3 There is a dynamic equilibrium in between the process of adsorption and desorption.

Postulate–4 All surface sides have equal tendency to attract and retain the particles of adsorbate.

$\frac{x}{m} = \frac{aP}{1+bP}$ where, a and b are Langmuir constant.

(i) At low P,

$$1 + bP \simeq 1$$

So, $\frac{x}{m} = aP$

$$\therefore \left[\frac{x}{m} \propto P\right]$$

(ii) At high P,

$$1 + bP \simeq bP$$

So, $\frac{x}{m} = \frac{aP}{bP} = \frac{a}{b}$

$$\therefore \left[\frac{x}{m} \propto P^{\circ}\text{(constant)}\right]$$

* As we know,

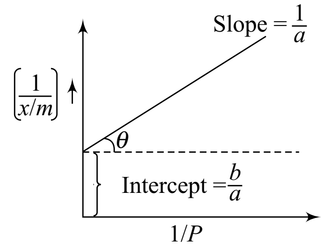
$$\frac{x}{m} = \frac{aP}{1+bP}$$

It can be written as

$$\frac{1}{(x/m)} = \frac{1+bP}{aP} = \frac{1}{aP} + \frac{b}{a}$$

$$\therefore \frac{1}{x/m} = \frac{1}{a} \times \frac{1}{P} + \frac{b}{a}$$

$$\equiv y = mx + C$$



Note: 2

Exception,

H_2 + Glass (Endothermic)

(II) Colloids → Colloids are heterogeneous system in which a substance (dispersed phase) is dispersed as very fine particles in dispersion medium.

→ **Colloid have two parts:**

(i) Dispersed phase ⇒ The substance which is present in lesser amount just like solute in true solution is known as dispersed phase.

(ii) Dispersion medium ⇒ The substance which is present in greater amounts just like solvent in true solution is known as dispersion medium.

*** Classification of solution on the basis of size of particles.**

Properties	**True Solution**	**Colloids**	**Suspension**
1. Size of particle	Less than 1 nm	between 1-1000 nm	Greater then 1000 nm
2. Nature	Homogenous	Heterogenous	Heterogenous
3. Visibility	Not visible	Visible under microscope	Visible with naked eye
4. Separation			
(i) Filter paper	×	×	√
(ii) Membrane	×	√	√
5. Tyndall effect	Do not show	Shows	May or may not show
6. Settling down of particles	Do not settle	Does not settles but under ultra centrifugation they can settle	Settles down
7. Ex-	$NaCl$, KCl in H_2O	Starch, Gum, Protein in H_2O	Sand Iron hails in H_2O

* Classification of Colloids:

(A) On the basis of physical state of dispersed phase and dispersion medium.

Dispersed Phase	**Dispersion medium**	**Colloids**	**Examples**
Solid	Solid	Solid Sol	Gem Stones
Solid	Liquid	Sol	Paints
Solid	Gas	Aerosol	Dust
Liquid	Solid	Gel	Cheese, Jellies
Liquid	Liquid	Emulsion	Milk, Hair Cream
Liquid	Gas	Aerosol	Fog, Cloud
Gas	Solid	Solid Sol	Pumice Stone
Gas	Liquid	Foam	Froth

(B) On the basis of Dispersion Medium

Dispersion Medium	**Colloid**
H_2O	Hydrosol OR Aquasol
Benzene	Benzosol
Air	Aerosol
Alcohol	Alcosol

(C) On the basis of Interaction in between dispersed phase and dispersion medium

Lyophilic (Solvent loving) **(Hydrophilic)** **Greater affinity**	**Lyophobic (Solvent lating)** **(Hydrophobic Lesser affinity)**
(i) When the particles of Dispresedphase have a greater affinity for the particles of dispersion medium, then the colloids are known as Lyophilic.	(i) When the particles of Dispresedphase have a lesser affinity for the particles of dispersion medium then the colloids are known as hyophobic.
(ii) Easily prepared just by mixing the dispersed phase with dispersion medium.	(ii) It requires special methods for preparation.
(iii) More stable	(iii) Less stable (requires, stabilising agent)
(iv) Reversible in nature	(iv) Irreversible in nature
(v) Coagulation is not so easy.	(v) Easily coagulated
(vi) Higher degree of solvation or hydration	(vi) Lower degree of hydration or solvation
(vii) Viscosity is more and surface tension is less as compared to that of dispersion medium	(vii) Viscosity and surface tension are nearly the same as that of dispersion medium.
For example, generally of organic nature like sols of protein, starch, etc.	For example, generally of inorganic nature like sols of metals metal sulphides, etc.

(D) On the basic of type of particles of dispersed phase

(i) Multi-molecular colloids

On dissolution a large number of atoms or smaller molecules aggregate together to form particles whose size lies in the colloidal range such type of systems are known as multi-molecular colloids.

For Example,

An (gold) sol and sulphur solution in sulphur sol

1 Dispresed phase particle = 1000 or more S_8 molecules

(ii) Macro-molecular colloids

Macro-molecules (having higher molecular mass) in a suitable solvent forms solution in which their size lies in the colloidal range such systems are known as macro-molecular colloids.

For example, Starch, protein (Natural macro-molecules) Nylon, polyethene (Man made macro-molecules)

(iii) Associated colloids

→ There are some substances which behave as strong electrolytes at lower concentration but at higher concentration they exhibit colloidal behaviour due to formation of aggregates. The aggregate thus formed are known as micelles and the system is known as associated colloids.

→ The temperature and the concentration above which the formation of micelles occurs is known as craft temperature and Critical Micelle Concentration (CMC).

For example, Surface acting agents (Surfactant's) like soap and detergent.

(A) Anionic Surfactants

Sodium stearate ⇒ $C_{17}H_{35}COO^{-}Na^{+}$ (Soap) sodium lauryl sulphate

$$CH_3(CH_2)_{11}SO_4^{-}Na^{+}\text{(Detergent)}$$

(B) Cationic surfactants

Catyl Trimethyl ammonium Chloride ⇒ $C_{16}H_{33}(CH_3)_3N^{+}Cl^{-}$

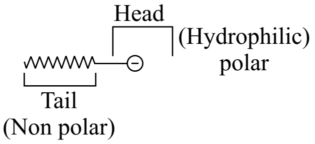
Octadecyl ammonium chloride ⇒ $C_{18}H_{37}NH_3^{+}Cl^{-}$

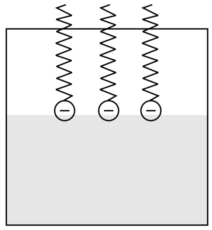
⇒ Associated colloids have both lyophilic and hyophobic part. A micelle may contain 100 or more ions.

Mechanism of micelle formation

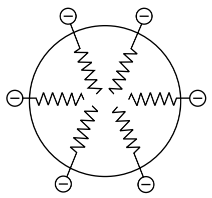
$C_{17}H_{35}COONa \rightarrow C_{17}H_{35}COO^{-}$ (stearate) + Na^{+}

or RCOONa and $RCOO^{-}$ and Na^{+}





(a) Arrangement of stearate ions on the surface of water before CMC.



(b) Micelle formation on at CMC. (Non-polar tails towards centre. Polar on surface of sphere.

Methods of Preparation

1. **Lyophilic colloids**

   They are easily prepared just by mixing the particles of dispersed phase with the dispersion medium.

2. **Lyophobic Colloids (intrinsic colloid)**

   These colloids are prepared by the following methods:

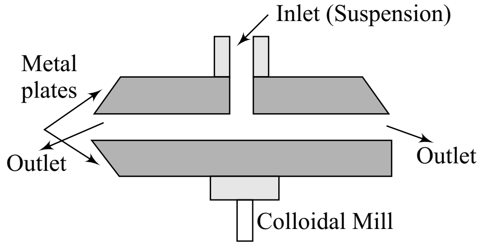
(A) Dispersion method

(B) Condensation method

(A) Dispersion Method

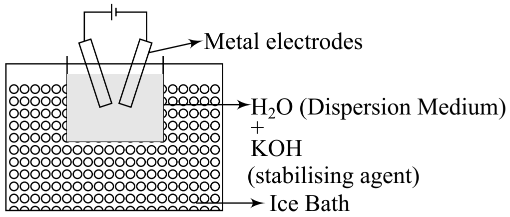
In these methods larger particles are broken into smaller particles.

(i) Mechanical Dispersion



In this method, the particles of the suspension are grinded to colloidal sized particles by placing it in between two metal plates that rotates in opposite direction in a Colloidal mill. This method is used for preparing the colloids of paints, varnises, dies, etc.

(ii) Electrical dispersion Bridics Arc Method



→ In this method, on striking an electric arc in between the metal electrodes result in the vapourisation of metal which is then condensed by the effect of ice bath. This metal disperses in water and hence forms a colloid. This method is used for preparing colloids of metal like Au, Ag, Pt, etc.

(iii) Peptisation

$$\underset{\text{Precipitate}}{Fe(OH)_3} + \underset{\text{Electrolyte}}{FeCl_3} \longrightarrow \underset{\text{Colloid}}{Fe(OH)_3|Fe^{3+}}$$

Precipitate + Dispersion Medium + Electrolyte (Small amount) ⇒ Sol.

$$\text{Electrolyte used as}\begin{bmatrix}\text{Peptidising agent}\\ \text{i.e., stabilising}\\ \text{agent}\end{bmatrix}$$

→ The process of converting a freshly prepared Precipitate into a colloidal solution by adding electrolyte is known as peptisation.

→ The electrolyte used in this process are known as peptising agents.

→ This process involves the adsorption of suitable ion (common ion) on the surface of Precipitate provided by the added electrolyte. As, a result the charged particles repell each other and thus forms a colloid.

(B) Condensation Method

In these methods smaller particle are aggregated together to the colloidal size.

(i) Chemical Method

$$\rightarrow As_2O_3 + 3H_2S \xrightarrow[\text{decomposition}]{\text{double}} As_2S_3(sol) + 3H_2O$$

$$\rightarrow H_2S + Br_2 \xrightarrow{\text{Oxidation}} 2HBr + S(sol)$$

$$\rightarrow 2AuCl_3 + 3SnCl_2 \xrightarrow{\text{Reduction}} 2Au(sol) + 3SnCl_4$$

$$\rightarrow FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3(sol) + 3HCl$$

→ In chemical reactions the molecules form aggregate together to form particles that lie in the colloidal range.

(ii) Physical Methods

(a) By exchange of solvent: In this method, a true solution is mixed with an excess of solvent in which the solute is less soluble and the solvent is completely miscible.

$$\begin{bmatrix} \text{Sulphur in } C_2H_5OH \\ \textbf{True solution} \end{bmatrix} + H_2O = \begin{bmatrix} \text{Sulphur in Alcoholic } H_2O \\ \textbf{Colloidal} \end{bmatrix}$$

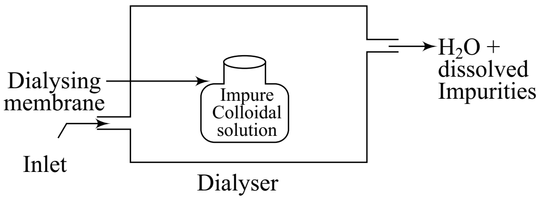
(b) By excessive cooling: In this method on excessive cooling, the molecules of a substance condense together to form particles of the colloidal range.

$$H_2O + CHCl_3 \xrightarrow[\text{Cooling}]{\text{On excessive}} \boxed{\text{ice} + CHCl_3} \Rightarrow \text{Colloidal}$$

(c) By condensing vapors: In this method the vapour of sulphur or Hg are passed through cold water containing ammonium nitrate.

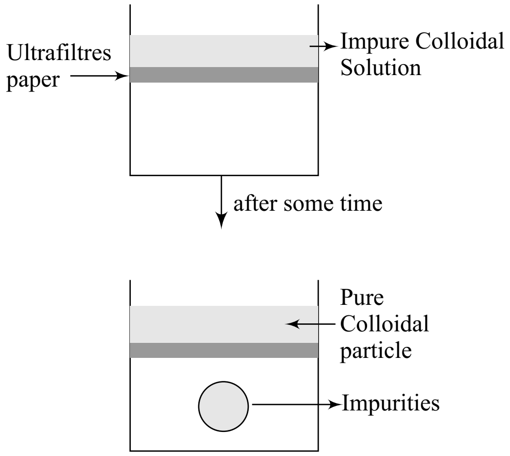
PURIFICATION OF COLLOIDS

1. **Dialysis:**



→ This process involves the diffusion of dissolved impurities through the membrane and leaving behind a pure colloidal solution.

2. **Electrodialysis:** This method is used when the impurities are electrolytes.
3. **Ultrafiltration:**
Ultra filter paper = Filter paper + Collodion solution
[4% Nitro – Cellulose is a mixture of alcohol and ether]



4. **Ultra centrifugation:** In this method, the tube is rotated at a very high speed as a result of which pure colloidal particles settle down and the impurities remain in the solution. These pure colloidal particles are collected and mixed with the dispersion medium to form colloidal solutions.

PROPERTIES OF COLLOIDAL SOLUTIONS

1. **Heterogeneous nature:**
2. **Visibility:** Colloidal particles are too small to be seen with naked eye, but they become visible as bright spots against dark background when viewed through an ultra microscope due to scattering of light caused by them.
3. **Filterability:** The size of solute particles is smaller than the pore size of filter paper, and therefore, they can readily pass through ultra filters, parchment paper, or animal membrane.
4. **Surface tension and viscosity:** The surface tension and viscosity of lyophobic sols are not very different from those of the dospersion medium. On the other hand, lyophilic sols show higher viscosity and lower surface tension in comparison to the dispersion medium.
5. **Colligative properties:** very low due to high molar mass.
6. **Brownian movement:** The colloidal particles of a colloidal solution when viewed through an ultramicroscope show a constant zig – zag motion. This type of motion was first observed by robert brown and is known as brownian movement. This motion is independent of the nature of the colloid but depends on the size of the par-

ticles and the viscosity of solution. Smaller the size and lesser the viscosity, faster is the motion. The Brownian movement is due to the unbalanced bombardment of the particles by the molecules of the dispersion medium.

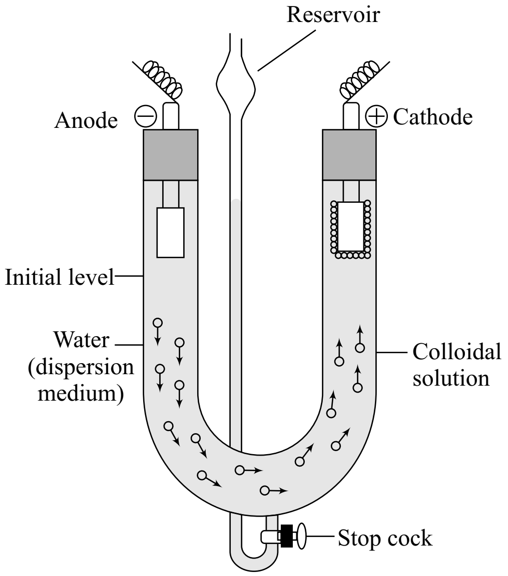
7. **Optical Properties: Tyndall effect:** The scattering of light by the colloidal particles in a colloidal solution is known as tyndall effect as it was first observed by Faraday and later studied in detail by Tyndall. Tyndall effect is caused by the scattering of blue part of light by the colloidal particles.

Tyndall effect is observed only when the following two conditions are satified:

The diameter of the dispersed particles is not much smaller than the wavelength of the light used. The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude.

Zsigmondy:- Tyndall effect to set up an apparatus known as ultramicroscope.

8. The electrical properties of colloidal solutions are related with two phenomena:



(i) **Electrophoresis:** The existance of charge on colloidal particles is determined by electrophoresis.

The phenomenon of the movement of colloidal particles under an applied electric field is called electrophoresis. The positive charged particles move towards the cathode while negatively charged particles move toward the anode.

(ii) **Electro – osmosis:** Electro – osmosis may be defined as a phenomenon in which the molecules of the dispersion medium are allowed to move under the influence of an electric field whereas colloidal particles are not allowed to move.

The direction of the flow of water (dispresion medium)depends on the charge of the colloid. For positively charged sols, the medium is negatively charged, and hence the flow will take place from one side to other. On the other hand, for negatively charged sols, the reverse will occur.

9. **Coagulation or precipitation or floculation of colloids:-**

The process of settling of colloidal particles is called coagulation or Precipitation of the sol. The coagulation of the lyophobic sols can be carried out in the following ways.

(a) By electrophoresis
(b) By mixing two oppositely charged sols
(c) By boiling
(d) By persistent dialysis
(e) By addition of electrolytes

Colloids Around US

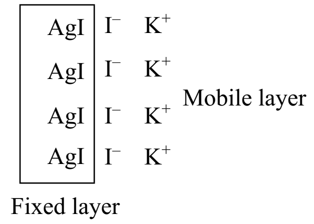
(a) Blue colour of the sky
(b) Fog, mist and rain
(c) Food articles :- Milk, butter, halwa
(d) Blood :- It is a colloidal solution of an albuminoid substance.
(e) Soils :-
(f) Formation of delta:-

Application of colloids

(a) Electrical precipitation of smoke
(b) Purification of drinking water
(c) Medicines
(d) Tanning
(e) Cleasing action of soaps and dettergents
(f) Photographic plates and films
(g) Rubber industry
(h) Industrial products

Zeta potential:

The potential difference between the fixed layer and the diffused layer of opposite charges is called electro kinetic potential or zeta potential.



Hordy sulzi rule: Greater the valency of the active ions or flocculating ion greater will be its flocculating power

For example,

(i) $Al^{+3} > Mg^{+2} > Na^{+}$ for –ve sol.

(ii) $[Fe(CN)_6]^{-4} > PO_4^{-3} > SO_4^{-2} > Cl^{-}$ for +ve sol

Gold Number: The protective power is measured in terms of gold number. It is defined as the number of milligrams of a lyophilic colloid that will just prevent the precipitation of 10 mL of a gold sol on the addition of 1 mL of 10% NaCl solution

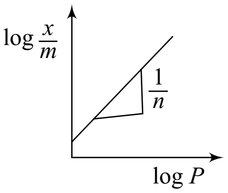
$$\text{Protective Power} \propto \frac{1}{\text{Gold Number}}$$

Positively charged colloid	Negatively charged colloid
Hydrated metallic oxide $Al_2O_3.\,xH_2O$, $CrO_3.\,xH_2O$, $Fe_2O_3.\,xH_2O$	Metals Cu, Ag, Au, Sol Metalic sulphides As_2S_3, Sb_2S_3, CdS sol
Basic dye stuffs methylene blue sol, Haemoglobin (blood)	Acid dye stuff eosin, congo red
Oxide TiO_2 Sol	Sols of starch, gum gelatin, clay

Solved Examples

1. For a linear plot of log (x/m) versus log P in a Freundlich adsorption isotherm, which of the following statements is correct? (k and n are constants)
(a) $1/n$ appears as the intercept.
(b) Only $1/n$ appears as the slope.
(c) log $(1/n)$ appears as the intercept
(d) Both k and $1/n$ appear in the slope term.

Sol. (b)



$$\frac{x}{m} = Kp^{\frac{1}{n}}$$

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log P$$

$$y = +C + mx$$

2. The coagulation values in millimoles per litre of the electrolytes used for the coagulation of As_2S_3 are given below:
I. (NaCl) = 52 II. ($BaCl_2$) = 0.69
III. ($MgSO_4$) = 0.22
The correct order of their coagulating power is
(a) III > I > II (b) I > II > III
(c) II > I > III (d) III > II > I

Sol. (d)

$$\text{Coagulation value} \propto \frac{1}{\text{Coagulating power}}$$

NaCl (52)	$BaCl_2$(0.69)	$MgSO_4$(0.22)
(I)	(II)	(III)

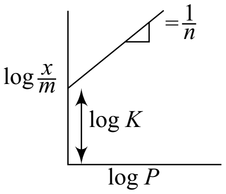
∴ coagulating power for As_2S_3

$MgSO_4 > BaCl_2 > NaCl$

III > II > I

3. Plot of log $\left(\frac{x}{m}\right)$ against log P is a straight line inclined at an angle of 45°. When the pressure is 0.5 atm and Freundlich parameter (K) is 10, then the amount of solute adsorbed per gram of adsorbent will be (log 5 = 0.699):
(a) 1 g (b) 6.99 g
(c) 3 g (d) 5 g

Sol. (d) $\log\frac{x}{m} = \log K + \frac{1}{n}\log P$



$y = +c + mx$

tan 45 = 1

$$\log\frac{x}{1} = \log 10 + 1\log(0.5)$$

$$\log x = \log 10 + 1 \times \log[5 \times 10^{-1}]$$

$$\log x = 1 + (-1) + .6990 = .6990 = \log 5$$

∴ x = 5 gram

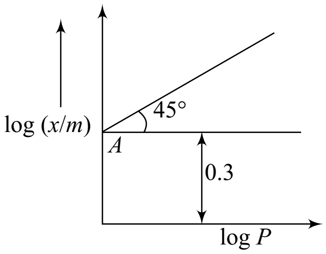
4. Gold number is a measure of
(a) stability of colloidal system.
(b) coagulating power of a colloid.
(c) size of colloidal particles.
(d) efficiency of the protective colloid.

Sol. (d) Smaller is the gold number, higher is its protecting power.

Gelatin	–	.005 to .01
Haemoglobin	–	0.03
Gum	–	0.15
Egg albumin	–	.08–.10
Starch	–	25–40

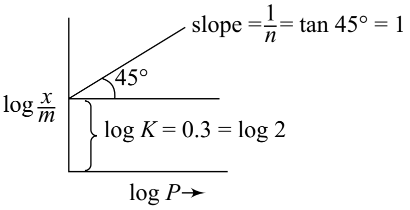
Gold No. The minimum amount in milligram of protective colloid which must be added to 10 mL gold sol in order to prevent its coagulation against 1 mL 10% NaCl solution.

5. Graph between log $\left(\frac{x}{m}\right)$ vs log P is provided for adsorption of NH_3 gas on metal surface.
Calculate weight of NH_3 gas adsorbed by 50 g of metal surface at 2 atm pressure.



(a) 100 g (b) 75 g
(c) 200 g (d) 50 g

Sol. **(c)** slope $= \frac{1}{n} = \tan 45° = 1$



$$\frac{x}{m} = KP^{\frac{1}{n}}$$

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log p$$

$$= \log 2 + \frac{1}{n} \log 2$$

$$\log \frac{x}{m} = \log 2 + (1) \log 2$$

$$\frac{x}{m} = 2 \times 2$$

$$\frac{x}{50} = 4$$

$$x = 200 \text{ g}$$

6. Which of the following parameter is correct regarding adsorption of gases over solid?
(a) $\Delta S_{\text{system}} > 0$ (b) $\Delta S_{\text{surrounding}} > 0$
(c) $\Delta G > 0$ (d) $\Delta H > 0$

Sol. **(b)** Adsorption
$\Delta H = -\text{ve}$
$\Delta S = -\text{ve}$
$\Delta G = -\text{ve}$
$\Delta\text{Surr.} = 0$

7. Fe $(SCN)_n^{3-n}$ absorb colour because of the complex $Fe(SCN)_n^{3-n}$ only, whereas Fe^{3+} and SCN^- both are colourless. In the given table, the equilibrium concentration of Fe^{3+} and SCN^- and corresponding absorbance are given–

Exp. No.	$[Fe^{3+}]$	$[SCN^-]$	Absorbance
1	3×10^{-3}(M)	(10 M)	3
2	3×10^{-3}(M)	$(10)^{2/3}$(M)	0.3

Considering absorbance proportional to concentration of the complex, the value of n is
(a) 3 (b) 6 (c) 4 (d) 2

Sol. **(a)** $Fe^{3+} + nSCN^- \rightleftharpoons Fe(SCN)_n^{3-n}$

$$K_{\text{form}} = \frac{[\text{Complex}]}{[Fe^{3+}][SCN^-]^n}$$

$\because$ [complex] $= K_{\text{form}} [Fe^{3+}][SCN^-]^n$

$\therefore$ log [complex] $= \log K_{\text{form}} + \log [Fe^{3+}] + n \log [SCN^-]$

$[Fe^{3+}]$ is constant, hence

$$\log \frac{[\text{Complex}]_1}{[\text{Complex}]_2} = n \log \frac{[SCN^-]_1}{[SCN^-]_2}$$

$$\therefore \quad \log 3/0.3 = n \log \frac{10}{(10)^{2/3}}$$

$$1 = n \times \frac{1}{3}$$

or $n = 3$

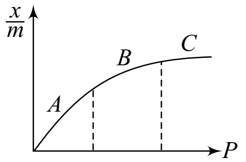
Exercise

LEVEL I

1. The formation of micelles (Associated colloids) takes place
(a) above CMC and at kraft temperature.
(b) at CMC and above kraft temperature.
(c) at CMC and at kraft temperature.
(d) above CMC and above kraft temperature.

2. Which of the following is an example of positively charged sols?
(a) As_2S_3 (b) Gold sol
(c) Congo red sol (d) Haemoglobin

3. When a graph is plotted between x/m versus pressure at constant temperature. The Freundlich equation at 'B' is (if $n > 1$)



(a) $\frac{x}{m} = kP^{\infty}$ (b) $\frac{x}{m} = kP^{\frac{1}{n}}$

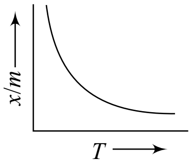
(c) $\frac{x}{m} = kP^{1}$ (d) $\frac{x}{m} = kP^{n}$

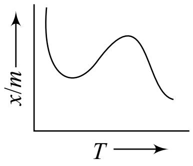
4. Gelatin is added in manufacture of icecream in order to
(a) prevent formation of a colloid.
(b) stabilise the colloid and prevent crystallisation.
(c) cause the mixture to solidify easily.
(d) improve flavour.

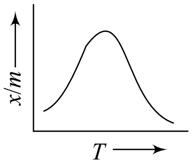
5. Which of the following statement is incorrect?

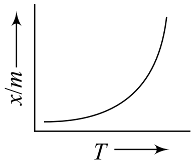
(a) Lyophilic sols are reversible.
(b) Lyophilic sols are more stable than lyophobic sols.
(c) Lyophobic sols require stabilising agent for their preservation.
(d) Lyophobic sols can be formed by direct mixing of dispersed phase and dispersion medium.

6. Which of the following graph represents the variation of amount of chemisorptions of a gas by a solid with temperature under constant pressure?

(a) 

(b) 

(c) 

(d) 

7. The colloidal sols are purified by

(a) Peptisation (b) Coagulation
(c) Dialysis (d) None of these

8. Which of the following is not heterogeneous?

(a) Emulsion (b) True solution
(c) Suspension (d) Colloidal solution

9. In multimolecular colloidal sols, atoms or molecules are held together by

(a) H-bonding (b) van der Waals forces
(c) ionic bonding (d) polar covalent bonding

10. Colloidal solution of gold prepared by different methods are of different colours because of

(a) variable valency of gold.
(b) different concentrations of gold particles.
(c) impurities produced by different methods.
(d) different diameters of colloidal gold particles.

11. Cod liver oil is

(a) fat dispersed in fat (b) fat dispersed in water
(c) water dispersed in fat (d) water dispersed in oil

12. Cellulose dispersed in ethanol is called

(a) emulsion (b) micelle
(c) collodion (d) hydrophilic solution

13. According to the adsorption theory of catalysis, the speed of reaction increases because

(a) adsorption lowers the activation energy of the reaction.
(b) the concentration of reactant molecules at the active centres of the catalyst becomes high due to adsorption.
(c) in the process of adsorption, the activation energy of the molecules becomes large.
(d) adsorption produces heat which increases the speed of the reaction.

14. Which one of the following characteristics is not correct for physical adsorption?

(a) Adsorption on solids is reversible.
(b) Adsorption increases with increase in temperature.
(c) Adsorption is spontaneous.
(d) Both enthalpy and entropy of adsorption are negative.

15. Identify the gas which is readily adsorbed by activated charcoal.

(a) N_2 (b) SO_2 (c) H_2 (d) O_2

16. The concentration of electrolyte required to coagulate a given amount of As_2S_3 sol is minimum in case of

(a) K_2SO_4 (b) $Al(NO_3)_3$
(c) $Mg(NO_3)_2$ (d) KNO_3

17. Plot of log x/m against log p is a straight line inclined at an angle of 45°. When the pressure is 4 atm and Freundlich parameter, k is 10, the amount of solute adsorbed per gram of adsorbent will be (log 5 = 0.6990)

(a) 2 g (b) 4 g (c) 16 g (d) 40 g

18. Which one of the following is an example for homogeneous catalysis?

(a) Manufacture of sulphuric acid by contact process.
(b) Manufacture of ammonia by Haber's process.
(c) Hydrolysis of sucrose in presence of dilute hydrochloric acid.
(d) Hydrogenation of oil.

19. The efficiency of enzyme catalysis is due to its capacity to

(a) form a strong enzyme-substrate complex.
(b) change the shape of the substrate.
(c) lower the activation energy of the reaction.
(d) form a colloidal solution in water.

20. Which of the following reaction is an example for homogeneous catalysis?

(a) $2H_2O_2(l) \xrightarrow{MnO_2(s)} 2H_2O(l) + O_2(g)$
(b) $2SO_2(g) + O_2(g) \xrightarrow{V_2O5(s)} 2SO_3(g)$
(c) $2CO(g) + O_2(g) \xrightarrow{NO(g)} 2CO_2(g)$
(d) $H_2(g) + C_2H_4(g) \xrightarrow{Ni(s)} C_2H_6(g)$

21. Which of the following electrolytes is least effective in coagulating ferric hydroxide solution?

(a) KNO_3 (b) K_2SO_4
(c) $K_2Cr_2O_7$ (d) $K_4[Fe(CN)_6]$

22. Example of intrinsic colloid is

(a) glue (b) sulplur (c) Fe (d) As_2S_3

23. Match the following colloids (in Column 1) with their specific name (in Column II) and choose the correct codes given below.

Column-I		Column-II	
A.	Smoke	1.	Foam
B.	Alloys	2.	Aerosol
C.	Froths	3.	Gel
D.	Cheese	4.	Solid sol

Codes

	A	B	C	D
(a)	4	3	1	2
(b)	2	3	4	1
(c)	2	4	1	3
(d)	3	2	4	1

24. In Freundlich adsorption isotherm, the value of $1/n$ is
(a) between 0 and 1 in all cases.
(b) between 2 and 4 in all cases.
(c) 1 in case of physical adsorption.
(d) 1 in case of chemisorption.

25. Which one of the following characteristics is associated with adsorption?
(a) ΔG is negative but ΔH and ΔS are positive.
(b) ΔG, ΔH and ΔS all are negative.
(c) ΔG and ΔH are negative but ΔS is positive.
(d) ΔG and ΔS are negative but ΔH is positive.

26. The addition of catalyst during a chemical reaction alters which of the following quantities?
(a) Entropy (b) Internal energy
(c) Enthalpy (d) Activation energy

27. Fog is a colloidal solution of
(a) Liquid in gas (b) Gas in liquid
(c) Solid in gas (d) Gas in gas

28. Substances whose solutions can readily diffuse through animal membranes are called
(a) Colloids (b) Crystalloids
(c) Electrolytes (d) Non-electrolytes

29. The size of the colloidal particles is in between
(a) $10^{-7} – 10^{9}$ cm (b) $10^{-9} – 10^{-11}$ cm
(c) $10^{-5} – 10^{-7}$ cm (d) $10^{-2} – 10^{-3}$ cm

30. The size of a colloidal particle is
(a) $> 0.1\mu$ (b) 1 mμ to 0.1 μ
(c) < 0.1 mμ (d) More than 3000 mμ

31. If dispersed phase is liquid and the dispersion medium is solid, the colloid is known as
(a) A sol (b) A gel
(c) An emulsion (d) A foam

32. An emulsion is a colloidal solution consisting of
(a) Two solids
(b) Two liquids
(c) Two gases
(d) One solid and one liquid

33. The colloidal solution of gelatin is known as
(a) Solvent loving (b) Reversible
(c) Hydrophilic (d) All of the above

34. Peptization is a process of
(a) precipitating the colloidal particles.
(b) purifying the colloidal sol.
(c) dispersing the precipitate in to colloidal sol.
(d) movement of colloidal particles towards the opposite charged electrodes.

LEVEL II

1. Colloids are purified by
(a) Brownian motion (b) Precipitation
(c) Dialysis (d) Filtration

2. Which of the following substance give a positively charged sol?
(a) Gold (b) Arsenious sulphide
(c) Starch (d) Ferric hydroxide

3. When excess of electrolyte is added to a colloid it
(a) Coagulates (b) Gets diluted
(c) Dissolved (d) Does not change

4. Gold number is a measure of the
(a) protective action by a lyophilic colloid on lyophobic colloid.
(b) protective action by a lyophobic colloid on lyophilic colloid.
(c) number of mg of gold in a standard red gold sol.
(d) None of the above

5. A liquid is found to scatter a beam of light but leaves no residue when passed through the filter paper. The liquid can be described as
(a) A suspension (b) Oil
(c) A colloidal sol (d) True solution

6. A catalyst is a substance which
(a) Increases the equilibrium concentration of the product.
(b) Change the equilibrium constant of the reaction.
(c) Shortens the time to reach equilibrium.
(d) Supplies energy to the reaction.

7. A catalyst
(a) Increases the free energy change in the reaction.
(b) Decreases the free energy change in the reaction.
(c) Does not increases and decreases the free energy change in the reaction.
(d) Can either decreases or increases the free energy change depending on what catalyst we use.

8. A catalytic poison renders the catalyst ineffective because
(a) It is preferentially adsorbed on the catalyst.
(b) It adsorbs the molecules of the reactants.
(c) It combines chemically with the catalyst.
(d) It combines with one of the reactant.

9. Regarding criteria of catalysis which one of the following statements is not true?
(a) The catalyst is unchanged chemically during the reaction.
(b) A small quantity of catalyst is often sufficient to bring about a considerable amount of the reaction.
(c) In reversible reaction, the catalyst alters the equilibrium position.
(d) The catalyst accelerates the rate of reaction.

10. Which of the following is lyophobic in nature?
(a) Gelatin (b) Phosphorus
(c) Starch (d) Agar-Agar

11. Gelatin is mostly used in making ice creams in order to
(a) prevent making of colloid.
(b) stabilise the colloid and prevent crystalisation.
(c) stabilise the mixture.
(d) enrich the aroma.

12. Blood may be purified by
(a) dialysis (b) electro osmosis
(c) coagulation (d) filtration

13. The slope of the straight line graph between log x/m and log P for the adsorption of a gas on solid is
(a) k (b) log k (c) n (d) $1/n$

14. The work of enzymes in living system is
(a) oxygen transfer.
(b) to provide immunity.
(c) to catalyse bio' chemical reactions.
(d) to provide energy.

15. A chemical reaction is catalysed by catalyst X. So X
(a) increases the activation energy of reaction.
(b) does not affect equilibrium constant of reaction.
(c) decreases the rate constant of reaction.
(d) decreases enthalpy of reaction.

16. When some special substances like protein particles. Blood corpuscles, etc., are separated by a permeable membrane, the process is called
(a) dialysis (b) diffusion
(c) exosmosis (d) endosmosis

17. Which is not the characteristic of hydrophobic sols?
(a) They are highly susceptible to coagulation by addition of electrolytes.
(b) They have nearly the same surface tensions and viscosity as that of dispersion medium.
(c) Their stability is due to both electric charge and salvation of the particles.
(d) Sol particles can be seen under ultramicroscope.

18. According to Hardy Schultz law the order of coagulation power of cations will be
(a) $Na^+ > Ba^{+2} > Al^{+3}$ (b) $Al^{+3} > Ba^{+2} > Na^+$
(c) $Ba^{+2} > Al^{+3} > Na^+$ (d) $Al^{+3} > Na^+ > Ba^{+2}$

19. Which one of the following method is commonly used for destruction of colloid?
(a) Dialysis
(b) Condensation
(c) Filtration by animal membrane
(d) By adding electrolyte

20. How enzymes increase the rate of reactions?
(a) By lowering activation energy.
(b) By increasing activation energy.
(c) By changing equilibrium constant.
(d) By forming enzyme substrate complex.

21. Which is not correct regarding the adsorption of a gas on surface of solid?
(a) On increasing temperature adsorption increases continuously.
(b) Enthalpy and entropy change is negative.
(c) Adsorption is more for some specific substance.
(d) Reversible

22. Position of non-polar and polar part in micelles:
(a) Polar at outer surface but non polar at inner surface.
(b) Polar at inner surface but non polar at outer surface.
(c) Distributed over all the surface.
(d) Are present in the surface only.

23. Milk is a colloidal
(a) liquid is dispersed in a liquid.
(b) solid is dispersed in a liquid.
(c) gas is dispersed in a liquid.
(d) sugar is dispersed in a liquid.

24. Adsorbed acetic acid on activated charcoal is
(a) adsorbed (b) absorber
(c) adsorbent (d) adsorbate

25. Who was Awarded Noble Prize for the study of catalytic reactions?
(a) Ostwald (b) Berzelius
(c) Vanthoff (d) Werner

26. Colloidal particles carry charge. This can be shown by
(a) Tyndall effect (b) electrophoresis
(c) Brownian movement (d) dialysis

27. Which forms a colloidal solution in water?
(a) NaCl (b) glucose
(c) strach (d) barium nitrate

28. Hydrophilic gels, when placed in water, absorb liquid resulting in an increase of their volume. This process of swelling of gels takes place with
(a) no change in volume
(b) net increase in volume
(c) net decrease in volume
(d) large reduction in volume

29. When dilute aqueous solution of $AgNO_3$ excess is added to KI solution, which of the following positively charged sol particles of AgI are formed due to adsorption of ion?
(a) KI^+ (b) Ag^+ (c) I^- (d) NO_3^-

30. The process which is catalysed by one of the products is called
(a) acid-base catalysis (b) autocatalysis
(c) negative catalysis (d) None of these

31. Which of the following statements about a catalyst is true?
(a) It lowers the energy of activation.
(b) The catalyst altered during the reaction is regenerated.
(c) It does not alter the equilibrium.
(d) All of the above

32. Colour of colloidal solution is due to
(a) different size of colloidal particles.
(b) due to formation of complex.
(c) due to formation of hydrated crystal.
(d) none of the above

33. Which of the following is a property of colloid?
(a) Scattering of light (b) They show attraction
(c) Dialysis (d) Emulsion

34. The size of particles in suspension, true solution and colloidal solution varies in the order?
(a) Suspension > Colloidal > True solution
(b) Suspension > (Colloidal + True solution)
(c) True solution > Suspension > Colloidal
(d) None of these

35. At the critical micelle concentration, the surfactant molecules
(a) decompose
(b) dissociate
(c) associate
(d) become completely soluble

36. The adsorption of a gas on a solid surface varies with pressure of the gas in which of the following manner?
(a) Fast → slow → independent of the pressure
(b) Slow → fast → independent of the pressure
(c) Independent of the pressure → fast → slow
(d) Independent of the pressure → slow → fast

37. If gold number of A, B, C and D are 0.005, 0.05, 0.5 and 5 respectively, then which of the following will have the greatest protective power?
(a) A (b) B (c) C (d) D

38. Which of the following colloids are formed when hydrogen sulphide gas is passed through a cold solution of arsenious oxide?
(a) As_2S_3 (b) As_2O_3 (c) As_2S (d) As_2H_2

39. The movement of colloidal particles towards the oppsitely charged electrodes on passing electricity is known as
(a) cataphoresis (b) Tyndall effect
(c) Brownian movement (d) None of these

40. Which of the following is used for the destruction of colloids?
(a) Dialysis (b) Condensation
(c) By ultrafiltration (d) By adding electrolyte

41. Brownian movement is
(a) Zig-zag motion of the colloidal particles.
(b) Migration of colloidal particles under the influence of electric field.
(c) Scattering of light by colloidal particles.
(d) None of these

42. Enzymes with two sites are called
(a) apoenzyme (b) holoenzyme
(c) allosteric enzyme (d) conjugate enzyem

43. Wood charcoal is used to decolourise sugar because it
(a) adsorbs coloured material
(b) absorbs decolorised material
(c) reduces coloured material
(d) None of these

44. A catalyst can effect reversible reaction by
(a) changing equilibrium
(b) slowing forward reaction
(c) attaining equilibrium in both direction
(d) None of these

45. Surface tension of lyophilic sols is
(a) lower than that of H_2O
(b) more than that of H_2O
(c) equal to that of H_2O
(d) None of these

46. The catalyst used in the manufacture of methanol from water gas is
(a) V_2O_5 (b) Ni + Mo
(c) $ZnO + Cr_2O_3$ (d) Pt + W

47. Which one of the following is an incorrect statement for physisorption?
(a) It is a reversible process.
(b) It requires less heat of adsorption.
(c) It requires activation energy.
(d) It takes place at low temperature.

48. The colligative property of a sol compared to the aqueous solution of glucose of same concentration will be
(a) Much smaller (b) Much higher
(c) The same (d) Slightly lower

49. Sodium lauryl sulphate is
(a) cationic sol (b) anionic sol
(c) neutral sol (d) None of these

50. Which of the following does not form sol?
(a) Electrophoresis
(b) Peptisation
(c) Electrical disintegration
(d) Solvent exchange

51. Which of the following is not an emulsion?
(a) Butter (b) Ice cream
(c) Milk (d) Cloud

52. Which of the following reaction is catalysed by enzyme maltase?
(a) Starch → Maltose
(b) Maltose → Glucose
(c) Lactose → Maltose
(d) Maltose → Glucose + Fructose

53. Which of the following factors affects the adsorption of a gas on solid?
(a) Tc (critical temperature)
(b) Temperature of gas
(c) Pressure of gas
(d) All of these

54. The volume of gases NH_3, CO_2 and CH_4 adsorbed by one gram of charcoal at 298 K are in
(a) $CH_4 > CO_2 > NH_3$ (b) $NH_3 > CH_4 > CO_2$
(c) $NH_3 > CO_2 > CH_4$ (d) $CO_2 > NH_3 > CH_4$

55. The heat of physisorption lie in the range of
(a) 1 to 10 kJ mol^{-1} (b) 20 to 40 kJ mol^{-1}
(c) 40 to 200 kJ mol^{-1} (d) 200 to 400 kJ mol^{-1}

56. Which of the following is not a gel?
(a) Cheese (b) Jellies
(c) Curd (d) Milk

57. Which of the following is used to adsorb water?
(a) Silica gel (b) Calcium acetate
(c) Hair gel (d) Cheese

58. An emulsion is a colloidal system of
(a) two solids
(b) two liquids
(c) one gas and one solid
(d) one gas and one liquid

59. Which of the following is a lyophobic colloid?
(a) Gelatin (b) Sulphur
(c) Starch (d) Gum arabic

60. The nature of bonding forces in adsorption is
(a) purely physical such as Van der Waal's forces.
(b) purely chemical.
(c) both chemical and physical always.
(d) None of these

61. The Tyndall effect associated with colloidal particles is due to
(a) presence of electrical charges.
(b) scattering of light.
(c) adsorption of light.
(d) reflection of light.

62. Which one of the following is not applicable to chemisorption?
(a) Its heat of adsorption is high.
(b) It takes place at high temperature.
(c) It is reversible.
(d) It forms mono-molecular layers.

63. In the colloidal state the particle size ranges
(a) below 1 nm.
(b) between 1 nm to 100 nm.
(c) more than 100 nm.
(d) None of the above.

64. All colloids
(a) are suspensions of one phase in another.
(b) are two phase systems.
(c) contain only water soluble particles.
(d) are true solutions.

65. When a colloidal solution is observed under ultramicroscope, we can see
(a) light scattered by colloidal particle.
(b) size of the colloidal particle.
(c) shape of the colloidal particle.
(d) relative size of the colloidal particle.

66. Colloidal solutions are classified on the basis of
(a) molecular size.
(b) organic or inorganic.
(c) surface tension value.
(d) pH value.

67. The electrical charge on a colloidal particle is indicated by
(a) Brownian movement (b) electrophoresis
(c) ultra microscope (d) molecular sieves

68. Crystalloids differ from colloids mainly in respect of
(a) electrical behaviour (b) particle nature
(c) particle size (d) solubility

69. Under the influence of an electric field, the particles in a sol migrate towards cathode. The coagulation of the same sol is studied using NaCl, Na_2SO_4, and Na_3PO_4 solutions. Their coagulating values will be in the order
(a) $NaCl > Na_2SO_4 > Na_3PO_4$
(b) $Na_2SO_4 > Na_3PO_4 > NaCl$
(c) $Na_3PO_4 > Na_2SO_4 > NaCl$
(d) $Na_2SO_4 > NaCl > Na_3PO_4$

70. Tyndall effect would be observed in a
(a) solution (b) solvent
(c) precipitate (d) colloidal solution

71. Adsorption is multilayer in case of
(a) physical adsorption (b) chemisorption
(c) both (d) None of these

72. A liquid is found to scatter a beam of light but leaves no residue when passed through the filter paper. The liquid can be described as
(a) a suspension (b) oil
(c) a colloidal sol (d) a true solution

73. The ability of an ion to bring about coagulation of a given colloid depends upon
(a) its charge.
(b) the sign of the charge alone.
(c) the magnitude of the charge.
(d) both magnitude and sign of charge.

74. Which of the following ionic substances will be most effective in precipitating the sulphursol ?
(a) KCl (b) $BaCl_2$
(c) $Fe_2 (SO_4)_3$ (d) Na_3PO_4

75. Which gas will be adsorbed on a solid to greater extent?
(a) A gas having non polar molecule.
(b) A gas having highest critical temperature (T_c).
(c) A gas having lowest critical temperature.
(d) A gas having highest critical pressure.

76. Colloidal particles in a solution can be coagulated by
(a) heating.
(b) adding an electrolyte.
(c) adding oppositely charged sol.
(d) all of these

77. Emulsifier is an agent which
(a) accelerates the dispersion.
(b) homogenises an emulsion.
(c) stabilizes an emulsion.
(d) aids the flocculation of an emulsion.

78. Given below are a few electrolytes, indicate which one among them will bring about the coagulation of a gold solution quickest and in the least of concentration?
(a) NaCl (b) $MgSO_4$
(c) $Al_2(SO_4)_3$ (d) $K_4[Fe(CN)_6]$

79. The minimum concentration of an electrolyte required to cause coagulation of a sol is called
(a) flocculation value (b) gold number
(c) protective value (d) None of these

80. Smoke precipitator works on the principle of
(a) distribution law.
(b) neutralisation of charge on colloids.
(c) Le-Chaterlier's principle.
(d) addition of electrolytes.

81. Which one of following statements is not correct in respect of lyophilic sols?
(a) There is a considerable interaction between the dispersed phase and dispersion medium.
(b) These are quite stable and are not easily coagulated.
(c) They carry charge.
(d) The particle are hydrated.

82. As_2S_3 sol is
(a) positive colloid (b) negative colloid
(c) neutral colloid (d) None of these

83. Which of the following electrolyte will be most effective in coagulation of gold sol?
(a) $NaNO_3$ (b) $K_4[Fe(CN)_6]$
(c) Na_3PO_4 (d) $MgCl_2$

84. During electro – osmosis of Fe $(OH)_3$ Sol
(a) Sol particles move towards anode
(b) Sol particles move towards cathode
(c) The dispersion medium move towards anode
(d) The sol particles do not move in either direction

85. Alums purify muddy water by
(a) dialysis (b) absorption
(c) coagulation (d) forming true solution

LEVEL III

1. Match the columns.

Column I		**Column II**	
(A)	Gas dispersed in liquid	(P)	Emulsion
(B)	Liquid dispersed in gas	(Q)	Foam
(C)	Liquid dispersed in solid	(R)	Gel
(D)	Liquid dispersed in liquid	(S)	Aerosol

2. Match the columns.

Column I		**Column II**	
(A)	Example of Coagulation	(P)	Scattering of light
(B)	Dialysis	(Q)	Converting precipitate into colloidal solution
(C)	Peptization	(R)	Purification of colloids
(D)	Tyndall effect	(S)	Formation of deltas

3. Match the columns.

Column I		**Column II**	
(A)	Protective colloids	(P)	Gold number
(B)	Example of lyophilic	(Q)	Gelatin Colloids
(C)	Dialysis	(R)	Purification of sols
(D)	As_2S_3 sol	(S)	Negatively charged sols

4. **Match the columns.**

Column I		Column II	
(A)	Fog	(P)	Gel
(B)	Milk	(Q)	Foam
(C)	Cheese	(R)	Emulsion
(D)	Soap lather	(S)	Aerosol

5. **Match the columns.**

Column I		**Column II**	
(A)	Electrophoresis	(P)	Movement of molecules of dispersion medium
(B)	Electro-osmosis	(Q)	Mechanical property
(C)	Tyndall effect	(R)	Optical property
(D)	Brownian motion	(S)	Determination of charge on colloidal particles

Comprehension 1 (Q. 6 to 8)

There are certain colloids which behave as normal strong electrolytes at low concentrations, but exhibit colloidal properties at higher concentrations due to the formation of aggregated particles. These are known as **micelles** or **associated colloids.** Surface active agents like soaps and synthetic detergents belong to this class.

- Critical micelle concentration (CMC) is the lowest concentration at which micelle formation appears. CMC increases with the total surfactant concentration. At concentration higher than CMC, they form extended parallel sheets known as **lamellar micelles** which resemble biological membranes. With two molecules thick, the individual molecule is perpendicular to the sheets such that hydrophilic groups are on the outside in aqueous solution and on the inside is a non-polar medium.
- In concentrated solution, micelles take the form of long cylinders packed in hexagonal arrays and are called **lyotropic mesomorphs.**
- In an aqueous solution (polar medium), the polar groups point towards the periphery and the hydrophobic hydrocarbon chains point towards the centre forming the core of the micelle.
- Micelles from the ionic surfactants can be formed only above a certain temperature called the **kraft temperature**.

- They are capable of forming ions.
- Molecules of soaps and detergents consist of lyophilic as well as lyophobic parts which associate together to form micelles.
- Micelles may contain as many as 100 molecules or more.

6. Select the incorrect statements (s).

(a) Surface active agents like soaps and synthetic detergents are micelles.
(b) Soaps are emulsifying agents.
(c) $C_{17}H_{35}$ (hydrocarbon part) and –COO (carboxylate) part of stearate ion ($C_{17}H_{35}$ COO^-) both are hydrophobic.
(d) All are incorrect statements.

7. In multimolecular colloidal sols, atoms or molecules are held together by

(a) H-bonding
(b) van der Waal's forces
(c) ionic bonding
(d) polar covalent bonding

8. Cleansing action of soap occurs because

(a) oil and grease can be absorbed into the hydrophobic centres of soap micelles and washed away.
(b) oil and grease can be absorbed into hydrophilic centres of soap micelles acid washed away.
(c) oil and grease can be absorbed into both hydrophilic and hydrophobic centres but not washed away.
(d) cleansing action is not related to micelles.

Comprehension 2
Question No. 9 to 12

The clouds consist of charged particles of water dispersed in air. Some of them are positively charged, others are negatively charged. When positively charged clouds come closer they have cause lightening and thundering whereas when positive and negative charged colloids come closer they cause heavy rain by aggregation of minute particles. It is possible to cause artificial rain by throwing electrified sand or silver iodide from an aeroplane and thus coagulation the mist hanging in air.

9. When excess of $AgNO_3$ is treated with KI solution, AgI forms

(a) positively charged sol
(b) negatively charged sol
(c) neutral sol
(d) true solution

10. Clouds are colloidol solution of

(a) liquid in gas (b) gas in liquid
(c) liquid in liquid (d) solid in liquid

11. AgI helps in artificial rain because

(a) It helps in coagulation
(b) It helps in dispersion process
(c) Both of these
(d) None of these

12. Electrical chimneys are made on the principle of

(a) Electroosmosis (b) Electrophoresis
(c) Coagulation (d) All of these

Comprehension 3
Question No. 13 to 14 (2 Questions)

The protective power of the lyophilic colloids is expressed in terms of gold number a term introduced by Zsigmondy. Gold number is the number of milligram of the protective colloid which prevent the coagulation of 10 mL of red gold sol. when 1 mL of a 10 percent solution of sodium chloride is added to it. Thus, smaller the gold number of lyophilic colloid, the greater is the protective power.

13. On addition of one mL of solution of 10% NaCl to 10 mL of red gold sol in presence of 0.025 g of starch, the coagulation is just prevented. The gold number of starch is

(a) 0.025 (b) 0.25 (c) 2.5 (d) 25

14. Gold number gives an indication of

(a) protective nature of colloids
(b) purity of gold in suspension
(c) the charge on a colloidal solution of gold
(d) g-mole of gold per litre

Assertion/Reason

These questions contains, Statement I (assertion) and Statement II (reason).

(a) Statement I is true, Statement II is true; Statement II is 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

15. **Statement I:** For adsorption ΔG, ΔH, ΔS all have –ve values.
Statement II: Adsorption is a exothermic process in which randomness decreases due to force of attraction between adsorbent and adsorbate.

16. **Statement:** IMore heat evolved in physisorption than in chemisorption.
Statement II: Molecules of adsorbate and adsorbent are held by van der Waals' forces in physisorption and by chemical bonds in chemisorption.

17. **Statement I:** Protein, starch are lyophilic colloids.
Statement II: They have strong interaction with the dispersion medium.

18. **Statement I:** Isoelectric point is pH at which colloidal can move towards either of electrode.
Because
Statement II: At isoelectric point, colloidal particles become electrically neutral.

19. **Statement I:** When $AgNO_3$ is treated with excess of potassium iodide, colloidal particles gets attracted towards anode.
Because

Statement II: Precipitate adsorb common ions (excess) and thus become charged.

20. **Statement I:** For adsorption ΔG, ΔH, all have –ve values

Statement II: Adsorption is a spontaneous exothermic process in which randomness decreases due to force of repulsion between adsorbent and adsorbate.

21. **Statement I:** A gas with higher critical temperature gets adsorbed to more extent than a gas with lower critical temperature.

Because

Statement II: The easily liquifiable gases get adsorbed to more extent due to high value of (a) Vander Waal constant.

22. **Statement I:** Micelles are formed by surfactant molecules above the critical micelle concentration (CMC).

Because

Statement II: The conductivity of a solution having surfactant molecules decreases sharply at the CMC.

23. Which among the following statement are correct with respect to adsorption of gases on a solid?
(a) The extent of adsorption is equal to kp^n according to Freundiich isotherm.
(b) The extent of adsorption is equal to $kp^{1/n}$ according to Freundlich isotherm.
(c) The extent of adsorption is equal to $(1 + bp)/ap$ according to Langmuir isotherm.
(d) The extent of adsorption is equal to $ap/(1 + ap)$ according to Langmuir isotherm.

24. Select the incorrect statement(s):
(a) Surface active agent like soaps and synthetic detergents are micelles.
(b) Soaps are emulsifying agents.
(c) $C_{17}H_{35}$ (hydrocarbon part) and –COO–(carboxylate part) of stearate ion ($C_{17}H_{35}COO^-$) both are hydrophobic.
(d) Micelles form above critical tempreture.

25. Which of the following statement(s) is/are correct?
(a) Higher the gold number, more protective power of colloid.
(b) Lower the gold number, more the protective power.
(c) Higher the coagulation value, more the coagulation power.
(d) Lower the coagulation value, higher the coagulation power.

26. The charge on the colloidal particles is due to
(a) self-dissociation.
(b) electron capture during Bredig's arc method.
(c) selective adsorption of ion on their surface.
(d) addition of protective colloids.

27. Which of the following aqueous solution is most effective in the coagulation of an arsenious sulphide sol?
(a) KCl (b) $MgCl_2$ (c) $AlCl_3$ (d) $FeCl_3$

28. Which of the following are multimolecular colloids?
(a) Sulphur sol (b) Egg albumin in water
(c) Gold sol (d) Soap solution

29. Which of the following colloidal solutions contain negatively charged colloidal particles?
(a) $Fe(OH)_3$sol (b) As_2S_3 sol
(c) Congored (d) Gold. sol.

30. Lyophilic sols among the following are
(a) Gelatin (b) Gold sol
(c) Starch (d) Sulphur

31. Which of the following statements are true?
(a) Soap solution contains ionic micelles as the colloidal particles.
(b) Physisorption reversible in nature
(c) Chemisorption is highly specific.
(d) Chemisorption needs high activation energy.

32. Which of the following statements are true for physisorption?
(a) Extent of adsorption increases with increase in pressure.
(b) It needs activation energy.
(c) It can be reversed easily.
(d) It occurs at high temperature.

33. A lyophobic colloidal solution can be precipitated by
(a) adding lyophilic colloid.
(b) heating.
(c) adding electrolyte.
(d) adding same charged colloid.

34. For physical adsorption of a gas on solid adsorbent
(a) ΔH is positive (b) ΔS is negative
(c) ΔG is negative (d) ΔE is positive

35. Which of the following statements is/are correct?
(a) In adsorption, the concentration of the adsorbate increases only at the surface of the adsorbent.
(b) In absorption, the concentration is uniform throughout the bulk of the solid.
(c) Adsorption is instantaneous, thus fast.
(d) Absorption is slow.

36. When negatively charged colloids like As_2S_3 sol is added to positively charged $Fe(OH)_3$ sol in suitable amounts
(a) Both the sols are precipitated simultaneously.
(b) This process is called mutual coagulation.
(c) They becomes positively charged colloids.
(d) They becomes negatively charged colloids.

37. Which of the following are colloids?
(a) Milk (b) Ice cream
(c) Urea solution (d) Blood

38. Which of the following is/are correct statements?
(a) Hardy Schulz rule is related to coagulation.
(b) Brownian movement and Tyndall effect are shown by colloids.
(c) When liquid is dispersed in liquid, it is called gel.
(d) Gold number is a measure of protective power of lyophillic colloid.

39. Which statement is/are correct?
- (a) Physical adsorption is multilayer non-directional and non-specific.
- (b) Chemical adsorption is generally monolayer and specific in nature.
- (c) Physical adsorption is due to free e^-
- (d) Chemical adsorption is stronger than physical adsorption.

40. Which is the following is/are correct for lyophillic sols?
- (a) Its surface tension is lower than that of H_2O.
- (b) Its viscosity is higher than that of water.
- (c) Its surface tension is higher than that of water.
- (d) Its viscosity is equal to that of water.

41. Which statement(s) is/are correct?
- (a) A solution is prepared by addition of excess of $AgNO_3$ solution in KI solution. The charge likely to develop on colloidal particle is positive.
- (b) The effects of pressure on physical adsorption is high if temperature is low.
- (c) Ultracentrifugation process is used for preparation of lyophobic colloids.
- (d) Gold number is the index for extent of gold plating done.

42. Colloidal solution can be purified by
(a) dialysis (b) electrodialysis
(c) electrophoresis (d) ultrafiltration

43. Coagulation of colloids can be achieved by
(a) centrifugation (b) adding electrolyte
(c) change in pH (d) adding water

44. Which are the properties of sols.
(a) Adsorption (b) Tyndall effect
(c) Flocculation (d) Paramagnetism

45. Which of the following is not lyophillic?
(a) gelatin sol (b) silver sol
(c) sulphur sol (d) As_2S_3 sol

46. Colloidal Gold can be prepared by
(a) Bredig's are method (b) reduction of $AuCl_3$
(c) hydrolysis (d) peptisation

47. The coagulation of sol particles may be brought about by
- (a) heating.
- (b) addition oppositely charged sol.
- (c) addition electrolyte.
- (d) persistent dialysis.

48. Which one is not lyophobic in nature?
(a) Gelatin (b) Sulphur
(c) Starch (d) Protein

49. On adding 1 mL of solution of 10% NaCl to 10 mL of gold sol in the presence of 0.25 g of starch, the coagulation is just prevented. The gold number of starch is
(1) 0.25 (2) 0.025 (3) 25 (4) 250

50. The density of gold is 19 g/cm^3. If 1.9×10^{-4} g of gold is dispersed in 1 L of water to give a sol having spherical gold particles of radius 10 nm, then the number of gold particles per mm^3 of the sol will be
(a) 1.9×10^{12} (b) 6.3×10^{14}
(c) 6.3×10^{10} (d) 2.4×10^{6}

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN AND ADVANCED)

1. The volume of a colloidal particle, V_C as compared to the volume of a solute particle in a true solution V_S, could be **[AIEEE, 2005]**
(a) $\frac{V_C}{V_S} \simeq 1$ (b) $\frac{V_C}{V_S} \simeq 10^{23}$
(c) $\frac{V_C}{V_S} \simeq 10^{-3}$ (d) $\frac{V_C}{V_S} \simeq 10^{3}$

2. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statement is NOT correct? **[AIEEE, 2005]**
- (a) Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol.
- (b) Sodium sulphate solution cause coagulation in both sols.
- (c) Mixing the sols has no effect.
- (d) Coagulation in both sols can be brought about by electrophoresis.

3. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is **[JEE, 2008]**
- (a) $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
- (b) $CH_3(CH_2)_{11}OSO_3^-Na^+$
- (c) $CH_3(CH_2)_6COO^-Na^+$
- (d) $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$

4. Which of the following statements is incorrect regarding physissorptions? **[AIEEE, 2009]**
- (a) Under high pressure it results into multi molecular layer on adsorbent surface.
- (b) Enthalpy of adsorption (ΔH adsorption) is low and positive.
- (c) It occurs because of Van der Waal's forces.
- (d) More easily liquefiable gases are adsorbed readily.

5. Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl, the most effective coagulation agent for Sb_2S_3 sol is **[JEE, 2009]**
(a) Na_2SO_4 (b) $CaCl_2$
(c) $Al_2(SO_4)_3$ (d) NH_4Cl

6. The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are)
- (a) Adsorption is always exothermic. **[JEE, 2011]**
- (b) Physisorption may transform into chemisorption at high temperature.
- (c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature.

(d) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation.

7. According to Freundlich adsorption isotherm, which of the following is correct? **[AIEEE, 2012]**

(a) $\frac{x}{m} \propto p^0$

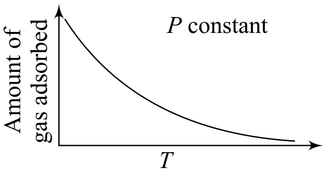
(b) $\frac{x}{m} \propto p^1$

(c) $\frac{x}{m} \propto p^{1/n}$

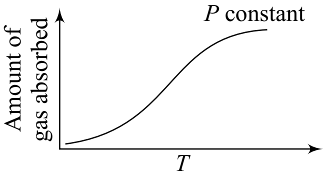
(d) All the above are correct for different ranges of pressure.

8. The given graphs/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is (are) correct? **[JEE, 2012]**

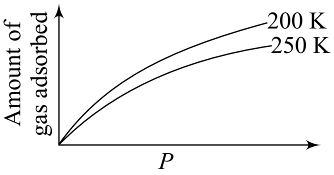
(I)



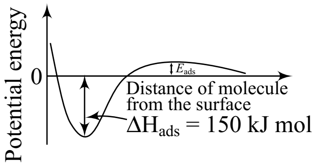
(II)



(III)



(IV)



(a) I is physisorption and II is chemisorption

(b) I is physisorption and III is chemisorption

(c) IV is chemisorption and II is chemisorption

(d) IV is chemisorption and III is chemisorption

9. Choose the correct reason(s) for the stability of the lyophobic colloidal particle. **[JEE, 2012]**

(a) Preferential adsorption of ions on their surface from the solution

(b) Preferential adsorption of solvent on their surface from the solution

(c) Attraction between different particles having opposite charges on their surface

(d) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles

10. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is **[2013 Adv.]**

(a) the adsorption requires activation at 25°C.

(b) the adsorption is accompanied by a decreases in enthalpy.

(c) the adsorption increases with increase of temperature.

(d) the adsorption is irreversible.

11. The coagulating power of electrolytes having ions Na^+, Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order **[2013 Adv.]**

(a) $Al^{3+} < Ba^{2+} < Na^+$ (b) $Na^+ < Ba^{2+} < Al^{3+}$

(c) $Ba^{2+} < Na^{2+} < Al^{3+}$ (d) $Al^{3+} < Na^+ < Ba^{2+}$

Answer Key

LEVEL I

1. (d)	2. (d)	3. (b)	4. (b)	5. (d)	6. (c)	7. (c)	8. (b)	9. (b)	10. (d)
11. (d)	12. (c)	13. (a)	14. (b)	15. (b)	16. (b)	17. (d)	18. (c)	19. (c)	20. (c)
21. (a)	22. (a)	23. (c)	24. (a)	25. (b)	26. (d)	27. (a)	28. (b)	29. (c)	30. (b)
31. (b)	32. (b)	33. (d)	34. (c)						

LEVEL II

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

31. (d) 32. (a) 33. (a) 34. (a) 35. (c) 36. (a) 37. (a) 38. (a) 39. (a) 40. (d)
41. (a) 42. (c) 43. (a) 44. (c) 45. (a) 46. (c) 47. (c) 48. (a) 49. (a) 50. (a)
51. (d) 52. (b) 53. (d) 54. (c) 55. (b) 56. (d) 57. (a) 58. (b) 59. (b) 60. (c)
61. (b) 62. (c) 63. (b) 64. (b) 65. (a) 66. (a) 67. (b) 68. (c) 69. (a) 70. (d)
71. (a) 72. (c) 73. (d) 74. (c) 75. (b) 76. (d) 77. (c) 78. (c) 79. (a) 80. (b)
81. (c) 82. (b) 83. (d) 84. (c, d) 85. (c)

LEVEL III

1. (A) → q; (B) → s; (C) → r; (D) → p   2. (A) → s; (B) → r; (C) → q; (D) → p
3. (A) → p, q; (B) → q; (C) → r; (D) → s   4. (A) → s; (B) → r; (C) → p; (D) → q
5. (A) → s; (B) → p; (C) → r; (D) → q
6. (c) 7. (b) 8. (a) 9. (a) 10. (a) 11. (c) 12. (b) 13. (d) 14. (a) 15. (a)
16. (d) 17. (a) 18. (b) 19. (c) 20. (d) 21. (a) 22. (b) 23. (b, d) 24. (c, d) 25. (b, d)
26. (a, b, c) 27. (c, d) 28. (a, c) 29. (b, c, b) 30. (a, c) 31. (a, b, c, d) 32. (a, c)
33. (b, c) 34. (b, c) 35. (a, b, c, d) 36. (a, b) 37. (a, b, d) 38. (a, b, d) 39. (a, b, d)
40. (a, b) 41. (a, b) 42. (a, b, d) 43. (a, b, c) 44. (a, b, c) 45. (b, c, d)
46. (a, b) 47. (a, b, c, d) 48. (a, c, d) 49. (d) 50. (d)

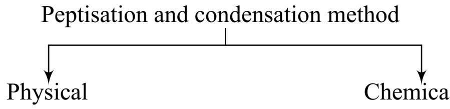
PREVIOUS YEARS' QUESTIONS OF JEE (MAIN AND ADVANCED)

1. (d) 2. (c) 3. (a) 4. (b) 5. (c) 6. (a, b, d) 7. (d) 8. (a, c) 9. (a, d) 10. (b)
11. (b)

Hints and Solutions

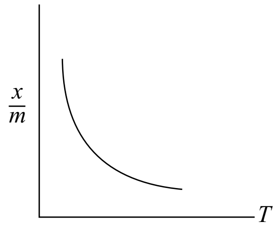
LEVEL I

1. **(d)** Micelles formation takes place only above CMC and above kraft temperature.
2. **(d)** positively charged sol.
   → Sols of metal hydroxide (Fe, Al, Cr)
   → Sols of basic dyes (methylene blue, methyl violet)
   → Haemoglobin, protein in acidic medium
   → Oxides TiO_2
   → Some metal sols like Bi, Pb, Fe, etc.
   –vely sols
   Metal sols Au, Ag, Pt, Cu metal sulphide AS_2S_3, CdS Starch, mud, charcoal, congored Eusin, Acidic dye, silicicacid Blood, Smoke, Soapmicelles
   Neutral colloid
   Tween-20 polyoxyethylene glycol derivative.
3. **(b)** At intermediate pressure in freundlich adsorption isotherm $\frac{x}{m} = kp^{1/n}$
4. **(b)** Theory based
5. **(d)** Lyophilic Colloids needs no special method and the sol is easily prepared by bringing the dispersed phase in the contact with dispersion medium example colloids of gum, gelatin starch, agar-agar, protein starch etc. may be prepared by just shaking them with water but *Special Methods* are needed to prepare lyophobic sols and the methods used are
   → mechanical method
   → electrical method
   → ultrasonic dispersion



→ By exchange of solvent	→ Double decomposition
→ Super cooling method	→ Hydrolysis
→ Vapour condensation	→ Oxidation
→ Reduction	

6. **(c)**

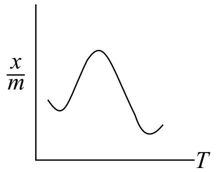


Physical adsorption

$Ea = 0$
$\Delta H = -ve$

So, according to Le Chatlier principle

$$\frac{x}{m} \propto \frac{1}{\text{temperature}}$$



Chemical adsorption

Extent of adsorption first increases up to certain temperature and then desorption is favoured at high temperature initial increase in the extent of chemisorption with temperature is because some *Ea* is required to cross energy barrier.

7. **(c)** Theory based

8. **(b)** True solution is a homogeneous mixture

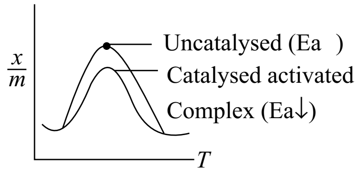
9. **(b)** Theory based

10. **(d)** Colour due to size of disperesed phase particle if size of Au different then colour different.

11. **(d)** Water in oil emulsion cod liver oil.

12. **(c)** Cellulose dispersed in ethanol called collodion.

13. **(a)** Threshold energy of intermediate adsorbed compound is less than unadsorbed intermediate.



Chemical adsorption

14. **(b)** Extent of adsorption decreases with increase in temperature.

15. **(b)** Adsorption ∝ Polarity or *M* mass

16. **(b)** According to Hardy Schulze rule, higher the valency of the active ion greater will be its power to precipitate the solution and reciprocal of coagulation value (or amount of electrolyte).

For As_2S_3 sol (–vely charged sol) amount of cation used for coagulation.

$$K^+ > Mg^{+2} > Al^{+3}$$

17. **(d)** $\frac{x}{m} = KP^{\frac{1}{n}}$

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

$$= \log 10 + \frac{1}{n}\log 4$$

$$\text{slop} = \frac{1}{n} = \tan\theta = \tan 45° = 1$$

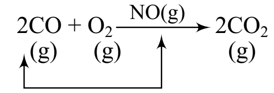
$$\log\frac{x}{m} = 1 + \frac{1}{1}\log 4$$

$$\log\frac{x}{m} = 1 + 0.6020 = 1.6020$$

$$\therefore \quad \frac{x}{m} = \text{antilog}\, 1.6020$$

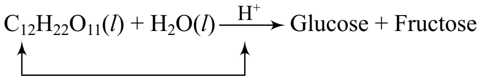
$$\therefore \quad \frac{x}{m} = 40 \text{ gram}$$

18. **(c)** Reactant and catalyst occur in same phase



$$\underset{(g)}{2CO} + \underset{(g)}{O_2} \xrightarrow{NO(g)} \underset{(g)}{2CO_2}$$

Same Phase ⇒ Gas Phase



$$C_{12}H_{22}O_{11}(l) + H_2O(l) \xrightarrow{H^+} \text{Glucose} + \text{Fructose}$$

Solution Phase catalysis

19. **(c)** Catalyst change the path of reaction positive catalyst Ea↓ Enzyme act as positive catalyst.

20. **(c)**

21. **(a)** Coagulating power ∝ charge

$$NO_3^- < SO_4^- \simeq Cr_2O_7^- < [Fe\,(CN)_6]^{-4}$$

22. **(a)** Intrinsic colloid or Lyophilic colloid, e.g., strach, rubber, protein, glue.

23. **(c)** Theory based

24. **(a)** In Freundlich adsorption isotherm $\frac{x}{m} = K \times p^{\frac{1}{n}}$

$$\therefore \quad n = 1 \text{ to } \infty$$

$$\therefore \quad \frac{1}{n} = 0 \text{ to } 1$$

25. **(b)** Adsorption is a spontaneous process so

$\Delta G = -\text{ve}$

$\Delta S = -\text{ve}$

Since bond formed so $\Delta H = -\text{ve}$.

26. **(d)** Catalyst change the path of reaction

or

Activation energy ↓ (+ve catalyst)

Activation energy ↑ (–ve catalyst)

27. **(a)** Fog ⇒ $\underset{\text{Dispersed Phase}}{\text{Liquid}}$ in $\underset{\text{Dispersion Medium}}{\text{gas}}$

28. **(b)**

29. **(c)** 1 nm to 1000 nm

⇒ 10^{-9}m to 10^{-6}m

10^{-7}cm to 10^{-5}cm

30. **(b)** 1 nm to 1000 nm

⇒ 10^{-9}m to 10^{-6}m

$$\frac{10^{-9}}{10^{-6}}\mu \text{ to } \frac{10^{-6}}{10^{-6}}\mu \Rightarrow 10^{-3}\mu \text{ to } 1\mu$$

⇒ 1 milliμ to 1μ

31. **(b)** Characterties of lyophilic calloid

32. **(b)**

33. **(d)** Gelatin when dissolve in water, is a calloid because the protein molecules dispersed through the water gelatin remains in liquid when warm becoming a gel (another colliod) when cooled.
34. **(c)**

LEVEL II

1. **(c)** Colloids are purified by dialysis, ultrafiltration.
2. **(d)** Gold, strach AS_2S_3 – vely charged colloid
3. **(a)** Coagulation is a process which involves coming together of colliodal particles by neutralising the charge of dispersed phase particle.
4. **(a)**
5. **(c)**
6. **(c)**
7. **(c)**
8. **(a)**
9. **(c)**
10. **(b)**
11. **(c)**
12. **(a)**
13. **(d)**
14. **(c)**
15. **(b)**
16. **(a)**
17. **(c)** The stability is attributed to electric charge on the sol particles.
18. **(b)**
19. **(d)**
20. **(a)**
21. **(a)**
22. **(a)**
23. **(a)**
24. **(d)**
25. **(b)**
26. **(b)**
27. **(c)**
28. **(c)** There will be net decrease in volume.
29. **(b)**
30. **(b)**
31. **(d)**
32. **(a)**
33. **(a)**
34. **(a)**
35. **(c)**
36. **(a)**
37. **(a)**
38. **(a)**
39. **(a)**
40. **(d)**
41. **(a)**
42. **(c)**
43. **(a)**
44. **(c)**
45. **(a)**
46. **(c)**
47. **(c)**
48. **(a)** Molar concentration of a sol is much smaller than that in a true solution of same strength (g L^{-1}) due to much larger particles.
49. **(a)**
50. **(a)**
51. **(d)**
52. **(b)**
53. **(d)**
54. **(c)**
55. **(b)**
56. **(d)**
57. **(a)**
58. **(b)**
59. **(b)**
60. **(c)**
61. **(b)**
62. **(c)**
63. **(b)**
64. **(b)**
65. **(a)**
66. **(a)**
67. **(b)**
68. **(c)**
69. **(a)** Since the sol particles migrate towards cathode, they are positively charged. Hence, anions would be effective in coagulation. Greater is the valence of effective ion, smaller will be its coagulation value.
70. **(d)**
71. **(a)**
72. **(c)**
73. **(d)**
74. **(a)** The sulphur sol is negatively charged and would be coagulated most effectively by Al^{3+}.
75. **(b)**
76. **(d)**
77. **(c)**
78. **(c)**
79. **(a)**
80. **(b)**
81. **(c)**
82. **(b)**
83. **(d)**
84. **(c, d)** In electro – osmosis, the sol particle are prevented from migration where as the dispersion medium migrates in the direction opposite to those of particles. Here the medium is negatively charged.
85. **(c)**

LEVEL III

1. **(A → Q, B → S, C → R, D → P)**
2. **(A → S; B → R; C → Q; D → P)**
3. **(A → P, Q; B → Q; C → R; D → S)**
4. **(A → S; B → R; C → P; D → Q)**
5. **(A → S; B → P; C → R; D → Q)**

Comprehension 1

6. **(c)**
7. **(b)**
8. **(a)**

Comprehension 2

9. **(a)**
10. **(a)**
11. **(c)**
12. **(b)**

Comprehension 3

13. **(d)**
14. **(a)**

Assertion and Reason

15. **(a)**
16. **(d)**

Physical Adsorption	**Chemical adsorption**
→ It arises due to weak Vanderwall forces	→ It arises due to formation of strong chemical bonds.
→ Heat of adsorption is low i.e., from –20 to –40 kJ mol^{-1}	→ Heat of adsorption is high i.e., from –80 to –240 kJ mol^{-1}
→ Reversible in Nature	→ Generally irreversible in nature

17. **(a)**

Lyophilic (Solvent living) (Hydrophilic) Greater affinity	**Lyophobic (Solvent lating) (Hydrophobic Lesser affinity)**
(i). When the particles of Dp have a greater affinity for the particles of dispersion medium, then the colloids is known as Lyophilic.	(i) When the particles of Dp have a lesser affinity for the particles of dispersion medium then the colloids is known as hyophobic
(ii) Easily prepared just by mixing the dispersed phase with dispersion medium	(ii) It require special methods for preparation
(iii) More stable	(iii) Less stable (Requires, stabilizing agent)
(iv) Reversible in nature	(iv) Irreversible in nature
(v) Coagulation is not so easy.	(v) Easily Coagulated
(vi) Higher degree of solvation or Hydration	(vi) Lower degree of hydration or Solvation
(vii) Viscosity is more and surface tension is less as compared to that of dispersion medium	(vii) Viscosity and surface tension are nearly the same as that of dispersion medium.
Ex. Generally of organic nature like sols of protein, starch etc.	Ex. Generally of in organic nature like sols of metals metal sulphides, etc.

18. **(b)**
19. **(c)**
20. **(d)**
21. **(a)**
22. **(b)**
23. **(b, d)** According to Freundlich isotherm

$$\frac{x}{m} \propto p^{\frac{1}{n}}$$

$$\frac{x}{m} = Kp^{\frac{1}{n}} \qquad n = 1 \ldots \infty$$

$$\frac{x}{m} = \text{extent of adsorption}$$

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log p$$

Following equilibrium is established:

$$A_{(g)} + M_{(S)} \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AM_{(s)}$$

Ra ∝ P × [$n(1-\theta)$] = Pressure × Number of sites available.

$$Ra = KaP_n\,(1-\theta)$$
$$Rd = K_d n\theta$$

At equilibrium

Rate of adsorb = Rate of desorption

$$Ka \times P \times n(1-\theta) = K_d \times n\theta$$

$$\frac{Ka}{Kd} \times p(1-\theta) = \theta$$

$$a \times p(1-\theta) = \theta$$

$$\frac{1-\theta}{\theta} = \frac{1}{\text{a.p.}}$$

$$\frac{1}{\theta} - 1 = \frac{1}{\text{a.p.}}$$

$$\theta = \frac{\text{ap}}{1+\text{ap}}$$

$$\theta = \frac{\text{Number of adsorption site occupied}}{\text{Number of adsorption available}}$$

24. (c, d)
25. (b, d)
26. (a, b, c)
27. (c, d)
28. (a, c)
29. (b, c, d)
30. (a, c)
31. (a, b, c, d)
32. (a, c)
33. (b, c)
34. (b, c)
35. (a, b, c, d)
36. (a, b)
37. (a, b, d)
38. (a, b, d)
39. (a, b, d)
40. (a, b)
41. (a, b)
42. (a, b, d)
43. (a, b, c)
44. (a, b, c)
45. (b, c, d)
46. (a, b)
47. (a, b, c, d)
48. (a, c, d)

49. (d) Minimum amount of protective colloid in milli grams which prevents a color change from red to violet of 10 ml gold sol by the addition of 1 ml of 10% NaCl solution.

Here protective colloid 0.25 gram starch = 0.25 × 1000 = 250 mg

$\therefore$ Gold No. = 250

50. (d) Volume of the gold dispersed in 1 L water =

$$\frac{m}{d} = \frac{1.9\times10^{-4}}{19\ \text{g/cm}^3} = 1\times10^{-5}$$

Radius of gold particle = 10 nm = 10^{-6} cm

$$\therefore\ \text{volume} = \frac{4}{3}\pi r^3 = \frac{4}{3}\times\frac{22}{7}\times(10^{-6})^3 = 4.19\times10^{-18}\,\text{cm}^3$$

$$\text{Number of particles in } 1\times10^{-5}\ \text{cm}^3 = \frac{1\times10^{-5}}{4.19\times10^{-18}} = 2.38\times10^{12}$$

$$\therefore\ \text{Number of gold particle in 1 mm}^3 = \frac{2.38\times10^{12}}{10^{6}} = 2.38\times10^{6}$$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN AND ADVANCED)

1. (d)
2. (c)
3. (a)
4. (b)
5. (c)
6. (a, b, d)
7. (d)

8. (a, c) Graph-I represent physisorption as in physisorption, absorbents are bonded to adsorbate through weak van der Waal's force. Increasing temperature increases kinetic energy of adsorbed particles increasing the rate of desorption, hence amount of adsorption decreases.

Graph-III also represents physical adsorption as extent of adsorption increasing with pressure.

Graph-II represents chemisorption as it is simple activation energy diagram of a chemical reaction.

Graph-IV represents chemisorption as it represents the potential energy diagram for the formation of a typical covalent bond.

9. (a, d)

10. (b)

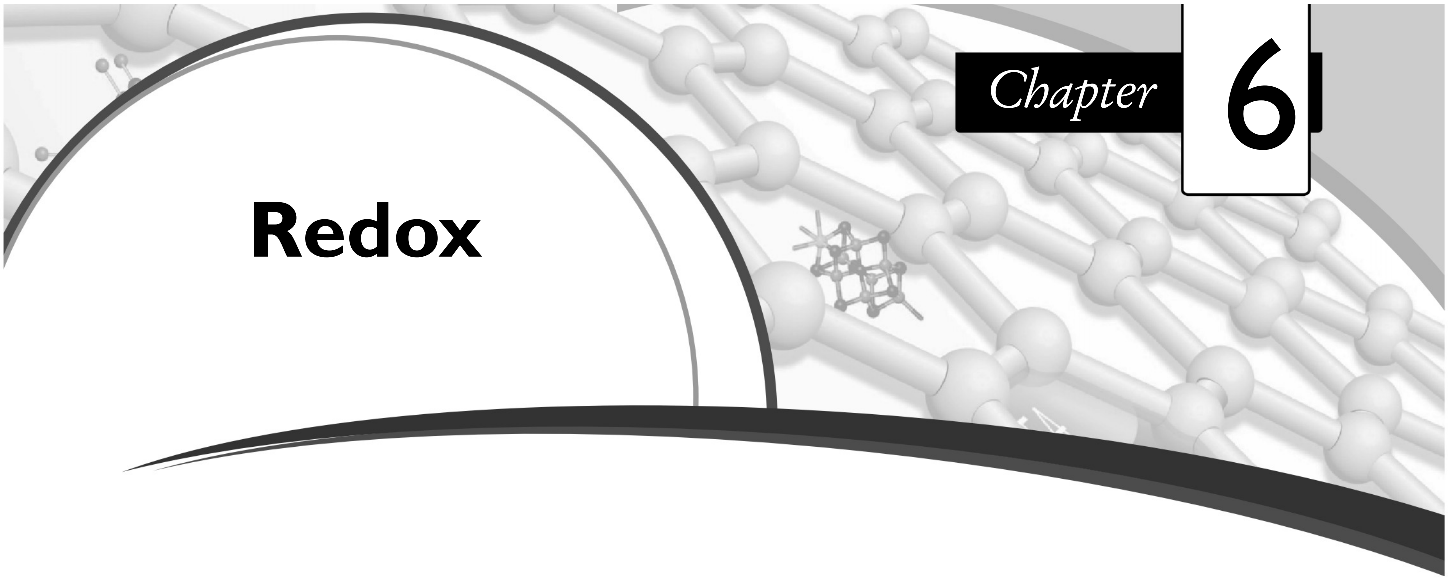
→ Physical adsorption takes place with decrease in enthalpy thus exothermic change. It is physical adsorption and does not require activation. Thus, (A) is incorrect.

→ Being physical adsorption $\Delta H < 0$ thus, (B) is correct.

→ Exothermic reaction is favoured at low temperature thus (c) is incorrect.

→ Physical adsorption is always reversible, thus (D) is incorrect.

11. (b) According to Hardy Schulze rule, greater the charge on oppositely charged ion, greater is its coagulating power. Since arsenic sulphide is a negatively charged sol, thus, the order of coagulating power is $Na^+ < Ba^{2+} < Al^{3+}$.



Chapter 6

Redox

Key Concepts

OXIDATION AND REDUCTION

Oxidation is the process of de-electronation during which oxidation number increases.

Oxidation reaction can also be defined as follows.

(i) Loss of hydrogen
(ii) Gain of oxygen
(iii) Loss of electron

Reduction: It is the process of electronation during which oxidation number decreases.

Reduction reaction can also be defined as follows.

(i) Gain of hydrogen
(ii) Loss of oxygen
(iii) Gain of electron

Oxidising Agent or Oxidant: It is the substance which undergoes reduction, and oxidises other substance. It gains electrons and its oxidation number decreases.
e.g. O_2, O_3, X_2, $KMnO_4$, $K_2Cr_2O_7$, H_2SO_4, HNO_3, etc., and oxides of metals and non metal (in heighest oxidation state)

Reducing Agent or Reductant: It is the substance, which undergoes oxidation and reduces other substance. It shows loss of electron during the process and its oxidation number increases. All the metals are reducing agents.

Reducing agent: [H], C, CO, H_2S, SO_2, $SnCl_2$, $Na_2S_2O_3$, A*l*, Na, CaH_2, LiA*l*H_4, $NaBH_4$

Alkali metals and alkaline earth metals in general are very strong reducing agents.

In general metals behave as reducing agent while non-metals behave as oxidising agents but it is not always true.

For example, $CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$

Here copper acts as non-reducing agent means as an oxidising agent.

Rules for Assigning Oxidation Numbers

(i) Sum of oxidation numbers of all atoms present in a neutral compound is equal to zero.
(ii) Sum of oxidation number of all atoms present in an ion is equal to charge on the ion.
(iii) The oxidation number of an atom in elementary state is zero.
(iv) The oxidation number of a mono-atomic ion is equal to charge on it.
(v) The oxidation number of oxygen in most of the compounds is –2. But in peroxides, it is –1 and in OF_2, It is +2.
(vi) The oxidation number of hydrogen is +1 in most of the compounds but in active metal hydrides (hydrides of group 1 and 2) it is –1.
(vii) The oxidation number of alkali metals in all the compounds is +1.
(viii) The oxidation number of alkali metals in all the compounds is +2.
(ix) The oxidation number of fluorine in all the compounds is –1.
(x) The oxidation number of all halogens is -1 except when the other atom present in the compound is oxygen.
(xi) The oxidation number of metals in amalgams is zero.
(xii) Maximum oxidation state of any element = Valance electron

Q. State which of the following changes are oxidation, reduction, both or none:

$$\underset{(0)}{Na} \longrightarrow \underset{(+1)}{NaOH}$$

Since ON of sodium increases means oxidation.

and $\overset{(+6)}{K_2CrO_4} \longrightarrow \overset{(+6)}{K_2Cr_2O_7}$

None since ON of chromium remains same

Reduction

$$\overset{0}{Cl_2} \longrightarrow \overset{-1}{Cl^-} + \overset{+5}{Cl_1O_3^-}$$

Oxidation

One chlorine oxidises and other one reduces

$$\overset{(+5)}{P_2O_5} \longrightarrow \overset{(+5)}{H_4P_2O_7}$$

Since ON of phosphorus remains same in both cases here no process takes place.

Q. Find oxidising agent (OA) and reducing agent (RA):

(A) $\underbrace{\overset{(0)}{Si}}_{R.A} + \underbrace{2\overset{(+1)(+1)}{KOH} + \overset{(+1)}{H_2O}}_{O.A} \longrightarrow \underset{(+1)}{\overset{(+4)}{K_2SiO_3}} + \overset{(0)}{2H_2}$

Hydrogen (Oxidising Agent) and Hydrogen Present in KOH and H_2O and Si Reducing agent

(B) $\overset{(+2)}{2Cu^{+2}} + \overset{(-1)}{4I^-} \longrightarrow \overset{(+1)}{2CuI} + \overset{(0)}{I_2}$

Reducing agent = I^-

Oxidising agent = Cu^{+2}

(C) $\underbrace{\overset{(-1)}{2I^{-2}}}_{R.A} + \underbrace{\overset{(-1)}{H_2O_2}}_{O.A} \longrightarrow \overset{(-2)}{2OH^-} + \overset{(0)}{I_2}$

(D) $\overset{(+1)}{Ag}(\overset{(-3)}{NH_3})_2^+ + 2H^+ \longrightarrow \overset{(+1)}{Ag^+} + 2\overset{(-3)}{NH_4^+}$ None

TYPES OF REDOX REACTIONS

Inter molecular redox reaction: If oxidation and reduction takes place in different substances then the reaction are called intermolecular redox reaction example.

$$\underbrace{Si}_{RA} + \underbrace{2KOH + H_2O}_{OA} \longrightarrow K_2SiO_3 + 2H_2$$

Disproportionation Reaction

If oxidation and reduction take place within same compound and of same element then the reaction are disproportionation reaction

Oxidation

For example, $\overset{0}{Cl_2} \longrightarrow \overset{-1}{Cl^-} + \overset{+5}{ClO_3^-}$

Reduction

Intramolecular redox reaction: If the oxidation and reduction take place with same compound and the elements involved are different or if same then in different oxidation number.

Reduction of Cl

e.g. $\overset{(+5)\,(-2)}{KClO_3} \longrightarrow \overset{(-1)}{KCl} + \overset{(0)}{O_2}$

Oxidation of O

Q. Identify the examples of intermolecular disproportion and intermolecular redox reaction.

Oxidation

1. $\overset{(-1)}{H_2O_2} \longrightarrow \overset{(-2)}{H_2O} + \frac{1}{2}\overset{(0)}{O_2}$

Reduction

Disproportionation reaction:

Reduction

2. $\overset{(-3)\ (+3)}{NH_4NO_2} \longrightarrow \overset{(0)}{N_2} + \overset{(-2)}{2H_2O}$

Oxidation

∴ Intramolecular reaction

(N) Reduced

3. $\overset{+2}{2Pb}\,(\overset{+5\,-2}{NO_3})_2 \longrightarrow \overset{+2}{2Pb} + \overset{+4}{4NO_2} + \overset{0}{O_2}$

(O) Oxidised

Intramolecular redox reaction

4. $\overset{0}{3Cl_2} + 6NaOH \longrightarrow Na\overset{-1}{Cl} + Na\overset{+5}{ClO_3} + 3H_2O$

Disproportionation reaction

5. $\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow 3NaH_2\overset{+1}{PO_2} + \overset{-3}{PH_3}$

Disproportionation reaction

6. $\overset{(+2)+(4)(-2)}{CaCO_3} \longrightarrow \overset{(+2)(-2)}{CaO} + \overset{(+4)(-2)}{CO_2}$

None (not a redox reaction)

7. $\overset{0}{Cl_2} + 2OH^- \longrightarrow \overset{+1}{ClO^-} + \overset{-1}{Cl^-} + H_2O$

Disproportion reaction

8. $\overset{+7\ -2}{MnO_4^-} \longrightarrow \overset{+6}{MnO_4^{-2}} + \overset{(0)}{O_2}$

Intramolecular

Balancing of Redox Reaction: Total no of e^- accepted by oxidising agent = total number of e^- given by reducing agent

1. Oxidation number method

Following rules are used to balance redox reaction by oxidation number method:

(i) Assign oxidation number to the atoms in the reaction and identify the atoms, which are undergoing oxidation and reduction.

(ii) Divide the redox reaction in two half-reaction; one representing oxidation and other reduction.

(iii) Find the change in oxidation number per atom in both half-reactions. Make equal changes in each half-reaction by multiplying them with suitable integers.

(iv) Balance all the atoms except hydrogen and oxygen atoms.

(v) In acidic medium, balance hydrogen atom by H^+ ions and oxygen atom by H_2O molecule.

(vi) In basic medium, balance hydrogen atom by OH^- ions and oxygen atom by H_2O molecule.

(vii) Balance the charge on each side of half-reaction by adding suitable number of electrons to the side deficient in it.

(viii) Add the two half–reaction to get balanced redox reaction.

Ex. (i) Balance the following reaction by the oxidation number method:

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

Sol. Write the oxidation number of all the atoms.

$$\overset{0}{Cu} + \overset{+1+5-2}{HNO_3} \longrightarrow \overset{+2+5-2}{Cu(NO_3)_2} + \overset{+4\;-2}{NO_2} + \overset{+1\;-2}{H_2O}$$

There is change in oxidation number of Cu and N.

$$\overset{0}{Cu} \longrightarrow \overset{+2}{Cu(NO_3)_2} \quad ....(1)$$

(Oxidation no. is increased by 2)

$$\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2} \quad .....(2)$$

(Oxidation no. is decreased by 1)

To make increase and decrease equal, equation (2) is multiplied by 2.

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

Balancing nitrates ions, hydrogen and oxygen, the following equation is obtained.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

This is the balanced equation.

Ex. (ii) Balance the following reaction by the oxidation number method :

$$MnO_4^- + Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$$

Sol. Write the oxidation number of all the atoms.

$$\overset{+7\,-2}{MnO_4^-} + Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$$

change in oxidation number has occurred in Mn and Fe.

$$\overset{+7}{MnO_4^-} \longrightarrow \overset{+2}{Mn} \qquad (1)$$

(Decrement in oxidation no. by 5)

$$Fe^{+2} \longrightarrow Fe^{+3} \qquad (2)$$

(Increment in oxidation no. by 1)

To make increase and decrease equal, equation (2) is multiplied by 5.

$$MnO_4^- + 5Fe^{+2} \longrightarrow Mn^{+2} + 5Fe^{+3}$$

To balance oxygen, $4H_2O$ are added to R.H.S. and to balance hydrogen, $8H^+$ are added to L.H.S.

$$MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$$

This is the balanced equation.

For example, (iii)

Reduction

$$\overset{+\frac{8}{3}}{Pb_3O_4} + \overset{-1}{HCl} \longrightarrow \overset{+2\;-1}{PbCl_2} + \overset{0}{Cl_2} + \overset{-2}{H_2O}$$

Oxidation

Oxidation	Reduction
$2Cl \longrightarrow Cl_2 + 2e^-$	$2e^- + Pb_3 \longrightarrow 3Pb$

Net Reaction:

$$2Cl + Pb_3 \longrightarrow 3Pb + Cl_2$$

$$6HCl + 2HCl + Pb_3O_4 \longrightarrow 3PbCl_2 + Cl_2 + H_2O$$

Balanced Reaction:

$$8HCl + Pb_3O_4 \longrightarrow Cl_2 + 3PbCl_2 + 4H_2O$$

For example, (iv)

Reduction

$$\overset{(-2)}{P_2H_4} \longrightarrow \overset{(-3)}{PH_3} + \overset{(-1/2)}{P_4H_2}$$

Oxidation

Oxidation	Reduction
$2P_2 \longrightarrow P_4 + 6e^-$	$[P_2 + 2e^- \longrightarrow 2P]3$

Net Reaction:

$$2P_2 + 3P_2 \longrightarrow P_4 + 6P$$

$$5P_2 \longrightarrow P_4 + 6P$$

$$5P_2H_4 \longrightarrow P_4H_2 + 6PH_3 \text{ (Balanced)}$$

For example, (v)

$$\overset{+3\;-2}{As_2S_3} + \overset{+5}{HNO_3} \longrightarrow H_3\overset{+5}{As}O_4 + H_2\overset{+6}{S}O_4 + \overset{+2}{N}O$$

Oxidation	**Reduction**
$As_2 \longrightarrow 2As + 4e^-$ $S_3 \longrightarrow 3S + 24e^-$	$(N + 3e^- \rightarrow N) \times 28$

$$As_2S_3 \longrightarrow 2As + 3S + 28e^-$$

Net Reaction:

$$3As_2S_3 + 28N \longrightarrow 6As + 9(S) + 28N$$

$$3As_2S_3 + 28HNO_3 \longrightarrow 6H_3AsO_4 + 9H_2SO_4 + 28NO$$

For example, (vi) $\overset{+2\;-1}{FeS_2} + \overset{0}{O_2} \longrightarrow \overset{+3\;-2}{Fe_2O_3} + \overset{+4\;-2}{SO_2}$

Oxidation	**Reduction**
$2Fe \longrightarrow \frac{1}{2}Fe_2 + e^-$ $S_2 \longrightarrow 2S + 10e^-$ $\left[FeS_2 \longrightarrow \frac{1}{2}Fe_2 + 2S + 11e^-\right]$	$[O_2 + 4e^- \longrightarrow 2O]11$

Net Reaction:

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2 + 8(S) + 22O$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

For example, (vii)

$$\overset{+4}{S}O_2 + Na_2\overset{+6}{Cr}O_4 + H_2\overset{+6}{S}O_4 \longrightarrow H_2O + \overset{+3}{Cr}_2(SO_4)_3 + Na_2SO_4$$

Oxidation | **Reduction**

$3[S \longrightarrow S + 2e^-]$ | $6e^- + 2Cr \longrightarrow Cr_2$

Net Reaction

$$3S + 2Cr \longrightarrow 3S + Cr_2$$

$$3SO_2 + 2Na_2CrO_4 \longrightarrow Cr_2(SO_4)_3 + 2Na_2SO_4$$

Balanced Reaction:

$$3SO_2 + 2Na_2CrO_4 + 2H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 2Na_2SO_4 + 2H_2O$$

2. Ion electron method

Following rules are used to balance redox reaction by ion electron method:

(i) Divide the redox reaction in two half-reactions; one representing oxidation and other reduction.
(ii) Balance all the atoms except hydrogen and oxygen atom.
(iii) In acidic medium, balance hydrogen atom by H^+ ions and oxygen atom by H_2O molecule.
(iv) In basic medium, balance hydrogen atom by OH^- ions and oxygen atom by H_2O molecule.
(v) Balance the charge on each side of half-reaction by adding suitable number of electrons to the side deficient in it.
(vi) Multiply one or both the half-reactions with such a number so that total number of electrons lost and gained are equal.
(vii) Add the two half-reactions to get balanced redox reaction.

For example, (i) $\overset{(+7)}{Mn}O_4^- + \overset{(+3)}{C}_2O_4^{--} \longrightarrow \overset{(+4)}{C}O_2 + \overset{(+2)}{Mn^{+2}}$

(Acidic medium)

Oxidation | **Reduction**

$5[C_2O_4^{--} \longrightarrow 2CO_2 + 2e^-]$ $[MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{+2}] \times 2$

Net Reaction:

$$5C_2O_4^{-2} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$$

For example, (ii) $\overset{+4}{Cl}O_2 + \overset{+3}{Sb}O_2^- \longrightarrow \overset{+3}{Cl}O_2^- + \overset{+5}{Sb}(OH)_6^-$

(Basic)

Reduction | **Oxidation**

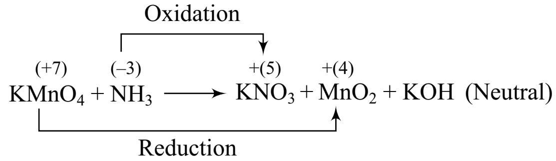
$[ClO_2 + e^- \longrightarrow ClO_2^-] \times 2$ $SbO_2^- + 2OH^- \longrightarrow Sb(OH)_6^- + 2e^-$

$$2ClO_2 + SbO_2^- + 2OH^- + 2H_2O \longrightarrow 2ClO_2^- + Sb(OH)_6^-$$

Balanced reaction:

$$2ClO_2 + SbO_2^- + 2OH^- + 2H_2O \longrightarrow 2ClO_2^- + Sb(OH)_6^-$$

For example, (iii)



$$K\overset{(+7)}{Mn}O_4 + \overset{(-3)}{N}H_3 \longrightarrow K\overset{+(5)}{N}O_3 + \overset{+(4)}{Mn}O_2 + KOH \text{ (Neutral)}$$

Oxidation | **Reduction**

$[NH_3 \longrightarrow KNO_3 + 8e^-] \times 3$ $[3e^- + 3KMnO_4 \longrightarrow MnO_2]8$

$$3NH_3 + 8KMnO_4 \longrightarrow 3KNO_3 + 8MnO_2 + 5KOH + 3H_2O$$

For example, (iv) $\overset{0}{Cl_2} \longrightarrow \overset{-1}{Cl^-} + \overset{+5}{Cl}O_3^-$ **(Basic)**

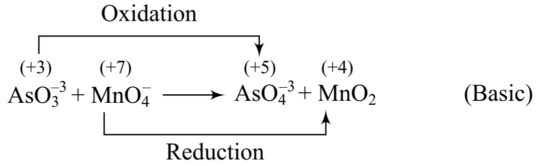
Oxidation | **Reduction**

$\frac{1}{2}Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5e^-$ $\left[\frac{1}{2}Cl_2 + e^- \longrightarrow Cl^-\right]5$

Balanced reaction

$$3Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$$

For example, (v)



$$\overset{(+3)}{As}O_3^{-3} + \overset{(+7)}{Mn}O_4^- \longrightarrow \overset{(+5)}{As}O_4^{-3} + \overset{(+4)}{Mn}O_2 \quad \text{(Basic)}$$

Oxidation

$$[2OH^- + AsO_3^{-3} \rightarrow AsO_4^{-3} + 2e^-] \times 3$$

Reduction

$$[3e^- + MnO_4^- \rightarrow MnO_2 + 4OH^-] \times 2$$

$$6OH^- + 3AsO_3^{-3} + 2MnO_4^- \longrightarrow 3AsO_4^{-3} + 2MnO_2 + 8OH^-$$

Balanced Reaction:

$$6OH^- + 3AsO_3^{-3} + 2MnO_4^- + 2H_2O \longrightarrow 3AsO_4^{-3} + 2MnO_2 + 8OH^-$$

Calculation of *n*-factor

For the calculation of n-factors reaction can be divided into three parts:

Acid-Base neutralisation reaction. Redox reaction and Substitution or exchange reaction.

Acid Base Neutralisation: For acid the number of H^+ ions donated or OH^- ions accepted or number of lone pair accepted by one molecule of acid is called its n-factor (Basicity of Acid). **For Base:** Number of H^+ ions accepted or OH^- ions released or lone pair donated by a molecule of a base in reaction is called *n*-factor (Acidity of Base)

For example, (i) $1H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

n-factor of $H_2SO_4 = 2$

n-factor of NaOH = 1

For example, (ii) $H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$

n-factor of $H_2SO_4 = 1$ and n_f of NaOH = 1

For example, (iii) $1\ Fe^{+2} + 6CN^- \longrightarrow [Fe(CN)_6]^{-4}$

n-factor 6 1

For example, (iv) $2H_3PO_4 + 3Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2 + H_2O$

n-factor 3 2

$$2H_3PO_4 + 3Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2 + 6H_2O$$

By observation we have balanced other elements in reaction.

Acid-Base Titration by using double indicators

For the titration of acids and bases, we use indicators which changes its colour in a particular PH range and indicate equivalence points in titration.

	PH range	Colour
Methyl orange (MeOH)	3.1–4.4	pink–yellow
phenolphthalein (HPH)	8.3–10	colourless–pink

For the titration of strong acid and strong bases we can use any indicator but for other titrations we used that indicator which has its pH range close to its equivalence point.

In case of polytrophic acid (H more than 1) and polyhydroxy bases (OH more than 1) we get more than 1 equivalence point so depending upon the choice of equivalence point we need a suitable indicator.

(i) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

first equivalence point

(ii) $NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

second equivalence point

(iii) $Na_2HPO_4 + NaOH \longrightarrow Na_3PO_4 + H_2O$

third equivalence point

⇒ In the titration of H_3PO_4 by NaOH in presence of methyl orange indicator the colour of solution changes at first equivalence point so n-factors in this case of H_3PO_4 is 1.

⇒ If we use phenolphthalein indicator in the same titration separately then change of colour occur at second equivalence point. In this case the n-factor of H_3PO_4 is 2.

Acidity of third acidic hydrogen is negligible.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

first equivalence point

$$NaHCO_3 + HCl \longrightarrow H_2CO_3 + NaCl$$

second equivalence point

***n*-factor in Redox reaction** = Total change in oxidation number per molecule either by oxidation or by reduction change in oxidation number per molecule during a reaction is called n-factor (in case of Redox reaction only)

Case-I $\overset{p}{A}x_1\,By_1 \longrightarrow \overset{q}{A}x_2\,By_2$

→ n-factor for $Ax_1By_1 = x_1|p - q|$

In the above case, there is no change in ON of B.

→ n-factor for $Ax_2By_2 = x_2|q - p|$

Important Reaction:

Permanganate ion

1. $\overset{+7}{Mn}O_4^- \longrightarrow Mn^{+2}$ (Acidic medium)
   (5) = n-factor
2. $\overset{+7}{Mn}O_4^- \longrightarrow \overset{+4}{Mn}O_2$ (Neutral medium) or weak basic
   (3) = n-factor
3. $\overset{+7}{Mn}O_4^- \longrightarrow \overset{+6}{Mn}O_4^{-2}$ (Basic medium)
   (1) = n-factor
4. $\overset{+6}{Cr_2}O_7^{--} \longrightarrow Cr^{+3}$ (Acidic/Basic)
   $2|6 - 3| = 6 = n$-factor
5. $\overset{+3}{C_2}O_4^{-2} \longrightarrow \overset{+4}{C}O_2$ (Any medium)
   $2|3 - 4| = n$-factor $= 2$
6. $\overset{+2}{S_2}O_3^{-2} \longrightarrow \overset{2.5}{S_4}O_6^{-2}$
   Thiosulphate
   $2|2 - 2.5| = 1 = n$-factor
   Some times its also called as hypo. ($Na_2S_2O_3.\ 2H_2O$)
7. $\overset{0}{I_2} \longrightarrow \overset{-1}{I^-}$ (Any medium)
   n-factor $= 2|0 + 1| = 2$
8. $Fe^{+2} \longrightarrow Fe^{+3}$
   n-factor $= |3 - 2| = 1$

Concentrated nitric acid behaves as strong oxidising agent and reduces itself into NO_2.

Concentrate $\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2}$

n-factor $= |5 - 4| = 1$

Case-II

$$\overset{p}{A}x_1\,\overset{r}{B}y_1 \longrightarrow \overset{q}{A}x_2\,\overset{s}{B}y_2$$

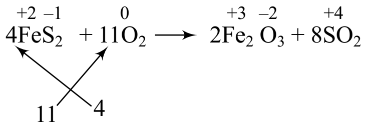
n-factor of $Ax_1By_1 = x_1\,|p - q| + y_1\,|r - s|$

Condition: In the above case either both A and B are oxidising or A and B are reducing.

$$4H_2O + 3\overset{+3\ -2}{As_2S_3} + 28\overset{+5}{HNO_3} \longrightarrow 6H_3\overset{+5}{As}O_4 + 9H_2\overset{+6}{S}AO_4 + \overset{+2}{N}O$$

n-factor 28 3

n-factor of $AS_2S_3 = 2|3 - 5| + 3|-2 - 6| = 28$
n-factor of $HNO_3 = 1|5 - 2| = 3$
All other remaining are balanced by observation.



$$\begin{aligned} n\text{-factor of } FeS_2 &= |2-3| + 2|-1-4| \\ &= 1 + 2(5) = 11 \end{aligned}$$

n-factor of $O_2 = 2|0 + 2| = 4$

∴ **balanced reaction**

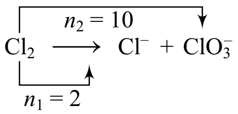
$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

Case-III Disproportionation Reaction

$n_1 = 2 =$ n-factor for reduction

$n_2 = 10 =$ n-factor for oxidation

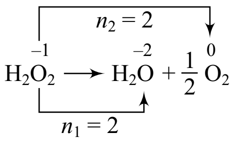
Ex. 1



$$\frac{1}{n} = \frac{1}{n_1} + \frac{1}{n_2} \text{ or } n = \left(\frac{n_1 n_2}{n_1 + n_2}\right)$$

$$\Rightarrow \quad n = \frac{|2 \times 10|}{10 + 2} = \frac{20}{12}$$

$$n = \frac{5}{3}$$



$$3Cl_2 + 6OH^- \longrightarrow 5Cl^- + ClO_3^- + 3H_2O$$

$$n = \frac{n_1 n_2}{n_1 + n_2}$$

$$n = \frac{2 \times 2}{2 + 2}$$

$$n = 1$$

Case-IV Complex Reaction occur in more than one step

For example,

(i) $3\overset{0}{Cu} + 8H\overset{+5}{N}O_3 \longrightarrow 3\overset{+2}{Cu}(\overset{+5}{N}O_3)_2 + 2\overset{+2}{N}O + 4H_2O$

$$\begin{array}{r} \text{Redox} \\ \text{Acid-Base} \end{array} \begin{bmatrix} 3Cu + 2HNO_3 \longrightarrow 3CuO + 2NO + H_2O \\ 3CuO + 6HNO_3 \longrightarrow 3Cu(NO_3)_2 + 3H_2O \end{bmatrix}$$

$$n_{\text{factor}} \begin{cases} Cu \quad + \quad HNO_3 & \\ n_1 \qquad\quad n_2 & n_1 = n_f \text{ of } Cu = 2 \\ \qquad\quad \Downarrow & n_2 = ? \end{cases}$$

$n_2Cu + n_1HNO_3$

$$\frac{1}{4}[3Cu + 8HNO_3]$$

$$\frac{3}{4}Cu + 2HNO_3$$

$$n_1 = 2 \quad \therefore \quad n_2 = \frac{3}{4}$$

$$\therefore \quad n\text{-factor of } HNO_3 = \frac{3}{4}$$

For example,

(ii) $4\overset{0}{Zn} + 10HNO_3 \longrightarrow 4\overset{+2}{Zn}(NO_3)_2 + NH_4NO_3 + 3H_2O$

$\quad 2 \qquad n$

$$\frac{1}{5}[4Zn + 10HNO_3]$$

$$\frac{4}{5}Zn + 2HNO_3$$

$$n\text{-factor of } HNO_3 = \frac{4}{5}$$

For example,

(iii) $\overset{0}{P_4} + 10HNO_3 + H_2O \longrightarrow 4H_3\overset{+5}{P}O_4 + 5NO + 5NO_2$

$\quad 20 \qquad x$

$2[P_4 + 10HNO_3]$

$2P_4 + 20HNO_3$

n-factor of HNO_3 is 2

Case-V $\overset{p}{Ax_1By_1} \longrightarrow \overset{q}{Ax_2By_2} + \overset{r}{Ax_3By_3}$

In the above case either the oxidation of A is taking place or reduction of A is taking place in product side.

If $\quad x_1 = x_2 + x_3$

$$\begin{aligned} n\text{-factor of } Ax_1By_1 &= |x_1p - x_2q - x_3r| \\ &= |x_2(p - q) + x_3(p - r)| \end{aligned}$$

If $\quad x_1 \neq x_2 + x_3$

$$aAx_1By_1 \longrightarrow bAx_2By_2 + cAx_3By_3$$

$$\Rightarrow \quad ax_1 = bx_2 + cx_3$$

$$\begin{aligned} n\text{-factor of } Ax_1By_1 &= \frac{|ax_1p - bx_2q - cx_3r|}{a} \\ &= \frac{|bx_2(p-q) + cx_3(p-r)|}{a} \end{aligned}$$

For example,

(i) $H_2O + P_4 + 10H\overset{+5}{N}O_3 \longrightarrow 4H_3PO_4 + 5\overset{+2}{N}O + 5\overset{+4}{N}O_2$

$$n\text{-factor of } HNO_3 = \frac{|10 \times 5 - 5 \times 2 - 5 \times 4|}{10}$$

For example,

(ii) $4\overset{+2}{Fe}(\overset{+3}{Cr}O_2)_2 + 8Na_2\overset{+4}{C}O_3 + 7\overset{0}{O_2} \longrightarrow$

$$2\overset{+3}{Fe_2}\overset{-2}{O_3} + 8Na_2\overset{+6}{Cr}O_4 + 8\overset{+4}{C}\overset{-2}{O_2}$$

n-factor of $Fe(CrO_2)_2 = 1|2-3| + 2|3-6| = 7$

n_{factor} of $O_2 = 2[0-(-2)] = 4$

Case-VI

Reduction

$n_2 = 3$

For example, $\overset{-3}{N}H_4\overset{+3}{N}O_2 \longrightarrow \overset{0}{N_2} + 2H_2O$

$n_1 = 3$

Oxidation

In this case, we will calculate either the n-factor for oxidation or the n-factor for reduction. The value of both is same and is equal to n-factor of the compound.

n-factor for NH_4NO_2
$= n$-factor for oxidation (n_1)
$= n$-factor for reduction (n_2)
$= 3$

Reduction

For example, $\overset{+7}{Mn_2}\overset{-2}{O_7} \longrightarrow \overset{+4}{Mn}\overset{-2}{O_2} + \overset{-2}{O_2}$

Oxidation

n-factor of Mn_2O_7 $= n$-factor for reduction
$= 2|7-4|$
$= 6$

n-factor of Mn_2O_7 calculated by Mn not by oxygen because few oxygen present in -2 oxidation state also in MnO_2 means No change in oxidation state.

$\therefore$ n-factor of Mn_2O_7 $= n$-factor for oxidation
$= 2|-2-0|$
$= 14$ (wrong)

$$Mn_2O_7 \longrightarrow 2MnO_2 + \frac{3}{2}O_2$$

$\therefore$ n-factor of $Mn_2O_7 = 3\,|-2-0|$
$= 6$ correct

Substitution or Exchange Reaction

In these type of reaction exchange of cations and anions occur between salts during the reaction and products may be some precipitate.

n-factor of the salt = (Number of metal ions) × (their charge)

For example, (i) $2AgNO_3 + 1CaCl_2 \longrightarrow \underset{\text{(ppt)}}{2AgCl} + Ca(NO_3)_2$

1 2

For example, (ii) $2(NH_4)_2SO_4 + 2BaCl_2 \longrightarrow \underset{\text{(ppt)}}{2BaSO_4} + 4NH_4Cl$

2 2

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

Whatever the substance is solute or solvent is slightly controversial and should be concluded in following case.

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

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

Amount 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 conc. Terms defined are applicable only for homogenous mixture not for heterogeneous mixture.

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

   Unit gm/ml or gm/L
   It is temperature dependent because Mass independent of temperature but volume depend upon temperature. ($T \propto V$)
   $\therefore$ T inversily proportional to density

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

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

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

   Temperature independent
   Eg.:- 20% mass of NaOH solution means 100 gm of solution contain 20 gm of NaOH and mass of solvent is 80 gm.

3. % Weight by volume or $\dfrac{W}{V}\%$ or % by volume :-

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

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

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

   Molarity :- $M = \dfrac{\text{Moles of solute}}{\text{Volume in liter}}$

   Temperature dependent
   Eg. 2 M NaCl solution means 1 Litre solution contains 2 moles of NaCl.

MOLARITY OF PURE SUBSTANCE

1 ml contain = 1 gm
1000 ml = 1000 gm = 55.56 moles
$\therefore$ moles in 1 L pure solution

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

MOLALITY [m]

Number of moles of solute in one kg solvent.
So temperature independent.
Eg. 2 m solution of NaCl means 2 mole of NaCl present in 1000 gram 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 $x_A + x_B = 1$

$$x_B = 1 - x_A$$

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

If $\Sigma n = 1$

$$x_A = n_A$$

It means mole fraction of A = mole of A.

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

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

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

(i) For gases

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

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

→ For gases parts = volume = moles

→ For solid/liquid parts = weight

(ii) For solid/liquid

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

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

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

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

SOME TYPICAL CONCENTRATION TERMS

These conc. terms are typical in the sence that they are defined exclusively for the substance concerned depending upon for what purpose substances are used.

(i) Concentration of H_2O_2: - H_2O_2 is used as a source of oxygen gas and hence the typical conc. 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 Litre of H_2O_2 gives x litre of O_2 gas at STP.

Eg. 20 volume H_2O_2 means 1 Litre of H_2O_2 gives 20 Litre of O_2 at STP. It can be converted to normal concentration.

"V volume H_2O_2" means 1 Litre of H_2O_2 gives V litre of O_2 gas at STP.

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

$$n_{O_2} = \frac{V}{22.4}$$

$$\therefore \quad n_{H_2O_2} = 2 \times n_{O_2}$$

$$= 2 \times \frac{V}{22.4} = \frac{V}{11.2} \text{mole}$$

$$\text{Molarity M} = \frac{\text{Number of moles}}{\text{Volume in L}} = \frac{\text{V/11.2}}{\text{1L}}$$

$$\therefore \quad \text{Molarity} = \frac{V}{11.2}\text{M}$$

$$\frac{V}{11.2} = \left(\frac{\text{W}}{\text{V}}\%\right) \times \frac{10}{34}$$

$$\frac{V}{11.2} = \left(\frac{\text{W}}{\text{W}}\%\right) \times \frac{10d}{34}$$

$$n_f \text{ of } H_2O_2 = 2$$

$$\because \quad N = n_f \cdot M$$

$$\therefore \quad N = 2 \times \frac{V}{11.2} = \frac{V}{5.6}$$

and H_2O_2 in gm/Liter = $N \times 17$ = strength in gm/L

$$= \frac{V}{5.6} \times 17 \text{ gm/L}$$

Molar mass of H_2O_2 = 34

and equivalent weight of $H_2O_2 = \frac{34}{2} = 17$

CONCENTRATION OF OLEUM

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

H_2SO_4	+	SO_3	$\longrightarrow$	$H_2S_2O_7$
Liq.		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 gm of this sample of oleum can maxima give x gm of H_2SO_4 by the addition of $(x - 100)$ gm of water.

For e.g. 109% oleum means 100 gm oleum is capable of giving 109 gm H_2SO_4 by adding 9 gm of H_2O in 100 gm of oleum.

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

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

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

Relation between concentration term

$$\text{Molality (m)} = \frac{1000\text{M}}{1000d - (M \times \text{Molar Mass of Solute})}$$

$$\text{Molarity (M)} = \left(\frac{\text{W}}{\text{V}}\%\right) \times \frac{10}{\text{Molar Mass of Solute}}$$

$$\text{Molarity (M)} = \left(\frac{\text{W}}{\text{W}}\%\right) \frac{10 \times d}{\text{Molar Mass of Solute}}$$

$$\text{Molality (m)} = \frac{\text{Mole Fraction of Solute}}{\text{Mole Fraction of Solvent}} \times \frac{1000}{\text{Molar Mass of Solvent}}$$

LAW OF EQUIVALENCE

In any chemical reaction, one equivalent of any substances will react with one equivalent of other substances and will produced one equivalent of products.

or

In any chemical reaction, the equivalents of substance react or the equivalent of product produced will always be same.

$$\text{Equivalent or gram equivalent} = \frac{\text{weight of substance}}{\text{equivalent weight}}$$

$$\Rightarrow \quad \text{Equivalent weight} = \frac{\text{Molar Mass(M)}}{n\text{-factor}}$$

$$E = \frac{M}{n\text{-factor}}$$

where M is molecular mass or molecular weight

$$\text{Equivalent} = \frac{\text{weight of substance}}{M/n\text{-factor}}$$

$$\text{Equivalent} = \frac{w}{M} \times n\text{-factor}$$

Equivalent = moles × n-factor

where $w \rightarrow$ weight of substance

Unbalanced Reaction

$$\begin{tikzcd} A + B \arrow[r] & C \arrow[d, "G"] & + & D \arrow[d, "E"] \\ & H & & F \end{tikzcd}$$

Equivalents of A reacted = equivalent of B reacted
= equivalent of C produced
= equivalent of G reacted
= equivalent of H produced
= equivalent of D produced
= equivalent of E reacted
= equivalent of F produced

NORMALITY

This is defined as the number of equivalent or gram equivalent of any substances dissolved in one litre of solution.

$$N = \frac{\text{Equivalent}}{\text{Volume (in litre)}}$$

$$N = \frac{\text{Moles} \times n\text{-factor}}{\text{Volume (in litre)}}$$

- Normality = Molarity × n-factor
- Equivalent = Volume (in litre) × N
- Milli-equivalent = volume (in mL) × N

On dilution moles and equivalent will not change or equivalent of substance will not change on dilution.

BACK TITRATION

Back titration is mainly used to calculate amount of agent used in excess or to find out percentage purity of any sample.

In this method, for the excess of agent we use some other agent and with the help of this we can find out the agent used initially for the reaction mixture and with this we can find out the initial composition.

IODOMERTRIC TITRATION

In iodomeric titration we use potassium iodide in solution which has some oxidising agent.

This oxidising agent oxidises iodide to iodine (I_2). The iodine librated can be measured by following ways:

Oxadising agent + KI (excess) $\longrightarrow$ Reduced form + I_2(solid)

I_2 react with any of the reducing agent.

1. $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$
2. $I_2 + I^- \longrightarrow I_3^-$ (dark brown)
3. $I_2 + AsO_3^{-3} \longrightarrow I^- + AsO_4^{-3}$

Some important reactions

$$\begin{array}{lcccccccc}
\text{(i)} & \overset{-1}{KI} & + & MnO_4^- & \longrightarrow & \overset{+5}{IO_3^-} & + & Mn^{+2} \\
 & x\text{ eq} & = & x\text{ eq} & = & x\text{ eq} & = & x\text{ eq} \\
 & & & & \multicolumn{4}{r}{\text{(According to law of equivalence)}} \\
 & (n_f)6 & & 5 & & 6 & & 5 \\
\text{(ii)} & \overset{+5}{IO_3^-} & + & \overset{+4}{SO_2} & \longrightarrow & \overset{+6}{SO_4^{-2}} & + & \overset{0}{I_2} \\
 & (n_f)5 & & 2 & & 2 & & 10 \\
\text{(iii)} & I^- & + & Cu^{+2} & \longrightarrow & Cu^+ & + & I_2 \\
 & (n_f)1 & & 1 & & 1 & & 2 \\
\text{(iv)} & I_2 & + & Na_2S_2O_3 & \longrightarrow & Na_2S_4O_6 & + & NaI \\
 & (n_f)2 & & 1 & & 1 & & 2
\end{array}$$

Back titration if HCl react with NaOH and excess HCl neutralise by $Ca(OH)_2$

$$NaOH + HCl \longrightarrow \text{salt} + \text{water}$$

(Equivalent of NaOH) = given HCl equivalent – [remaining equivalent of HCl]

$$HCl + Ca(OH)_2 \longrightarrow \text{Product}$$

[Remaining equivalent of HCl] = [equivalent of $Ca(OH)_2$]

Results

1. Remaining equivalent of HCl = equivalent of $Ca(OH)_2$
2. Equivalent of NaOH = [given equivalent of HCl] – [Remaining equivalent of HCl]
3. Equivalent of NaOH = [given equivalent of HCl] – [equivalent of $Ca(OH)_2$]

Hardness of Water

Hard water is that which does not gives foam with soap.

Classification of Hardness of Water

1. Permanent hardness
2. Temporary hardness

Temporary Hardness

This type of hardness easily removed by heating of water sample.

$$Ca(HCO_3)_2 \text{ (soluble)} \xrightarrow{\Delta} CaCO_3 \downarrow + CO_2 + H_2O$$

It is generated by bicarbonate of calcium and magnesium.

Permanent Hardness

It is removed by suitable chemical process. It is generated by chloride, sulphate of calcium and magnesium.

Degree of Hardness

$$\text{(Parts per million) PPM} = \frac{\text{weight of solute}}{\text{weight of solvent}} \times 10^6$$

	$CaCO_3$	$CaCl_2$	$MgCO_3$	$MgCl_2$
weight of 1 equivalent	$\frac{100}{2}$	$\frac{111}{2}$	$\frac{84}{2}$	$\frac{95}{2}$

It is defined as mass of $CaCO_3$ equivalent to the mass of various calcium and magnesium salts present. in 10^6 gram of water in dilute solution where the density is approximately equal to 1 gm/ml.

Solved Examples

1. Balance the following reaction

$$V + H_2O \longrightarrow H_4V_6O_{17} + H_2$$

Sol. $\overset{0}{V} + \overset{+1}{H_2}O \longrightarrow H_4\overset{+5}{V_6}O_{17} + \overset{0}{H_2}$

Oxidation	**Reduction**
$6V \longrightarrow V_6 + 30e^-$	$[H_2 + 2e^- \longrightarrow H_2]15$

Net reaction:

$$6V + 15\,H_2 \longrightarrow V_6 + 15H_2$$

$$6V + 15H_2O + 2H_2O \longrightarrow H_2V_6O_{17} + 15H_2$$

Final reaction:

$$6V + 17\,H_2O \longrightarrow H_4V_6O_{17} + 15H_2$$

2. Balance the following reaction

$$NH_4OH + Br_2 \longrightarrow NH_4Br + H_2O + N_2$$

Sol. $\overset{(-3)}{N}H_4OH + \overset{(0)}{Br_2} \longrightarrow \overset{(-3)}{N}H_4\overset{(-1)}{Br} + H_2O + \overset{(0)}{N_2}$

Reduction

Oxidation

Oxidation	**Reduction**
$2N \longrightarrow N_2 + 6e^-$	$[2e^- + Br_2 \longrightarrow 2\,Br]3$

Net reaction:

$$2N + 3Br_2 \longrightarrow N_2 + 6Br$$

$$2NH_4OH + 3Br_2 + 6NH_4OH \longrightarrow N_2 + 6NH_4Br + 8H_2O$$

Balanced Reaction:

$$6NH_4OH + 3Br_2 \longrightarrow N_2 + 6NH_4Br + 8H_2O$$

3. Find valency factor of H_2SO_4 in given reaction
$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$
Base Acid

Sol. Valency factor of base = 1
Valency factor of acid = 2
Here two molecules of NaOH replaced $2H^+$ ion from the H_2SO_4, therefore, per molecule of NaOH replaced only one H^+ ion of acid so valency factor = 1

4. Find valency factor of H_2SO_4 in given reaction
$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$
Base acid

Sol. Valence factor of acid = 1
Here one of molecule of H_2SO_4 replaced one OH^- from NaOH therefore valency factor for H_2SO_4 is = 1.

$$E = \frac{\text{molecular weight of } H_2SO_4}{1}$$

5. Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

Sol. Normality (N) = $\dfrac{W \times 1000}{E \times \text{VmL}}$

where $W = 15.8$ g, $V = 50$ mL

$$E = \frac{\text{Molar mass of } KMnO_4}{\text{Valence factor}} = 158/5 = 31.6$$

So, $N = \dfrac{15.8 \times 1000}{31.6 \times 50} = 10.$

6. Calculate the normality of a solution containing 50 mL of 5 M solution $K_2Cr_2O_7$ in acidic medium.

Sol. In acidic medium Cr change its oxidation state +6 to +3
$\therefore \quad n_f = (6 – 3) \times 2 = 6$
Normality (N) = Molarity × Valence factor
= 5 × 6 = 30 N

7. Find the number of moles of $KMnO_4$ needed to oxidise one mole Cu_2S in acidic medium.
The reaction is $KMnO_4 + Cu_2S \longrightarrow Mn^{2+} + Cu^{2+} + SO_2$

Sol. Valence factor of $\overset{+1}{Cu_2}\overset{-2}{S} \longrightarrow Cu^{+2}$ and $\overset{+4}{S}$

$n_f = 2[2 – 1] + 1|–2 –4| = 8$

Valence factor of $K\overset{+7}{Mn}O_4 \longrightarrow \overset{+2}{Mn}$

$n_f = 1|7 – 2| = 5$

From law of equivalence
Equivalents of Cu_2S = Equivalents of $KMnO_4$
Moles of Cu_2S × v.f = moles of $KMnO_4$ × Valence factor
Moles of Cu_2S × 8 = 1 × 5 ⇒ Moles of Cu_2S = 5/8

8. What is the equivalent weight of $C_{12}H_{22}O_{11}$ in the following reaction?

Sol. $\overset{0}{C_{12}}H_{22}O_{11} + 36HNO_3 \longrightarrow$

$$6H_2\overset{+3}{C_2}O_4 + 36NO_2 + 23H_2O$$

$$\text{Equivalent wt} = \frac{\text{Molar mass}}{n\text{-factor}}$$

n-factor for $C_{12}H_{22}O_{11} = 12|0 – 3| = 36$

$$E = \frac{342}{36} = 9.5$$

9. What is the equivalent weight of phosphorous in the following reaction?

$$P_4 + NaOH \longrightarrow NaH_2PO_2 + PH_3$$

Sol. $n_2 = 4|0 – 1| = 4$

$$\overset{0}{P_4} + NaOH \longrightarrow NaH_2\overset{+1}{P}O_2 + \overset{-3}{P}H_3$$

$4|0 – 3| = 12 = n_1$

$$P_4^0 + NaOH \longrightarrow NaH_2PO_2 + PH_3$$

n_f for disproportion ation $n_f = \dfrac{n_1 n_2}{n_1 + n_2}$

$n_1 = 12$ (reduction)
$n_2 = 4$ (oxidation)

$$n_f = \frac{12 \times 4}{12 + 4}$$

$n_f = 3$

$$\text{Equivalent weight} = \frac{\text{Molar mass}}{n_f}$$

$$\therefore \quad \text{Equivalent weight} = \frac{4 \times 31}{3} = \frac{124}{3} = 41.33$$

10. What mass of N_2H_4 can be oxidised to N_2 by 24 g of K_2CrO_4 which is reduced to $Cr(OH)_4^-$?

Sol. $\overset{-2}{N_2}H_4 + \underset{24gm}{K_2\overset{+6}{Cr}O_4} \longrightarrow \overset{+3}{Cr}(OH)_4^- + \overset{0}{N_2}$

Atomic weight of chromium = 52
n-factor of N_2H_4 = 4 = Δ O.N of nitrogen in N_2H_4
n-factor of K_2CrO_4 = 3 = Δ O.N of cromium in K_2CrO_4
Equivalent of N_2H_4 = Equivalent of K_2CrO_4

$$\left(\frac{w}{32/4}\right) = \left(\frac{24}{194/3}\right)$$

$$w = \frac{24 \times 3}{194} \times \frac{32}{4}$$

$$= \frac{18 \times 32}{194}$$

$w = 2.969$ g

11. What will be the moles of permaganate ion that will be needed to react with one mole of Ferrous oxylate in acidic condition?

Sol. $\overset{+2}{Fe}(\overset{+3}{C_2}O_4) + \overset{+7}{Mn}O_4^- \longrightarrow Mn^{+2} + \overset{+4}{C}O_2 + Fe^{+3}$

n-factor of $Fe(C_2O_4) = 1[3 – 2] + 2[4 – 3] = 3$

n-factor of $MnO_4^- = [2 – 7] = 5$

Equivalent of FeC_2O_4 = Equivalent of MnO_4^-

$$1 \times 3 = n \times 5$$

$$n = \frac{3}{5} \text{ moles}$$

12. 2.68×10^{-3} moles of an ion in a solution requires 1.61×10^{-3} moles of permaganate ion for oxidation of A^{+n} to AO_3^- in Acidic medium? What is the value of n?

Sol. Here MnO_4^- reduced into Mn^{+2} and A^{+n} oxdise into +5 means $n < 5$ and n_f of $A^{+n} = (5 - n)$

Oxidise $n_f = (5 - n)$

$$A^{+n} + \overset{+7}{MnO_4^-} \longrightarrow \overset{+5}{AO_3^-} + \overset{+2}{Mn^{+2}}$$

reduce and $n_f = (7 - 2) = 5$

Equivalence of A^{+n} = Equivalence of MnO_4^-

$$(5 - n) \times 2.68 \times 10^{-3} = 5 \times 1.61 \times 10^{-3}$$

$$\therefore \quad 5 - n = \frac{5 \times 1.61}{2.68}$$

$$\therefore \quad -n = \frac{5 \times 1.61}{2.68} - 5$$

$$n = \frac{5 \times 2.68 - 5 \times 1.61}{2.68}$$

$$n = \frac{5(1.07)}{2.68} \approx 2$$

13. A sample weighing 2.186 g containing a mixture AO and A_2O_3 takes .015 moles of potassium dichromate ($K_2Cr_2O_7$) to oxidise the sample completely to form AO_4^- and Cr^{+3}. If 0.0187 moles of AO_4^- is formed, what is atomic weight of A?

Sol. $\overset{+2}{AO} + \overset{+3}{A_2O_3} + \overset{+6}{K_2Cr_2O_7} \longrightarrow \overset{+7}{AO_4^-} + \overset{+3}{Cr^{+3}}$

Reduction

n-factor of $K_2Cr_2O_7 = 2|6 - 3|$
$= 2 \times 3$
$= 6$

n-factor of AO $[7 - 2] = 5$

n-factor of $A_2O_3 = 2(7 - 3) = 8$

If x mole AO and y mole A_2O_3 present in mixture.

x mole

$$\overset{+2}{AO} + K_2Cr_2O_7 \longrightarrow \overset{+7}{AO_4^-} + Cr^{+3}$$

$$\overset{+3}{A_2O_3} + K_2Cr_2O_7 \longrightarrow \overset{+7}{AO_4^-} + Cr^{+3}$$

y mole

$$x \times 5 + y \times 8 = 0.015 \times 6$$

$5x + 8y = 0.015 \times 6$ ...(i)

$x[M + 16] + y[2M + 48] = 2.186$ ...(ii)

Given $x + 2y = 0.0187$ ...(iii)

Solving the above three equations we get x, y and M (atomic mass of A)

OR

Equivalent of AO + Equivalent of A_2O_3
= Equivalent of $K_2Cr_2O_7$
= Equivalent of AO_4^-

14. To a 25 mL H_2O_2 solution excess of acidified solution of potassium iodide was added. The iodine liberate require 20 mL of 0.3 N solution $Na_2S_2O_3$. Calculate volume strength of H_2O_2 solution?

Sol. $\underset{25\text{ mL}}{H_2O_2} + \underset{\text{excess}}{KI} \longrightarrow I_2 + H_2O$

$$I_2 \xrightarrow{Na_2S_2O_3\ (20\text{ mL, }0.3\text{ N})} NaI + Na_2S_4O_6$$

Equivalent of H_2O_2 = Equivalent of KI reacted
= Equivalent of I_2 formed
= Equivalent of $Na_2S_2O_3$

$$N \times 25 = 20 \times 0.3$$

$$N = \frac{6}{25} = M \times 2$$

$$M = \frac{V}{11.2} = \frac{3}{25}$$

$$M = \frac{3}{25}$$

$$\text{V.S.} = \frac{11.2 \times 3}{25}$$

$$\text{V.S.} = 1.344$$

Since Volume strength $= 11.2 \times M = \dfrac{11.2 \times N}{2}$

or Volume strength $= 5.6 \times N$

15. If a 1 L sample of water has 50 mg calcium chloride then calculate degree of hardness of this water sample.

Sol. 111 g $CaCl_2$ equivalent to 100 g $CaCO_3$

1 g $CaCl_2$ equivalent to 100 g $CaCO_3$ $\dfrac{100}{111}$ gram $CaCO_3$

$\therefore$ 50 mg $CaCl_2$ equivalent to $\dfrac{100}{111} \times 50$ mg $CaCO_3$

Degree of hardness

$$= \frac{\frac{100}{111} \times 50 \text{ mg}}{1000 \text{ mL} = 1000 \text{ g}} \times 10^6 \text{ PPM}$$

$$= \frac{100 \times 50 \times 10^{-3} \text{ g}}{111 \times 1000 \text{ g}} \times 10^6$$

$$= \frac{100 \times 50}{111} = 45 \text{ PPM}$$

16. What weight of Na_2CO_3 of 85% purity would be required for 45.6 mL of 0.235 N H_2SO_4 for complete reaction.

Sol. Milliequivalents of Na_2CO_3 = Milliequivalents of H_2SO_4
$= 45.6 \times 0.235$

$$\therefore \quad \frac{W_{Na_2CO_3}}{E_{Na_2CO_3}} \times 1000 = 45.6 \times 0.235$$

$$\Rightarrow \quad \frac{W_{Na_2CO_3}}{106/2} \times 1000 = 45.6 \times 0.235$$

$$\therefore \quad W_{Na_2CO_3} = 0.5679 \text{ g}$$

For 85 g of pure Na_2CO_3, weighed sample = 100 g

$\therefore$ for 0.5679 g of pure Na_2CO_3, weighed sample = $\frac{100}{85} \times 0.5679 = 0.6681$ g

17. 20 mL of H_2O_2 after acidification with dil H_2SO_4 required 30 mL of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. The strength of H_2O_2 solution is [Molar mass of H_2O_2 = 34]

Sol. $30 \times \frac{1}{12} = 20 \times N'$

$$N' = \frac{30}{12 \times 20} = \frac{1}{8}$$

$\therefore$ strength = N′ × equivalent mass = $\frac{1}{8} \times 17 = 2.12$ g/L

18. 3.55 g sample of bleaching powder suspended in H_2O was treated with enough acetic acid and KI solution. Iodine thus liberated requires 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine.

[Available Chlorine = Mass of chlorine liberated/mass of bleaching powder × 100]

Sol. Moles of iodine = Moles of chlorine = $\frac{80 \times 0.2}{2} \times 10^{-3}$ = 8×10^{-3}

so required % = $\frac{8 \times 71 \times 10^{-3}}{3.55} \times 100\% = 16\%$

19. Calculate the molar ratio in which the following two substances would react?

$Ba_3(PO_4)_2$ and $AlCl_3$

Sol. n-factor of $Ba_3(PO_4)_2 = 3 \times (+2) = 6 = n_1$

While n-factor of $AlCl_3 = 1 \times (+3) = 3 = n_2$

$$\frac{n_1}{n_2} = \frac{6}{3} \text{ If } \frac{n_1}{n_2} = \frac{x}{y}$$

Molar ratio = $\frac{y}{x}$ (inverse of equivalent ratio)

$\therefore$ molar ratio in which $Ba_3(PO_4)_2$ and $AlCl_3$ will react = 3:6 = 1:2

20. 1.20 g sample of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 mL of solution. 20 mL of this solution required 40 mL of 0.1 N HCl for complete neutralisation. Calculate the weight of Na_2CO_3 in the mixture. If another 20 mL of this solution is treated with excess of $BaCl_2$ what will be the weight of the precipitate?

Sol. Let weight of $Na_2CO_3 = x$ g

Weight of $K_2CO_3 = y$ g

$\therefore x + y = 1.20$ g …(i)

For neutralisation reaction of 100 mL

Milliequivalents of Na_2CO_3 + Milliequivalents of K_2CO_3 = Milliequivalents of HCl

$$\Rightarrow \frac{x}{106} \times 2 \times 1000 + \frac{y}{138} \times 2 \times 1000 = \frac{40 \times 0.1 \times 100}{20}$$

$\therefore \quad 69x + 53y = 73.14$ …(ii)

From Eqs. (i) and (ii), we get

$x = 0.5962$ g

$y = 0.604$ g

Solutions of Na_2CO_3 and K_2CO_3 gives ppt. of $BaCO_3$ with $BaCl_2$

(Milliequivalents of Na_2CO_3 + Milliequivalents of K_2CO_3) in 20 mL = Milliequivalents of $BaCO_3$

$\Rightarrow$ Milliequivalents of HCl for 20 mL mixture = Milliequivalents of $BaCO_3$

$\Rightarrow$ Milliequivalents of $BaCO_3 = 40 \times 0.1 = 4$

$$\frac{W_{BaCO_3}}{M_{BaCO_3}} \times 1000 = 40 \times 0.1 = 4$$

$$\frac{W_{BaCO_3}}{197} \times 2 \times 1000 = 4$$

$$\therefore \quad W_{BaCO_3} = 0.394 \text{ g}$$

21. A 20 g sample of only CuS and Cu_2S was treated with 100 mL of 1.25 M $K_2Cr_2O_7$. The products obtained were Cr^{3+}, Cu^{2+} and SO_2. The excess oxidant was reacted with 50 mL of Fe^{2+} Solution:25 mL of the same Fe^{2+} solution required 0.875 M $KMnO_4$ under acidic condition, the volume of $KMnO_4$ used was 20 mL. Find the % of CuS and Cu_2S in the sample.

Sol. Equivalents of dichromate initially

$$= \frac{1.25 \times 6 \times 100}{1000} = 0.75$$

Equivalents of Fe^{2+} in 25 mL

$$= \frac{0.875 \times 5 \times 5 \times 20}{1000} = 0.0875$$

Equivalents of Fe^{2+} in 50 mL = 0.0875 × 2 = 0.175

Equivalents of excess dichromate = 0.175

$\therefore$ equivalents of dichromate consumed by (CuS and Cu_2S)

$= 0.75 - 0.175 = 0.575$

If x g is the mass of CuS, the mass of Cu_2S is $(20 - x)$ g

$$\frac{x}{95.5} \times 6 + \frac{(20-x)}{159} \times 8 = 0.475$$

$\therefore \quad x = 5.74$ g

$$\% \quad CuS = \frac{5.74}{20} \times 100 = 28.7\ \%$$

$\% \quad Cu_2S = 71.3\%$

22. 2.249 g of a sample of pure $BaCO_3$ and impure $CaCO_3$ containing some CaO was treated with dil. HCl and it evolved 168 mL of CO_2 at N.T.P. From this solution, $BaCrO_4$ was precipitated filtered and washed. The precipitate was dissolved in dil. H_2SO_4 and diluted to 100 mL. 10 mL of this solution when treated with KI solution liberated iodine which required exactly 20 mL of 0.05 N $Na_2S_2O_3$. Calculate the percentage of CaO in the sample.

Sol. Let weight of $BaCO_3$, $CaCO_3$ and CaO are x, y and z respectively.

$\therefore \quad x + y + z = 2.249$

$$BaCO_3 \longrightarrow BaCrO_4$$

Redox change $Cr^{6+} + 3e^- \longrightarrow Cr^{3+}$

$$2I^- \longrightarrow I_2 + 2e^-$$

Milliequivalents of $BaCO_3$ = Milliequivalents of $BaCrO_4$ = Milliequivalents of I_2

$$\therefore \quad \frac{x}{197/3} \times 1000 = 20 \times 0.05 \times \frac{100}{10}$$

$$\therefore \quad x = 0.657 \text{ g} \qquad ....(1)$$

The equivalent weight of $BaCrO_4$ is M/3, therefore for $BaCO_3$, it should be M/3 also because mole ratio of $BaCO_3$ and $BaCrO_4$ is 1:1.

Applying POAC for C atom,

Moles of C in $BaCO_3$ + Moles of C in $CaCO_3$ = Moles of C in CO_2

$$\therefore \quad \frac{x}{197} + \frac{y}{100} = \frac{168}{22400}$$

$$\Rightarrow \quad 200x + 294y = 295.5 \qquad ....(2)$$

From Eqs. (1) and (2)

$y = 0.416$ g

$\therefore \quad 0.657 + 0.416 + z = 2.249$

$z = 1.176$

$$\% \text{ of CaO} = \frac{1.176}{2.249} = 52.29\%$$

23. For estimating ozone in the air, a certain volume of air is passed through an alkaline KI solution when O_2 is evolved and iodide is oxidised to iodine. When such a solution is acidified, free iodine is evolved which can be titrated with standard $Na_2S_2O_3$ solution: In an experiment, 10 L of air at 1 atm and 27°C were passed through an alkaline KI solution, and at the end, the iodine was entrapped in a solution which on titration as above required 1.5 mL of 0.02 N $Na_2S_2O_3$ solution. Calculate volume percentage of ozone in the sample.

Sol. The chemical reaction is $H_2O + KI + O_3 \longrightarrow I_2 + O_2 + KOH$

Milliequivalents of iodine = Milliequivalents of KI = Milliequivalents of O_3 reacted

Milliequivalents of $Na_2S_2O_3 = 1.5 \times 0.02 = 3 \times 10^{-2}$

$$\text{Millimoles of iodine} = \frac{3 \times 10^{-2}}{2} = 1.5 \times 10^{-2}$$

[∵ n-factor for iodine = 2]

Millimoles of ozone $= 1.5 \times 10^{-2} = 1.5 \times 10^{-5}$ moles

$$\text{Volume of ozone} = \frac{nRT}{P} = \frac{1.5 \times 10^{-5} \times 0.0821 \times 300}{1}$$

$$= 36.945 \times 10^{-5} \text{ L}$$

$$\text{Volume percent of ozone} = \frac{36.945 \times 10^{-5}}{10} \times 100$$

$$= 3.6945 \times 10^{-3}$$

24. Find the volume strength of H_2O_2 solution prepared by mixing of 250 mL of 3N H_2O_2 & 750 mL of 1 N H_2O_2 solution:-

Sol. $$N = \left(\frac{N_1V_1 + N_2V_2}{V_1 + V_2}\right) = \frac{3 \times 250 + 750 \times 1}{1000}$$

$$= \frac{1500}{1000} = 1.5$$

$$\text{Molarity} = \frac{1.5}{2} = 0.75 = \frac{3}{4}$$

$$\Rightarrow \quad H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

in 1L H_2O_2, 1 Mole H_2O_2 give O_2 = 11.2 L

$$1\text{L } H_2O_2, 0.75\ H_2O_2 \longrightarrow = 11.2 \times \frac{3}{4}$$

$$\longrightarrow = 8.4 \text{V } O_2$$

$\Rightarrow \quad$ Volume strength = 8.4 V

Alternative volume strength $= 5.6 \times N = 5.6 \times 1.5 = 8.4$ V

25. Mg can reduce NO_3^- to NH_3 in basic medium.

$$NO_3^- + Mg\,(s) + H_2O \rightarrow Mg\,(OH)_2\,(s) + OH^-\,(aq.) + NH_3(g)$$

A 25.0 mL sample of NO_3^- solution was treated with Mg. The NH_3 (g) was passed into 100 mL of 0.15 N HCl. The excess of HCl required 32.10 mL of 0.10 N NaOH for neutralisation. What was the molarity of NO_3^- ions in the original sample?

Sol. Milliequivalents of NH_3 formed

= Milliequivalents of HCl used

$= 100 \times 0.15 - 32.10 \times 0.10$

$= 11.79$

Here, n-factor of NH_3 is 1 (acid - base reaction)

For redox change,

$$\overset{+5}{NO_3^-} \xrightarrow{+8e^-} \overset{-3}{NH_3} \quad (n\text{-factor} = 8)$$

∴ Milliequivalents of NH_3 for n-factor 8 = 8 × 11.79 = 94.32

$$\therefore \text{ normality of } NO_3^- = \frac{\text{miliequivalent}}{\text{V(ml)}} = \frac{94.32}{25} = 3.77$$

$$\text{Molarity of } NO_3^- = \frac{3.77}{8} = 0.41725$$

26. 30 mL of a solution containing 9.15 g/L of an oxalate $K_xH_y\,(C_2O_4)_z.nH_2O$ are required for titrating 27 mL of 0.12 N NaOH and 36 mL of 0.12 N $KMnO_4$ separately. Calculate x, y, z and n. Assume all H atoms (except H_2O) are replaceable and x, y, z are in the simple ratio of g atoms.

Sol. Let molecular weight of oxalate salt is M

(i) n-factor in acid-base reaction = y

(ii) n-factor in redox titration = $2 \times z$

$(C_2O_4^{2-} \longrightarrow 2CO_2 + 2e)$

∴ Milliequivalents of acid in 30 mL = Milliequivalents of NaOH used

$$30 \times \frac{9.15}{M} \times y = 27 \times 0.12 \qquad \text{(i)}$$

$$\text{Also, } 30 \times \frac{9.15}{M} \times (2z) = 36 \times 0.12 \qquad \text{(ii)}$$

$$\text{From Eqs. (i) and (ii) } \frac{y}{2z} = \frac{27}{36} \Rightarrow \frac{y}{z} = \frac{3}{2} \qquad \text{(iii)}$$

Also, total cationic charge = total anionic charge

$$\therefore \quad x + y = 2z \qquad \text{(iv)}$$

By Eqs. (iii) and (iv)

$x{:}y{:}z{::}1{:}3{:}2$

These are in simplest ratio and molecular formula is $KH_3\,(C_2O_4)_2.nH_2O$

Molecular weight of salt = $39 + 3 + 176 + 18n = 218 + 18n$

$$\text{From Eq. (i), } M = \frac{30 \times 9.15 \times 3}{27 \times 0.12} = 254.16$$

$\therefore \quad 218 + 18n = 254.15$

$\therefore \quad n = 2$

∴ **Oxalate salt is $KH_3(C_2O_4)_2.2H_2O$**

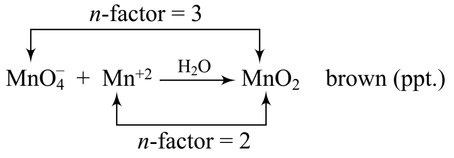
27. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolourised by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 20 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the volume strength of H_2O_2.

Sol. Milliequivalents of MnO_2 = Milliequivalents of $Na_2C_2O_4$

$= 20 \times 0.2 \times 2 = 8$

$(C_2O_4^{2-} \rightarrow 2CO_2,\ n\text{-factor} = 2)$

$$\text{Millimoles of } MnO_2 = \frac{8}{4} = 4$$



$$\overset{n\text{-factor} = 3}{\underset{n\text{-factor} = 2}{MnO_4^- + Mn^{+2} \xrightarrow{H_2O} MnO_2}} \quad \text{brown (ppt.)}$$

or $\quad 2MnO_4^- + 3Mn^{2+} \rightarrow 5MnO_2$

(Mole ratio is reciprocal of n-factor ratio)

$$\frac{\text{Millimoles of } MnO_4^-}{\text{Millimoles of } MnO_2} = \frac{2}{5}$$

$$\text{Millimoles } MnO_4^- = \frac{2}{5} \times \text{Millimoles of } MnO_2$$

$$= \frac{2}{5} \times 4 = \frac{8}{5}$$

$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow$
$2\,MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

$$\frac{\text{Millimoles of } H_2O_2}{\text{Millimoles of } MnO_4^-} = \frac{5}{2}$$

$$\therefore \quad \text{millimoles of } H_2O_2 = \frac{5}{2} \times \frac{8}{5} = 4$$

$N_{H_2O_2} \times 20 = 4 \times 2 \qquad (n\text{-factor for } H_2O_2 = 2)$

$\therefore \quad N_{H_2O_2} = 0.4$

Volume strength of H_2O_2 = $5.6 \times N_{H_2O_2}$

$= 5.6 \times 0.4 = 2.24$

Exercise

LEVEL I

1. The number of moles of $CaCl_2$ needed to react with excess of $AgNO_3$ to produce 4.31 g of AgCl.

(a) 0.030 (b) 0.015 (c) 0.045 (d) 0.060

2. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction, $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$.

The mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl is

(a) 0.1 g (b) 0.5 g (c) 1.5 g (d) 0.94 g

3. If ten volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be

(a) 10 (b) 20 (c) 48 (d) 12

4. 1.60 g of a metal were dissolved in HNO_3 to prepare its nitrate. The nitrate on strong heating gives 2 g oxide. The equivalent weight of metal is

(a) 16 (b) 32 (c) 48 (d) 12

5. How many moles of electron is needed for the reduction of each mole of Cr in the reaction,

$$CrO_5 + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + H_2O + O_2$$

(a) 4 (b) 3 (c) 5 (d) 7

6. The incorrect order of decreasing oxidation number of S in compounds is

(a) $H_2S_2O_7 > Na_2S_4O_6 > Na_2S_2O_3 > S_8$

(b) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$

(c) $SO_3 > SO_2 > H_2S > S_8$

(d) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$

7. Which reaction does not represent autoredox or disproportionation:
(a) $Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$
(b) $2H_2O_2 \longrightarrow H_2O + O_2$
(c) $2Cu^+ \longrightarrow Cu^{+2} + Cu$
(d) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

8. Which of the following is a redox reaction?
(a) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$
(b) $CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]\,SO_4$
(c) $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + NaI$
(d) $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

9. In the reaction
xHI + yHNO$_3$ $\longrightarrow$ NO + I$_2$ + H$_2$O
(a) $x = 3, y = 2$ (b) $x = 2, y = 3$
(c) $x = 6, y = 2$ (d) $x = 6, y = 1$

10. For the redox reaction

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

the correct stoichiometric coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+ are respectively
(a) 2,5,16 (b) 16,5,2 (c) 5,16,2 (d) 2,16,5

11. Which of the following relations is incorrect?
(a) $3NAl_2(SO_4)_3 = 0.5\ M\ Al_2(SO_4)_3$
(b) $3M\ H_2SO_4 = 6NH_2\ SO_4$
(c) $1\ M\ H_3PO_4 = 1/3\ N\ H_3PO_4$
(d) $1\ M\ Al_2(SO_4)_3 = 6\ N\ Al_2(SO_4)_3$

12. In the reaction $CrO_5 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O + O_2$, one mole of CrO_5 will liberate how many moles of O_2?
(a) 5/2 (b) 5/4 (c) 9/2 (d) 7/4

13. One gram of Na_3AsO_4 is boiled with excess of solid Kl in presence of strong HCl. The iodine evolved is absorbed in Kl solution and titrated against 0.2 N hyposolution. Assuming the reaction to be

$$AsO_4^{3-} + 2H^+ + 2I^- \longrightarrow AsO_3^{3-} + H_2O + I_2,$$

calculate the volume of thiosulphate hypo consumed. [Atomic weight of As = 75]
(a) 48.1 mL (b) 38.4 mL
(c) 24.7 mL (d) 30.3 mL

14. 25 mL of 0.50 M H_2O_2 solution is added to 50 mL of 0.20 M $KMnO_4$ in acid solution. Which of the following statement is true:
(a) 0.010 mole of oxygen is liberated.
(b) 0.005 mole of $KMnO_4$ are left.
(c) 0.030 g atom of oxygen gas is evolved.
(d) 0.0025 mole H_2O_2 does not react with $KMnO_4$.

15. Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation

$$2H_2O_2\,(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

Under conditions where 1 mole of gas occupies 24 dm^3. 100 cm^3 of XM solution of H_2O_2 produces 3 dm^3 of O_2. Thus X is
(a) 2.5 (b) 1 (c) 0.5 (d) 0.25

16. Temporary hardness is due to HCO^{3-} of Mg^{2+} and Ca^{2+}. It is removed by addition of CaO.

$$Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3 + H_2O$$

Mass of CaO required to precipitate 2 g $CaCO_3$ is
(a) 2.00 (b) 0.56 g (c) 0.28 g (d) 1.12 g

17. Bottle (A) contains 320 mL of H_2O_2 solution and labelled with 10 V H_2O_2 and bottle (B) contains 80 mL H_2O_2 having normality 5 N. Bottle (A) and bottle (B) are mixed and solution filled in bottle (C). Select the correct label for bottle (C) in terms of volume strength and in terms of g/litre.
(a) 13.6 "V" and 41.285 g/L
(b) 11.2 "V"and 0.68 g/L
(c) 5.6 "V" and 0.68 g/L
(d) 5.6 "V" and 41.285 g/L

18. 1 mol of iron (Fe) reacts completely with 0.65 mol O_2 to give a mixture of only FeO and Fe_2O_3. Mole ratio of ferrous oxide to ferric oxide is
(a) 3:2 (b) 4:3
(c) 20:13 (d) none of these

19. The molar ratio of Fe^{++} to Fe^{+++} in a mixture of $FeSO_4$ and $Fe_2(SO_4)_3$ having equal number of sulphate ion in both ferrous and ferric sulphate is
(a) 1:2 (b) 3:2
(c) 2:3 (d) Cannot be determined

20. If a piece of iron gains 10% of its weight due to partial rusting into Fe_2O_3. The percentage of total iron that has rusted is
(a) 23 (b) 13 (c) 23.3 (d) 25.67

21. HNO_3 oxidises NH_4^+ ions to nitrogen and itself gets reduced to NO_2. The moles of HNO_3 required by 1 mol of $(NH_4)_2SO_4$ is
(a) 4 (b) 5 (c) 6 (d) 2

22. 25 mL of a 0.1 M solution of a stable cation of transition metal Z reacts exactly with 25 mL of 0.04 mL acidified $KMnO_4$ solution. Which of the following is most likely to represent the change in oxidation state of Z correctly?
(a) $Z^+ \rightarrow Z^{2+}$ (b) $Z^{3+} \rightarrow Z^{1+}$
(c) $Z^{3+} \rightarrow Z^{4+}$ (d) $Z^{2+} \rightarrow Z^{4+}$

23. How many litres of Cl_2 at S.T.P. will be liberated by oxidation of NaCl with 10 g $KMnO_4$?
(a) 3.54 L (b) 7.08 L
(c) 1.77 L (d) None of these

24. During the disproportionation of iodine to iodide and iodate ions, the ratio of iodate and iodide ions formed in alkaline medium is
(a) 1:5 (b) 5:1 (c) 3:1 (d) 1: 3

25. $28NO_3^- + 3As_2S_3 + 4H_2O$

$$\rightarrow 6AsO_4^{3-} + 28NO + 9SO_4^{2-} + H^+$$

What will be the equivalent mass of As_2S_3 in above reaction?

(a) $\dfrac{\text{Molecular weight}}{2}$ (b) $\dfrac{\text{Molecular weight}}{4}$

(c) $\dfrac{\text{Molecular weight}}{24}$ (d) $\dfrac{\text{Molecular weight}}{28}$

26. When ZnS is boiled with a strong nitric acid, the products are zinc nitrate, sulphuric acid and nitrogen dioxide. What are the changes in the oxidation numbers of Zn, S and N?

(a) +2, +4, –1 (b) +2, +6, –2
(c) 0, +4, –2 (d) 0, +8, –1

27. Which of the following solutions will exactly oxidise 25 mL of an acid solution of 0.1 M Fe (II) oxalate?

(a) 25 mL of 0.1 M $KMnO_4$
(b) 25 mL of 0.2 M $KMnO_4$
(c) 25 mL of 0.6 M $KMnO_4$
(d) 15 mL of 0.1 M $KMnO_4$

28. 4.9 g of $K_2Cr_2O_7$ is taken to prepare 0.1 L of the solution. 10 mL of this solution is further taken to oxidise Sn^{2+} ion into Sn^{4+} ion. Sn^{4+} so produced is used in second reaction to prepare Fe^{3+} ion from ferous ion then the millimoles of Fe^{3+} ion formed will be (assume all other components are in sufficient amount)? [Molar mass of $K_2Cr_2O_7$ = 294 g]

(a) 5 (b) 20
(c) 10 (d) None of these

29. 35 mL sample of hydrogen peroxide gives of 500 mL of O_2 at 27°C and 1 atm pressure. Volume strength of H_2O_2 sample will be

(a) 10 volume (b) 13 volume
(c) 11 volume (d) 12 volume

30. 20 mL of 0.1 M solution of compound Na_2CO_3. $NaHCO_3.2H_2O$ is titrated against 0.05 M HCl, x mL of HCl is used when phenolphthalein is used as an indicator and y mL of HCl is used when methyl orange is the indicator in two separate titrations. Hence $(y - x)$ is

(a) 40 mL (b) 80 mL
(c) 120 mL (d) None of these

31. 0.3 g of an oxalate salt was dissolved in 100 mL solution. The solution required 90 mL of N/20 $KMnO_4$ for complete oxidation. The % of oxalate ion in salt is

(a) 33% (b) 66% (c) 70% (d) 40%

32. A 0.518 g sample of limestone is dissolved in HCl and then the calcium is precipitated as CaC_2O_4. After filtering and washing the precipitate, it requires 40.0 mL of 0.250 N $KMnO_4$ solution acidified with H_2SO_4 to titrate it. The percentage of CaO in the sample is

$$MnO_4^- + H^+ + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2 + 2H_2O$$

(a) 54.0% (b) 27.1% (c) 42% (d) 84%

33. The mass of oxalic acid crystals ($H_2C_2O_4$. $2H_2O$) required to prepare 50 mL of a 0.2 N solution is

(a) 4.5 g (b) 6.3 g (c) 0.63 g (d) 0.45 g

34. What volume of 6 M HNO_3 is needed to oxidise 8 g of Fe^{2+} to Fe^{3+}, HNO_3 gets converted to NO?

(a) 80 mL (b) 7.936 mL
(c) 32 mL (d) 64 mL

35. A certain weight of pure $CaCO_3$ is made to react completely with 200 mL of an HCl solution to give 224 mL of CO_2 gas at STP. The normality of the HCl is

(a) 0.05 N (b) 0.1 N (c) 1.0 N (d) 0.2 N

36. Volume V_1 mL of 0.1 M$K_2Cr_2O_7$ is needed for complete oxidation of 0.678 g N_2H_4 in acidic medium. The volume of 0.3 M $KMnO_4$ needed for same oxidation in acidic medium will be

(a) $\frac{2}{5}V_1$ (b) $\frac{5}{2}V_1$ (c) 113 V_1 (d) can't say

37. If equal volumes of 0.1 M $KMnO_4$ and 0.1 M $K_2Cr_2O_7$ solutions are allowed to oxidise Fe^{2+} to Fe^{3+} in acidic medium, then Fe^{2+} oxidised will be

(a) more by $KMnO_4$ (b) more by $K_2Cr_2O_7$
(c) equal in both cases (d) cannot be determined

38. 25.4 g of iodine and 12.2 g of chlorine are made to react completely to yield a mixture of ICl and ICl_3. Calculate the ratio of moles of ICl and ICl_3.

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

39. Calculate the weight of iron which will be converted into its oxide by the action of 18 g of steam on it.

(a) 37.3 g (b) 3.73 g
(c) 56 g (d) 5.6 g

40. A 0.1097 g sample of As_2O_3 required 36.10 mL of $KMnO_4$ solution for its titration. The molarity of $KMnO_4$ solution is

(a) 0.02 (b) 0.04 (c) 0.0122 (d) 0.3

41. In basic medium, CrO_4^{2-} oxidise $S_2O_3^{2-}$ to form SO_4^{2-} and itself changes to $Cr(OH)_4^-$. How many mL of 0.154 M CrO_4^{2-} are required to react with 40 mL of 0.246 M $S_2O_3^{2-}$?

(a) 200 mL (b) 156.4 mL
(c) 170.4 mL (d) 190.4 mL

42. 10 mL of 0.4 M $Al_2(SO_4)_3$ is mixed with 20 mL of 0.6 M $BaCl_2$. Concentration of Al^{3+} ion in the solution will be

(a) 0.266 M (b) 10.3 M
(c) 0.1 M (d) 0.25 M

43. The weight of sodium bromate required to prepare 55.5 mL of 0.672 N solution for cell reaction,

$$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O, \text{ is}$$

(a) 1.56 g (b) 0.9386 g (c) 1.23 g (d) 1.32 g

44. $NaIO_3$ reacts with $NaHSO_3$ according to equation

$$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{2-}$$

The weight of $NaHSO_3$ required to react with 100 mL of solution containing 0.68 g of $NaIO_3$ is

(a) 5.2 g (b) 0.2143 g
(c) 2.3 g (d) None of these

45. If 0.5 moles of $BaCl_2$ is mixed with 0.1 moles of Na_3PO_4, the maximum amount of $Ba_3(PO_4)_2$ that can be formed is

(a) 0.7 mol (b) 0.5 mol (c) 0.2 mol (d) 0.05 mol

46. 0.52 g of a dibasic acid required 100 mL of 0.2 N NaOH for complete neutralisation.
The equivalent weight of acid is

(a) 26 (b) 52 (c) 104 (d) 156

47. 34 g hydrogen peroxide is present in 1120 mL of solution. This solution is called

(a) 10 volume (b) 20 volume
(c) 30 volume (d) 32 volume

48. The number of moles of $KMnO_4$ that will be required to react with 2 mol of ferrous oxalate is

(a) $\frac{6}{5}$ (b) $\frac{2}{5}$ (c) $\frac{4}{5}$ (d) 1

49. What volume of 0.1 M $KMnO_4$ is needed to oxidise 100 mg of FeC_2O_4 in acid solution?

(a) 4.1 mL (b) 8.2 mL (c) 10.2 mL (d) 4.6 mL

LEVEL II

1. Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction
$4HCl(aq) + MnO_2(s) \rightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$
The grams of HCl react with 5.0 g of manganese dioxide will be [Atomic mass of Mn = 55]

(a) 84 g (b) 0.84 g (c) 8.4g (d) 4.2 g

2. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. The empirical formula, molar mass of the gas and molecular formula will be respectively

(a) CH_2, 30, C_2H_4 (b) CH, 30, C_2H_2
(c) CH, 26, C_2H_2 (d) CH_2, 26, C_2H_4

3. It takes 0.15 mole of ClO^- to oxidise 12.6 g of chromium oxide of a specific formula to $Cr_2O_7^{2-}$. ClO^- became Cl^-. The formula of the oxide is (atomic weight Cr = 52, O = 16)

(a) CrO_3 (b) CrO_2 (c) CrO_4 (d) CrO

4. 8 g of sulphur is burnt to form SO_2 which is oxidised by Cl_2 water. The solution is treated with $BaCl_2$ solution. The amount of $BaSO_4$, precipitate is

(a) 1 mole (b) 0.5 mole
(c) 0.24 mole (d) 0.25 mole

5. 25.0 mL of HCl solution gave, on reaction with excess $AgNO_3$ solution 2.125 g of AgCl. The normality of HCl solution is

(a) 0.25 (b) 0.6 (c) 1.0 (d) 0.75

6. 50 mL of 0.1 M solution of a salt reacted with 25 mL of 0.1 M solution of sodium sulphite. The half-reaction for the oxidation of sulphite ion is

$$SO_3^{2-}\,(aq) + H_2O\,(l) \longrightarrow SO_4^{2-}\,(aq) + 2H^+(aq) + 2e^-$$

If the oxidation number of metal in the salt was 3, what would be the new oxidation number of metal?

(a) 0 (b) 1 (c) 2 (d) 4

7. An element A in a compound ABD has oxidation number A^{n-}. It is oxidised by $Cr_2O_7^{2-}$ in acid medium. In the experiment 1.68×10^{-3} moles of $K_2Cr_2O_7$ were used for 3.26×10^{-3} moles of ABD. The new oxidation number of A after oxidation is

(a) 3 (b) $3 - n$ (c) $n - 3$ (d) $+n$

8. Match List-I (Compounds) with List-II (Oxidation states of nitrogen) and select answer using the codes given below the lists:

	List-I		**List-II**
(A)	NaN_3	1.	+5
(B)	N_2H_2	2.	+2
(C)	NO	3.	–1/3
(D)	N_2O_5	4.	–1

Code:	(A)	(B)	(C)	(D)
(a)	3	4	2	1
(b)	4	3	2	1
(c)	3	4	1	2
(d)	4	3	1	2

9. 125 mL of 63% (w/v) $H_2C_2O_4 . 2H_2O$ is made to react with 125 mL of a 40% (w/v) NaOH solution. The resulting solution is

(a) neutral (b) acidic
(c) strongly acidic (d) alkaline

10. If 10 g of V_2O_5 is dissolved in acid and is reduced to V^{2+} by zinc metal, how many mole I_2 could be reduced by the resulting solution if it is further oxidised to VO^{2+} ions ?
[Assume no change in state of Zn^{2+} ions] (V = 51, O = 16, I = 127):

(a) 0.11 mole of I_2 (b) 0.22 mole of I_2
(c) 0.055 mole of I_2 (d) 0.44 mole of I_2

11. 0.10 g of a sample containing $CuCO_3$ and some inert impurity was dissolved in dilute sulphuric acid and volume made up to 50 mL. This solution was added into 50 mL of 0.04 M KI solution where copper precipitates as CuI and I^- is oxidised into I_3^-. A 10 mL portion of this solution is taken for analysis, filtered and made up free I_3^- and then treated with excess of acidic permanganate solution. Liberated iodine required 20 mL of 2.5 mM sodium thiosulphate solution to reach the end point. Determine weight percentage of $CuCO_3$ in the original sample.

(a) 7.41 (b) 74.1
(c) 61.75 (d) none of these

12. A 150 mL of solution of I_2 is divided into two unequal parts. I part reacts with hyposolution in acidic medium. 15 mL of 0.4 M hypo was consumed. II part was added with 100 mL of 0.3 M NaOH solution. Residual base required 10 mL of 0.3 M H_2SO_4 solution for complete neutralisation. What was the initial concentration of I_2?
(a) 0.08 M (b) 0.1 M
(c) 0.2 M (d) none of these

13. A mixture of H_2SO_4 and $H_2C_2O_4$ (oxalic acid) and some inert impurity weighing 3.185 g was dissolved in water and the solution made up to 1 L, 10 mL of this solution required 3 mL of 0.1 N NaOH for complete neutralisation. In another experiment 100 mL of the same solution in hot condition required 4 mL of 0.02M $KMnO_4$ solution for complete reaction. The weight % of H_2SO_4 in the mixture was
(a) 40 (b) 50 (c) 60 (d) 80

14. 0.80 g of sample of impure potassium dichromate was dissolved in water and made up to 500 mL solution. 25 mL of this solution treated with excess of KI in acidic medium and I_2 liberated required 24 mL of a sodium thiosulphate solution. 30 mL of this sodium thiosulphate solution required 15 mL of N/20 solution of pure potassium dichromate. What was the percentage of $K_2Cr_2O_7$ in given sample?
(a) 73.5 % (b) 75.3 %
(c) 36.75 % (d) none of these

15. A 10.0 g samples of a mixture of calcium chloride and sodium chloride is treated with Na_2CO_3 to precipitate the calcium as calcium carbonate. This $CaCO_3$ is heated to convert all the calcium to CaO and the final mass of CaO is 1.62 g. The % by mass of $CaCl_2$ in the original mixture is
(a) 15.2% (b) 32.1% (c) 21.8% (d) 11.7%

16. Hydroxyl amine reduces iron (III) according to following equation:

$$NH_2OH + Fe_2(SO_4)_3 \longrightarrow N_2(g) + H_2O + FeSO_4 + H_2SO_4$$

Which statement is correct?
(a) *n*-factor for Hydroxyl amines is 1.
(b) equivalent weight of $Fe_2(SO_4)_3$ is M/2.
(c) 6 meq of $Fe_2(SO_4)_3$ is contained in 3 millimoles of ferric sulphate.
(d) All of these.

17. Equal volumes of 1 M each of $KMnO_4$ and $K_2Cr_2O_7$ are used to oxidise Sn(II) solution in acidic medium. The amount of Fe oxidised will be
(a) more with $KMnO_4$
(b) more with $K_2Cr_2O_7$
(c) equal with both oxidising agents
(d) more with $KMnO_4$ in basic medium

18. The normality of a mixture obtained by mixing 100 mL of 0.2 M H_2SO_4 with 100 mL of 0.2 M NaOH will be
(a) 0.05 N (b) 0.1 N (c) 0.15 N (d) 0.2 N

19. A solution of $KMnO_4$ is reduced to MnO_2. The normality of solution is 1.8. The molariy will be
(a) 0.1 M (b) 0.6 M (c) 1.8 M (d) 0.3 M

20. 40 g $Ba(MnO_4)_2$ (molecular weight = 375) sample containing some inert impurities in acidic medium is completely reacted with 125 mL of "33.6 V" of H_2O_2. What is the percentage purity of the sample?
(a) 28.12 % (b) 70.31 %
(c) 85 % (d) None of these

LEVEL III

1. Match the columns.

Column I (Reaction)		**Column II (Equivalent weight)**	
(a)	$NH_3 \longrightarrow NO_3^-$	(p)	M/3
(b)	$FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_3^{2-}$	(q)	M/6
(c)	$H_2SO_5 \longrightarrow S_8$	(r)	M/8
(d)	$KMnO_4 \longrightarrow Mn^{2+}$	(s)	M/5
		(t)	Reducing agent

2. Match the column

Column I (Acid)		**Column II (Nature)**	
(a)	H_3PO_4	(p)	Monobasic
(b)	H_3PO_3	(q)	Pentabasic
(c)	H_3BO_3	(r)	Tri basic
(d)	EDTA	(s)	Tetra basic
		(t)	Dibasic

3. Match the following

Column I		**Column II**	
(a)	$KMnO_4 \xrightarrow{H^+} Mn^{+2}$	(p)	M/2
(b)	$MgC_2O_4 \longrightarrow Mg^{2+} + CO_2$	(q)	M/5
(c)	$K_2Cr_2O_7 \longrightarrow Cr^{+3}$	(r)	M/6
(d)	$CrO_5 \longrightarrow Cr_2O_3$	(s)	M/3
		(t)	Oxidising agent

Comprehension 1 (Question No. 4 to 7)

Oleum is considered as a solution of SO_3 in H_2SO_4, which is obtained by passing SO_3 in solution of H_2SO_4. When 100 g sample of oleum is diluted with desired weight of H_2O then the total mass of H_2SO_4 obtained after dilution is known as % labelling in oleum.

For example, a oleum bottle labelled as '109% H_2SO_4' means the 109 g total mass of pure H_2SO_4 will be formed when 100 g of oleum is diluted by 9 g of H_2O which combines with all the free SO_3 present in oleum to form H_2SO_4 as $SO_3 + H_2O \longrightarrow H_2SO_4$

4. What is the % of free SO_3 in an oleum that is labelled as '104.5 % H_2SO_4'?
(a) 10 (b) 20
(c) 40 (d) None of these

5. 9.0 g water is added into oleum sample labelled as '112% H_2SO_4' then the amount of free SO_3 remaining in the solution is
(a) 14.93 L at STP (b) 7.46 L at STP
(c) 3.73 L at STP (d) 11.2 L at STP

6. If excess water is added into a bottle sample labelled as '112 % H_2SO_4' and is reacted with 5.3 g Na_2CO_3, then find the volume of CO_2 evolved at 1 atm pressure and 300 K temperature after the completion of the reaction.
(a) 2.46 L (b) 24.6 L (c) 1.23 L (d) 12.3 L

7. 1 g of oleum sample is diluted with water. The solution required 54 mL of 0.4 N NaOH for complete neutralisation. The % of free SO_3 in the sample is
(a) 74 (b) 26
(c) 20 (d) None of these

Comprehension 2 (Question No. 8 to 10)

The strength of H_2O_2 is expressed in several ways like molarity, normality, % (w/V), volume strength, etc. The strength of "10 V" means 1 volume of H_2O_2 on decomposition gives 10 volumes of oxygen at STP or 1 L of H_2O_2 gives 10 L of O_2 at STP. The decomposition of H_2O_2 is shown as under.

$$H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$$

H_2O_2 can acts as oxidising as well as reducing agent. As oxidising agent H_2O_2 is converted into H_2O and as reducing agent H_2O_2 is converted into O_2. In both cases its *n*-factor is 2.

$\therefore$ Normality of H_2O_2 solution $= 2 \times$ Molarity of H_2O_2 solution

8. What is the molarity of "11.2 V" of H_2O_2?
(a) 1 M (b) 2 M (c) 5.6 M (d) 11.2 M

9. What is the percentage strength (% w/V) of "11.2 V" H_2O_2?
(a) 1.7 (b) 3.4
(c) 34 (d) none of these

10. 20 mL of H_2O_2 solution is reacted with 80 mL of 0.05 M $KMnO_4$ in acidic medium then what is the volume strength of H_2O_2?
(a) 2.8 (b) 5.6
(c) 11.2 (d) none of these

Comprehension 3 (Question No. 11 to 14)

All such titration which involves the direct titration of iodine with a reducing agent are grouped under iodimetry. Iodimetry is employed to determine the strength of reducing agent such as sodium those sulphate:

$$I_2 + Na_2S_2O_3 \longrightarrow I^- + S_4O_6^{--}$$

If iodine is liberated as a result of chemical reaction involving oxidation of an idodide ion by a strong oxidising agent in neutral or acidic medium, the liberated iodine is then titrated with reducing agent. Iodometry is used to estimate the strength of oxidising agent.

For example, the estimation of Cu^{++} with thiosulphate.

$$Cu^{++} + I^- \longrightarrow Cu_2I_2 + I_2$$

$$I_2 + S_2O_3^{--} \longrightarrow S_4O_6^{--} + I^-$$

Starch used as indicator near the end point which form blue colour complex with I_3^-. The blue colour disappears when there is no more of free I_2.

11. In iodine titration, iodine remains in solution in the form of
(a) I_3^- (b) I_2 (c) I_3^+ (d) I^-

12. In the reaction, $2CuSO_4 + 4KI \rightarrow Cu_2I_2 + 2K_2SO_4 + I_2$ the ratio of equivalent weight of $CuSO_4$ to its molecular weight is
(a) 1/8 (b) 1/4 (c) 1/2 (d) 1

13. When 159.50 g of $CuSO_4$ in a solution is reacted with KI, then the liberated iodine required 100 mL 1 M $Na_2S_2O_3$ for complete reaction, then what is the percentage purity of sample used in making the solution.
(a) 10% (b) 20%
(c) 5% (d) None of these

14. 100 mL of 0.1 N hypo decolourised iodine by the addition of *x* g of crystalline blue vitriol to excess of KI. The value of *x* is
(a) 5 g (b) 2.5 g (c) 10 g (d) 1.25 g

Comprehension 4 (Question No. 15 to 18)

Iodine titrations: Compounds containing iodine are widely used in titrations, commonly known as iodine titration. It is of two kinds:

(i) Iodometric titrations
(ii) Iodimetric titrations

(i) Iodometric titrations: It is nothing but an indirect method of estimating the iodine. In this type of titration, an oxidising agent is made to react with excess of KI, in acidic medium or, basic medium in which I^- oxidises into I_2. Now the liberated I_2 can be titrated with $Na_2S_2O_3$ solution.

$$KI \xrightarrow{\text{Oxidising Agent}} I_2 \xrightarrow{Na_2S_2O_3/H^+} I^- + Na_2S_4O_6$$

Although solid I_2 is black and insoluble in water, but it converts into soluble I_3 ions

$$\underset{\text{Black}}{I_2(s)} + I^- \rightleftharpoons \underset{\text{dark brown}}{I_3^-}$$

Starch is used as indicator near the end point or equivalence point. Even small amount of I_2 molecules, gives blue colour with starch. The completion of the reaction can be detected when blue colour disappears at the end point. In iodimetric titration, the strength of reducing agent is determined by reacting it with I_2.

15. When 79.75 g of $CuSO_4$ sample containing inert impurity is reacted with KI, the liberated I_2 is reacted with 50 mL (1M) $Na_2S_2O_3$ in basic medium, where it oxidises into SO_4^{-2} ions, and I_2 reduces into I^-, then what will be the % purity of $CuSO_4$ in sample?

(a) 60% (b) 75% (c) 50% (d) 95%

16. When 214 g of KIO_3 reacts with excess of KI in presence of H^+, then it produces I_2. Now I_2 is completely reacted with 1 M $Na_2S_2O_3$ solution in basic medium, where it converts into SO_4^{-2} ions. Then what volume of $Na_2S_2O_3$ is needed to react the end point of the reaction?

(a) 500 mL (b) 800 mL (c) 1500 mL (d) 750 mL

17. A solution containing Cu^{+2} and $C_2O_4^{-2}$ ions which on titration with M/10 $KMnO_4$ requires 50 mL. The resulting solution is neutralised with K_2CO_3, then treated with excess of KI. The liberated I_2 required 25 mL M/10 $Na_2S_2O_3$ in acidic solution, then what is the difference of the number of m mole of Cu^{+2} and $C_2O_4^{-2}$ ions in the solution?

(a) 40 (b) 10 (c) 30 (d) 50

18. When 1.66 g of KI is reacted with excess of KIO_3 in presence of diluted HCl, then I_2 is produced. The amount of KIO_3 reacted and the I_2 formed are respectively.

(a) 4×10^{-2} mole, 3×10^{-3} mole
(b) 1.5×10^{-2} mole, 5×10^{-3} mole
(c) 5×10^{-2} mole, 1.5×10^{-3} mole
(d) 2×10^{-3} mole, 6×10^{-3} mole

Comprehension 5 (Question No. 19 to 22)

The percentage labelling of oleum is a unique process by means of which, the percentage composition of H_2SO_4, SO_3 (free) and SO_3 (combined) is calculated.

Oleum is nothing but it is a mixture of H_2SO_4 and SO_3 i.e., $H_2S_2O_7$, which is obtained by passing SO_3 in solution of H_2SO_4. In order to dissolve free SO_3 in oleum, dilution of oleum is done, in which oleum converts into pure H_2SO_4. It is shown by the reaction as given below.

$$H_2SO_4 + SO_3 + H_2O \longrightarrow 2H_2SO_4\,(\text{pure}) \text{ or, } SO_3 + H_2O \longrightarrow H_2SO_4\,(\text{pure})$$

When 100 g sample of oleum is diluted with desired weight of H_2O (in g), then the total mass of pure H_2SO_4 obtained after dilution is known as percentage labelling in oleum.

For example, if the oleum sample is labelled as "109% H_2SO_4" it means that 100 g of oleum on dilution with 9 g of H_2O provides 109 g pure H_2SO_4, in which all free SO_3 in 100 g of oleum is dissolved.

19. For 109% labelled oleum if the number of moles of H_2SO_4 and free SO_3 be x and y respectively, then what will be the value of $\dfrac{x+y}{x-y}$?

(a) 1 (b) 18 (c) 1/3 (d) 9.9

20. In the above question number 19, what is the percentage of free SO_3 and H_2SO_4 in the oleum sample respectively?

(a) 60%, 40% (b) 30%, 70%
(c) 85%, 15% (d) 40%, 60%

21. In the above question number 19, what will be the % of combined SO_3 in the given oleum sample?

(a) 20% (b) 30% (c) 48.98% (d) 51%

22. What volume of 1 M NaOH (in mL) will be required to react completely with H_2SO_4 and SO_3 in 109% labelled oleum?

(a) 250 mL (b) 2224 mL
(c) 750 mL (d) 1800 mL

Multiple Correct Type Questions

23. Which of the following samples of reducing agents is/are chemically equivalent to 25 mL of 0.2 N $KMnO_4$ to be reduced to Mn^{2+} and water?

(a) 25 mL of 0.2 M $FeSO_4$ to be oxidised to Fe^{3+}
(b) 50 mL of 0.1 M H_3AsO_3 to be oxidised to H_3AsO_4
(c) 25 mL of 0.1 M H_2O_2 to be oxidised to O_2
(d) 25 mL of 0.1 M $SnCl_2$ to be oxidised to Sn^{4+}

24. For the following balanced redox reaction,

$$2MnO_4^- + 4H^+ + Br_2 \rightleftharpoons 2Mn^{+2} + 2BrO_3^- + 2H_2O$$

If the molecular weight of MnO_4^-, Br_2 be Mx, My respectively, then

(a) equivalent weight of MnO_4^- is Mx/5
(b) equivalent weight of Br_2 is My/10
(c) the n-factor ratio of Mn^{+2} to BrO_3^- is 1:1
(d) None of these

25. When non-stoichiometric compound $Fe_{0.95}O$ is heated in the presence of oxygen, it converts into Fe_2O_3, then which of the following statements are correct?

(a) Equivalent weight of $Fe_{0.95}O$ is M/0.5 where M is molecular weight of $Fe_{0.95}O$.
(b) The number of moles of Fe^{+3} and Fe^{+2} 1 moles $Fe_{0.95}O$ and 0.1 and 0.85 respectively.
(c) The number of moles of Fe^{+3} and Fe^{+2} in 1 mole of $Fe_{0.95}O$ are 0.85 and 0.10 respectively
(d) The % composition of Fe^{+2} and Fe^{+3} in the non stoichiometric compound is 89.47% and 10.53% respectively.

26. When FeS_2 is oxidised with sufficient O_2, then its oxidation product is found to be Fe_2O_3 and SO_2, if the molecular weight of FeS_2, Fe_2O_3 and SO_2 are M, M′ and M″, then which of the following statements are correct?

(a) Equivalent weight of FeS_2 is M/11
(b) The molar ratio of FeS_2 to O_2 is 4:11
(c) The molar ratio of FeS_2 to O_2 is 11:4
(d) The molar ratio of Fe_2O_3 and SO_2 is 1:4

27. 40 g NaOH, 106 g Na_2CO_3 and 84 g $NaHCO_3$ is dissolved in water and the solution is made 1 L. 20 mL of this stock solution is titrated with 1N HCl, hence which of the following statements are correct?

(a) The titre reading of HCl will be 40 mL, if phenolphthalein is used indicator from the very beginning.

(b) The titre reading of HCl will be 60 mL if phenolphthalein is used indicator from the very beginning.

(c) The titre reading of HCl will be 40 mL if the methyl orange is used indicator after the first end point.

(d) The tire reading of HCl will be 80 mL, if methyl orange is used as indicator from the very beginning.

28. 150 mL $\frac{M}{10}$ $Ba(MnO_4)_2$ in acidic medium can oxidise completely

(a) 150 mL 1M Fe^{+2}

(b) 50 mL 1M FeC_2O_4

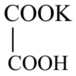
(c) 75 mL 1M $C_2O_4^{-2}$

(d) 25 mL 1M $K_2Cr_2O_7$ solution

29. Which of the following quantities are dependent on temperature?

(a) Molarity (b) Normality

(c) Molality (d) Mole fraction

30  $\begin{array}{c}COOH\\|\\COOH\end{array}$ and  $\begin{array}{c}COOK\\|\\COOH\end{array}$ behave as acid are well as reducing agent. Then which of the following are the correct statements regarding  $\begin{array}{c}COOH\\|\\COOH\end{array}$ and  $\begin{array}{c}COOK\\|\\COOH\end{array}$?

(a) When behaves as reducing agent, then its equivalent weights are equal to half of its molecular weight respectively.

(b) 1000 mL of 1 N solution of each is neutralised by 1000 mL 1 N $Ca(OH)_2$.

(c) 1000 mL of 1 M solution of each is neutralised by 1000 mL of 1 M $Ca(OH)_2$.

(d) 1000 mL of 1 M solution of each is neutralised by 200 mL 2 M of $KMnO_4$ in acidic medium.

31. For the reaction,

$$\underset{1\text{ mole}}{H_3PO_4} + \underset{1\text{ mole}}{Ca(OH)_2} \longrightarrow CaHPO_4 + 2H_2O$$

then which of the following statements are correct?

(a) The equivalent weight of H_3PO_4 is 49.

(b) The resulting solution is neutralised by 1 mole of KOH

(c) 1 mole of H_3PO_4 is completely neutralised by 1.5 mole of $Ca(OH)_2$

(d) None of these

32. 1 mol of H_2SO_4 will exactly neutralise

(a) 2 mol of ammonia (b) 1 mol of $Ca(OH)_2$

(c) 0.5 mol of $Ba(OH)_2$ (d) 2 mol of NaOH

33. During the titration of a mixture of NaOH, Na_2CO_3 and inert substances against HCl.

(a) Phenolpthalein is used to detect the end point when half equivalent of Na_2CO_3 and full equivalent NaOH is consumed.

(b) Phenolpthalein is used to detect the second end point.

(c) Methyl orange is used to detect the final end point.

(d) Methyl orange is used to detect the first end point.

34. The reaction, $3ClO^-(aq) \longrightarrow ClO_3^-\ (aq) + 2Cl^-(aq)$ is an example of

(a) Oxidation reaction

(b) Reduction reaction

(c) Disproportionation reaction

(d) Decomposition reaction

Assertion/Reason

(a) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.

(b) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.

(c) Statement 1 is True, Statement 2 is False.

(d) Statement 1 is False, Statement 2 is True.

35. **Statement 1**: In the titrations of Na_2CO_3 with HCl using methyl orange indicator, the volume required at the equivalence point is twice that of acid required using phenolphthalein indicator.

Statement 2: Two moles of HCl are required for complete neutralization of one mole of Na_2CO_3.

36. **Statement 1:** The molality of the solution does not change with temperature.

Statement 2: The moltiy is expressed in units of moles per 1000 gm of solvent.

37. **Statement 1:** In the roasting of FeS_2, ore is converted into ferric oxide and SO_2 gas. The equivalent mass of FeS_2 is equal to molecular weight /11.

Statement 2: The *n*-factor for reducing agent is total net change in oxidation number per formula unit.

38. **Statement 1:** Molarity and molality of solution change with temperature

Statement 2: On changing temperature the density of the solution is changed

39. **Statement 1:** Atomic weight of *P* atom in the molecule P_xO_y is $\frac{2yE_p}{x}$ where E_p is the equivalent mass of *P* atom

Statement 2: The *n* factor of *P* is = $\frac{x}{y}$

40. **Statement 1:** 109% H_2SO_4 represent a way to express concentration of industrial H_2SO_4 because

Statement 2: It represents that 9 g H_2O reacts with 40 g SO_3 to produce 49 g H_2SO_4 in addition to 100 g H_2SO_4

Integer and Subjective Type Questions

41. $KMnO_4$ oxidises X^{n+} ion to XO_3^-, itself changing to Mn^{2+} in acid medium. 2.68×10^{-3} mole of X^{n+} requires 1.61×10^{-3} mole of MnO_4^-. Calculate the atomic mass of X, if the weight of 1 g equivalent of XCl_n is 56.

42. A solution of a 0.4 g sample of H_2O_2 reacted with 0.632 g of $KMnO_4$ in the presence of sulphuric acid. Calculate the percentage purity of the sample of H_2O_2.

43. 5 L of a solution of H_2O_2 with x N strength is diluted to 5.5 L. This 5.5 L H_2O_2 solution gives 28 L O_2 at NTP. Find the value of x.

44. A dilute solution of H_2SO_4 is made by adding 5 mL of 3N H_2SO_4 to 245 mL of water. Find molarity of the solution × 100.

45. V litre volume of 0.40 M H_2SO_4 is required to produce 34.0 g of H_2S by the reaction,

$$8KI + 5H_2SO_4 \rightarrow 4K_2SO_4 + 4I_2 + H_2S + 4H_2O?$$

Find 10 × V.

46. To 50 L of 0.2 N NaOH, 2.5 L of 2N HCl and 15 L of 0.1 N $FeCl_3$ solutions are added. What weight of Fe_2O_3 in gram can be obtained from the precipitate?

47. Hemoglobin contains 0.25% iron by weight. The molecular weight of Hemoglobin is 89600. Calculate the number of iron atom per molecule of Hemoglobin.

48. Copper froms two oxides. For the same amount of copper, twice as much oxygen was used to form first oxide than to form second one. If valency of Cu in I oxide is 2, then find valency of Cu in second oxide?

49. 1.575 g of oxalic acid $(COOH)_2.xH_2O$ are dissolved in water and the volume made upto 250 mL. On titration 16.68 mL of this solution requires 25mL of N/15 NaOH solution for complete neutralisation. Calculate x.

50. A solution containing 4.2 g of KOH and $Ca(OH_2)$ is neutralised by an acid. It consums 0.1 equivalent of acid, calculate the percentage composition of KOH.

51. 10 g $CaCO_3$ were dissolved in 250 mL of molar HCl and the solution was boiled. What volume of 2 M KOH in ml would be required to equivalence point after boiling? Assume no change in volume during boiling.

52. H_3PO_4 is a tri basic acid and one of its salt is NaH_2PO_4. What volume of 1 M NaOH solution in ml should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4?

53. It required 40.05 mL of 1 M Ce^{4+} to titrate 20 mL of 1 M Sn^{2+} to Sn^{4+}. What is the oxidation state of the cerium in the product?

54. A volume of 12.53 mL of 0.05093 M SeO_2 reacted with exactly 25.52 mL of 0.1 M $CrSO_4$. In the reaction, Cr^{2+} was oxidised to $Cr^{3+.}$ To what oxidation state was selenium converted by the reaction?

55. How many mL of 0.1 N HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two?

56. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. The solution requires 26.7 mL of 0.4N NaOH for complete neutralisation. Find the % of free SO_3 in the sample of oleum.

57. 1.64 g of mixture of $CaCO_3$ and $MgCO_3$ was dissolved in 50 mL of 0.8 M HCl. The excess of acid required 16 mL of 0.25 M NaOH for neutralisation. Calculate the percentage of $CaCO_3$ and $MgCO_3$ in the sample.

58. 1.5 g of chalk were treated with 10 mL of 4N – HCl. The chalk was dissolved and the solution made to 100 mL, 25 mL of this solution required 18.75 mL of 0.2 N – NaOH solution for complete neutralisation. Calculate the percentage of pure $CaCO_3$ in the sample of chalk?

59. A solution contains Na_2CO_3 and $NaHCO_3$. 20 mL of this solution required 4 mL of 1N – HCl for titration with Ph indicator. The titration was repeated with the same volume of the solution but with MeOH. 10.5 mL of 1 – N HCl was required this time. Calculate the amount of Na_2CO_3 and $NaHCO_3$.

60. A solution contains a mix of Na_2CO_3 and NaOH. Using Ph as indicator 25 mL of mixture required 19.5 mL of 0.995 N HCl for the end point. With MeOH, 25 mL of the solution required 25 mL of the same HCl for the end point. Calculate g/L of each substance in the mixture.

61. 200 mL of a solution of mixture of NaOH and Na_2CO_3 was first titrated with Ph and M/10 HCl. 17.5 mL of HCl was required for end point. After this MeOH was added and 2.5 mL of same HCl was again required for next end point. Find out amounts of NaOH and Na_2CO_3 in the mix.

62. A solution contains Na_2CO_3 and $NaHCO_3$. 10 mL of this requires 2 mL of 0.1 M H_2SO_4 for neutralisation using Ph indicator. MeOH is then added when a further 2.5 mL of 0.2 M H_2SO_4 was needed. Calculate milliequilivalent strength of Na_2CO_3 and $NaHCO_3$ in 10 ml.

63. Pottasium acid oxalate $K_2C_2O_4.3H_2C_2O_4.4H_2O$ can be oxidised by MnO_4 in acid medium. Calculate the volume of 0.1 M $KMnO_4$ reacting in acid solution with 1 g of the acid oxalate.

64. A 1.0 g sample of H_2O_2 solution containing x% H_2O_2 by mass requires x cm^3 of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution.

65. Metallic tin in the presence of HCl is oxidised by $K_2Cr_2O_7$ to stannic chloride, $SnCl_4$. What volume of deci-normal dichromate solution would be reduced by 1 g of tin.

66. 5 g sample of brass was dissolved in 1 L dilute H_2SO_4. 20 mL of this solution were mixed with KI, liberating I_2 and Cu^+ and the I_2 required 20 mL of 0.0327 N hypo solution for complete titration. Calculate the percentage of Cu in the alloy.

67. 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x mL of a dichromatic solution for oxidising the iron content to ferric state. Calculate the strength of dichromatic solution.

68. The neutralisation of a solution of 1.2 g of a substance containing a mixture of $H_2C_2O_4.2H_2O$, $KHC_2O_4.H_2O$ and different impurities of a neutral salt consumed 18.9 mL of 0.5 N NaOH solution. On titration with $KMnO_4$ solution, 0.4 g, of the same substance needed 21.55 mL of 0.25 N $KMnO_4$. Calculate the % composition of the substance.

69. 50 g of a sample of $Ca(OH)_2$ is dissolved in 50 mL of 0.5 N HCl solution. The excess of HCl was titrated with 0.3 N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of $Ca(OH)_2$.

70. 1 g of impure sodium carbonate is dissolved in water and the solution is made up to 250 mL. To 50 mL of this made up solution, 50 mL of 0.1 N – HCl is added and the mix after shaking well required 10 mL of 0.16 N – NaOH solution for complete titration. Calculate the % purity of the sample.

71. What amount of substance containing 60% NaCl, 37% KCl should be weighed out for analysis so that after the action of 25 mL of 0.1 N $AgNO_3$ solution, excess of Ag^+ is back titrates with 5 mL of NH_4SCN solution. Given that 1 mL of NH_4SCN = 1.1. mL of $AgNO_3$.

72. A bottle labelled with “12 V H_2O_2” contain 700 mL solution. If a student mix 300 mL water in it what is the g/litre strength volume strength of final solution.

73. 50 mL of an aqueous solution of H_2O_2 were treated with an excess of KI solution and dilute H_2SO_4, the liberated iodine required 20 mL of 0.1 N $Na_2S_2O_3$ solution for complete interaction. Calculate the concentration of H_2O_2 in g/L.

74. 100 kg hard water contains 5 g $MgSO_4$. Find hardness.

75. 1 L hard water contains 1 mg $CaCl_2$ and 1 mg $MgSO_4$. Find hardness.

76. Calculate the hardness of water sample which contains 0.001 mol $MgSO_4$ per litre of water.

77. Calculate the amount of lime $Ca(OH)_2$ required to remove the hardness in 60 L of pond water containing 1.62 mg of calcium bicarbonate per 100 mL of water.

78. What volume at NTP of gaseous ammonia will be required to be passed into 30 cc of N – H_2SO_4 solution to bring down the acid strength of the latter to 0.2 N.

79. Calculate the amount (in milligrams) of SeO_3^{-2} in solution on the basis of following data 20 mL of M/60 solution of $KBrO_3$ was added to a definite volume of SeO_3^{-2} solution. The bromine evolved was removed by boiling and excess of $KBrO_3$ was back titrated with 5 mL of M/25 solution of $NaAsO_2$. The reactions are given below. (Atomic mass of K = 39, Br = 80, As = 75, Na = 23, O = 16, Se = 79)

(a) $SeO_3^{-2} + BrO_3^- + H^+ \rightarrow SeO_4^{-2} + Br_2 + H_2O$

(b) $BrO_3^- + AsO_2^- + H_2O \rightarrow Br^- + AsO_4^{-3} + H^+$

80. A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of moles of electrons taken up by the oxidant in the reaction of the above titration.

81. 1.2475 g of crystalline copper sulphate was dissolved in water and excess of KI was added. The liberated iodine consumed 50 mL N/10 $Na_2S_2O_3$ solution to reach the end point of the titration. Calculate the number of water molecules of hydration in crystalline copper sulphate salt.

82. A 1g sample of $K_2Cr_2O_7$ containing some inert material was entirely reduced with concentrated. HCl. The chlorine liberated was passed through hot solution of NaOH at 800C, and it completely diproportionates to form ClO_3^- and Cl^-. This $NaClO_3$ was isolated and its reduction with KI (aq) liberated iodine, giving Cl^-.The iodine thus liberated required 100 mL of decinormal hypo solution for complete titration. What is the percentage purity of the dichromate sample?

83. 2.5 g of mixture of crystalline oxalic acid ($H_2C_2O_4$. $2H_2O$) and sodium oxalate ($Na_2C_2O_4$) was dissolved in 100 mL of water. 50 mL of this solution was titrated against N/10 NaOH solution when 119.05 mL of the base was found necessary to reach the end point with phenolphthalein as the indicator. 1 g of the mixture was dissolved in water and the solution titrated against N/10 $KMnO_4$ in the presence of dilute H_2SO_4. What is the volume of $KMnO_4$ needed for getting the end point with 0.5 g of the mixture?

84. 25 mL of a solution containing HCl was treated with excess of M/5 KIO_3 and KI solution of unknown concentration where I_2 liberated is titrated against a standard solution of 0.021 M $Na_2S_2O_3$ solution whose 24 mL were used up. Find the strength of HCl and volume of KIO_3 solution consumed.

85. 0.6213 g of sample contains an unknown amount of As_2O_3. The sample was treated with HCl resulting information of $AsCl_3$ (g) which was distilled into a beaker of water. The hydrolysis reaction is as follows:

$$AsCl_3 + 2H_2O \rightarrow HAsO_2 + 3H^+ + 3Cl^-$$

The amount of $HAsO_2$ was determined by titration with 0.04134 M I_2, requiring 23.04 mL to reach the equivalence point. The redox products in the titration were H_3AsO_4 and I^-. Find the amount of $KMnO_4$ needed to oxidise As in As_2O_3 to its maximum possible oxidation state in acidic medium.

86. A sample of steel weighing 0.6 g and containing S as an impurity was burnt in a stream of O_2, when S was converted to its oxide SO_2.SO_2 was then oxidised to SO_4^{--} by using H_2O_2 solution containing 30 mL of 0.04 M

NaOH. 22.48 mL of 0.024 M HCl was required to neutralise the base remaining after oxidation. Calculate the % of S in the sample>

87. The mixture of CuS (molar weight = M_1) and Cu_2S (molecular weight = M_2) oxidised by $KMnO_4$ (molecular weight = M_3) in acidic medium, the product obtained are Cu^{2+}, SO_2. Find the equivalent weight of CuS, Cu_2S and $KMnO_4$ respectively.

88. A mixture of two gases, H_2S and SO_2 is passed through three beakers successively. The first beaker contains Pb^{2+} ions, which absorbs S^{2-} forming PbS. The second beaker contains 25 mL of 0.0396 N I_2 to oxidise SO_2 to SO_4^{2-}. The third contains 10 mL of 0.0345 N thiosulphate solution to retain any I_2 carried over from the second absorber. A 25 L gas sample was passed through the apparatus followed by an additional amount of N_2 to sweep last traces of SO_2 from first and second absorber. The solution from the first absorber was made acidic and treated with 20 mL of 0.0066 M $K_2Cr_2O_7$ which converted S^{2-} to SO_2. The excess dichromate was reacted with solid KI and the liberated iodine required 7.45 mL of 0.0345 N $Na_2S_2O_3$ solution. The solutions in the second and third absorbers were combined and the resultant iodine was titrated with 2.44 mL of the same thiosulphate solution. Calculate the concentrations of SO_2 and H_2S in mg/L of the sample

89. A 1 g sample containing NaOH as the only basic substance and some inert impurity was left exposed to atmosphere for a very long time so that part of NaOH got converted into Na_2CO_3 by absorbing CO_2 from atmosphere. The resulting sample was dissolved in water and volume made up to 100 mL. A 20 mL portion of this solution required 16 mL 0.25 M HCl solution to reach the equivalence point when methyl orange was used as indicator. In a separate analysis, 20 mL portion of the same solution was taken along with phenolphthalein indicator and mixed with 50 mL of 0.1 M HCl solution. An additional 9.00 mL 0.1 M $Ba(OH)_2$ solution was required to just restore the pink colour of solution. Determine mass percentage of NaOH in the original sample and mass percentage of Na_2CO_3 in the sample after exposure to atmosphere.

90. Calculate the weight of MnO_2 and the volume of HCl of specific gravity 1.2 g mL^{-1} and 4% nature by weight needed to produce 1.78 L of Cl_2 at STP by the reaction.

91. 3.2 g of pyrolusite was treated with 50 mL of 0.5 M oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 mL in a flask. 25 mL of this solution when treated with 0.02 M $KMnO_4$ required 32 mL of the solution. Find the % of MnO_2 in the sample and also the percentage of available oxygen.

92. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 mL. A 1.5 g of the sample requires 150 mL of M/10 HCl for complete neutralisation. Calculate the percentage composition of the components of the mixture.

93. 1 L of a mixture of O_2 and O_3 at STP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of M/10 sodium thiosulphate solution for titration. What is the mass per cent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture?

94. Potassium selenate is isomorphous with potassium sulphate and contains 45.52% selenium by weight. Calculate the atomic weight of selenium. Also report the equivalent weight of potassium selenate.

95. Borax in water gives

$$B_4O_7^{2-} + 7H_2O \longrightarrow 4H_3BO_3 + 2OH^-$$

How many gram of borax ($Na_2B_4O_7 \cdot 10H_2O$) are required to

(a) prepare 50 mL of 0.2 M solution?

(b) neutralise 25 mL of 0.1934 M of HCl and H_2SO_4 separately?

96. For estimating ozone in the air, a certain volume of air is passed through an acidified or neutral KI solution when oxygen is evolved and iodide is oxidised to give iodine. When such a solution is acidified, free iodine is evolved which can be titrated with standard $Na_2S_2O_3$ solution. In an experiment, 10 L of air at 1 atm and 27°C were passed through an alkaline KI solution, at the end, the iodine entrapped in a solution on titration as above required 1.5 mL of 0.01 N $Na_2S_2O_3$ solution. Calculate volume % of O_3 in sample.

97. 1.249 g of a sample of pure $BaCO_3$ and impure $CaCO_3$ containing some CaO was treated with diluted HCl and it evolved 168 mL of CO_2 at NTP. From this solution, $BaCrO_4$ was precipitated, filtered and washed. The precipitate was dissolved in dilute sulphuric acid and diluted to 100 mL. 10 mL of this solution, when treated with KI solution, liberated iodine which required exactly 20 mL of 0.05N $Na_2S_2O_3$. Calculate the percentage of CaO in the sample.

98. In a quality control analysis for sulphur impurity 5.6 g steel sample was burnt in a stream of oxygen and sulphur was converted into SO_2 gas. The SO_2 was then oxidised to sulphate by using H_2O_2 solution to which had been added 30 mL of 0.04M NaOH. The equation for reaction is

$$SO_2(g) + H_2O_2(aq) + 2OH^-_{(aq)} \longrightarrow SO_4^{-2}{}_{(aq)} + 2H_2O(l)$$

22.48 mL of 0.024M HCl was required to neutralise the base remaining after oxidation reaction. Calculate % of sulphur in given sample.

99. A granulated sample of aircraft alloy (Al, Mg, Cu) weighing 8.72 g was first treated with alkali and then with very dilute HCl, leaving a residue. The residue after alkali boiling weighed 2.10 g and the acid insoluble residue weighed 0.69 g. What is the composition of the alloy?

100. 2.480 g of $KClO_3$ are dissolved in concentrated HCl and the solution was boiled. Chlorine gas evolved in the reaction was then passed through a solution of KI and liberated iodine was titrated with 100 mL of hypo. 12.3 mL of same hyposolution required 24.6 mL of 0.5 N iodine for complete neutralisation. Calculate % purity of $KClO_3$ sample.

101. P and Q are two elements which forms P_2Q_3 and PQ_2. If 0.15 mole of P_2Q_3 weights 15.9 g and 0.15 mole of PQ_2 weights 9.3 g, what are atomic weights of P and Q?

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is **[JEE, 1990]**

(a) +3 (b) +2 (c) +1 (d) –1

2. The oxidation states of the most electronegative element in the products of the reaction of BaO_2 with dilute H_2SO_4. **[JEE, 1991]**

(a) 0 and –1 (b) –1 and –2

(c) –2 and 0 (d) –2 and +2

3. For the redox reaction, **[JEE, 1992]**

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are:

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

4. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper II carbonate? **[JEE, 1999]**

5. Among the following species, in which oxidation state of the element is +6? **[JEE, 2000]**

(a) MnO_4^- (b) $Cr(CN)_6^{3-}$

(c) NiF_6^{2-} (d) CrO_2Cl_2

6. How many moles of electron weigh 1 kg: **[JEE, 2002]**

(a) 6.023×10^{23} (b) $\dfrac{1}{9.108} \times 10^{31}$

(c) $\dfrac{6.023}{9.108} \times 10^{54}$ (d) $\dfrac{1}{9.108 \times 6.023} \times 10^{8}$

7. MnO_4^- is good oxidising agent in different medium changing to **[AIEEE, 2002]**

$$\begin{aligned} MnO_4^- &\longrightarrow Mn^{2+} \\ &\longrightarrow MnO_4^{2-} \\ &\longrightarrow MnO_2 \\ &\longrightarrow Mn_2O_3 \end{aligned}$$

Changes in oxidation number respectively are

(a) 1, 3, 4, 5 (b) 5, 4, 3, 2

(c) 5, 1, 3, 4 (d) 2, 6, 4, 3

8. Oxidation number of Cl in $CaOCl_2$ (bleaching powder is) **[AIEEE, 02]**

(a) Zero, since it contains Cl_2

(b) –1, since it contains Cl^-

(c) +1, since it contains ClO^-

(d) +1 and –1 since it contains ClO^- and Cl^-

9. Which of the following is a redox? **[AIEEE, 02]**

(a) $2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Ag$

(b) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

(c) $N_2O_5 + H_2O \rightarrow 2HNO_3$

(d) $AgNO_3 + KI \rightarrow AgI + KNO_3$

10. In the coordination compound, $K_4[Ni(CN)_6]$, the oxidation state of nickel is **[AIEEE, 03]**

(a) +1 (b) +2 (c) –1 (d) 0

11. Amongst the following, the pair having both the metals in their highest oxidation state is **[JEE, 2004]**

(a) $[Fe(CN)_6]^{3-}$ and $[Co(CN)_6]^{3-}$

(b) $[CrO_2Cl_2]$ and $[MnO_4^-]$

(c) TiO_3 and MnO_2

(d) $[MnCl_4]^{2-}$ and $[NiF_6]^{-2}$

12. The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is **[AIEEE, 2005]**

(a) +2 (b) +3 (c) 0 (d) +1

13. The oxidation state of chromium in the final product formed by the reaction between Kl and acidified potassium dichromate solution is **[AIEEE, 05]**

(a) +6 (b) +4 (c) +3 (d) +2

14. Which of the following chemical reaction depicts the oxidising behaviour of H_2SO_4? **[AIEEE, 2006]**

(a) $2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

(b) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2$

(c) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$

(d) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

15. 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 titrations 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.

16. Among the following, the number of elements showing only one non-zero oxidation state is O, Cl, F, N, P, Sn, Tl, Na, Ti. **[IIT JEE, 2010]**

17. The difference in the oxidation numbers of two types of sulphur atoms in $Na_2S_4O_6$ is …… **[IIT JEE, 2011]**

18. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are **[IIT JEE, 2011]**

(a) II, III in haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III is haematite and II, III in magnetite

19. Consider the following reaction:

$$x\mathrm{MnO_4^-} + y\mathrm{C_2O_4^{2-}} + z\mathrm{H^+} \rightarrow x\mathrm{Mn^{2+}} + 2y\mathrm{CO_2} + \frac{z}{2}\mathrm{H_2O}$$

The values of x, y and z in the reaction are, respectively. **[JEE Main, 2013]**

(a) 5, 2 and 16 (b) 2, 5 and 8
(c) 2, 5 and 16 (d) 5, 2 and 8

20. For the reaction **[JEE Advanced, 2014]**

$$\mathrm{I^-} + \mathrm{ClO_3^-} + \mathrm{H_2SO_4} \rightarrow \mathrm{Cl^-} + \mathrm{HSO_4^-} + \mathrm{I_2}$$

The correct statement(s) in the balanced equation is/are

(a) Stoichiometric coefficient of HSO_4^- is 6
(b) Iodide is oxidised
(c) Sulphur is reduced
(d) H_2O is one of the products

21. Match the reactions in Column I with the nature of the reactions/type of the products listed in Column II.

Column I	**Column II**
a. $O_2^{\ominus} \rightarrow O_2 + O_2^{-2}$	p. Redox reaction
b. $CrO_4^{2-} + H^+ \rightarrow$	q. One of the products has trigonal planar structure
c. $MnO_4^{\ominus} + NO_2^{\ominus} + H^+ \rightarrow$	r. Dimetic bridged tetrahedral metal ion
d. $NO_3^{\ominus} + H_2SO_4 + Fe^{+2}$	s. Disproportionation

Answer Key

LEVEL I

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

LEVEL II

1. (c) 2. (c) 3. (b) 4. (d) 5. (b) 6. (c) 7. (b) 8. (a) 9. (a) 10. (a)
11. (b) 12. (b) 13. (a) 14. (a) 15. (b) 16. (d) 17. (b) 18. (b) 19. (b) 20. (b)

LEVEL III

1. (A) → r, t; (B) → p, t; (C) → q; (D) → s 2. (A) → r; (B) → t; (C) → p; (D) → s
3. (A) → q, t; (B) → p; (C) → r, t; (D) → s, t
4. (b) 5. (c) 6. (c) 7. (b) 8. (a) 9. (b) 10. (b) 11. (a) 12. (d) 13. (a)
14. (b) 15. (b) 16. (d) 17. (b) 18. (d) 19. (d) 20. (d) 21. (c) 22. (b) 23. (a, c, d)
24. (a, b, c) 25. (b, d) 26. (a, b, d) 27. (a, c, d) 28. (a, b, c, d) 29. (a, b)
30. (a, b, d) 31. (a, b, c) 32. (a, b, d) 33. (a, c) 34. (a, b, c) 35. (a)
36. (b) 37. (a) 38. (d) 39. (c) 40. (b) 41. (41) 42. (85) 43. (1) 44. (2) 45. (125)
46. (40) 47. (4) 48. (1) 49. (2) 50. (35) 51. (25) 52. (200) 53. (3) 54. (0)
55. 157.89 ml 56. 20.72 % 57. (48.78%, 51.22%) 58. 83.33% 59. 0.424 mg, 0.21 mg
60. 23.2 gm/lit., 22.28 gm/lit. 61. 0.06 gm, 0.0265 gm 62. 0.4 & 0.6 63. 31.5 ml
64. 0.588 N 65. 337.8 ml 66. 41.53% 67. 0.15 N 68. 14.36 % & 81.7%
69. 1.406% 70. 90.1% 71. 0.1281 gm 72. 25.5 gm/L, 8.4 V 73. 0.68gm/L
74. 41.66 ppm 75. 1.734 ppm 76. 100 ppm 77. 0.444 gm 78. (537.6 ml)

79. 84 mg 80. (3) 81. (5) 82. 58.8 % 83. 77.46 mL 84. 0.168N & 0.42 mL 85. 0.06 g
86. 1.76% 87. $M_1/6$, $M_2/8$, $M_3/5$ 88. 0.1212 mg/L & 0.7178 mg SO_2/L 89. 80% & 36.05 %
90. 241.66 ml 91. (24.44% and 4.5%) 92. 42%, 26.5%, 31.5% 93. 1.2×10^{21}
94. 118.2 & 130.1 95. (a) 3.82 g (b) 0.9235 g & 1.847g 96. 1.847×10^{-3}% 97. 14.09%
98. 0.1875% 99. Al = 75.9%, Mg = 16.2%, Cu = 7.9% 100. 82.32% 101. $P = 26$, $Q = 18$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (c) 2. (b) 3. (a) 4. 8.097 ml 5. (d) 6. (d) 7. (c) 8. (d) 9. (a)
10. (b) 11. (b) 12. (d) 13. (c) 14. (b) 15. (c) 16. (2) 17 (5) 18. (d) 19. (c)
20. (a), (b), (d) 21. (a) → p, s ; (b) → r ; (c) → p, q ; (d) → p

Hints and Solutions

LEVEL I

1. (b) $CaCl_2 + 2AgNO_3 \rightarrow 2AgCl + Ca(NO_3)_2$

$$n = \frac{4.31}{143.5}$$

$$\text{Moles of } CaCl_2 = \frac{4.31}{143.5} \times \frac{1}{2} = 0.015$$

2. (d) $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$

$$n = \frac{25 \times 0.75}{1000} = \text{No. of moles of HCl}$$

$$\text{Moles of } CaCO_3 \text{ required} = \frac{25 \times 0.75}{1000} \times \frac{1}{2}$$

$$\text{Mass of } CaCO_3 = \frac{25 \times 0.75}{1000} \times \frac{1}{2} \times 100 = 0.9375 \text{ g}$$

3. (a) $2H_2 + O_2 \rightarrow 2H_2O$

10 5

2 vol. H_2 give 2 vol. of H_2O vapours

∴ 10 vol. H_2O vapour will form 10 volume H_2O

4. (b) Mass of oxide = 2 g

Mass of metal = 1.6 g

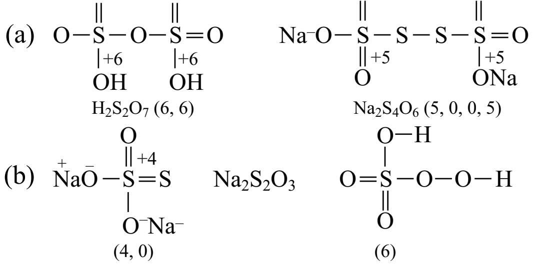
Mass of oxygen = 0.4 g

$$\text{Equivalent weight of metal} = \frac{1.6 \times 8}{0.4} = 32$$

5. (b) $\overset{+6}{C}rO_5 \rightarrow \overset{+3}{C}r_2(SO_4)_3$

Number of moles of electron required = 3

6. (d)


(a) $H_2S_2O_7$ (6, 6) $Na_2S_4O_6$ (5, 0, 0, 5)

(b) (4, 0) $Na_2S_2O_3$ (6)

(c) $SO_3 > SO_2 > H_2S > S_8$

↓ ↓ ↓ ↓

+6 +4 –2 0

(d) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$.

+6 +4 –2 (6, 6)

7. (d) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

Decomposition reaction

8. (c) $\overset{2.0}{S_2O_5^{-2}} + \overset{0}{I_2} \longrightarrow \overset{2.5}{S_2O_6^{-2}} + \overset{-1}{I^-}$

$\Rightarrow$ Redox reaction $I_2^o \xrightarrow{\text{Redn}} I^-$

$$\underset{(4,\,0)}{S_2O_3^{-2}} \xrightarrow{\text{Oxd.}} \underset{(5,\,0,\,0,\,5)}{S_2O_6^{-2}}$$

9. (c) $xHI + yHNO_3 \longrightarrow NO + I_2 + H_2O$

$$\left[\begin{array}{l} (2I^- \longrightarrow I_2 + 2e) \times 3 \\ (\overset{+5}{NO_3^-} + 3e \longrightarrow \overset{+2}{N}O) \times 2 \end{array}\right] \begin{array}{l} \text{.....(1)} \\ \text{.....(2)} \end{array}$$

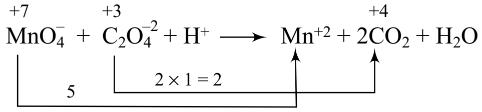
Adding (1) and (2)

$\Rightarrow$ $6I^- + 2NO_3^- \longrightarrow 2NO + 3I_2$

$6HI + 2HNO_3 \longrightarrow 2NO + 3I_2 + 4H_2O$

$\Rightarrow$ $x = 6, y = 2$

10. (a)


$$\overset{+7}{MnO_4^-} + \overset{+3}{C_2O_4^{-2}} + H^+ \longrightarrow Mn^{+2} + 2\overset{+4}{C}O_2 + H_2O$$

5

2 × 1 = 2

$$2MnO_4^- + 5C_2O_4^{-2} + 16H^+ \rightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

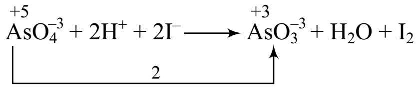
11. (c) $\text{Molarity} = \dfrac{\text{Normality}}{n \text{ factor}}$

1 M H_3PO_4 = 3N H_3PO_4

12. (d) $2CrO_5 + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3H_2O + 7/2O_2$

1 mole CrO_5 Liberate $\longrightarrow$ 7/4 mole of O_2

13. (a)


$$\overset{+5}{AsO_4^{-3}} + 2H^+ + 2I^- \longrightarrow \overset{+3}{AsO_3^{-3}} + H_2O + I_2$$

2

Molar mass Na_3AsO_4 = 23 × 3 + 75 + 15 × 4

Molar mass = 208

$$\text{Equivalent of AsO}_4^- = \frac{1}{\left(\frac{208}{2}\right)} = \left(\frac{1}{104}\right)$$

Equivalent of Na_3AsO_4 = Equivalent of I_2
= Equivalent of $Na_2S_2O_3$

$$\frac{1}{104} = 0.2 \times V$$

$$\frac{1}{104 \times 0.2} L = V = 48.1 \text{ mL}$$

14. (b) Milliequivalent of $KMnO_4$ = .2 × 50 × 5 = 50
Milliequivalent of H_2O_2 = 2 × 25 × .5 = 25
Milliequivalent of $KMnO_4$ remaining = (50 – 25) = 25

$$\text{Mole of KMnO}_4 = \frac{25}{5} \times 10^{-3} = 5 \times 10^{-3} = .005$$

15. (a) $$\frac{100X}{1000} = \left(\frac{3}{24}\right) \times 2$$

$$X = \frac{20}{8} = 2.5$$

16. (b) $Ca(HCO_3)_2 + CaO \longrightarrow 2CaCO_3 + H_2O$
1 mole CaO required for precipitation of 2 mole $CaCO_3$
OR
2 × 100 gram $CaCO_3$ obtained by 1 × 56 gram CaO

$$\therefore \quad 2 \text{ gram CaCO}_3 \text{ obtained by } \frac{56}{200} \times 2 = 0.56 \text{ gram}$$

17. (a) (320 mL, 10V H_2O_2) + (80 mL, 5NH_2O_2)
(A) (B)

$$N_A = \left(\frac{10}{5.6}\right)$$

$$\Rightarrow \quad N_C = \frac{N_AV_A + N_BV_B}{V_A + V_B} = \frac{\frac{10}{5.6} \times 320 + 5 \times 80}{320 + 80}$$

$$= \frac{571.42 + 400}{400}$$

$$= 2.4285$$

$$\text{volume strength} = \frac{N}{5.6}$$

∴ volume strength = 5.6 × 2.4285 = 13.6 V
volume strength in gram/L = $N \times 17$
= 2.4285 × 17
= 41.285 gram L^{-1}

18. (b)

$$\begin{array}{llll} \text{Fe} & + \ \frac{1}{2}\text{O}_2 & \longrightarrow & \text{FeO} \\ 1 & \quad 0.65 & & \\ 0 & \quad 0.15 & & 1 \\ 2\text{FeO} & + \ \frac{1}{2}\text{O}_2 & \longrightarrow & \text{Fe}_2\text{O}_3 \\ 1 & \quad 0.15 & & \\ (1 - 0.60) & & & 0.30 \\ 0.4 & & & 0.30 \end{array}$$

$$\text{Mole ratio } \frac{\text{FeO}}{\text{Fe}_2\text{O}_3} = \frac{0.40}{0.30} \Rightarrow \frac{4}{3}$$

19. (b) 1 mole of $FeSO_4$ gives 1 mole Fe^{2+} and 1 mole SO_4^{2-} while a mole $Fe_2(SO_4)_3$ gives 2 *a* mole Fe^{2+} and 3 *a* mole SO_4^{2-}.

according to question.

$$[\text{SO}_4^{--}]_{\text{FeSO}_4} = [\text{SO}_4^{--}]_{\text{Fe}_2(\text{SO}_4)_3}$$

$$1 \times \text{SO}_4^{--} = a \times 3 \times \text{SO}_4^{--}$$

$$a = \frac{1}{3} \text{mole}$$

$$\therefore \quad \text{number of moles of Fe}^{3+} = 2a = \frac{2}{3} \text{mole}$$

$$\therefore \quad \frac{\text{Fe}^{2+}}{\text{Fe}^{+3}} = \frac{1}{2/3} = \frac{3}{2}$$

$$\text{Fe}^{+2} : \text{Fe}^{+3} := 3 : 2$$

20. (c)

$$\begin{array}{llll} & 2\text{Fe} & + \ \frac{3}{2}\text{O}_2 \longrightarrow & \text{Fe}_2\text{O}_3 \\ \text{Initial} & n & \text{excess} & 0 \\ & n - x & & \frac{x}{2} \end{array}$$

$$\text{weight } (n - x) \times 56 + \left(\frac{x}{2}\right) \times 160 = n \times 56 \times 1.1$$

$$24x = 5.6n$$

$$\left(\frac{x}{n}\right) = 0.2323$$

% total iron = 23.3%

21. (c) $$\overbrace{\text{HNO}_3 + (\underbrace{\text{NH}_4)_2\text{SO}_4 \longrightarrow \text{N}_2}_{2 \times 3 = 6} + \text{NO}_2}^{1}$$

Milliequivalent of HNO_3 = Milliequivalent of NH_4^+
Mole × *n*-factor = Mole × *n*-factor
1 × Mole = 1 × 6
Mole of HNO_3 = 6

22. (d) $Z^{+x} + KMnO_4 \xrightarrow{H^+} Mn^{2+} + Z^{+y}$

Milliequivalent of Z^{+x} = Milliequivalent of $KMnO_4$

$$25 \times 0.1 \times (y - x) = 25 \times 0.04 \times 5$$

$$(y - x) = \frac{0.04 \times 5}{0.1} = 2$$

$$Z^{2+} \longrightarrow Z^{4+}$$

$$(4 - 2) = 2$$

$|y| > |x|$ ∴ Correct Ans. (d)

23. (a) $Cl^- + KMnO_4 \longrightarrow Mn^{2+} + Cl_2$
Milliequivalent of NaCl = Milliequivalent of $KMnO_4$

$$\text{Mole} \times n\text{-factor} = \frac{10}{158} \times \frac{5}{2}$$

$$\text{Mole} \times 1 = \frac{10}{158} \times \frac{5}{2}$$

$$\text{Volume of } Cl_2 = \frac{10}{158} \times \frac{5}{2} \times 22.4 = 3.54 \text{ L}$$

24. **(a)** $I_2 \longrightarrow I^- + IO_3^-$

$I_2 \rightarrow 2I^-$

$[2e^- + I_2 \rightarrow 2I^-] \times 5$

$10e^- + 5I_2 \rightarrow 10I^-$

$I_2 \longrightarrow 2IO_3^-$

$I_2 + 6H_2O \longrightarrow 2IO_3^-$

$I_2 + 6H_2O + 12OH^- \longrightarrow 2IO_3^- + 12H_2O + 10e^-$

$\therefore$ $I_2 + 12OH^- \longrightarrow 2IO_3^- + 6H_2O + 10e^-$

$\therefore$ net reaction

$12OH^- + 6I_2 \longrightarrow 10I^- + 2IO_3^- + 6H_2O$

$$\text{Ratio of } \frac{IO_3^-}{I^-} = \frac{2}{10} = 1:5$$

25. **(d)** Equivalent mass

$$= \frac{\text{Molecular mass}}{n\text{-factor}}$$

$\overset{+3}{As_2} \longrightarrow 2\overset{+5}{As}$ $\quad$ n-factor 4

$\overset{-2}{S_2} \longrightarrow 3\overset{+6}{S}$ $\quad$ 24

Total n-factor = 28

$$\text{Equivalent mass} = \frac{\text{Molecular weight}}{28}$$

26. **(d)** $\overset{+2}{Zn}\overset{-2}{S} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Zn}(\overset{+5}{N}O_3)_2 + H_2\overset{+6}{S}O_4 + \overset{+4}{N}O_2$

Change in O.N. of Zn

Zn = 0

S = 6 – (–2) = 8

N = 5 – 4 = 1

27. **(d)** $Fe(C_2O_4) + KMnO_4 \longrightarrow Fe^{+3} + CO_2 + Mn^{+2} + H_2O$

$(1 \times 1 + 2 \times 1) = 3$

1×5

for [*a*, *b*, *c*]

$3 \times 0.1 \times 25 = 5 \times M \times 25$

$$M = \frac{0.3}{5} = 0.06 \text{ M}$$

for [*d*]

$3 \times 0.1 \times 25 = 5 \times 15 \times M$

$\therefore$ molarity = 0.1 M

$\therefore$ Correct Ans. (d)

28. **(c)** $K_2Cr_2O_7 + Sn^{2+} \longrightarrow Sn^{4+} + Cr^{3+}$

$Sn^{4+} + Fe^{2+} \longrightarrow Fe^{3+}$

Milliequivalent of Sn^{4+} = Milliequivalent of $K_2Cr_2O_7$

Milliequivalent of Sn^{4+} = Milliequivalent of Fe^{3+}

Milliequivalent of Fe^{3+} = Milliequivalent of $K_2Cr_2O_7$

$$N_{K_2Cr_2O_7} = \frac{4.9 \times 6}{294 \times 0.1} = 1$$

Millimol × n-factor = NV = $n_f \times$ MV = 1 × 1 × 10

Millimol = 10

29. **(b)** Volume of O_2 at NTP

$$V_{O_2} = \frac{500 \times 1 \times 273}{300}$$

$V_{O_2} = 455$ mL

35 mL of H_2O_2 gives 455 mL at N.T.P.

$$\therefore \quad 1 \text{ mL of } H_2O_2 \text{ gives} = \frac{455}{35} = 13$$

= 13 mL of O_2 at NTP

Hence volume strength of H_2O_2 = ‘13 V’

30. **(b)** Half milliequivalent of salt (Na_2CO_3) in neutralise using Hph indicator because HPh work in basic medium.

$\frac{1}{2}$ milliequivalent of salt = milliequivalent of HCl

$\frac{1}{2}(20 \times 0.1 \times 2) = 0.05x$ (i)

Complete milliequivalent of salt ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is neutralise using MeOH indicator (Work in acidic medium)

Milliequivalent of salt = Meq of HCl

$20 \times 0.1 \times 3 = 0.05y$ (ii)

Eq. (ii) – Eq. (i)

$0.05(y - x) = (6 - 2)$

$$(y - x) = \frac{4}{0.05}$$

$(y - x) = 80$ mL

31. **(b)** Milliequivalent of $KMnO_4$ = Milliequivalent of $C_2O_4^{-2}$

$$90 \times \frac{1}{20} = 100 \times N_{C_2O_4^{-2}} = 100 \times 2 \times M_{C_2O_4^{-2}}$$

$$\text{mole of oxalate} = \frac{9}{2 \times 2} \times 10^{-3} = \frac{9}{4} \times 10^{-3} \text{ mole}$$

$$\text{Weight of oxalate} = \frac{9}{4} \times 88 \times 10^{-3} = 0.198 \text{ gram}$$

$$\%\ C_2O_4^{-2} = \frac{0.198}{0.300} \times 100 = 66\%$$

32. **(a)** Milliequivalent of $KMnO_4$ = Milliequivalent of $C_2O_4^{-2}$ = Milliequivalent of $CaCO_3$

40 × .25 = Milliequivelent of CaO

$$\frac{10 \times 10^{-3}}{2} = \text{Mole of CaO}$$

$$\%\ \text{CaO} = \frac{5 \times 10^{-3} \times 56 \times 100}{.518}$$

CaO = 54%

33. **(c)** $M = \dfrac{\text{Number of equivalent}}{\text{Volume of sol (in } L)}$

$\Rightarrow$ Milliequivalent = 50 × 0.2 = 10

$$\therefore \quad \text{mole} = \frac{10 \times 10^{-3}}{2} = 5 \times 10^{-3}$$

Molar mass = 24 + 16 × 4 + 2 + 2 × 18 = 126 gm.

⇒ Mass of $H_2C_2O_4.2H_2O$

$= 126 \times 5 \times 10^{-3} = 0.63$ gm

34. **(b)** Milliequivalent of HNO_3 = Milliequivalent of Fe^{2+}

$$\overbrace{\overset{+5}{(NO_3} \longrightarrow \overset{2+}{NO)}}^{n\text{-factor} = 3}$$

or $6 \times 3 \times V = \dfrac{8}{56}$

$V = 7.936 \times 10^{-3}$ L = 7.936 ml

35. **(a)** $CaCO_3 + HCl \to CaCl_2 + H_2O + CO_2$ (224 mL)

$$CO_2 \text{ mole} = \frac{224}{22400} = 10^{-2}$$

$$HCl\ (M) = HCl\ (N) = \frac{10^{-2}}{200 \times 10^{-3}} = \frac{1}{20} = 0.05$$

36. **(a)** $KMnO_4$ (*n* factor in acidic medium) = 5

$K_2Cr_2O_7$ (*n* factor in acidic medium) = 6

$6 \times 0.1 \times V_1 = 5 \times 0.3 \times V_2$

$$\frac{6}{15}V_1 = V_2$$

$$V_2 = \frac{2}{5}V_1$$

37. **(b)** $K_2Cr_2O_7$ have greater *n* factor as compared to $KMnO_4$ so same volume of $K_2Cr_2O_7$ will oxidise more amount of Fe^{+2}.

38. **(a)**

I_2	+	$2Cl_2$	→	ICl	+	ICl_3
254 g		142 g		1	:	1
25.4 g		14.2 g		0.1	:	0.1

but Cl_2 given is only 12.2 g (less than normal ratio hence limiting reagent)

14.2 g Cl_2 produces → 0.1 moles of each

$$12.2 \text{ g} \to = \frac{0.1}{14.2} \times 12.2 = 0.086 \text{ mole of each}$$

hence molar ratio remain equal (1:1)

39. **(a)** $2Fe + 3H_2O \to Fe_2O_3 + 3H_2$

54 g $H_2O(g)$ convert 112 g Fe to its oxide

∴ 18 gram $H_2O(g)$ convert $\dfrac{112}{54} \times 18 = 37.3$ g

n-factor = 5

40. **(c)** $As_2O_3 + MnO_4^- \longrightarrow 2AsO_4^{3-} + Mn^{2+}$

n-factor = 4

Let, molarity of $KMnO_4$ solution be M

∴ Equivalent of As_2O_3 = Equivalent of $KMnO_4$ solution

$$\frac{0.1097}{198} \times 4 = \frac{36.10 \times M \times 5}{1000}$$

$$\left(\text{Equivalent weight } As_2O_3 = \frac{198}{4}\right)$$

Molarity = 0.0122 M

41. **(c)** Milliequivalent of $S_2O_3^{2-}$ = Milliequivalent of CrO_4^{2-}

$40 \times 0.246 \times 8 = V \times 0.154 \times 3$

∴ $V = 170.4$ mL

42. **(a)**

	$Al_2(SO_4)_3$	+ $BaCl_2$ ⟶	$BaSO_4$ ↓	+ $AlCl_3$
Initial	$10 \times 0.4 \times 6$	$20 \times 0.6 \times 2$	0	0
	24	24		
Finally	0	0	24	24

$$[Al^{3+}] = \frac{24}{30 \times 3} = 0.266 \text{ M}$$

43. **(b)** Milliequivalent of $NaBrO_3 = 55.5 \times 0.672 = 37.296$

Let weight of $NaBrO_3$ = W

$$\therefore \quad \frac{W}{M_{NaBrO_3}} \times 6 \times 1000 = 37.296$$

$$\therefore \quad \frac{W}{151} \times 6 \times 1000 = 37.296$$

∴ $W = 0.9386$ gram

44. **(b)** Milliequivalent of $NaHSO_3$ = Milliequivalent of $NaIO_3 = N \times V = \dfrac{0.68}{198} \times 6 \times 1000$

$$\therefore \quad \frac{W_{NaHSO_3}}{M_{NaHSO_3}} \times 2 \times 1000 = \frac{0.68}{198} \times 6 \times 100$$

$$W_{NaHSO_3} = \frac{0.68 \times 6 \times 100 \times 104}{198 \times 1000} = 0.2143$$

45. **(d)** Let us first solve this problem by writing the complete balanced reaction.

$$3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 \downarrow + 6NaCl$$

We can see that the moles of $BaCl_2$ used are $\dfrac{3}{2}$ times the moles of Na_3PO_4. Therefore, to react with 0.1 mol of Na_3PO_4, the moles of $BaCl_2$ required would be 0.1 $\times \dfrac{3}{2}$ = 0.15. Since $BaCl_2$ is 0.5 mol, we can conclude that Na_3PO_4 is the limiting reagent. Therefore, moles of $Ba_3(PO_4)_2$ formed is

$$0.1 \times \frac{1}{2} = 0.05 \text{ mol}$$

46. **(a)** Milliequivalent of Acid = Milliequivalent of NaOH

$$\frac{0.52}{E} \times 1000 = 100 \times 0.2$$

∴ $E = 26$

47. **(a)** Weight of H_2O_2 in 1 mL = $\dfrac{34}{1120}$g

$$H_2O_2 \to H_2O + \frac{1}{2}O_2$$

34 g of H_2O_2 gives 11200 mL of O_2 at STP

$$\therefore \quad \frac{34}{1120} \text{g of } H_2O_2 \equiv \frac{11200}{34} \times \frac{34}{1120}$$

= 10 mL of O_2 at STP.

48. **(a)** $Mn^{7+} + 5e^- \to Mn^{2+}] \times 3$

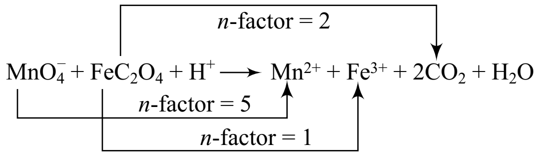
$Fe^{2+} \to Fe^{3+} + e^-$

$C_2O_4^{2-} \to 2CO_2 + 2e^-$

3 moles of $KMnO_4$ = 5 moles of FeC_2O_4

$\therefore$ 2 mol of ferrous oxalate $\equiv \frac{6}{5}$ mole of $KMnO_4$

49. **(a)** Milliequivalent of $KMnO_4$ = Milliequivalent of FeC_2O_4



$$MnO_4^- + FeC_2O_4 + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + 2CO_2 + H_2O$$

LEVEL II

1. **(c)** $4HCl + MnO_2 \rightarrow MnCl_2 + Cl_2 + 2H_2O$

$$n = \frac{5}{87}$$

Moles of HCl reacted = $\frac{5}{87} \times 4$

Mass of HCl = $\frac{5}{87} \times 4 \times 36.5 = 8.4$ gram

2. **(c)** $\therefore$ 10 L volume at STP = 11.6 g

$\therefore$ 22.4 L volume = $\frac{11.6 \times 22.4}{10}$

M.W = 26

EF = CH, MF = C_2H_2

3. **(b)** $ClO^- + \underset{2(6-x)}{Cr_2O_X} \rightarrow Cl^- + Cr_2O_7^{2-}$

Number of equivalent of ClO^- = Number of equivalent of Cr_2O_X

$$0.15 \times 2 = \frac{12.6}{(104 + 16x)} \times 2(6 - x)$$

or $31.2 + 4.8x = 151.2 - 25.2x$

$x = 4$

Hence formula = Cr_2O_4 or CrO_2

4. **(d)** $S + O_2 \rightarrow SO_2$

Moles of SO_2 produced from 8 g of sulphur = $\frac{8}{32} = 0.25$

$SO_2 + Cl_2$ water $\rightarrow SO_4^{2-} + 2Cl^-$

Moles of SO_4^{2-} produced = Moles of SO_2 = 0.25

Now $SO_4^{2-} + BaCl_2 \rightarrow BaSO_4 + 2Cl^-$

Moles of $BaSO_4$ produced = moles of SO_4^{2-} = 0.25

5. **(b)** $\underset{170\text{ g}}{AgNO_3} + HCl \rightarrow \underset{143.5\text{ g}}{AgCl} + H^+ + NO_3^-$

$\because$ 143.5 g AgCl is produced by 170 gm of $AgNO_3$

$\therefore$ 2.125 g AgCl is produced by $\frac{170 \times 2.125}{143.5}$

= 2.517 of $AgNO_3$

Now for the reaction equivalent of $AgNO_3$ = equivalent of HCl

or $\frac{2.517}{170} = \frac{25}{1000} \times N$

Hence $N = 0.6$

6. **(c)** Number of equivalent = Mole × n-factor

$$SO_3^{-2} + H_2O \longrightarrow SO_4^{-2} + 2H^+ + 2e^- \quad (1)$$

n-factor for reaction is 2

$\Rightarrow$ $50 \times .1 \times n = 25 \times .1 \times 2$

$$n = \frac{2.5 \times 2}{5}$$

$n = 1$

$\Rightarrow$ Final oxidation state will be $(3 - 1) = 2$

7. **(b)** Milliequivalent of $K_2Cr_2O_7$ = Milliequivalent of ABD

n-factor of $K_2Cr_2O_7$ in acidic medium = 6.

$6 \times 1.68 \times 10^{-3} = x \times 3.26 \times 10^{-3}$

$x = 3$

$\Rightarrow$ New oxidation state of A^{-n} will be $= -n + 3$

8. **(a)** $NaN_3 \longrightarrow N_3^- \longrightarrow N \longrightarrow -1/3$

$N_2H_2 \longrightarrow N \longrightarrow -1$

$NO \longrightarrow N \longrightarrow +2 \Rightarrow 5(A)$

$N_2O_5 \longrightarrow N \longrightarrow +5$

9. **(a)** 63% (w/v) $H_2C_2O_4.2H_2O$

$\Rightarrow$ 100 mL contains = 63 g

125 mL $\longrightarrow = \frac{63}{100} \times 125$ g

Mole of $H_2C_2O_4 = \frac{63 \times 125}{126 \times 100} = \left(\frac{5}{8}\right)$

for NaOH $\frac{40}{100} = \frac{x}{125}$

Mole of NaOH = $\frac{125 \times 40}{100 \times 40} = \left(\frac{5}{4}\right)$

$$H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O$$

2 × mole of Acid = Mole of NaOH for neutralisation = 5/4

and will have $\left(\frac{5}{4}\right)$ mole of NaOH

$\therefore$ Solution is neutral

10. **(a)** Mole of $V_2O_5 = \frac{10}{51 \times 2 + 5 \times 16} = \frac{10}{102 + 80} = \frac{10}{182}$

= .055

Mole of V^{+2} = .055 × 2

= .1098 mole ≃ 0.11

$$V^{+2} \longrightarrow \overset{+4}{V}O^{+2} + 2e$$

$$I_2 + 2e \longrightarrow 2I^-$$

$\Rightarrow$ Mole of I_2 = Mole of V^{+2} = 0.11 mole

11. **(b)** Milliequivalent of I_2 = Milliequivalent of Hypo solution

$= 20 \times 2.5 \times 10^{-3}$

Milliequivelent of 10 ml I^- = Milliequivelent of I_2 = 20 × 2.5 × 10^{-3} = 0.05
Milliequivelent of 100 mL I^- = 0.5
Milliequivelent of $CuCO_3$ = 0.5

$$\frac{w}{123.5} \times 1000 = 0.5 \qquad w = 0.06175$$

$$\% \text{ purity} = \frac{0.06175}{0.1} \times 100 = 61.75\%$$

12. **(b)** $I_2 + Na_2S_2O_3 \rightarrow I^- + S_4O_6^{2-}$
let x mL of I_2 react with Hypo
milliequivelent of I_2 = milliequivelent of Hypo

$$xN = 15 \times 0.4 \qquad xN = 6 \qquad \text{(i)}$$

milliequivelent of H_2SO_4 used by base = $10 \times 0.3 \times 2 = 6$
milliequivelent of NaOH used by I_2 = (30 – 6)

$$(150 - x)\,N = 24 \qquad \text{(ii)}$$

Equation (ii) divided by (i)

$$\frac{150 - x}{x} = 4 \quad \Rightarrow \quad 5x = 150$$

$$x = 30 \text{ mL} \qquad 30\,N = 6$$

$$N = \frac{1}{5} \qquad N = M \times n\text{-factor}$$

$$\frac{1}{5} = M \times 2$$

$$M = \frac{1}{10} = 0.1$$

13. **(a)** Let a g H_2SO_4 and $(3.185 - a)$ g $H_2C_2O_4$
milliequivelent of 10 mL mixture = 0.3
milliequivelent of 1000 mL mixture = 0.3 × 1000 = 30
milliequivelent of H_2SO_4 + milliequivelent of $H_2C_2O_4$ = 30

$$\frac{a}{49} \times 1000 + \frac{(3.185 - a)}{45} \times 1000 = 30 \qquad \text{(i)}$$

In another example
milliequivelent of 100 mL mixture = milliequivelent of $KMnO_4$ = 4 × 0.02 × 5
milliequivelent of 100 mL mixture = 0.4
milliequivelent of 1000 mL mixture = 4
milliequivelent of $H_2C_2O_4$ = 4

$$\frac{3.185 - a}{45} \times 1000 = 4 \qquad \text{(ii)}$$

$$\therefore \quad \frac{a}{49} \times 1000 = 30 - 4 = 26$$

$$a = \frac{26 \times 49}{1000} = 1.274$$

$$\% \text{ of } H_2SO_4 = \frac{1.274}{3.184} \times 100 = 40\%$$

14. **(a)** $K_2Cr_2O_7 + KI \longrightarrow I_2 + Cr^{3+}$

$I_2 + Na_2S_2O_3 \longrightarrow I_2 + S_4O_6^{2-}$

$Na_2S_2O_3 + K_2Cr_2O_7 \longrightarrow$

milliequivelent of $Na_2S_2O_3 \longrightarrow$ milliequivelent of $K_2Cr_2O_7$

$$30 \times N = 15 \times \frac{1}{20} \qquad N = \frac{1}{40}$$

milliequivelent of I_2 = milliequivelent of Hypo
milliequivelent of I_2 = milliequivelent of KI
milliequivelent of KI = milliequivelent of $K_2Cr_2O_7$

$$24 \times \frac{1}{40} = \text{milliequivelent of 25 mL } K_2Cr_2O_7$$

milliequivelent of 500 mL $K_2Cr_2O_7 = \frac{24}{40} \times \frac{500}{25}$

$$\frac{w \times 6}{294} \times 1000 = 12 \qquad w = 0.588$$

$$\% \text{ purity} = \frac{0.588}{0.8} \times 100 = 73.5\%$$

15. **(b)** Let the mass of $CaCl_2$ in sample = x g
$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$
111 g 100 g
∴ 111 g $CaCl_2$ produces → 100 g $CaCO_3$

x g $CaCl_2$ produces $\frac{100x}{111}$ g $CaCO_3$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

100 g 56 g
∴ 100 g $CaCO_3$ produces → 56 g CaO

$\left(\frac{100x}{111}\right)$ $CaCO_3$ produces → $\frac{56}{100} \times \frac{100}{111}$ g CaO = $\frac{56x}{111}$ g CaO

since mass of CaO finally produced = 1.62 g = 56x/111

$$x = 3.21 \text{ g}$$

$$\% \text{ of CaO in sample} = \frac{3.21}{10} \times 100 = 32.1\%$$

16. **(d)** $2\overset{-1}{N}H_2OH \rightarrow \overset{0}{N}_2$

n-factor = 1

$$\overset{+3}{F}e_2(SO_4)_3 \rightarrow 2\overset{+2}{F}eSO_4$$

n-factor = 2

$$\text{Equivalent weight} = \frac{\text{Molar mass}}{2}$$

17. **(b)** In acidic medium

$$MnO_4^- \longrightarrow Mn^{+2} \qquad n_f = 5$$

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{+3} \qquad n_f = 6$$

Hence the amount of Fe(II) oxidised is more with $Cr_2O_7^{2-}$

18. **(b)** Milliequivelent of H_2SO_4 = 100 × 0.2 × 2 = 4
Milliequivelent of NaOH = 100 × 0.2 × 1 = 20
milliequivelent of H_2SO_4 remains un neutralised = 20
Number of g equivalent of H_2SO_4 = N × V

$$\frac{200}{100} = N \times \frac{200}{1000,}, N = 0.1$$

or $$N_{\text{mix}} = \frac{N_aV_a - N_bV_b}{V_a + V_b}$$

19. **(b)** $K\overset{7+}{Mn}O_4 \longrightarrow \overset{4+}{Mn}O_2$

$n = 3$

$$\text{Molarity} = \frac{\text{Normality}}{n\text{-factor}} = \frac{1.8}{3} = 0.6$$

20. **(b)** milliequivalent of $Ba(MnO_4)_2$ = milliequivelent of $H_2O_2 \left(\therefore M = \frac{33.6}{11.2} \Rightarrow 3\right)$ $\quad n_f$ of $Ba(MnO_4)_2 = 10$

$$\frac{w}{375} \times 10 \times 1000 = \frac{3 \times 125 \times 2}{1000}$$

$w = 28.125$

$$\%\text{ purity} = \frac{w}{40} \times 100 = \frac{28.125}{40} \times 100 = 70.31$$

LEVEL III

1. **(a - r,t), (b - p,t), (c - q), (d - s)**

$\overset{-3}{N}H_3 \longrightarrow \overset{+5}{N}O_3^-$ n-factor = 8,
Equivalent weight = Mw/8

$\overset{+2}{Fe}\overset{+3}{C_2}O_4 \longrightarrow \overset{+3}{Fe}^{+++} + 2\overset{+4}{C}O_3^{--}$ n-factor = 3,
Equivalent weight = Mw/3

$H_2\overset{+6}{S}O_5 \longrightarrow \overset{0}{S_8}$ n-factor = 6,
Equivalent weight = Mw/6

$KMnO_4 \longrightarrow \overset{+2}{Mn}$ n-factor = 5,
Equivalent weight = Mw/5

2. **(a - r), (b - t), (c - p), (d - s)**

H_3PO_4 is tribasic acid ($n = 3$); H_3PO_3 is dibasic acid ($n = 2$); H_3BO_3 is monobasic acid ($n = 1$) and EDTA is tetrabasic acid ($n = 4$)

3. **(a – q,t), (b – p), (c – r,t), (d – s,t)**

$K\overset{+7}{Mn}O_4 \longrightarrow \overset{+2}{Mn}^{+2}$ (n-factor = 5)

$Mg\overset{+3}{C_2}O_4 \longrightarrow Mg^{+2} + 2\overset{+4}{C}O_2$ (n-factor = 2)

$K_2\overset{+6}{Cr_2}O_7 \longrightarrow 2\overset{+3}{Cr}^{+3}$ (n-factor = 6)

$\overset{+6}{Cr}O_5 \longrightarrow \overset{+3}{Cr_2}O_3$ (n-factor = 3)

Comprehension 1

4. **(b)** $H_2O + SO_3 \longrightarrow H_2SO_4$;

18 g water combines with 80 g SO_3

∴ 4.5 g of H_2O combines with 20 g of SO_3

∴ 100 g of oleum contains 20 g of SO_3 or 20% free SO_3

5. **(c)** Initial moles of free SO_3 present in oleum

$$= \frac{12}{18} = \frac{2}{3}\text{ moles}$$

$$= \text{moles of } SO_3 \text{ combined with water} = \frac{9}{18} = \frac{1}{2}\text{ mole}$$

$$\therefore \text{ moles of free } SO_3 \text{ remains} = \frac{2}{3} - \frac{1}{2} = \frac{1}{6}\text{ mole}$$

$$\therefore \text{ volume of free } SO_3 \text{ at STP} = \frac{1}{6} \times 22.4 = 3.73\text{L}$$

6. **(c)** $Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$

Moles of CO_2 formed = moles of Na_2CO_3 reacted = $\frac{5.3}{106} = 0.05$

Volume of CO_2 formed at 1 atm pressure and 300 K = $0.05 \times 24.63 = 1.23$ L

7. **(b)** Equivalent of H_2SO_4 + Equivalent of SO_3 = Equivalent of NaOH

$$\frac{x}{98} \times 2 + \frac{(1-x) \times 2}{80} = 54 \times 0.4 \times 10^{-3}$$

$$\%\text{ of free } SO_3 = \frac{1 - 0.74}{1} \times 100 = 26\%$$

Comprehension 2

8. **(a)** 1 L of H_2O_2(aq.) provide 11.2 L of O_2 at STP

$$\text{Moles of } O_2 = \frac{11.2}{22.4} = 0.5$$

$n_{H_2O_2}$ required 0.5×2

$$M_{H_2O_2} = \frac{n_{H_2O_2}}{V_{\text{solution}}} = 1\text{ M}$$

9. **(b)** Strength in percentage mean how many g H_2O_2 present per 100 mL

∵ M ⇒ 1 and molecular weight of $H_2O_2 = 34$

∴ 34 gram H_2O_2 present per litre of solution or 3.4 gram H_2O_2 present per 100 mL of solution.

10. **(b)** Milliequivalent of H_2O_2 = Milliequivalent of $KMnO_4$

$20 \times N = 0.05 \times 5 \times 80 \Rightarrow N = 1$

$$N = \frac{\text{Volume strength of } H_2O_2}{5.6}$$

⇒ Volume strength of $H_2O_2 = 5.6$

Comprehension 3

11. **(a)** In aqueous solution iodine exist in polyiodide ion (I_3^-)

12. **(d)** $2\overset{+2}{Cu}SO_4 \longrightarrow \overset{+1}{Cu}_2I_2$, n-factor = 1

13. **(a)** Equivalent of $CuSO_4$ = Equivalent of I_2 = Equivalent of hypo

$$\frac{\text{Weight}}{\text{Equivalent weight } CuSO_4} \times 1000 = 100 \times 1 \times 1$$

$$\text{Weight of } CuSO_4 = \frac{100}{1000} \times 159.5 = 15.95\text{ gm}$$

∴ % purity = 10%

14. **(b)** Equivalent of Hypo = Equivalent of $CuSO_4.5H_2O$

$$100 \times 0.1 = \frac{x}{249.5} \times 1000, x = 2.5 \text{ gm}$$

Comprehension 4

15. **(b)** Milliequivalent of $CuSO_4$ reacted = Milliequivalent of $Na_2S_2O_3$ reacted ($n_f = 8$) = 50 × 1 × 8 = 400

$$\overset{+2}{S_2}O_3^{-2} \longrightarrow \overset{+6}{S}O_4^{-2}$$

$$n_f = 2(6-2) = 8$$

$$\frac{\text{Weight}}{\text{Equivalent weight}} = \frac{400}{1000} = \frac{\text{Weight}}{149.5}$$

$$\therefore \quad \text{Weight} = 59.8 \text{ g}; \% \text{ purity } \frac{59.8}{79.75} \times 100 = 75\%$$

16. **(d)** 214 g KIO_3 = 1 mole of KIO_3 ($n_f = 5$)
= 3 mole of I_2 (in the balanced chemical reaction) = 6
Equivalent of I_2 ($n f = 2$) = 6000 Milliequivelent of I_2
Let the volume of $Na_2S_2O_3 = x$ mL, then

$$(x \times 1) \times 8 = 6000 \quad x = 750 \text{ mL}$$

17. **(b)** $5KI + KIO_3 + 6HCl \longrightarrow 3I_2 + 6KCl + 3H_2O$

m mole of $KMnO_4$ used $= 50 \times \frac{1}{10} = 5$

Milliequivalent of $KMnO_4$ used ($n_f = 5$) = 25 Milliequivalent of $C_2O_4^{-2}$

m mole of $C_2O_4^{-2}$ $(n_f = 2) = \frac{25}{2} = 12.5$

Milliequivalent of $Na_2S_2O_3$ = 2.5 = Milliequivalent of Cu^{+2} (n = 1) Milliequivalent of Cu^{+2} (n = 1) = 2.5

Difference in number of m moles of Cu^{+2} and $C_2O_4^{-2}$ = 12.5 – 2.5 = 10

18. **(d)** $5KI + KIO_3 + 6HCl \longrightarrow 3I_2 + KCl + 3H_2O$

$$\frac{1.66}{166} = 10^{-2} \text{mole KI}$$

Moles of KIO_3 reacted $= \frac{1}{5} \times 10^{-2} = 2 \times 10^{-3}$

Moles of I_2 formed $= 3 \times 2 \times 10^{-3} = 6 \times 10^{-3}$

Comprehension 5

19. **(d)** 109% labelled oleum will contain $\frac{9}{18}$ mole SO_3 = 40 g free SO_3, & 60 g H_2SO_4
40 g (free) SO_3 = mole SO_3 (free) = y = 0.5
60 g (H_2SO_4) = 0.6122 mole $H_2SO_4 = x$

$$\Rightarrow \quad \frac{x+y}{x-y} = \frac{1.1122}{0.1122} = 9.9$$

20. **(d)** In 100 g oleum sample
Weight of SO_3 = 40 g
Weight of H_2SO_4 = 60 g
% of SO_3 = 40% and
% of H_2SO_4 = 60%

21. **(c)** 98 g H_2SO_4 contains 80 g SO_3
∴ 60 g H_2SO_4 contains = 48.98 g
% of combined SO_3 in oleum = 48.98%

22. **(b)** Use, Milliequivalent of NaOH = Milliequivalent of SO_3 + Milliequivalent of H_2SO_4

23. **(a, c, d)** Milliequivelent of $KMnO_4 = 25 \times .2 = 5$
   (a) Milliequivelent of $FeSO_4 = \frac{25 \times .2}{1} = 5$
   (c) Milliequivelent of $H_2O_2 = 25 \times .1 \times 2 = 2.5 \times 2 = 5$
   (d) Milliequivelent of $SnCl_2 = 25 \times .1 \times 2 = 5$

24. **(a, b, c)**

$$n_f = 2[5-0] = 10$$

$$2\overset{+7}{M}nO_4^- + 4H^+ + \overset{0}{Br_2} \rightarrow 2\overset{+2}{M}n^{+2} + 2\overset{+5}{Br}O_3^- + 2H_2O$$

$$n_f = 1 \times [7-2] = 5$$

n-factor for $MnO_4^- = 5$
Equivalent weight = $M_x/5$
n-factor for Br_2 = 10
Equivalent weight = $M_y/10$
Ratio of n-factor $\overset{+2}{M}n^{+2} \rightarrow \overset{+7}{M}nO_4^-, n_f = 5$

$$2\overset{+5}{B}rO_3^- \rightarrow \overset{0}{B}r_2 = n_f = 5 \quad \therefore \text{ratio } 1:1$$

25. **(b, d)** $Fe_{0.95}O + O_2 \rightarrow Fe_2O_3$
Let x is the fraction of Fe^{+3} in the compound then Fe^{+2} = $(0.95 - x)$

$$x \times 3 + (0.95 - x) \times 2 - 2 = 0 \qquad x = 0.1$$

$$\% \text{ of } Fe^{+2} = \frac{0.85}{0.95} \times 100 = 89.47\%$$

26. **(a, b, d)** $2FeS_2 + \frac{11}{2}O_2 \rightarrow Fe_2O_3 + 4SO_2$
n-factor = 11
Equivalent weight = M/11

27. **(a, c, d)** NaOH and $NaHCO_3$ in solution react together

$$\begin{array}{llll} NaOH & + \; NaHCO_3 & \rightarrow Na_2CO_3 & + \; H_2O \\ 40 \text{ g} & 84 \text{ g} & & \end{array}$$

$$\frac{40}{40} = 1 \text{ mol} \qquad \frac{84}{84} = 1 \text{ mol}$$

After reaction solution will have two moles of Na_2CO_3 in 1 L
For phenolphthalein Milliequivalent of Na_2CO_3 = Milliequivalent of HCl

$$20 \times 2 \times 1 = V \times 1 \Rightarrow V = 40 \text{ mL}$$

For methyl orange after first end point
Milliequivalent of $NaHCO_3$ = Milliequivalent of Na_2CO_3 = Milliequivalent of HCl

$$2 \times 20 \times 1 = 1 \times V \Rightarrow V = 40 \text{ mL}$$

For methyl orange if used from very begining
Milliequivalent Na_2CO_3 + Milliequivalent of $NaHCO_3$ = Milliequivalent of HCl

$2 \times$ Milliequivalent of Na_2CO_3 = Milliequivalent of HCl

$2 \times 20 \times 2 = 1 \times V \Rightarrow V = 80$ mL

28. (a, b, c, d) $Ba(\overset{+7}{M}nO_4)_2 \rightarrow 2\overset{+2}{M}n^{++}$

n-factor = 10

Milliequivelent of $Ba(MnO_4)$ in 150 mL

$\Rightarrow \quad 150 \times 10 \times \frac{1}{10} = 150$ Milliequivelent

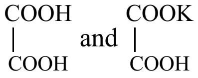
Milliequivelent of 1 M $Fe^{+2} \rightarrow Fe^{+3} = 150 \times 1 = 150$

Milliequivelent of 50 mL 1 M $\overset{+2}{Fe}\overset{+3}{C_2}O_4 \rightarrow Fe^{+3} + 2\overset{+4}{C}O_2$
$= 50 \times 3 = 150$ Milliequivelent

Milliequivelent of 75 mL 1 M $\overset{+3}{C_2}O_4^{--} \rightarrow 2\overset{+4}{C}O_2$
$= 75 \times 2 = 150$ Milliequivelent

Milliequivelent of 25 mL 1 M $Cr_2O_7^{--} \rightarrow 2Cr^{+3}$
$= 75 \times 2 = 150$ Milliequivelent

29. (a, b) ∵ molarity and normality involves the use of volume of solution and we know $V \propto T$

30. (a, b, d) For 
$\begin{array}{c}COOH\\|\\COOH\end{array}$ and $\begin{array}{c}COOK\\|\\COOH\end{array}$

When behave as reducing agent

$(COOH)_2$ $\quad 2CO_2$ $\quad n$-factor = 2, eq wt. = $M/2$


$\begin{array}{c}COOK\\|\\COOH\end{array} \longrightarrow 2CO_2$ $\quad n$-factor = 2, eq wt. = M/2

for neutralization Milliequivelent of one reactant = Milliequivelent of other reactant can be neutralised $1000 \times 2 = 1000 \times 2$

31. (a, b, c) $H_3PO_4 + Ca(OH)_2 \longrightarrow CaHPO_4 + 2H_2O$
n-factor for $H_3PO_4 = 2$ (since $2H^+$ ions are replaced)

$$\text{Equivalent weight} = \frac{M}{2} = \frac{98}{2} = 49$$

resulting solution of $CaHPO_4$ have only are replacable H^+

so $\quad nf = 1$

hence number of equivalent = 1 for 1 mole so can be neutralised by 1 mole of KOH

equivalent of $CaHPO_4$ = equivalent of KOH

For complete neutralisation - Number of equivalent of H_3PO_4

= Number of equivalent of $Ca(OH)_2$

$= 1 \times 3 = 1.5 \times 2$ can be neutralised.

32. (a, b, d) number. of equivalent of H_2SO_4 = moles × n factor = $1 \times 2 = 2$

Number of equivalent of $Ca(OH)_2 = 1 \times 2 = 2$ (neutralised)

Number of equivalent of $NaOH = 2 \times 1 = 2$ (neutralised)

Number of equivalent of $NH_3 = 2 \times 1 = 2$ (neutralised)

$$H_2SO_4 + Ca(OH)_2 = CaSO_4 + 2H_2O$$

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

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

33. (a, c) In presence of phenolphthalein to detect first end point.

$NaOH + HCl \longrightarrow NaCl + H_2O$ (Full equivalent of NaOH)

$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$ (1/2 equivalent of Na_2CO_3)

methyl orange is used to detect final end point. Where rest of 1/2 equivalent of Na_2CO_3 will be neutralised.

$NaHCO_3 + HCl \longrightarrow NaCl + H_2CO_3 \longrightarrow (H_2O + CO_2)$

34. (a, b, c) $3\overset{+1}{C}lO^- \rightarrow \overset{+5}{C}lO_3^- + 2\overset{-1}{C}l^-$

It is a disproportionation reaction, which incluces both oxidation and reduction of same element.

Assertion/Reason

35. (a) $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

From the above reactions it is clear that two moles of HCl are required for complete neutralisation of Na_2CO_3. The titre value with methyl orange correspond to complete neutralisation of Na_2CO_3 and with phenolphthalein correspond to half neutralisation of Na_2CO_3.

36. (b) Molality does not depend upon volume thus it does not depend upon temperature.

37. (a) $\overset{2+}{Fe}\overset{1-}{S_2} \xrightarrow{O_2} \overset{3+}{Fe_2}O_3 + \overset{4+}{S}O_2$

38. (d) Density change means ($m = d \times V$) mass of solution per unit volume changed hence mass of solute per unit volume changed and therefore molarity will be changed but molality independent of temperature.

39. (c) n factor of P will be $\frac{2y}{x}$ and atomic mass = Equivalent mass of $P \times n$-factor of

$$P = E_p \times \frac{2y}{x}$$

40. (b) Industiral H_2SO_4 is Oleum ($H_2S_2O_7$) in which concentration is represented by this method.

9 g water is added

$SO_3 + H_2O \rightarrow H_2SO_4$
0.5 mL $\qquad$ 0.5 mL

SO_3 also present as 0.5 mol or 40 g

41. $KMnO_4 \quad + \quad X^{+n} \quad \longrightarrow \quad XO_3^- \ + Mn^{+2}$
$1.61 \times 10^{-3} \quad 2.63 \times 10^{-3}$

Equivalent of $KMnO_4$ = Equivalent of X^{+n}

$1.61 \times 10^{-3} \times 5 = 2.63 \times 10^{-3} \times (5 - n)$

$n = 2 \quad \Rightarrow \quad 56 = \frac{M}{2} \quad M = 41$

42. Milliequivalent of H_2O_2 = Milliequivalent of $KMnO_4$

$$\frac{\text{weight}}{\text{Equivalent weight}} = \frac{x}{34/2} = \frac{0.632}{158/5}$$

$\therefore \quad x = 0.34$

$\therefore \quad \%\ \text{Purity} = \frac{x}{0.4} \times 100 = 85\%$

43. Normality of 5.5 L H_2O_2

$$= \frac{4}{5.6} = \frac{28}{5.6} \times \frac{1}{5.5\,L}$$

Now, $5 \times x = 5.5 \times \frac{28}{5.6} \times \frac{1}{5.5} \quad \therefore \quad x = 1$

44. $N = \left(\frac{5 \times 3}{250}\right) = 0.06 \quad M = \frac{0.06}{2} = 0.03$ n-factor = 2

45. 1 mole of $H_2S \equiv 5$ moles of H_2SO_4

34 g of $H_2S \equiv 5$ moles of H_2SO_4

$$0.40 \times V_{H_2SO_4} = 5$$

$$\therefore \quad V_{H_2SO_4} = \frac{5}{0.40} = 12.5\text{ L}$$

46. Equivalent of NaOH = 50 × 0.2 = 10

Equivalent of HCl = 2.5 × 2 = 5

Equivalent of NaOH left after reaction with HCl

= 10 – 5 = 5

$FeCl_3 + NaOH \rightarrow Fe(OH)_3\downarrow \xrightarrow{\Delta} Fe_2O_3$

$FeCl_3$ reacts with NaOH to give $Fe(OH)_3$ which on ignition gives Fe_2O_3

$\therefore$ Equivalent of NaOH used for $FeCl_3$ = Equivalent of $Fe(OH)_3$

= Equivalent of Fe_2O_3 = 15 × 0.1 = 1.5

$\therefore$ Equivalent of NaOH left finally = 5 – 1.5 = 3.5

$$\frac{W_{Fe_2O_3}}{M_{Fe_2O_3}} \times 6 = 1.5 \qquad (n\text{-factor for } Fe_2O_3 = 6)$$

$$W_{Fe_2O_3} = \frac{1.5 \times 160}{6} = 40\text{ g}$$

47. $\because$ 100 g Haemoglobin has = 0.25 g Fe

$\therefore$ 86600 g Haemoglobin has $= \frac{0.25 \times 86600}{100}$ g

= 224 g Fe

i.e., 1 mole or N_A molecules of Haemoglobin has $= \frac{224}{56}$ g atom Fe = 4 g atom Fe

$\therefore$ 1 molecule of Haemoglobin has 4 atom of Fe.

48. Let valencies of Cu in two oxides be x and y, then I oxide is Cu_2O_x; II oxide is Cu_2O_y

In I oxide: Equivalent of Cu = equivalent of oxygen

$$\frac{w}{A/x} = \frac{a}{8} \qquad (1)$$

where w, x, A and a are weight of Cu, atomic weight of Cu, valency of Cu and weight of oxygen.

In II oxide: $\frac{w}{A/y} = \frac{a}{2 \times 8}$ (2)

($\because$ Oxygen used half of I)

By Eqs. (1) and (2)

$$\frac{x}{y} = \frac{2}{1} \qquad 2/y = 2/1 \Rightarrow y = 1$$

the valancy of Cu second oxide is 1

49. Milliequivalent of oxalic acid in 16.68 mL = Milliequivalent of NaOH $= 25 \times \frac{1}{15}$

$\therefore$ Milliequivalent of oxalic acid in 250 mL

$$= 25 \times \frac{1}{15} \times \frac{250}{16.68} = \frac{w}{\text{Equivalent}} \times 1000$$

$$\therefore \quad 24.98 = \frac{1.575}{(90 + 18x)/2} \times 1000$$

$\therefore \quad x \approx 2$

50. $n_1 \times 56 + n_2 \times 74 = 4.2$ (1)

$n_1 \times 1 + n_2 \times 2 = 0.1$ (2)

% of KOH $= \frac{n_1 \times 56}{4.2} \times 100 = 35\%$

$Ca(OH)_2 = 65\%$

51. $CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$

0.1 mole 0.25

– 0.05

$HCl + KOH \longrightarrow KCl + H_2O$

0.05 2 × V

$V = \frac{.05}{2}$ L = 25 mL

52. $2NaOH + NaH_2PO_4 \longrightarrow Na_3PO_4 + 2H_2O$

$1 \times V \qquad \frac{12}{120} = 0.1$ Mole

$V \times 1 = 0.1 \times 2$

$V = 0.2$ L = 200 mL

53. $Ce^{+4} + Sn^{+2} \longrightarrow Sn^{+4} + C_e^{n}$

40.05 + 20 mL

1 M 1 M

Milliequivalent of Ce^{+4} = Milliequivalent Sn^{+2}

$40.05 \times 1 \times (4 - n) = 20 \times 1 \times 2$

$(4 - n) = \frac{20 \times 2}{40.05} \simeq 1$

$n = 3$

54. $\overset{+4}{Se}O_2 + CrSO_4 \longrightarrow Cr^{+3} + S_e^{n}$

Milliequivalent of SeO_2 = Milliequivalent of $CrSO_4$

$12.53 \times 0.05093 \times (4 - n) = 25.52 \times .1 \times 1$

$4 - n \simeq 4 \Rightarrow n = 0$

55. $n \times 106 + n \times 84 = 1$ (1)

$n \times 2 + n \times 1 = 0.1 \times V \times 1000$ (2)

$V = 157.89$ mL

56. Equivalent of H_2SO_4 = Equivalent of NaOH

$n \times 2 = 0.0267 \times 0.4$

$n = [0.0267 \times 0.2]$ mole of H_2SO_4 total.

$[n \times 98 - 0.5]$ = mass of H_2O added

mole of H_2O = mole of SO_3

% of SO_3 = 20.72%

57. $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

x mole $2x$

$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2$

y mole $2y$

$$2x + 2y = \frac{(50 \times 0.8 - 16 \times 0.25)}{1000} \Rightarrow x + y = 0.018 \quad (1)$$

$$x \times 100 + y \times 84 = 1.64 \quad (2)$$

$$\% \ CaCO_3 = \frac{x \times 100}{1.64} \times 100 = 48.78\%$$

$$\% \ MgCO_3 = 51.22\%$$

58. Milliequivalent of $CaCO_3$ = Milliequivalent of HCl – Milliequivalent of NaOH

$$\frac{w}{(100/2)} \times 1000 = 10 \times 4 - \frac{100}{25} \times 18.75 \times 0.2 = 25$$

$$w = 1.25 \text{ g}$$

$$\% \ CaCO_3 = \left(\frac{1.25}{1.5}\right) \times 100 = 83.33\%$$

59. Na_2CO_3 + $NaHCO_3$
x y milli mole

$$x = 4 \times 1 \quad (1)$$

$$2x + 4 = 10.5 \times 1$$

$$y = 2.5, x = 4$$

$Na_2CO_3 = 4 \times 106$ mg = 0.424 mg
$NaHCO_3$ = 0.21 gm

60. Na_2CO_3 NaOH
x y m mole

$$x + y = 19.5 \times 0.995 = 19.4025 \quad (1)$$

$$2x + y = 25 \times 0.995 = 24.875 \quad (2)$$

$x = 5.4775$ m mole in 25 ml

$$Na_2CO_3 = \frac{5.4725 \times 106}{25} = 23.2 \text{ g/L}$$

NaOH = 22.28 g/L

61. NaOH + Na_2CO_3
x y m mole

$$x + y = \frac{1}{10} \times 17.5 = 1.75 \quad (1)$$

$$y = \frac{1}{10} \times 2.5 = 0.25 \quad (2)$$

$x = 1.5, y = 0.25$ m mole

$$NaOH = \frac{1.5 \times 40}{1000} \text{ g} = 0.06 \text{ g}$$

$$Na_2CO_3 = \frac{0.25 \times 106}{1000} = 0.0265 \text{ g}$$

62. Na_2CO_3 $NaHCO_3$
x y Milliequivalent

$$x = 2 \times 0.2 = 0.4 \quad \ldots(1)$$

$$y + x = 2.5 \times 0.4 = 1 \quad \ldots(2)$$

$$y = 0.6 \qquad x = 0.4$$

63. $K_2\overset{+3}{C_2}O_4 \cdot 3H_2\overset{+3}{C_2}O_4 \cdot 4H_2O + MnO_4^- \rightarrow Mn^{+2} + \overset{+4}{C}O_2$
V ml. 0.1M

$$\left[\frac{1}{508}\right] \times 8 \times 1000 = V \times 0.1 \times 5$$

$$\Rightarrow \quad V = 31.68 \text{ mL}$$

64. $H_2O_2 + KMnO_4 \longrightarrow Mn^{+2} + O_2$

$$\frac{1 \times x/100}{(34/2)} \times 1000 = x \times N$$

$$N = \frac{20}{34} = 0.5882$$

65. Sn + $K_2Cr_2O_7$ $\longrightarrow$ $SnCl_4$ + Cr^{+3}
1 0.1 N V ml

$$\left(\frac{1}{118.7/4}\right) \times 1000 = 0.1 \times V \Rightarrow V = 337.8 \text{ mL}$$

66. Milliequivalent of Cu $= \frac{1000}{20}[20 \times 0.0327] = 32.7$

$$\frac{w}{(63.5/1)} \times 1000 = 32.7 \Rightarrow w = 2.07645 \text{ g}$$

$$\% \ Cu = \frac{2.07645}{5} \times 100 = 41.53\%$$

67. Milliequivalent of Fe = Milliequivalent of $K_2Cr_2O_7$

$$\frac{0.84 \times x/100}{56} \times 1000 = x \times N$$

$$N = 0.15$$

68. $H_2C_2O_4 \cdot 2H_2O \cdot KHC_2O_4 \cdot H_2O + NaOH \rightarrow$ product
x mole y mole 18.9 ml, 0.5 N
$H_2C_2O_4 \cdot 2H_2O \, KHC_2O_4 \cdot H_2O + KMnO_4 \rightarrow Mn^{+2} + CO_2$
$\frac{x}{4}$mol $\frac{y}{4}$mol 21.55 mL, 0.25 N

$$x \times 2 + y \times 1 = \frac{18.9 \times 0.5}{1000} \quad (1)$$

$$\left(\frac{x}{4} + \frac{y}{4}\right) \times 2 \times 1000 = 21.55 \times 0.25 \quad (2)$$

$\% \ H_2C_2O_4 \cdot 2H_2O = 14.36\%$
$\% \ KH_2C_2O_4 \cdot H_2O = 81.7\%$

69. Milliequivalent of $Ca(OH)_2$ = Milliequivalent of HCl – Milliequivalent of NaOH

$$\left(\frac{w}{74/2}\right) \times 1000 = (50 \times 0.5 - 0.3 \times 20)$$

$$w = 0.703$$

$$\% \ Ca(OH)_2 = \frac{0.703}{50} \times 100 = 1.406\%$$

70. Milliequivalent of Na_2CO_3 = Milliequivalent of HCl – Milliequivalent of NaOH

$$\frac{w}{106/2} \times 1000 = 50 \times 0.1 - 10 \times 0.16$$

$$\% \text{ purity} = \frac{w}{1} \times 100 = 90.1\%$$

71. x g substance
0.6 x g NaCl, 0.37 x g KCl

$$\left(\frac{0.6x}{58.5} + \frac{0.37x}{74.5}\right) \times 1000 = 25 \times 0.1 - 5.5 \times 0.1$$

$$x = 0.1281 \text{ g}$$

72. $12 = 5.6 \times N \Rightarrow N = 2.1428.57$

$700 \times 2.1428 = 1000 \times N$

$N_1 = 1.5 = M_1 \times 2$

$M_1 = 0.75 \quad \Rightarrow \quad g/L = 0.75 \times 34 = 25.5$ gram/L

Volume strength of final solution $= 5.6 \times 1.5$

$= 8.4$ volume

73. $50 \times N = 20 \times 0.1$

$N = 0.04 = M \times 2$

$M = 0.02 \Rightarrow g/L = 0.02 \times 34 = 0.68$ gram/L

74. $\dfrac{5}{120} \times 100 \times \dfrac{10^6}{100 \times 10^3} = 41.66$ ppm

75. $\dfrac{\left(\dfrac{1}{111} + \dfrac{1}{120}\right) \times 10^{-3} \times 100}{1000} \times 10^6 = 1.734$ ppm

76. $\dfrac{0.001 \times 100}{1000} \times 10^6 = 100$ ppm

77. $100 \text{ mL} \longrightarrow 1.62 \text{ mg } Ca(HCO_3)_2$

$60 \times 10^3 \text{ mL} \longrightarrow \dfrac{1.62}{100} \times 60 \times 10^3 = 972 \text{ mg}$

$$\begin{array}{ll} Ca(OH)_2 + & Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + 2H_2O \\ \dfrac{w}{74} & \left[\dfrac{0.972}{162}\right] \end{array}$$

$w = \left(\dfrac{0.972}{162}\right) \times 74 = 0.444$ g

78. $$\begin{array}{lll} H_2SO_4 & + & 2NH_3 \longrightarrow (NH_4)_2SO_4 \\ (30 - 25) \text{ Milliequivalent} & & 25 \text{ Milliequivalent} \\ (30 \times 0.2) \text{ Milliequivalent} & & \end{array}$$

$V_{NH_3} = 25 \times 10^{-3} \times 22400 = 537.6$ mL

79. Milliequivalent of SeO_3^{-2} = Milliequivalent of BrO_3^- used

$\dfrac{w}{M} \times 2 \times 1000 = \left[20 \times \dfrac{1}{60} \times 5 - 5 \times \dfrac{1}{25} \times 2\right]$

$w = 0.084$ g $= 84$ mg

80. $\dfrac{1 \times 0.552}{160} \times 1000 = \dfrac{100}{25} \times 17 \times 0.0167 \times n$

$\therefore \quad n = 3$

81. Milliequivalent of Hypo = 5 = Milliequivalent of I_2

Moles of I_2 = 2.5 m moles

$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

From reaction moles of $CuSO_4 = 2.5 \times 2 = 5$ m moles

M_w of hydrated $CuSO_4 = 159.5 + 18x$

so $\dfrac{1.2475}{159.5 + 18x} = 5 \times 10^{-3} x = 5.$

82. Milliequivalent of Hypo $= 100 \times \dfrac{1}{10} = 10$ = Milliequivalent of I_2

Milliequivalent of $ClO_3^- = 10$

$\because \quad n_f$ of $ClO_3^- = 5$

m moles of $ClO_3^- = 2$

$6H_2O + 6Cl_2 \longrightarrow 10Cl^- + 2ClO_3^- + 12H^+$

2 m moles so moles of Cl_2 = 6 m moles

$6e^- + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$(2Cl^- \longrightarrow Cl_2 + 2e^-)\, 3$

$14H^+ + Cr_2O_7^{-2} + 6Cl^- \longrightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O$

$6m$ moles

$\therefore \quad m$ moles of $Cr_2O_7^{-2} = 2$ m moles

Weight of $Cr_2O_7^{-2} = 2 \times 10^{-3} \times 294 = 0.588$ g

$(Cr_2O_7^{-2})$ % purity = 58.8%

83. Let $H_2C_2O_4 \,.\, 2H_2O \rightarrow x$ g in 100 mL

On reaction with NaOH with phenolphthalein

g equivalent of acid in 50 mL $= \dfrac{x \times 2}{2 \times 126}$

g equivalent of NaOH $= \dfrac{1}{10} \times 0.11905$

so $\dfrac{x \times 2}{2 \times 126} = \dfrac{0.11905}{10} \Rightarrow x = 1.5$ g

so mass of $Na_2C_2O_4 = 2.5 - 1.5 = 1$ g

Now, in 0.5 g of same mixture

$H_2C_2O_4 \cdot 2H_2O \longrightarrow 0.3$ g

$Na_2C_2O_4 \longrightarrow 0.2$ g

g equivalent of $H_2C_2O_4 \cdot 2H_2O = \dfrac{0.3 \times 2}{126}$

g equivalent of $Na_2C_2O_4 = \dfrac{0.2 \times 2}{134}$

g equivalent of $KMnO_4 = \dfrac{V}{10} \times 10^{-3}$

so $\dfrac{0.3 \times 2}{126} + \dfrac{0.2 \times 2}{134} = \dfrac{V \times 10^{-3}}{10}$

$\therefore \quad V = 77.46$ mL

84. First HCl will react with KIO_3 to from I_2 and Cl_2 then this Cl_2 produced will again react with KI to form I_2. Let initially x moles of KIO_3 were mixed with y moles of HCl then

$$\begin{array}{cccccc} 2IO_3^- & + & 10Cl^- & \longrightarrow & I_2 & + \quad 5Cl_2 \\ x & & y & & & \\ & & - & & \dfrac{y}{10} & \quad \dfrac{y}{2} \end{array}$$

$$\begin{array}{cccc} Cl_2 + & 2KI \longrightarrow & I_2 + & 2KCl \\ \dfrac{y}{2} & \text{excess} & 0 & 0 \\ - & - & \dfrac{y}{2} & y \end{array}$$

Total moles of I_2 formed $= \dfrac{y}{10} + \dfrac{y}{2} = \dfrac{3y}{5}$

so $\dfrac{3y}{5} = \dfrac{0.021 \times 24 \times 10^{-3}}{2} \Rightarrow y = 0.00042$ mole

so concentration of HCl $= \dfrac{0.00042}{0.025} = 0.0168$ M
$= 0.0168$ N

Moles of KIO_3 consumed $= \dfrac{0.00042}{5}$

Volume of KIO_3 consumed $= \dfrac{0.00042 \times 5}{5} = 0.00042\,L = 0.42$ mL

85. $As_2O_3 + 6HCl \longrightarrow 2AsCl_3 + 3H_2O$

$AsCl_3 + 2H_2O \longrightarrow HAsO_2 + 3H^+ + 3Cl^-$

Gram equivalent of I_2 = Gram equivalent of $HAsO_2$ = Gram equivalent of $AsCl_3$ = Gram equivalent of As_2O_3

Gram equivalent of $As_2O_3 = 2 \times 0.04134 \times 23.04 \times 10^{-3}$
$= 0.9524 \times 10^{-3} \times 2$

Gram equivalent of $KMnO_4 = 0.9524 \times 10^{-3} \times 2$

Let amount of $KMnO_4$ used $= w$ g then

$$\frac{w \times 5}{158.5} = 0.9524 \times 10^{-3} \times 2$$

$w = 0.06$ g

86. $4OH^- + 2H_2O + SO_2 \longrightarrow SO_4^{2-} + 4H_2O + 2e^-$

$$4OH^- + SO_2 \longrightarrow SO_4^{2-} + 2H_2O + 2e^- \quad (1)$$
$$2H_2O + H_2O_2 + 2e^- \longrightarrow 2H_2O + 2OH^-$$
$$H_2O_2 + 2e^- \longrightarrow 2OH^- \quad (2)$$

Eq. (1) + (2)

$$2OH^- + H_2O_2 + SO_2 \longrightarrow SO_4^{2-} + 2H_2O \quad (3)$$

∵	NaOH +	HCl	⟶	NaCl	+ H_2O
Milliequivalent					
	30×0.04	0.024×22.48		–	–
	1.2	0.53952			
0.66048×10^{-3}		0			

From Eq. (3)

$\therefore$ moles of $SO_2 = 0.33024 \times 10^{-3} = n_{NaOH} \times \dfrac{1}{2}$

weight of sulphur $= 0.33024 \times 10^{-3} \times 32$
$= 10.5676 \times 10^{-3}$

% of S in sample $= \dfrac{10.5676 \times 10^{-3}}{0.6} \times 100 = 1.76\%$

87. $CuS + Cu_2S + KMnO_4 \longrightarrow Mn^{+2} + Cu^{+2} + SO_2$

6 8 5

Equivalent weight of CuS $= M_1/6$

Equivalent weight of $Cu_2S = M_2/8$

Equivalent weight of $KMnO_4 = M_3/5$

88. H_2S + SO_2

x y

$S^{-2} \longrightarrow SO_4^{2-}$ (n-factor = 6)

for H_2S $\dfrac{x}{34} \times 6 = 0.534975 \times 10^{-3} = (20 \times 0.0066 \times 6 - 7.45 \times 0.0345) \times 10^{-3}$

$x = 3.031525 \times 10^{-3}$

$SO_2 \longrightarrow SO_4^{2-}$ (n-factor = 2)

for SO_2 $\dfrac{y}{64} \times 2$

$$\frac{2y}{64} = (25 \times 0.0396 - 12.44 \times 0.0345) \times 10^{-3}$$

$$\frac{2y}{64} = 0.56082 \times 10^{-3}$$

$y = 17.94624$ g

Concentration of H_2S

$$= \frac{3.031525}{25} \times 10^{-3} = 0.1212 \text{ mg/L}$$

Concentration of SO_2

$$= \frac{17.94624}{25} = 0.7178 \text{ mg } SO_2\text{/L}$$

89. In presence of methyl orange, the whole NaOH and Na_2CO_3 are neutralised

$\Rightarrow$ milliequivalent of HCl $= 16 \times 0.25 = 4$ = milliequivalent of (NaOH + Na_2CO_3) = milliequivalent of NaOH original

$\Rightarrow$ Total milliequivalent of NaOH in original 1.0 g sample $= 4 \times \dfrac{100}{20} = 20$

$\Rightarrow$ mass % of NaOH (original) $= \dfrac{20 \times 40 \times 100}{1000} = 80$

Now, let us assume that in 20 mL, x m mol of NaOH has got converted to Na_2CO_3

$\Rightarrow$ In 20 mL, m mol of NaOH $= 4 - x$

m mol of $Na_2CO_3 = \dfrac{x}{2}$

In second titration, HCl used in titration of NaOH + $Na_2CO_3 = 50 \times 0.1 - 9 \times 0.2 = 3.2$

$\Rightarrow$ Up to phenolphthalein end point, m mol of HCl required $= 4 - x + \dfrac{x}{2} = 4 - \dfrac{x}{2} = 3.2$

$\Rightarrow$ $x = 1.6$

$\Rightarrow$ Total Na_2CO_3 formed $= \dfrac{x}{2} \times 5 = \dfrac{5x}{2} = 4$

m mol of NaOH left unreacted $= 20 - 4 \times 2 = 12$

$\Rightarrow$ weight of 1.0 g of exposed sample

$$= 1 - \frac{8 \times 40}{1000} + \frac{8 \times 40}{1000} = 1.176 \text{ g}$$

$\Rightarrow$ weight % of Na_2CO_3 in exposed sample

$$= \frac{4 \times 106}{1000 \times 1.176} \times 100 = 36.05\%$$

90. $MnO_2 + 4\,HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

Number of moles of $Cl_2 = \dfrac{1.78}{22.4} = 0.07946$

Number of moles of $MnO_2 = 0.07946$

$\therefore$ mass of $MnO_2 = 0.0794 \times 87 = 6.913$ g

$\therefore$ number of moles of HCl $= 4 \times 0.07946 = 0.3178$

Mass of HCl $= 0.3178 \times 36.5$. Let the volume of HCl $= V$ mL

$$\therefore \quad V \times 1.2 \times \frac{4}{100} = \times 0.3178 \times 36.5 = 241.66 \text{ mL}$$

91. Redox changes are

$$C_2O_4^{2-} \longrightarrow 2CO_2 \quad (n\text{-factor} = 2)$$

$$MnO_4^- \longrightarrow Mn^{2+} \quad (n\text{-factor} = 5)$$

$$MnO_2 \longrightarrow Mn^{2+} \quad (n\text{-factor} = 2)$$

Milliequivalent of MnO_2 = Milliequivalent of oxalic acid taken – Milliequivalent of oxalic acid left

$$= 50 \times 0.5 \times 2 - 32 \times 0.02 \times 5 \times \frac{250}{25} \text{ (in 250 mL)} = 18$$

$$\frac{W_{MnO_2}}{\text{Molar mass}} \times 2 \times 1000 = 18$$

$$\Rightarrow \quad \frac{W_{MnO_2}}{87} \times 2 \times 1000 = 18,$$

$$\therefore \quad W_{MnO_2} = 0.7821 \text{ g}$$

$$\therefore \quad \% \text{ of } MnO_2 = \frac{0.7821}{3.2} \times 100 = 24.44\ \%$$

Milliequivalent of MnO_2 = Milliequivalent of O_2

$$\frac{W_{O_2}}{32} \times 4 \times 1000 = 18, \therefore W_{O_2} = 0.144 \text{ g}$$

$$\% \text{ of available } O_2 = \frac{0.144}{3.2} \times 100 = 4.5\%$$

92. Out of Na_2CO_3, $NaHCO_3$ and Na_2SO_4 only $NaHCO_3$ decomposes on heating to give CO_2 gas, according to the equation $2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$ moles

$$\text{of } CO_2 = \frac{PV}{RT} = \frac{750 \times 123.9}{760 \times 1000 \times 0.082 \times 298} = 5 \times 10^{-3}$$

$\therefore$ moles of $NaHCO_3 = 2 \times 5 \times 10^{-3} = 0.01$

$$\text{Equivalents of HCl used} = \frac{150 \times (1/10)}{1000} = 1.5 \times 10^{-2}$$

$$\text{Equivalents of } NaHCO_3 \text{ in 1.5 g} = 0.01 \times \frac{1.5}{2}$$

$$= 7.5 \times 10^{-3}$$

$$\therefore \quad \text{equivalents of } Na_2CO_3 = 1.5 \times 10^{-2} - 7.5 \times 10^{-3}$$

$$= 7.5 \times 10^{-3}$$

$$\text{Moles of } Na_2CO_3 = \frac{7.5 \times 10^{-3}}{2}$$

(when Na_2CO_3 reacts with HCl it gives NaCl, CO_2 and H_2O. No atom undergoes change in oxidation state. $\therefore$ 'n' factor of $Na_2CO_3 = 2$)

$$= 3.75 \times 10^{-3}$$

Mass of $NaHCO_3$ in 1.5 g $= 7.5 \times 10^{-3} \times 84 = 0.63$ g

Mass of Na_2CO_3 in 1.5 g $= 3.75 \times 10^{-3} \times 106 = 0.3975$ g

$\therefore$ mass of $Na_2SO_4 = 1.5 - 0.63 - 0.3975 = 0.4725$ g

$$\text{Percentage of } NaHCO_3 = \frac{0.63}{1.5} \times 100 = 42\%$$

$$\text{Percentage of } Na_2CO_3 = \frac{0.3975}{1.5} \times 100 = 26.5\%$$

$$\text{Percentage of } Na_2SO_4 = \frac{0.4725}{1.5} \times 100 = 31.5\%$$

93. $\text{Total moles of the mixture} = \dfrac{1}{22.4}$

$$= 0.0446 = 4.46 \times 10^{-2}$$

$$\text{Equivalents of } Na_2S_2O_3 \text{ solution} = \frac{40}{1000} \times \frac{1}{10} = 4 \times 10^{-3}$$

Equivalents of $I_2 = 4 \times 10^{-3}$

Equivalents of KI $= 4 \times 10^{-3}$

Equivalents of $O_3 = 4 \times 10^{-3}$

when O_3 reacts with KI it converts to O_2 and O^{-2}

the 'n' factor for O_3 in this reaction is 2

$$\text{Moles of } O_3 = \frac{4 \times 10^{-3}}{2} = 2 \times 10^{-3}$$

Moles of $O_2 = 4.46 \times 10^{-2} - 2 \times 10^{-3} = 4.26 \times 10^{-2}$

Mass percent of ozone in the mixture =

$$\frac{2 \times 10^{-3} \times 48}{2 \times 10^{-3} \times 48 + 4.26 \times 10^{-2} \times 32} \times 100 = 6.57\%$$

Number of O_3 molecules $= 2 \times 10^{-3} \times 6.023 \times 10^{23} = 1.2 \times 10^{21}$

Number of photons required $= 1.2 \times 10^{21}$

94. Potassium selenate is isomorphous to K_2SO_4 and thus its molecular formula is K_2SeO_4.

Now molecular weight of $K_2SeO_4 = (39 \times 2 + a + 4 \times 16)$

$= (142 + a)$

where a is atomic weight of Se

$(142 + a)$g K_2SeO_4 has Se = a gram

$$\therefore \quad 100 \text{ g } K_2SeO_4 \text{ has Se} = \frac{a \times 100}{142 + a}$$

$\therefore$ % of Se = 45.52

$\therefore$ = 45.52

$\therefore$ $a = 118.2$

Also equivalent of K_2SeO_4

$$= \frac{\text{Molecular weight}}{2} = \frac{2 \times 39 + 118.2 + 64}{2} = 130.1$$

95. $\left(\text{Molarity} = \dfrac{\text{Normality}}{\text{Number of replaceable } OH^-}\right)$

$$N = M \times 2$$

Thus Milliequivalent of borax in solution $= 50 \times 0.2 \times 2 = 20$

$$\therefore \quad \frac{w}{m/2} \times 1000 = 20$$

$$\therefore \quad \frac{w}{382/2} \times 1000 = 20/w = 3.82 \text{ g}$$

For neutralisation of HCl

Milliequivalent of HCl = Milliequivalent of borax

$$25 \times 0.1934 = \frac{w}{382/2} \times 1000$$

$\therefore$ Weight of borax = 0.9235 g

For neutralisation of H_2SO_4
Milliequivalent of borax = Milliequivalent of H_2SO_4

$$\frac{w}{382/2}\times 1000 = 25\times 0.1934\times 2$$

∴ Weight of borax = 1.847 g

96. The reactions are

$$H_2O + 2KI + O_3 \longrightarrow 2KOH + I_2 + O_2$$

Also $2e^- + I_2 \longrightarrow 2I^-$

And $2S_2^{2+} \longrightarrow S_4^{+5/2} + 2e^-$

∴ Milliequivalent of I_2 = Milliequivalent of $Na_2S_2O_3 = 1.5 \times 0.01 = 1.5 \times 10^{-2}$

or mM of $I_2 = 7.5 \times 10^{-3}$

mM of O_3 = mM of $I_2 = 7.5 \times 10^{-3}$

∵ (Mole ratio of $O_3 : I_2 :: 1 : 1$)

$$P_{O_3} = \frac{nRT}{V} = \frac{7.5\times 10^{-6}\times 0.0821\times 300}{10}$$

$$= 184.725\times 10^{-7}\,\text{atm}$$

∴ Volume % of $O_3 = 184.725 \times 10^{-7} \times 100$
$= 1.847 \times 10^{-3}\%$

97. $n_{CaCO_3} + n_{BaCO_3} = \frac{168}{22400} = 7.5\times 10^{-3}$ (1)

$2BaCO_3 \longrightarrow 2BaCrO_4 \longrightarrow BaCr_2O_7 \longrightarrow I_2 + Na_2S_2O_3$

Equivalent of $Na_2S_2O_3$ = Equivalent of I_2 = Equivalent of $BaCr_2O_7$

$$= \frac{20\times 10^{-3}\times 0.05\times 100}{10} = 1 \times 10^{-2}$$

Moles of $BaCr_2O_7 = \frac{1}{2} \times 10^{-2}$

Moles of $BaCrO_4 = \frac{2}{6}\ (1 \times 10^{-2})$

Moles of $BaCO_3 = \frac{1}{3} \times 10^{-2} = 3.33 \times 10^{-3}$ (2)

Weight of $BaCO_3$ = 0.650 g
From Eqs. (1) and (2), we get
$= 4.17 \times 10^{-3}$
Weight of $CaCO_3 = 100 \times 4.17 \times 10^{-3} = 0.417$ g
Weight of CaO = 1.249 – 0.656 – 0.417 = 0.176

$$\%\text{ of CaO} = \frac{0.176}{1.249} \times 100 = 14.09\%$$

98. Milliequivalent of alkali added = 30 × 0.04 = 1.2
Milliequivalent of alkali left = 22.48 × 0.024 = 0.54
Milliequivalent of alkali for SO_2 and H_2O_2 = 1.2 – 0.54
= 0.66

$$\text{Weight of alkali used} = \frac{0.66\times 40}{1000} = 0.0264$$

80g NaOH reacts with 64g SO_2

$$0.0264\text{ g NaOH reacts} = \frac{64\times 0.0264}{80} = 0.021\text{g } SO_2$$

Now 64 g SO_2 required = 32g S

$$0.021\text{g } SO_2 \text{ required} = \frac{32\times 0.021}{64} = 0.0105\text{ g}$$

$$\%\text{ of S} = \frac{0.0105}{5.6}\times 100 = 0.1875\%$$

99. Let Al, Mg and Cu be *a*, *b* and *c* g respectively.

$$2Al + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2$$
$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$
$$Cu + HCl \longrightarrow \text{No reaction}$$

i.e., only Al reacts with NaOH and then only Mg reacts with HCl

∴ $a + b + c = 8.72$
$b + c = 2.10$ (Residue left after alkali treatment)
$c = 0.69$ (Residue left after acid treatment)
∴ $b = 6.62$g

∴ $\%\text{ of Al} = \frac{6.62}{8.72}\times 100 = 75.9$

$\%\text{ of Mg} = \frac{1.41}{8.72}\times 100 = 16.2$

$\%\text{ of Cu} = \frac{0.69}{8.72}\times 100 = 7.9$

100. $2KClO_3 + 12HCl \longrightarrow 2KCl + 6H_2O + 6Cl_2$
$Cl_2 + 2KI \longrightarrow 2KCl + I_2$

[∵ $N_{Hypo}12.3 = 24.6 \times 0.5$; ∴ $N_{Hypo} = 1$]

Also Milliequivalent of Cl_2 = Milliequivalent of Hypo
= 100 × 1

$$\text{Also mM of } KClO_3 = \frac{2\times \text{mM of } Cl_2}{6} = \frac{2\times 50}{6} = \frac{50}{3}$$

$$\text{Also } \frac{w}{122.5}\times 1000 = \frac{50}{3}$$

$$\left[\text{milli-mole (mM)} = \frac{\text{Weight}\times 1000}{\text{Molecular weight}}\right]$$

$$\%\text{ of } KClO_3 = \frac{2.042}{2.48}\times 100 = 82.32\%$$

101. Let atomic weight of *P* and *Q* are *a* and *b* respectively
Molecular weight of $P_2Q_3 = 2a + 3b$ and Molecular weight of $PQ_2 = a + 2b$
Now given that 0.15 mole of P_2Q_3 weigh 15.9 g

$$(2a + 3b) = \frac{15.9}{0.15} \qquad \left(\because \frac{\text{Weight}}{\text{Molecular weight}} = \text{mole}\right)$$

$$\text{Similarly, } (a + 2b) = \frac{9.3}{0.15}$$

Solving these two equations
$b = 18$, $a = 26$ ∴ $P = 26$ and $Q = 18$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. **(c)** $2 + 2(2 + x - 4) = 0$ [∵ $Ba(H_2PO_2)$ is neutral molecule] or $2x - 2 = 0 \Rightarrow x = +1$
2. **(b)**
   (i) Write balance chemical equation for given change.
   $$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$
   (ii) Identify most electronegative element in the reaction and has the oxidation states of –1 (in H_2O_2) and –2(in $BaSO_4$). In H_2O_2, peroxide ion is present.
3. **(a)** Balanced the reaction by ion electron method

   Oxidation reaction: $[C_2O_4^{-2} \rightarrow 2CO_2 + 2e] \times 5$

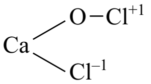
   Reduction reaction:
   $$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
   Net reaction:
   $$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow$$
   $$2Mn^{2+} + 10CO_2 + 8H_2O$$
4. Use molarity equation to find volume of H_2SO_4 solutions.
   $$\underset{\substack{63.5+12+48.98\\=123.5g}}{CuCO_3} + \underset{98g}{H_2SO_4} \longrightarrow CuSO_4 + H_2O + CO_2\uparrow$$
   ∴ For 123.5 g of Cu(II) carbonate 98 g of H_2SO_4 are required. For 0.5 g of Cu(II) carbonate weight of H_2SO_4 required $= \frac{98 \times 0.5}{123.5} g = 0.39676$ g H_2SO_4

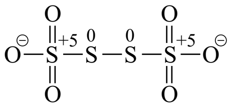
   Weight of required $H_2SO_4 = 0.39676$ g
   $$M = \frac{0.39676}{98} \times \frac{1000}{V(ml)}$$
   $$\therefore \quad V = \frac{0.39676 \times 1000}{90 \times 0.5} mL = 8.097 \text{ mL}$$
5. **(d)** Oxidation state of Mn in $MnO_4^- = +7$

   Oxidation state of Cr in $Cr(CN)_6^{3-} = +3$

   Oxidation state of Ni in $NiF_6^{2-} = +4$

   Oxidation state of Cr in $CrO_2Cl_2 = +6$
6. **(d)**
   (i) Mass of one electron $= 9.108 \times 10^{-31}$
   (ii) 1 mole of electron $= 6.023 \times 10^{23}$ electrons ∴ weight of 1 mole of electron
   = Mass of one electron × Avogadro number
   $= 9.108 \times 10^{-31} \times 6.023 \times 10^{23}$ kg

   ∴ Number of moles of electrons in 1 kg
   $$= \frac{1}{9.108 \times 10^{-31} \times 6.023 \times 10^{23}}$$
   $$= \frac{1}{9.108 \times 6.023} \times 10^8$$
7. **(c)**
   (i) $7 - 2 = 5$
   (ii) $7 - 6 = 1$
   (iii) $7 - 4 = 3$
   (iv) $7 - 3 = 4$
8. **(d)** 

9. **(a)** In this oxidation number of N is changing
10. **(b)** $+4 + x - 6 = 0 \Rightarrow x = 2$
11. **TIPS/Formulae:**
    The highest O.S. of an element is equal to the number of its valence electrons
    (a) $[Fe(CN)_6]^{3-}$, O.N. of Fe = +3
    $[Co(CN)_6]^{3-}$, O.N. Of Co = +3
    (b) CrO_2Cl_2, O.N. of Cr = +6,
    (Highest O.S. of Cr)
    $[MnO_4]^-$ O.N. of Mn = +7,
    (Highest O.S. of Mn)
    (c) TiO_3, O.N. of Ti = +6,
    MnO_2 O.N. of Mn = +4
    (d) $[MnCl_4]^{-2}$, O.N of Mn = +2
    $[NiF_6]^{-2}$ O.N of Ni = +4
12. **(d)** $x + 4(0) - 2 = +1$
    $x = 3$
13. **(c)** Final product will be Cr_2O_3 in this oxidation state of Cr is +3
14. **(b)** $2e + S^{6+} \rightarrow S^{4+}$
    $2I^- \rightarrow I_2 + 2e$
15. **(c)** HCl being stronger reducing agent reduces MnO_4^- to Mn^{2+} and result of the titration becomes unsatisfactory.
16. **(2)** Na, F show only one non-zero oxidation state.
    Na = +1
    F = –1
17. **(5)** $S_4O_6^{2-}$: 
    $$\overset{\ominus}{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{\overset{+5}{S}}}-\overset{0}{S}-\overset{0}{S}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{\overset{+5}{S}}}-\overset{\ominus}{O}$$
    So difference in oxidation numbers of two types of $S = (5 - 0) = 5$.
18. **(d)** Haematite:$Fe_2O_3 \Rightarrow$ Oxidation state of Fe = III
    Magnetite: $Fe_3O_4 \equiv FeO.Fe_2O_3$
    Oxidation state of Fe = II, III
19. **(c)** The half-equations of the reaction are
    $$MnO_4^- \rightarrow Mn^{2+}$$
    $$C_2O_4^{2-} \rightarrow CO_2$$
    The balanced half-equations are
    $$MnO_4^- + 8H^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

On equating number of electrons, we get

$$2MnO_4^- + 16H + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$

$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$

On adding both the equations, we get

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^- \rightarrow$$

$$2Mn^{2+} + 2 \times 5CO_2 + \frac{16}{2}H_2O$$

∴ x, y and z are 2, 5 and 16 are respectively.

20. (a, b, d)

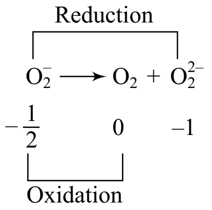
$$ClO_3^- + 6e^- + 6H^+ \rightarrow Cl^- + 3H_2O$$

$$ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O$$

$$ClO_3^- + 6I^- + 6H_2SO_4 \rightarrow 3I_2 + Cl^- + 3H_2O + 6HSO_4^-$$

21. (a) → p, s; (b) → r; (c) → p, q; (d) → p

(a) → p, s

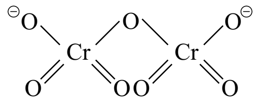


(b) → r

$$2\overset{+6}{Cr}O_4^{2-} + H^+ \rightarrow \overset{+6}{Cr_2}O_7^{2-} + H_2O$$

(no change in +6 oxidation state of Cr)

Structure is

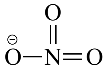


It is a dimeric bridged tetrahedral metal ion

(c) → p, q

$[5e^- + MnO_4^\ominus \rightarrow Mn^{2+}]$ (Reduction)

$[NO_2^\ominus \rightarrow NO_3^\ominus + e^-]$ (Oxidation)

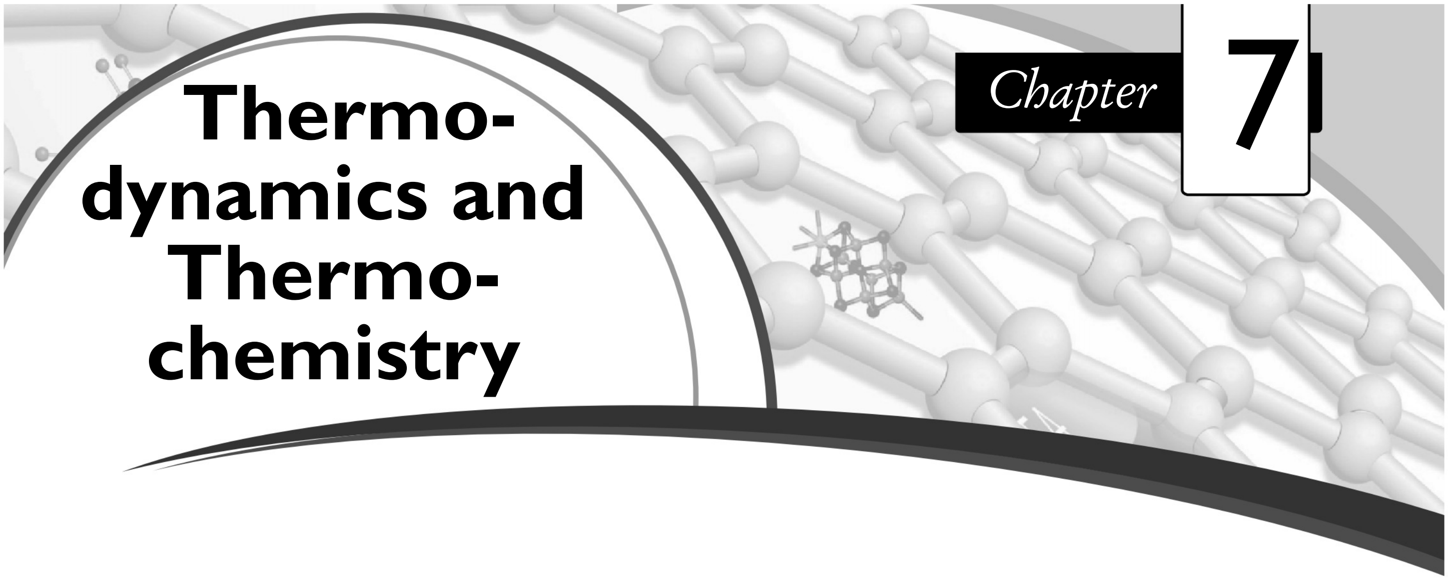
Structure of $NO_3^\ominus$:

$\overset{\ominus}{O}-\overset{\overset{O}{||}}{N}=O$

[sp^2 hybridisation and hence trigonal planar in shape]

(d) → p

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (Oxidation)

$3e^- + NO_3^\ominus \rightarrow NO$ (Reduction)



Chapter 7

Thermodynamics and Thermochemistry

Key Concepts

A large portion of thermodynamics deals with flow of energy and its impact on the properties of the substance.

Thermodynamic laws are applicable on macro scopic levels.

Few terms used in thermodynamics

$$PV = \frac{1}{3}\text{mn } V_{\text{rms}}^2$$

Sum of microscopic properties give macroscopic properties.

System: That region in space which is studied for thermodynamics aspect is known as system.

System may be very small, or as large as earth.

System is further classified as

1. Open system
2. Closed system
3. Isolated system

	Mass Exchange	Energy Exchange	Example
Open	Possible	Possible	Hot cup of coffee
Closed	Not possible	Possible	Hot cup of coffee covered with lid.
Isolated	Not possible	Not possible	Hot cup of coffee covered isolately.

Laws of thermodynamics are not applicable on open system because mass is changing.

Earth is treated as an isolated system for small thermodynamic changes.

Universe is treated as an isolated system and laws applicable on isolated system will be applicable on universe as well.

Surroundings

Everything except system is known as surrounding.

Surrounding is very large but only that part of surrounding is significant in which appreciable change is taking place.

Any change taking place in surrounding is very small compared to the change in the system.

System + Surrounding = Universe

Boundary

The interface at which mass and energy are/may be exchanged between system and surrounding.

Boundary may be real or imaginary, rigid or non-rigid.

* **Properties of the system:** Property defines the state of any system.

* **Extensive Properties:** Those properties of the system which depend upon the amount of the substance are known as extensive properties.

Extensive properties are additive in nature.

For example, mass, length, area, volume, heat capacity (ms)

E or U (internal Energy), H(Enthalpy), S(Entropy), G(Gibbs free entropy)

* **Intensive Properties**

Those properties of the system which is independent of the amount and depend on the nature are known as intensive properties.

For example, pressure, temperature, boiling point, melting point, surface tension, vapour pressure, refractive index, $\frac{m}{L}, \frac{m}{A}, \frac{m}{V}$ = density

Ratio of extensive property is intensive properties

$$\frac{ms}{n} = \text{heat capacity per mole}$$
$$= \text{molar heat capacity}$$
$$= \text{(intensive properties)}$$

Standard emf of the cell ($E°$) is intensive property.

$Fe \longrightarrow Fe^{+2} + 2e$ $\quad E° = +0.44$ V $\quad \Delta H = x$

$2Fe \longrightarrow 2Fe^{+2} + 4e^-$ $\quad E° = +0.44$ V $\quad \Delta H = 2x$

*** State and Path function**

State functions are those functions which do not depend upon the process and depend only on the state.

For example, E(U), H, G, A, S, P, V, T

Path Function

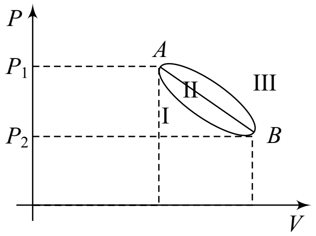
Those properties of the system which depend on the state as well as on the process by which the state has been achieved, are called path function.

For example, w, q

$$\oint SF = 0$$

* Characteristic of state function

1.



ΔSF is same for all path ($A \rightarrow B$)

$(\Delta P_{A\rightarrow B})_I = (\Delta P_{A\rightarrow B})_{II} = (P_{A\rightarrow B})_{III}$

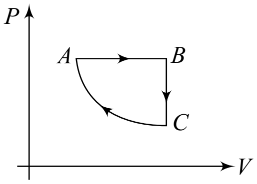
$= P_2 - P_1$

$W_I < W_{II} < W_{III}$

2. $\oint SF = 0, \oint \text{path function} \neq 0$

$w \neq 0$

$q \neq 0$



Internal Energy (U) and total energy of the system at constant volume (E)

$E = KE + PE + U$

KE = due to motion

PE = External electric or magnetic field

$U = (TKE + RKE + VKE + \ldots)$

TKE = Translational Kinetic Energy

RKE = Rotational Kinetic Energy

VKE = Vibrational Kinetic Energy

In thermodynamics, usually system is at rest $KE = 0$ and external electric or magnetic field not applied

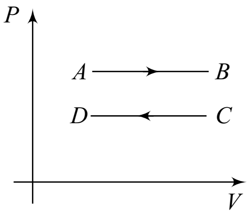
$\therefore \quad PE = 0$ and $\therefore \quad E = U$

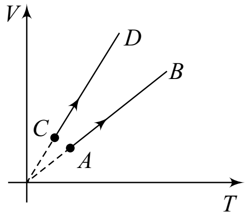
Process: Change in state is known as process:

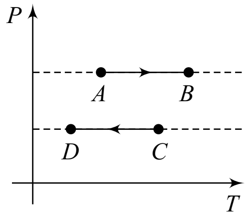
1. **Isobaric process**

P = constant

$dp = 0$





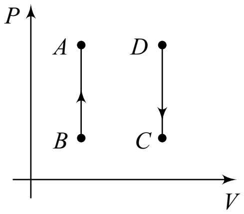


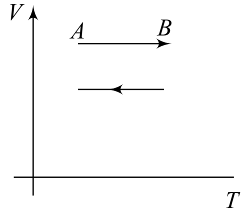
2. **Isochoric process**

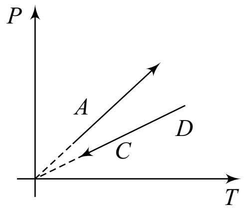
V = constant

$dV = 0$

$\therefore$ work = 0





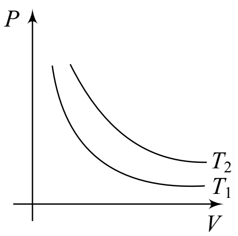


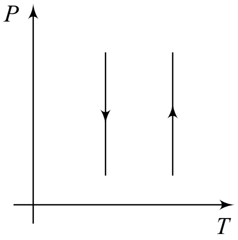
3. **Isothermal process**

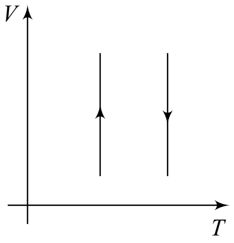
T = constant

$dT = 0$

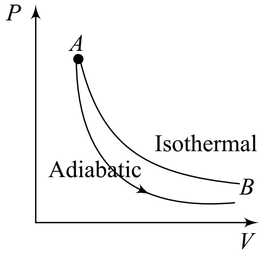
$dE = 0 \Rightarrow$ (If phase change is not taking place)





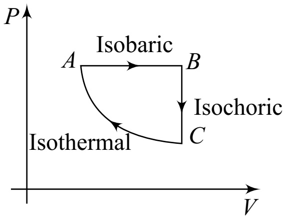


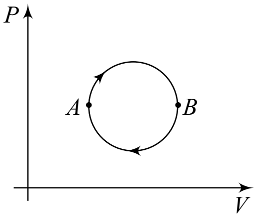
4. Adiabatic process
   for adiabatic process;
   $dq = 0$
   i.e., no heat will enter into the system or leave the system.



Cyclic Process

If any system undergoes different processes and finally comes to its initial state, then such processes are called cyclic process.





$$\Delta P = \Delta V = \Delta T = \Delta E = \Delta H = \Delta S = 0$$

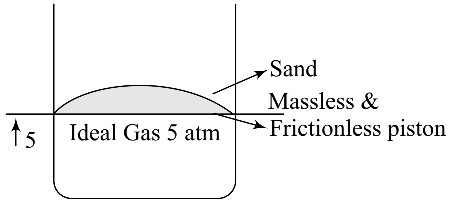
$$w \neq 0$$

$$q \neq 0$$

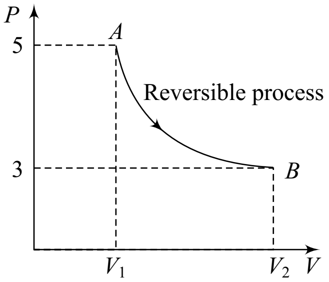
Reversible and Irreversible Process

Reversible: Those processes in which driving force is infinitesimally greater than opposing force, such processes are called reversible process.

$DF = F + dF$ and $OF = F$



If sand is removed slowly, state A comes to state B.

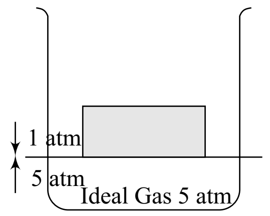


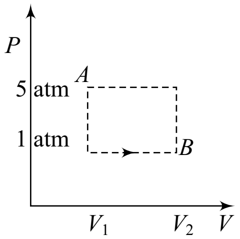
*** Characteristics of Reversible Process**

1. Reversible process is a slow process.
2. It takes infinite time for the completion.
3. Reversible process is imaginary process because massless and frictionless piston do not exist.
4. When reversible process $A \longrightarrow B$ is changed into $B \longrightarrow A$, it traces its original path.
5. Work done in reversible process is maximum.
6. Each state between A to B, system is in equilibrium with the surrounding.

Irreversible Process: Those processes in which driving force is much greater than opposing force.

$DF = F$ or $OF = dF$





Characteristics of Irreversible Process

- Irreversible processes are fast process.
- Between A and B, system will not be at equilibrium.
- All naturally occurring processes are irreversible process.
- It takes place in finite time.
- Work done in irreversible process is less as compared to reversible process.
- Exact path of irreversible process can be obtained only by experiments.
- A to B and B to A do not follow same path.

Reasons for Irreversibility

Most important reason are:

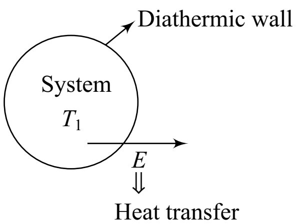
⇒ Friction

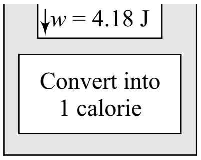
⇒ May be temperature gradient

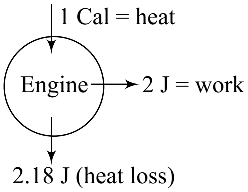
⇒ Any reversible process $A \longrightarrow B$ and $B \longrightarrow A$ has effect on the surrounding.

HEAT AND WORK

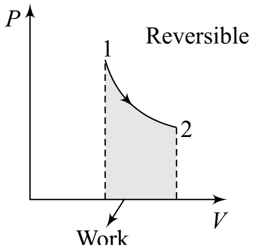
- **Heat and Work:** Energy transfer or energy exchanged by system and surrounding by virtue of temperature difference only is known as heat, rest all form of energy transfer is referred as work.
- Work is a high quality energy while heat is a low quality energy.

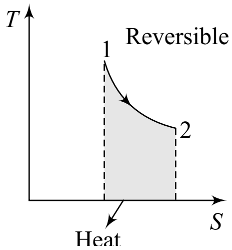






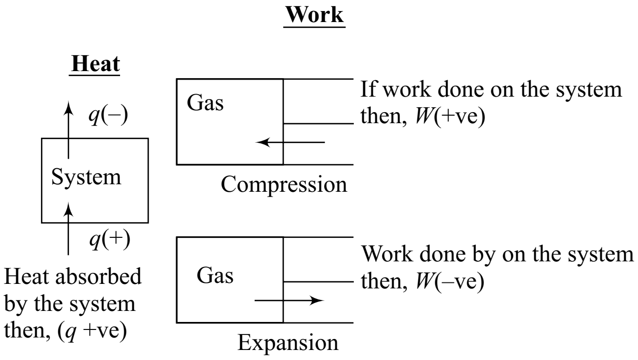
Both heat and work are path function and are not the property of the system.





Both work and heat are boundary phenomena and work transfer or heat transfer takes place at the interface of system and surrounding.

Sign Convection:



Thermodynamic Equilibrium

Any isolated process is said to be thermodynamic equilibrium when no changes occur in its macroscopic properties spontaneously.

All isolated system tends towards thermodynamic equilibrium.

For existence of thermodynamic equilibrium, following three equilibrium must be held:

⇒ Thermal Equilibrium: When system and surrounding are at same temperature.

⇒ Mechanical Equilibrium: No net force should exist on the system.

Material Equilibrium

Physical Equilibrium:
Phase Change
$H_2O(s) \rightleftharpoons H_2O(l)$ at 1 atm and 0°C

Chemical Equilibrium
$N_2 + 3H_2 \rightleftharpoons 2NH_3$

At standard state

$$\left.\begin{array}{lcl} \Delta H & = & \Delta H^\circ \\ \Delta G & = & \Delta G^\circ \\ E & = & E^\circ \end{array}\right\}$$

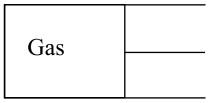
Pressure = 1 bar (1 atm = 1.01 bar)
≃ 1 atm
Temprature : 25°C (298 K)
or
else specified
Concentration: 1 Mole L^{-1}

Q. Whenever heat is added to the system, its temperature will rise. ⇒ false statement.

$$H_2O(l) \longrightarrow H_2O(g) \text{ [in phase change}$$

$$100^\circ C \qquad 100^\circ C \text{ [temperature constant]}$$

Relation between total energy of the system at constant volume (E) and total energy of the system at constant pressure (H) enthalpy:



$$H = E + PV \tag{1}$$

$$H = f(P, V, T, n)$$

$$E = f(P, V, T, n)$$

$$\Delta H = \Delta E + \Delta(PV) \tag{2}$$

$$= \Delta E + (P_2V_2 - P_1V_1)$$

If pressure is constant.

$$\Delta H = \Delta E + P\Delta V \tag{3}$$

$$= \Delta E + P(V_2 - V_1)$$

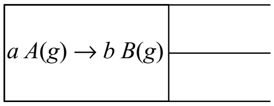
For any ideal gas undergoing through certain process at constant pressure P, we can say that

$$V = \frac{nRT}{P}$$

$$\Delta V = \frac{nR}{P} \cdot \Delta T$$

$$\Delta H = \Delta E + nR\Delta T \tag{4}$$

For chemical reaction:



$$H = E + PV$$

$$\Delta H = \Delta E + \Delta(PV)$$

If P is constant

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = \Delta E + P\Delta V = \Delta E + (P_2V_2 - P_1V_1)$$

Assuming gas to be ideal

$$V = \frac{nRT}{P}$$

If T and P are constant then,

$$\Delta V = \frac{RT}{P}\Delta n$$

$$\Delta H = \Delta E + RT\Delta n$$

$$\Delta n = \Delta n_g = \Sigma n_{(\text{gas})\,\text{Product}} - \Sigma n_{(\text{gas})\,\text{Reactant}}$$

$$\Rightarrow \quad \Delta H = \Delta E + \Delta n_g RT$$

If $\Delta n_g > 0 \quad \Rightarrow \quad \Delta H > \Delta E$

If $\Delta n_g = 0 \quad \Rightarrow \quad \Delta H = \Delta E$

$\Delta n_g < 0 \quad \Rightarrow \quad \Delta H < \Delta E$

Homogenous and Heterogeneous System

Homogenous	Heterogeneous
1. Only one Phase present. e.g., Pure solid Pure liquid Gas (X) + Gas (Y) $H_2O(l) + NaCl(s)$ = Solution $H_2O(l) + NH_3(g)$ = Solution 2. In homogenous system composition is same throughout.	1. More than one phase. e.g., Solid + Solid $H_2O(l)$ + Oil(l) $H_2O(l) + H_2O(g)$ at equilibrium $H_2O(S) + H_2O(l)$ at equilibrium

HEAT CAPACITY (HC)

$$q = ms\Delta t \qquad \text{(In Physics)}$$

$$q = mc\Delta t \qquad \text{(In Chemistry)}$$

$$\text{H.C} = mc = \frac{q}{\Delta t} \text{ or } \frac{dq}{dT}$$

$$\text{Unit}: \frac{\text{Cal}}{°\text{C}}, \frac{\text{J}}{°\text{C}}$$

Heat capacity is a extensive property of the system.

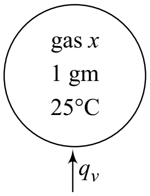
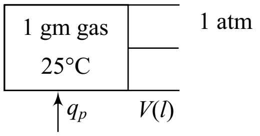
SPECIFIC HEAT

$$q = ms\Delta t$$

$$C = S = \frac{q}{m\Delta t}\left(\frac{\text{Cal}}{\text{gm} - °\text{C}}\right) \text{ (intensive property)}$$

For solids and liquids, specific heat depends upon nature of the substance.

For gases, C depends upon nature as well as the process.

At constant volume (CV)	At constant Pressure (CP)
	
Purpose: ($\Delta t = +1°C$) Work = 0	($\Delta t = +1°C$) ∴ Work done by the system

$$CV = \frac{q}{m\Delta t} \qquad CP = \frac{q}{m\Delta t}\left(\frac{\text{Cal}}{\text{gm} - r}\right)$$

Molar Specific Heat

Molar Specific Heat are of two types:

C_P = Molar specific heat at constant pressure = CV × Molar Mass

C_V = Molar specific heat at constant pressure = CP × Molar Mass

Prove $C_P - C_V = R$ (For 1 mole ideal gas)

For one mole gas ($PV = RT$)

$$H = E + RT$$

$$\therefore \quad \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + R$$

$$C_P = C_V + R$$

$$C_P - C_V = R$$

RELATION BETWEEN CHANGE IN ENTHALPY AND C_P FOR ANY PROCESS

$$H = f(P, T, V, n)$$

$H = f(P, T)$ in closed system for any process.

$$\therefore \quad dH = \left(\frac{\partial H}{\partial T}\right)_P \cdot \partial T + \left(\frac{\partial H}{\partial P}\right)_T \cdot dP \qquad (1)$$

d_H = change in enthalpy due to change in temperature and change in pressure.

$\left(\frac{\partial H}{\partial T}\right)_P \cdot \partial T$ = change in enthalpy due to change in temperature only.

For Ideal gas,

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

For Real gas

$$\left(\frac{\partial H}{\partial P}\right)_T \neq 0$$

For Solids and Liquids

$$dp \simeq 0$$

Under above set of condition; Eq. (1) may be written as

$$dH = \left(\frac{\partial H}{\partial T}\right)_P \cdot dT$$

$$dE = dq + w$$

$$dE = dq - PdV$$

$$dq = dE + PdV$$

$$dq_p = d_H \qquad (2)$$

$$\{H = E + PV \quad \therefore \quad d_H = dE + PdV\}$$

At constant pressure

$$\Delta H = \Delta U + V(P_2 - P_1)$$

$$\frac{dH}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\Rightarrow \quad \frac{dq_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\Rightarrow \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\Rightarrow \quad \int \partial H = \int C_P \partial T \qquad (3)$$

Case 1:
Where C_P is temperature independent

$$\Delta H = C_P \int_{T_1}^{T_2} dT$$

$$= C_P(T_2 - T_1) \qquad \text{(For one mole)}$$

For '*n*' moles

$$\Delta H = nC_P\Delta T \qquad (4)$$

Case 2:
C_P is temperature dependent.

$$C_P = a + bT + cT^2$$

$$\int dH = \int_{T_1}^{T_2} (a + bT + cT^2)dT$$

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) \qquad (5)$$

Internal energy and specific heat at constant volume

$U = f(P, T, V, n)$

$U = f(T, V)$- in closed system for any process

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \cdot dT + \left(\frac{\partial U}{\partial V}\right)_T \cdot dV \qquad (1)$$

For ideal gas

$$\left(\frac{\partial U}{dV}\right)_T \cdot dV = 0 \qquad [\text{isochoric condition } dV = 0]$$

For real gas,

$$\left(\frac{\partial U}{dV}\right)_T \neq 0;$$

For solid/liquid,

$$dV \simeq 0$$

Under these set of condition

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \cdot dT \qquad \left\{\begin{array}{l} dU = dq + W \\ \therefore dU = dq_V \end{array}\right\} \text{Since } W = PdV = 0$$

$$\frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V dT}$$

$$\int \partial U = \int C_V \partial T \qquad (3)$$

Case 1: If C_V is temperature independent

$$\Delta U = C_V \int_{T_1}^{T_2} dT$$

$$\Rightarrow \qquad \Delta U = C_V(T_2 - T_1) \qquad \text{(for 1 mole)}$$

For '*n*' moles

$$\Delta U = n \times C_V(T_2 - T_1) \qquad (4)$$

Case 2: If C_V is temperature dependent

$$C_V = a + bT + cT^2$$

$$\int dU = \int (a + bT + cT^2)\partial T$$

1 mole

$$\Delta U = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) \qquad (5)$$

KIRCHOFF'S EQUATION (For Chemical Equation)

Reaction	N_2	+	$3H_2$	$\rightarrow$	$2NH_3$
C_P	$\frac{7}{2}R$		$\frac{7}{2}R$		$4R$

$$\Delta_r C_P = \Sigma(v_P C_P)_{\text{Product}} - \Sigma(v_R C_P)\text{Reactant}$$

$$= [2 \times 4R] - \left[1 \times \frac{7}{2}R + 3 \times \frac{7}{2}R\right]$$

$$= 8R - 14R \Rightarrow -6R$$

Gas.	C_P	C_V
Mono atomic, He, Ne	5/2R	3/2R
Diatomic H_2, O_2	7/2R	5/2R
Polyatomic Linear (CO_2)	9/2R	7/2R
Polyatomic Non-linear NH_3	4R	3R

$$\Delta_r H^\circ = S(v_p \Delta H_f^\circ)_{\text{Products}} - \Sigma(v_R \Delta H_f^\circ)_{\text{Reactants}}$$

ΔH_f: Heat of formation in $\left(\frac{\text{KJ}}{\text{mole}}\right)$

$dH = C_P dT$: Process

$d\,\Delta rH = \Delta rC_P.dT$: For chemical reaction

$$\int_{T_1}^{T_2} d\,\Delta rH = \int_{T_1}^{T_2} \Delta r\,C_P \cdot dT$$

$$[\Delta H_{T_2} - \Delta H_{T_2}] = \int_{T_1}^{T_2} \Delta r\,C_P \cdot dT$$

Case 1: If C_P is independent of temperature

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta rC_P(T_2 - T_1)$$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta rC_P$$

Similarly,

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta rC_V$$

Case 2: If C_P and C_V are temperature dependent

$$A \longrightarrow B + C$$

$$(C_P)_A = a + bT$$

$$(C_P)_B = a' + b'T$$

$$(C_P)_C = a'' + b''T$$

$$\Delta rC_P = (a' + a'' - a) + (b' + b'' - b)T$$

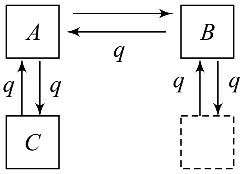
$$= \Delta a + \Delta bT$$

$$\int_{T_1}^{T_2} d\,\Delta rH = \int_{T_1}^{T_2} \Delta C_P \cdot dT$$

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} (\Delta a + \Delta bT) \cdot dT$$

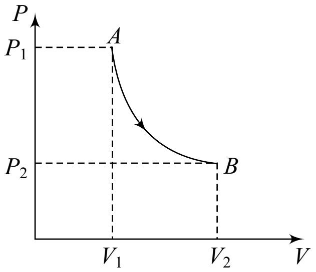
$$= \Delta a(T_2 - T_1) + \frac{\Delta b}{2}(T_2^2 - T_1^2)$$

Zeroth law of thermodynamics: If A and B is in thermal equilibrium and A and C are in thermal equilibrium then, B and C must be in thermal equilibrium.



Calculation of Work in Different Process

1. Reversible isothermal expansion of ideal gas.



$$d_W = -P_{\text{ext.}} \cdot dV$$

$$d_W = -P_{\text{gas}} \cdot dV$$

$$W = \int dW = -\int PdV$$

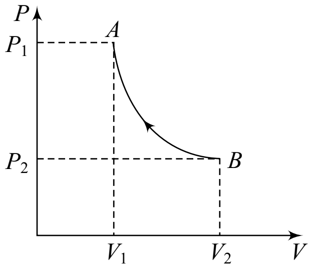
$$= -nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$= -nRT \left[\ln V\right]_{V_1}^{V_2}$$

$$W = -nRT \ln \frac{V_2}{V_1} \because P \propto \frac{1}{V}$$

$$W = -nRT \ln \frac{P_1}{P_2}$$

2. Isothermal reversible compression of ideal gas.



$$\underset{(-)}{|W_{\text{rev.iso.exp.}}|} = \underset{(+)}{|W_{\text{rev.iso.comp.}}|}$$

$W_{AB} + W_{BA} = 0$ (For entire reversible cycle)

Applying first law of thermodynamic for cycle $A \to B, B \to A$

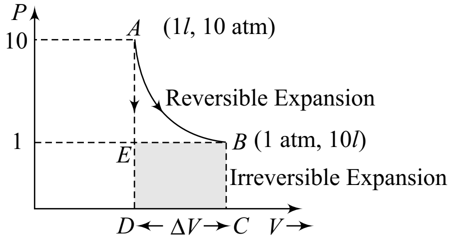
$$\Delta E = q + w$$

$$q = 0$$

$$\Delta H = \Delta E + nR\Delta T$$

$$= 0$$

3. Irreversible isothermal expansion of ideal gas.



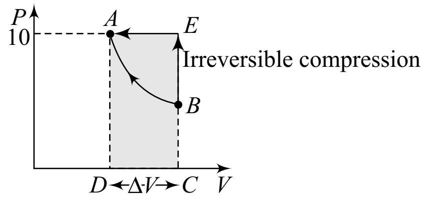
$$|W_{\text{rev.exp.}}| > |W_{\text{irr.exp.}}|$$

$\Rightarrow$ Area $ABCDA$ > Area $BCDEB$

4. Irreversible isothermal expansion of ideal gas in two stages.

$$|W_{\text{rev., exp.}}| > |W_{\text{irr.2stage, exp.}}| > |W_{\text{irr.one stage, exp.}}|$$

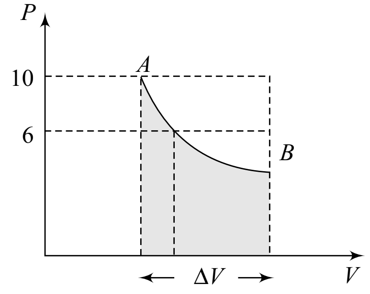
5. Irreversible isothermal compression of ideal gas



$$|W_{\text{rev.comp.iso.}}| < |W_{\text{irr.comp.iso.}}|$$

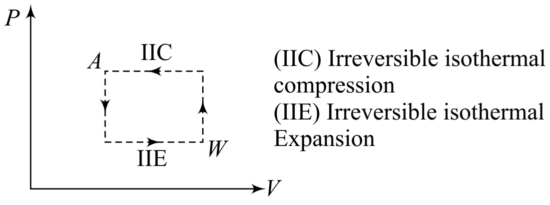
$\Rightarrow$ Area $ABCDA$ > Area $AECDA$

6. Irreversible isothermal two-stage compression of ideal gas.



$$|W_{\text{rev.comp.iso.}}| < |W_{\text{irr.two stage}}| < |W_{\text{irr.one stage}}|$$

7. Work done in entire irreversible cycle.



$$|W_{AB}| \neq |W_{BA}|$$

$$W_{AB} + W_{BA} \neq 0$$

here $|W_{BA}| > |W_{AB}|$ means work done on the system greater than work done by the system. $\therefore$ network +ve.

8. Work done during chemical equation taking place in closed rigid vessel.

$W = 0$ because $dv = 0$

9. Work done in chemical reaction occurring at constant pressure 'P' and constant temprature 'T'.

$$A(g) \longrightarrow B(g) + C(g) \qquad V = \frac{nRT}{P}; \therefore \Delta V = \frac{\Delta n_g RT}{P}$$

$$\int dW = -P_{ext.}\int dV$$

$$W = -P_{ext.}(V_2 - V_1)$$

$$= -P_{ext.}\Delta V$$

$$= -P \cdot \frac{\Delta n_g \cdot RT}{P}$$

$$W = -\Delta n_g \times RT$$

Adiabatic Process

$$dq = 0 \qquad (1)$$

$$dE = dq + dw$$

$$dE = dw \qquad (2)$$

For ideal gas

$$dE = nC_V dT$$

$$dW = -P_{ext}\, dV \qquad P_{ext} = \text{External Pressure}$$

$$\int_{T_1}^{T_2} nCvdT = -P_{ext}\int_{V_1}^{V_2} dV$$

Assuming C_V temperature independent

$$nC_V(T_2 - T_1) = P_{ext}(V_2 - V_1) \qquad (3)$$

$$\frac{P_2V_2}{nR} = T_2 \qquad (4)$$

Putting values of Eq. (4) into Eq. (3)

$$V_2 = \frac{P_{ext}V_1 + nC_VT_1}{P_{ext.} + \frac{P_2C_V}{R}} \qquad (5)$$

In reversible process $P_{external} = P_{gas}$

$$dW = -P_{ext.}\, dV = -P_{gas} \cdot dV$$

and $\quad dE = nC_VdT = -PdV = dw$

$$W = nC_V(T_2 - T_1)$$

$$C_P - C_V = R$$

$$\Rightarrow \quad \frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$$\Rightarrow \quad \gamma - 1 = \frac{R}{C_V}$$

$$\Rightarrow \quad C_V = \frac{R}{\gamma - 1}$$

$$W = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_2V_1}{\gamma - 1}$$

Calculation of work done

$$W = -P_{ext.}\,\Delta V \qquad V_1 = \frac{nRT_1}{P_1} \qquad (6)$$

$$= -P_{ext.}(V_2 - V_1) \qquad V_2 = \frac{nRT_2}{P_2}$$

Prove $TV^{\gamma-1}$ = constant for reversible adiabatic process.

$$dq = 0 \text{ or } q = 0$$

$$dU = dq + dw$$

$$nCvdT = -\frac{nRT}{V}dV$$

$$\frac{dT}{T} = -\frac{R}{Cv}\frac{dV}{V}$$

$$\int_{T_1}^{T_2}\frac{dT}{T} = \int_{V_1}^{V_2} -(\gamma - 1)\frac{dV}{V}$$

$$\ln\frac{T_2}{T_1} = -(\gamma - 1)\ln\frac{V_2}{V_1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

OR

$$TV^{\gamma-1} = \text{Constant.}$$

$$\therefore \quad PV^{\gamma} = \text{Constant}$$

$$\therefore \quad P^{1-\gamma}T^{\gamma} = \text{Constant}$$

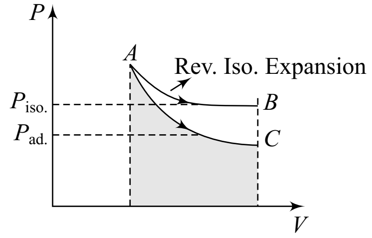
Work done in irreversible adiabatic expansion

$$nCv\int dT = -P_{ext}\int dV$$

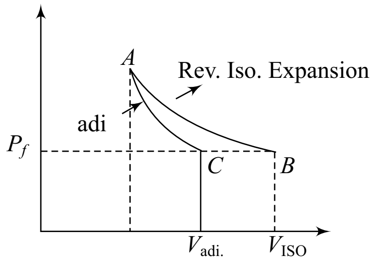
$$nCv[T_2 - T_1] = -P_{ext}\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]$$

Compression of isothermal expansion (reversible) and adiabatic expansion (reversible) of ideal gas.

Case 1: When final volume is same.

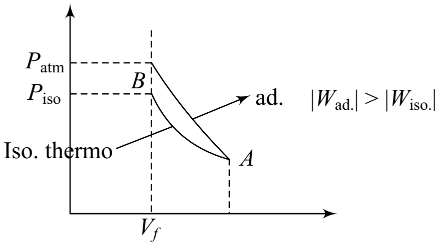


Case 2: When final pressure is same.

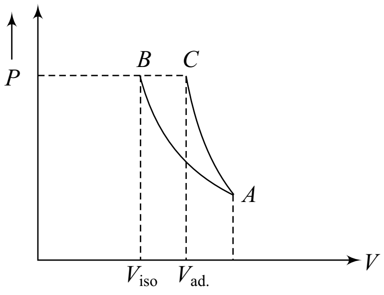


Comparison of work done in reversible isothermal compression of ideal gas and reversible adiabatic compression of ideal gas.

Case 1: When final volume is same.



Case 2: When final pressure is same.



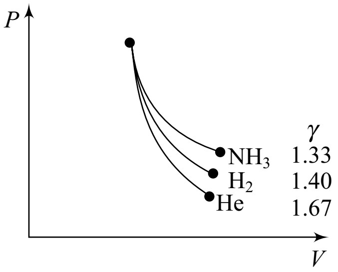
Slope of reversible adiabatic process:

$$PV^{\gamma} = \text{constant}$$

$$PV = nRT$$

$$\frac{dP}{dv} = -\gamma\frac{P}{V}$$

$$|\text{slope}| \propto |\gamma|$$



Polytrophic process

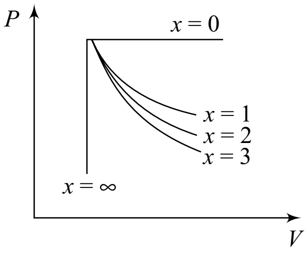
$$PV^{x} = \text{constant } (x \neq \gamma)$$

Ideal gas reversible polytrophic process,

$$PV = nRT$$

$$\Rightarrow \quad K.V^{-x} \cdot V = nRT$$

$$\Rightarrow \quad KV^{-x+1} = nRT$$



$$\Rightarrow \quad K(-x+1)\cdot V^{-x}\cdot\frac{dV}{dT} = nR$$

$$\frac{dV}{dT} = \frac{n.R.V^{x}}{K(1-x)}$$

$$\Rightarrow \quad \frac{dV}{dT} = \frac{nR}{P(1-x)}$$

Calculation of molar specific heat for any polytopic process. (Cm)

According to first law of thermodynamics,

$$dE = dq + dw$$

$$\Rightarrow \quad n.C_V \cdot dT = nC_m dT - PdV$$

$$\Rightarrow \quad n.C_m dT = n.C_V.dT + PdV$$

$$C_m = C_V + \frac{P}{n}\cdot\frac{dV}{dT} \Rightarrow C_V + \frac{P}{n}\cdot\frac{nR}{P(1-x)}$$

$$C_m = C_V + \frac{R}{(1-x)}$$

$$C_m = \frac{R}{\gamma - 1} + \frac{R}{1-x}$$

Work done in polytropic process:

For any ideal gas undergoing through reversible polytropic process.

$$PV^{x} = K = P_1V_1^{x} = P_2V_2^{x}$$

$$dw = -P_{\text{ext.}}dV$$

$$\Rightarrow \quad dw = -P_{\text{gas}} \cdot \text{dV} \quad \text{(for reversible process)}$$

$$\Rightarrow \quad W = \int dw = -\int_{V_1}^{V_2} KV^{-x}\cdot dV$$

$$= \frac{-K}{(-x+1)}[V^{-x+1}]_{V_1}^{V_2}$$

$$= \frac{K}{(x-1)}[V_2^{1-x} - V_1^{1-x}]$$

$$\boxed{W = \frac{1}{(x-1)}[P_2V_2 - P_1V_1]}$$

Limitations of first law of thermodynamics:

1. First law of thermodynamics does not tell us about the direction of flow of energy.
2. According to first law of thermodynamics, PMM-2 is possible which is not possible.
3. First law doesnot tells about feasibility, i.e., where the process will be spontaneous or non-spontaneous.
4. First law does not tells about extent of reaction.

ENTROPY(S)

Entropy is a measure of randomness or disorder of molecules. Higher the disorder, higher will be entropy. It is extensive property.

$$\text{Unit} \rightarrow \left[\frac{\text{J}}{\text{K} - \text{mole}}\right]$$

Entropy is a state function.

Measurement of entropy measurement of entropy is difficult. However, change in entropy can be measured.

Order of Entropy:

Crystalline Solid < Amorphous Solid < Liquid < Gas

Entropy is proportional to complexcity of molecule.

(i) $NO_2 < N_2O_4$
(ii) Hg < MeOH < EtOH
(iii) $H < H_2$
(iv) $H_2O + NaCl > H_2O$

Entropy is also proportional to molecular weight.

$$O_2 > N_2$$

Entropy change is always positive in the following process:

⇒ Expansion of ideal gas.
⇒ Following phase transformation.

$$\left.\begin{array}{l}\text{Solid} \rightarrow \text{Liquid}\\ \text{Liquid} \rightarrow \text{Gas}\\ \text{Solid} \rightarrow \text{Gas}\end{array}\right]\Delta S > 0$$

⇒ Dissolution of solute in solvent.
⇒ In a chemical reaction where $\Delta n_g > 0$, in such case $\Delta S > 0$.

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

If $n_g = 0 \Delta S \simeq 0$

$$2HI \longrightarrow H_2 + I_2$$

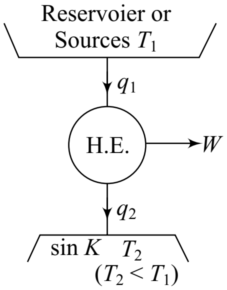
Spontaneous and non-spontaneous process

Those process in which $\Delta S_{\text{universe}} \geq 0$, are known as spontaneous process and ΔS universe < 0 are known as non-spontaneous process.

$$\Delta S = 0 \text{ reversible}$$

$$\Delta S > 0 \text{ irreversible}$$

Carnot's Heat Engine



First Law

$$q_1 = w + q_2$$

$$\eta = \frac{w}{q_1} = \frac{q_1 + (-q_2)}{q_1}$$

$$= 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

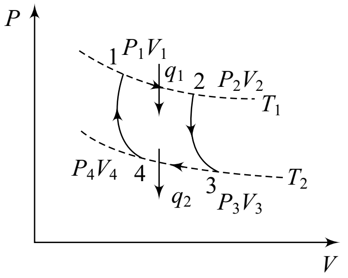
* T_2 is always less than T_1. Hence, efficiency of heat engine is always less than 1.

* If $\left.\begin{array}{l} T_1 \rightarrow \infty \text{ then } \eta \rightarrow 1 \\ T_2 \rightarrow 0\,K \text{ then } \eta \rightarrow 1 \end{array}\right]$ which is not possible

Carnot's Cycle

Carnot's cycle consist of following four reversible steps:

(a) Reversible isothermal expansion of ideal gas at $T = T_1$.
(b) Reversible adiabatic expansion of ideal gas.
(c) Reversible isothermal compression of ideal gas at $T = T_2$.
(d) Reversible adiabatic compression of ideal gas.



Process 1-2

$$\Delta E_1 = 0 = q_1 + w_1$$

⇒ $$q_1 = -w_1$$

$$q_1 = +nRT_1 \ln \frac{V_2}{V_1} \qquad (1)$$

Process 2-3

$$q = 0$$

$$\Delta E_2 = w_2$$

$$w_2 = nC_V(T_2 - T_1)$$

Process 3-4

$$\Delta E_3 = 0$$

⇒ $$q_2 = -w_3$$

⇒ $$nRT_2 \ln \frac{V_4}{V_3} \qquad (2)$$

Process 4-1

$$q = 0$$

⇒ $$\Delta E_4 = w_4$$

⇒ $$w_4 = nC_V(T_1 - T_2)$$

For entire cycle

$$\Delta E_T = 0$$

$$\Delta E_T = (q_1 + q_2) + (w_1 + w_2 + w_3 + w_4)$$

Process 2-3

$$T_1 \times V_2^{\gamma-1} = T_2 \times V_3^{\gamma-1} \qquad (3)$$

Process 4-1

$$T_2 \times V_4^{\gamma-1} = T_1 \times V_1^{\gamma-1} \qquad (4)$$

Equation (3)/(4)

$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \qquad (5)$$

Putting Eq. (5) in Eq. (2)

$$q_2 = -\mathrm{nRT}_2 \ln \frac{V_2}{V_1} \qquad (6)$$

Efficiency of Carnot Cycle:

$$\eta = \frac{q_1 + q_2}{q_1}$$

Putting values of q_1 and q_2 from Eqs. (1) and (6),

$$\eta = \frac{nRT_1 \ln\frac{V_2}{V_1} - nRT_2 \ln\frac{V_2}{V_1}}{nRT_1 \ln\frac{V_2}{V_1}}$$

$$\eta = \frac{T_1 - T_2}{T_1}$$

Claussius Inequality:

$$\eta_{\text{rev.}} = \left(\frac{q_1 + q_2}{q_1}\right) = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \qquad 1 + \frac{q_{2\,\text{rev.}}}{q_{1\,\text{rev.}}} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \qquad \frac{(q_1)_{\text{rev.}}}{T_1} + \frac{(q_2)_{\text{rev.}}}{T_2} = 0$$

$$\Rightarrow \qquad \Sigma \frac{q_{\text{rev.}}}{T} = 0$$

$$\Rightarrow \qquad \oint \frac{q_{\text{rev.}}}{T} = 0$$

$\frac{q_{\text{rev.}}}{T}$ is a state function and is named change in entropy.

$$\oint \frac{q_{\text{rev.}}}{T} = 0$$

If Cycle is irreversible then,

$$\eta_{\text{irr.}} < \eta_{\text{rev.}}$$

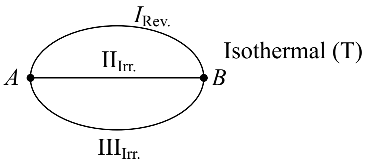
$$\Rightarrow \qquad \left(\frac{q_1 + q_2}{q_1}\right)_{\text{irr.}} < 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \qquad \frac{(q_1)_{\text{irr.}}}{T_1} + \frac{(q_2)_{\text{irr.}}}{T_2} < 0$$

$$\Sigma \frac{q_{\text{irr.}}}{T} < 0$$

$\frac{q_{\text{irr.}}}{T}$ does not specify any state.

Change in Entropy from *A* to *B* (isothermal condition)



$$\Delta S = S_B - S_A = \Delta S_{\text{I}} = \Delta S_{\text{II}} = \Delta S_{\text{III}} = \frac{q_{\text{rev.}}}{T} = \frac{q_1}{T} \neq \frac{q_{2\text{irr.}}}{T} \neq \frac{q_{3\text{irr.}}}{T}$$

$$\Delta E = q + w$$

$$(\text{for } T \text{ constant}) \quad \Delta E = 0$$

$$q = -w$$

Since $\quad w_1 \neq w_2 \neq w_3$

$\therefore \quad q_1 \neq q_2 \neq q_3$

Calculation of entropy for different cases:

A. General heating or cooling

$$dS = \frac{dq}{T}$$

$$dS = \frac{nCdT}{T}$$

$$\Rightarrow \qquad \int dS = n\int_{T_1}^{T_2} \frac{CdT}{T}$$

If C is temperature Independent

$$\Delta S = nC_P \ln\frac{T_2}{T_1} \qquad \text{at constant pressure}$$

$$\Delta S = nC_V \ln\frac{T_2}{T_1} \qquad \text{at constant volume}$$

If C is temperature dependent

$$C = a + bT + cT^2$$

$$= n\int_{T_1}^{T_2} \left(\frac{a + bT + cT^2}{T}\right) dT$$

$$\Delta S = n\left[a \ln\frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2)\right]$$

B. Entropy change during phase change:

$$A(\text{s}) + \text{heat(x)} \rightleftharpoons A(\text{l}); \quad \Delta H = +x$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T}$$

$$A(\text{l}) + \text{heat (y)} \rightleftharpoons A(\text{g}); \quad \Delta H_{\text{vap}} = +y$$

$$y = \Delta H_{\text{vapourisation}} \text{ at } T = \text{Boiling point } T_B$$

$$\Delta S_{\text{vaporisation}} = \frac{\Delta H_{\text{vaporisation}}}{T_B}$$

$$\Delta S_{\text{vaporisation}} > \Delta S_{\text{fusion}} > 0$$

Entropy change during allotropic transition

$$\underset{\text{white phosphorus}}{nP_4} \rightleftharpoons \underset{\text{Red phosphorus}}{4P_n}$$

$$\Delta S \text{ trans.} = \frac{\Delta H_{\text{trans.}}}{T_{\text{trans.}}}$$

C. Entropy change during chemical reaction:

$$aA + bB \longrightarrow cC$$

$$(\Delta S)_f = \Sigma v_p(S_f)_P - \Sigma v_R(S_f)_R$$

$$= [c.(S_f)_C] - [a.(S_f)_A + b.(S_f)_B]$$

$$\Delta rC_P = \Sigma v_P(C_P)_P - \Sigma v_R \cdot (C_P)_R$$

$$c(C_P)_C - [a(C_P)_A + b(C_P)_B]$$

$$\int dS = \int \frac{nC}{T} dT$$

⇒ for chemical reaction

$$\int d(\Delta_r S) = \int \frac{\Delta_r C.}{T} dT$$

⇒ at constant pressure

$$\int_{T_1}^{T_2} d(\Delta_r S) = \int_{T_1}^{T_2} \frac{\Delta_r C_P}{T} \cdot dT$$

(i) If $\Delta_r C_P$ is temperature independent:

$$(\Delta_r S)_{T_2} - (\Delta_r S)_{T_1} = \Delta_r C_P \ln \frac{T_2}{T_1}$$

If C_V is temperature independent:

$$(\Delta_r)S_{T_2} - (\Delta_r)S_{T_1} = \Delta r C_v \ln \frac{T_2}{T_1}$$

(ii) $\Delta_r C_P$ is temperature dependent:
If $\Delta_r C_P = a + bT + cT^2$

$$(\Delta_r)S_{T_2} - (\Delta r)S_{T_1} = \int_{T_1}^{T_2} \frac{(a + bT + cT^2)}{T} \cdot dT$$

$$= a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}[T_2^2 - T_1^2]$$

D. Entropy change involving ideal gas:

First law

$$dU = dq + dw$$

$$\Rightarrow \quad nC_V dT = TdS - PdV$$

$$\Rightarrow \quad TdS = nC_V dT + PdV$$

$$\Rightarrow \quad \int dS = \int_{T_1}^{T_2} nC_V \frac{dT}{T} + \int_{V_1}^{V_2} \frac{nR}{V} dV \Bigg] \qquad \because P = \frac{nRT}{V}$$

(i) If C_V of ideal gas is temperature independent

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

We know $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\therefore \quad \frac{P_1}{P_2} \cdot \frac{T_2}{T_1} = \frac{V_2}{V_1}$$

So $$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR\left[\ln \frac{P_1}{P_2} + \ln \frac{T_2}{T_1}\right]$$

$$= (nC_V + nR) \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$\Delta S = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

(ii) If C_V is temperature dependent and is given by
$C_V = a + bT + cT^2$

$$\int dS = \int_{T_1}^{T_2} \frac{nC_V}{T} \cdot dT + \int_{V_1}^{V_2} \frac{nR}{V} \cdot dV$$

$$= n\int_{T_1}^{T_2} \frac{(a + bT + cT^2)}{T_2} \cdot dT + nR\int_{V_1}^{V_2} \frac{1}{V} \cdot dV$$

$$= n\left[a \ln \frac{T_2}{T_1} + b(T_2 - T_2) + C(T_2^2 - T_1^2) + nR\left(\ln \frac{T_2}{T_1}\right)\right]$$

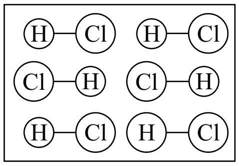
Second law of thermodynamics:

1. PMM-2 is not possible.
2. Heat cannot be completely converted in to work.
3. Entropy of the universe always increases during irreversible spontaneous process
4. Efficiency of engine can not be equal to 1.

Third law of thermodynamics:

According to third law of thermodynamics, entropy of perfect crystalline solid is 0 at 0K.

H – C*l* at 0K



S_{HCL} (0K) ≠ 0
Size of H, Cl is not comparable

NO/CO at 0K

CO	CO	CO
OC	OC	OC
CO	CO	CO
OC	OC	OC

S_{CO} (0K) = 0
Size of C, O is comparable

However, there are substances in which even at 0K there will be some disorder and hence there will be some residual entropy even at 0K.

Measurement of entropy

$$\underset{\substack{\text{at 0K assuming} \\ \text{perfect crystalline}}}{A(s)} \xrightarrow{\text{I}} \underset{\text{at } T_m}{A(s)} \xrightarrow{\text{II}} \underset{\text{at } T_m}{A(l)} \xrightarrow{\text{III}}$$

$$\underset{\text{at } T_B}{A(l)} \xrightarrow{\text{IV}} \underset{\text{at } T_B}{A(g)} \xrightarrow{\text{V}} \underset{\text{at } TK}{A(g)}$$

$$\Delta \text{S} = \Delta S_{\text{I}} + \Delta S_{\text{II}} + \Delta S_{\text{III}} + \Delta S_{\text{IV}} + \Delta S_{\text{V}}$$

assuming molar entropy of A gas at TK to be S_T.

$$S_T - 0 = \int_0^{T_m} \frac{C_{Pm(S)}}{T} dT + \frac{\Delta H_{\text{fussion}}}{T_m} +$$

$$\int_{T_m}^{T_B} \frac{C_{P \cdot m}(l) dT}{T} + \frac{\Delta H_{\text{vap.}}}{T_B} + \int_{T_B}^{T} \frac{C_{P,m(g)}}{T} dT$$

GIBB'S ENERGY (*G*)

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \frac{\Delta H_{\text{surrunding}}}{T}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

$\Rightarrow$ $-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$

$\because$ $\Delta H_{\text{System}} = -\Delta H_{\text{surrounding}}$

$\Rightarrow$ $\Delta G = \Delta H - T\Delta S$ (at constant T and P)

For feasible/spontaneous	**Non-spontaneous**
1. $\Delta S_{\text{universe}} > 0$	1. $\Delta S_{\text{universe}} < 0$
2. $\Delta G < 0$	2. $\Delta G > 0$

In reversible reaction at equilibrium

1. $\Delta S_{\text{universe}} = 0$
2. $\Delta G = 0$

Now, $\Delta G = \Delta H - T\Delta S$

No.	ΔH	ΔS	T	ΔG	Example
1.	(–)	(+)	high	–	$C_2H_5OH(l) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2(g) + \text{heat}$
2.	(–)	(+)	low	–	
3.	(+)	(–)	high	+	$2CO_2 + 3H_2O \rightarrow C_2H_5OH + \frac{7}{2}O_2$
4.	(+)	(–)	low	+	
5.	(–)	(–)	high	+	$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) + \text{heat}$
6.	(–)	(–)	low	–	
7.	(+)	(+)	high	–	
8.	(+)	(+)	low	+	$CaCO_3(s) + \text{heat} \xrightarrow{\Delta} CaO(s) + CO_2(g)$

Since $G = H - TS$

$$\begin{aligned}
\therefore \quad \Delta G &= \Delta H - T\Delta S \\
&= -nFE \\
&= \Delta G^\circ + RT\ln Q \qquad Q = \text{Reaction Quotient} \\
&= -W_{\text{useful}} = (\text{maximum available non PV work})
\end{aligned}$$

$$\left.\begin{aligned}
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
&= -nFE^\circ \\
&= -RT\ln K_{\text{eq}}
\end{aligned}\right] \Rightarrow \text{At Standard Condition}$$

We know $G = H - TS$

$$\begin{aligned}
\Rightarrow \quad \Delta G &= dH - d(TS) \\
&= dE + d(PV) - d(TS) \\
&= dq + dw + d(PV) - d(TS) \\
&= TdS - PdV + PdV + VdP - TdS - SdT \\
&= VdP - SdT \\
dG &= VdP - SdT
\end{aligned}$$

at constant temperature

$$dG = VdP$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

For chemical reaction

$$aR \longrightarrow bP$$

$$\int d(\Delta rG) = \int_{P_1}^{P_2} (\Delta rV) \cdot dP$$

$$\Delta rG_{P_2} - \Delta rG_{P_1} = \Delta rV \cdot (P_2 - P_1)$$

For ideal gas:

$$\int dG = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

$$\Delta G = nRT \ln\frac{P_2}{P_1}$$

at constant pressure

$$dG = -SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$aR \longrightarrow bP$$

$$= \int_{T_1}^{T_2} d(\Delta rG) = -\Delta rS\int_{T_1}^{T_2} dT$$

$$\Delta rG_{T_2} - \Delta rG_{T_1} = -\Delta rS[T_2 - T_1]$$

Standard Gibb's Energy of Formation: (ΔG_f^o)

When 1 mole of any compound is formed from its most stable constituents. Then, change in Gibb's energy under standard condition is said as ΔG_f^o

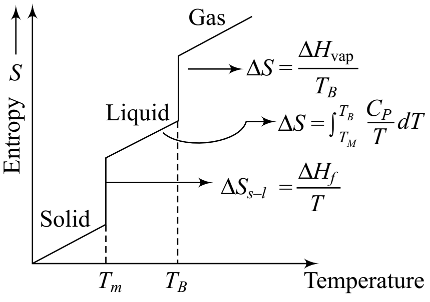
For element and molecules in their most stable form, ΔG_f^o assumed to be 0.

here (s) = solid, (l) = liquid, (g) gas

C(graphite)
S(rhombic)
$H_2(g)$
$O_2(g)$
Fe(s)
$F_2(g)$
$Cl_2(g)$
$Br_2(l)$
$I_2(s)$

Na(s)
Ca(s)
Fe(s)
Hg(l)

$\Rightarrow$ for all $\Delta G_f^\text{o} = 0$



and $\Delta S_{\text{S–l}} < \Delta S_{\text{l-}g}$

Entropy change of ideal gas in following expansion process:

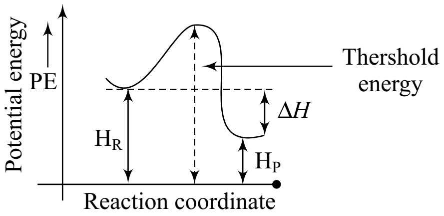
Process	ΔS_{system}	$\Delta S_{\text{surrounding}}$	ΔS_T
(1) Reversible isothermal	$\Delta S = nR\ln\frac{V_2}{V_1} = \frac{q_{\text{rev.}}}{T}$	$-\Delta S_{\text{system}}$	0
(2) Irreversible isothermal free expansion $\Delta\cancel{E}^{\circ} = q + \cancel{w}^{\circ}$	$\Delta S = nR\ln\frac{V_2}{V_1}$	0	> 0
(3) Irreversible intermediate isothermal Expansion $\Delta\cancel{E}^{\circ} = q + w$	(+ve)	$\Delta S = \frac{-q}{T}$	> 0
(4) Reversible adiabatic Expansion $\Delta E = \cancel{q}^{\circ} + w_{\text{rev}}$	$\Delta S = nR\ln\frac{V_2}{V_1} + nC_V\ln\frac{T_2}{T_1} = 0$ (+ve) (–ve)	0	> 0
(5) Irreversible adiabatic free expansion $\Delta E = \cancel{q}^{\circ} + \cancel{w}^{\circ}$	$\Delta S = nR\ln\frac{V_2}{V_1}$ (+ve)	0	> 0
(6) Irreversible adiabatic intermediate Expansion $\Delta E = \cancel{q}^{\circ} + w_{\text{irr.}}$	$\Delta S = nR\ln\frac{V_2}{V_1} + nC_V\ln\frac{T_2}{T_1} + ve$ (+ve)	0	> 0

THERMOCHEMISTRY

Thermochemistry is that part of thermodynamics which deals with heat exchanged between system and surrounding during any chemical reaction or phase change.

Exothermic and endothermic reaction:

$$R \longrightarrow P + q \text{ (heat)}$$



H_R = Enthalpy of reactant, H_p = Enthalpy of Product

First law $H_R = H_P + q$

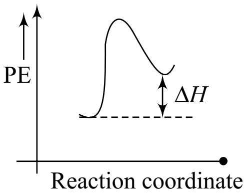
$$\Delta H = H_P - H_R$$
$$= -q$$
$$E_{af} = E_{ab} + \Delta H \text{ (including sign)}$$

ΔH in magnitude is always less than E_{ab}.

Examples of exothermic reaction:

(a) Combustion reaction
(b) Addition reaction
(c) Acid-base neutraliation

Endothermic Reaction:



$$q_{\text{(heat)}} + R \longrightarrow P$$
$$q + H_R = H_P$$
$$\Rightarrow \quad \Delta H = H_P - H_R$$
$$= +q$$
$$E_{af} = E_{ab} + \Delta H$$

Examples:

(a) Decomposition reaction
(b) Elimination reaction

ΔH or ΔE for the reaction

Enthalpy change of the reaction at constant pressure is known as ΔH.

Enthalpy change of the reaction at constant volume is known as ΔE.

ΔH and ΔE depends on following factors:

1. Reaction condition, i.e., whether pressure is constant or volume is constant.

$$\Delta H = \Delta E + \Delta ngRT$$

If $\Delta ng > 0 \Rightarrow \Delta H > \Delta E$
$\Delta ng = 0 \Rightarrow \Delta H = \Delta E$
$\Delta ng < 0 \quad \Delta H < \Delta E$

In Bomb calorimeter: V-constant

2. Temperature:

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta r C_P$$

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta r C_V$$

$\Rightarrow$ **if** $T_2 > T_1$

If $\Delta r C_P > 0$ $\quad \Delta H_2 > \Delta H_1$

$\Delta r C_P = 0$ $\quad \Delta H_2 = \Delta H_1$

$\Delta r C_P < 0$ $\quad \Delta H_2 < \Delta H_1$

3. Pressure:

   ΔH, ΔE depends on pressure:

4. Different allotropic forms:

   $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) + 393.5$ kJ/mole

   $C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g) + 395.4$ kJ/mole

5. Different isomeric form:

   $C_4H_8 + 6O_2 \longrightarrow 4CO_2 + 4H_2O + x$ kJ/mole

   Cis-2-butene

   $C_4H_8 + 6O_2(g) \longrightarrow 4CO_2 + 4H_2O + y$ kJ/mole

   trans-2-butene $\quad x > y$

6. Phase:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) + x$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + y \quad x < y$$

Standard Conditions:

Pressure = 1 bar

Temperature = Specified (298 K)

activity = 1

for dilute solution

|activity| = |concentration| in Molarity |M|

7. Solvent:

   $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) \qquad \Delta H_1$

   $Na^+(aq) + Cl^-(aq) \longrightarrow NaCl(s) \qquad \Delta H_2$

   $Na^+(alc) + Cl^-(alc) \longrightarrow NaCl(s) \qquad \Delta H_3$

   $\Delta H_1 \neq \Delta H_2 \neq \Delta H_3$

Standard enthalpy of formation ΔH_f^o :

When 1 mole compound is formed from its most stable constituents then, enthalpy change of reaction is termed as ΔH_f^o .

For elements and molecules listed below ΔH_f^o is taken as 0.

C(graphite), $H_2(g)$ $N_2(g)$ S(rhombic) *P* (White)

ΔH_f^o may be +ve or –ve.

Write down thermochemical equation for the formation following compounds:

$CO_2(g)$, $H_2O(l)$, $C_2H_2(g)$, $CH_3OH(l)$, $C_6H_5COOH(s)$, CH_3–CN(g), $NH_4Cl(s)$, $H_2SO_4(l)$, HCl(g), $H_3PO_4(l)$

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

$$2C(\text{graphite}) + H_2(g) \longrightarrow C_2H_2(g)$$

$$C(\text{graphite}) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l)$$

$$7C(\text{graphite}) + 3H_2(g) + O_2(g) \longrightarrow C_6H_5COOH(s)$$

$$2C(\text{graphite}) + \frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \longrightarrow CH_3 - CN(g)$$

$$\frac{1}{2}N_2(g) + 2H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow NH_4Cl(s)$$

$$H_2(g) + S(\text{rhombic}) + 2O_2(g) \longrightarrow H_2SO_4(l)$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$$

$$\frac{3}{2}H_2(g) + P(\text{white}) + 2O_2(g) \longrightarrow H_3PO_4(l)$$

Application of ΔH_f^o

1. Calculation of standard enthalpy of the reaction:

$$\Delta_r H^\circ = \Sigma v_p (\Delta H_f^o)_p - \Sigma v_R (\Delta H_f^o)_R \quad v = \text{No of moles}$$

2. Calculation of relative stability of isomers and allotropes:

$$\text{Stability} \propto \frac{1}{\Delta H_f^o} (\text{including sign})$$

   If ΔH_f^o for *A* 10 J and for *A′* (12 J) then *A* is more stable

   Explosive compound should have high +ve value of ΔH_f^o

Standard enthalpy change of combustion:

When 1 mole compound is completely combusted in the presence of sufficient oxygen then, enthalpy of the reaction under standard conditions is known as $\Delta H^o_{\text{combustion}}$

$\Delta H^o_{\text{combustion}}$ is always negative or else reaction is not considered to be combustion reaction.

$$\left[\begin{array}{l} \text{heat} + F_2 + 1/2O_2 \longrightarrow OF_2 \\ \text{heat} + N_2 + O_2 \longrightarrow 2NO \end{array}\right] \text{not a combustion reaction}$$

Reason: BDE of N ≡ N More than 900 kJ/mole

$$C + \frac{1}{2}O_2 \longrightarrow CO(g) + \text{heat (parital combustion)}$$

Normal combustion products of element:

CHSPNOLiCa $\longrightarrow$ $CO_2(g)$ $N_2(g)$

$H_2O(l)$ $Li_2O(s)$

$SO_2(g)$ $CaO(s)$

$P_4O_{10}(s)$

Q. Write down thermo-chemical equation for the combustion of following compounds:

C(graphite), *C*(diamond), H_2(graphite), S(rhombic), *P*(white),

$CH_4(g)$, $C_2H_4(g)$, $C_2H_2(g)$, $CH_3OH(l)$, $C_6H_5COOH(s)$

$CH_3 - CN(g)$, $PH_3(g)$

$C(\text{graphite}) + O_2 \longrightarrow CO_2(g)$

$$C(\text{diamond}) + O_2 \longrightarrow CO_2(g)$$

$$H_2(g) + \frac{1}{2}O_2 \longrightarrow H_2O(g)$$

$$S(\text{rhombic}) + O_2 \longrightarrow SO_2(g)$$

$$P(\text{white}) + \frac{5}{4}O_2 \longrightarrow \frac{1}{4}P_4O_{10}(s)$$

$$CH_4(g) + 2O_2 \longrightarrow CO_2(g) + 2H_2O(l)$$

$$C_2H_4(g) + 3O_2 \longrightarrow 2CO_2(g) + 2H_2O(l)$$

$$C_2H_2(g) + \frac{5}{2}O_2 \longrightarrow 2CO_2(g) + H_2O(l)$$

$$CH_3OH(l) + \frac{3}{2}O_2 \longrightarrow CO_2(g) + 2H_2O(l)$$

$$C_6H_5COOH(s) + \frac{15}{2}O_2 \longrightarrow 7CO_2(g) + 3H_2O(l)$$

$$CH_3 - CN(g) + \frac{11}{4}O_2 \longrightarrow 2CO_2(g) + \frac{3}{2}\underset{(l)}{H_2O} + \frac{1}{2}\underset{(g)}{N_2}$$

$$PH_3(g) + 2O_2 \longrightarrow \frac{1}{4}P_4O_{10}(s) + \frac{3}{2}H_2O(l)$$

Application of $\Delta H^o_{\text{combutation}}$

⇒ In calculation of = $\Delta_r H^\circ = \Delta H^o_{\text{reaction}}$

$$\Delta rH^\circ = \Sigma \nu_R(\Delta H^o_{\text{comb}})_R - \Sigma \nu p(\Delta H^o_{\text{comb.}})p$$

for reaction $CH_4(g) + SO_2(g) \longrightarrow CO_2 + H_2O + S$

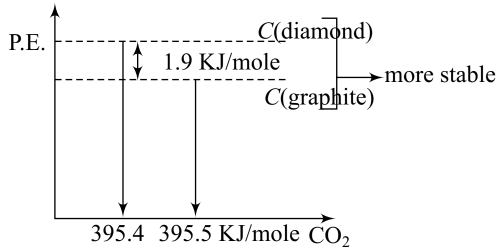
Since ΔH° combution for SO_2, CO_2, H_2O = 0

$$\Delta rH^\circ = (\Delta H_{\text{Comb.}})CH_4 - (\Delta H_{\text{comb.}})S$$

⇒ $C_3H_8 + H_2 \longrightarrow C_2H_6 + CH_4 \quad \Delta rH^\circ = -55.7 \text{ kJ}$

⇒ $-55.7 = [(1 \times \Delta H^o_{\text{comb.}}\ C_3H_8) + (1 \times \Delta H^o_{\text{comb.}}\ H_2)]$
$-[(1 \times \Delta H^o_{\text{comb.}}\ (C_2H_6) + 1 \times \Delta H^o_{\text{comb.}}\ CH_4)]$

In estimation of stability of allotropes



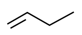
∴ $|\Delta H^o_{\text{comb.}}| \propto \frac{1}{\text{Stability}}$

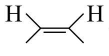
∴ graphite more stable.

In comparing stability of different isomers

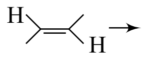
$C_4H_8 + O_2(g) \longrightarrow 4CO_2(g) + 4H_2O(l) +$ Heat of combution

$C_4H_8 + O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l) +$ Heat of combution


$\rightarrow 4CO_2(g) + 4H_2O + x$ kJ/mole



$\rightarrow 4CO_2(g) + 4H_2O + y$ kJ/mole



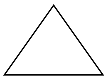
$\rightarrow 4CO_2(g) + 4H_2O + z$ kJ/mole

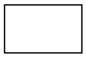
HOC order $x > y > z$

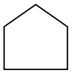
Since stability order *trans*-2 butene > *Cis*-2 butene > 1-butene

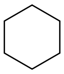
In comparing stability of different members of homologous series.

Cyclo alkane → C_nH_{2n}


$+ O_2 \longrightarrow 3CO_2 + 3H_2O + x$ kJ/mole


$+ O_2 \longrightarrow 4CO_2 + 4H_2O + y$ kJ/mole


$+ O_2 \longrightarrow 5CO_2 + 5H_2O + z$ kJ/mole


$+ O_2 \longrightarrow 6CO_2 + 6H_2O + w$ kJ/mole

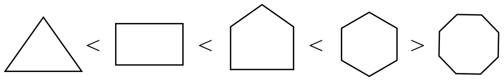
HOC = $x < y < z < w$

Since, HOC ∝ No of Carbon or Molar mass

∴ $|\Delta H^o_{\text{comb.}}|$ per $CH_2 \propto \frac{1}{\text{Stability}}$

$$\frac{x}{3} > \frac{y}{4} > \frac{z}{5} > \frac{w}{6}$$

Since **stability of cycloalkane**



In estimating calorific value of any fuel.

$$\text{C.V.} = \frac{|\Delta H^o_{\text{comb.}}|}{\text{GMM}} \text{KJ/g}$$

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 800$ kJ/mole $\qquad \frac{800}{16} = 50$ KJ/g

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O + 300$ KJ/mole $\qquad \frac{300}{2} = 150$ KJ/g

If calorific value ↑ fuel more efficient.

ΔH^o_{BDE} (Bond dissociation energy)

When 1 mole bonds are broken from gaseous reactants to gaseous products then, enthalpy change of reaction under standard conditions is known as ΔH^o_{BDE}.

It is always positive.

(i) $H_2(g) \rightarrow 2H(g) \qquad \Delta H^\circ = \Delta H^o_{\text{BDE}}$

(ii) $Cl_2(g) \rightarrow 2Cl(g)$

(iii) $O_2(g) \rightarrow 2O(g)$

(iv) $CH_4(g) \rightarrow CH_3(g) + H(g) \qquad \Delta H_1$
$CH_3(g) \rightarrow CH_2(g) + H(g) \qquad \Delta H_2$
$CH_2(g) \rightarrow CH(g) + H(g) \qquad \Delta H_3$
$CH(g) \rightarrow C(g) + H(g) \qquad \Delta H_4$

$CH_4(g) \rightarrow C(g) + 4H(g)\ \Delta H$

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$

$$\Delta H_{\text{B.D.E.}} \text{ of } C-H \text{ in } CH_4 = \frac{\Delta H}{4}$$

$Br_2(l) \rightarrow 2Br \qquad \Delta H^\circ \neq \Delta H^o_{\text{BDE}}$

Application of B.E. data

⇒ **In comparing stability of bonds:**

1. $C-C > Si-Si > Ge-Ge > S_n-S_n > P_b-P_b$
2. $P-P > N-N$
3. $Cl-Cl > Br-Br > F-F > I-I$
4. $S-S > O-O$

⇒ **In calculating ΔH for the reaction:**

$$\Delta H = \Sigma(\text{B.D.E.})_R - \Sigma(\text{B.D.E.})_P$$

It is applicable for only gaseous reactants and gaseous products.

If reactants and products are not in gaseous state (any one) then, calculate ΔH for reaction by the following method:

$$\Delta H = E_{\text{absorbed}} - E_{\text{released}}$$

Q. Calculate ΔH for following reaction:
$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ B.D.E. = kJ/mol.
$E_{H-H} = x$, $E_{Cl-Cl} = y$, $E_{H-Cl} = z$
$\Delta H = (x + y) - 2z$

Q. Calculate ΔH for the following reaction:
$H_2(l) + Cl_2(s) \rightarrow 2HCl(l)$
B.DE = kJ/mol
$E_{H-H} = x$, $E_{Cl-Cl} = y$, $E_{H-Cl} = z$, $(\Delta H_{vap})_{H_2} = m$,
$(\Delta H_{sub})_{Cl_2} = p$, $(\Delta H_{vap})_{HCl} = n$

Sol.

$$\begin{array}{llll} H_2(l)\ + & Cl_2(s) & \rightarrow & 2HCl(l) \\ \uparrow m + x & \uparrow p + y & & \downarrow 2n + 2z \end{array}$$

$$\Delta H = (m + x + p + y) - 2(n + z)$$

ΔH$_{\text{atomisation}}$

When 1 mole gaseous atoms are formed from any substance then, $\Delta H_{\text{reaction}}$ is known as $\Delta H_{\text{atomisation.}}$

It is always +ve.

$$\left.\begin{array}{l} C(dia) \rightarrow C(g) \\ C(gr) \rightarrow C(g) \\ \frac{1}{2}H_2(g) \rightarrow H(g) \\ \frac{1}{2}Br_2(l) \rightarrow Br(g) \end{array}\right\} \Delta H^\circ = \Delta H^\circ_{\text{atom}}$$

Enthaphly of phase change:

ΔH$_{\text{sublimation}}$

A(s) + heat → A(g) $\Delta H = \Delta H_{Sub}$ always +ve

1 mole A at temperature $T\ (< T_m)$

ΔH fusion

A(s) + heat → A(l) $\Delta H = \Delta H_{\text{fusion}}$ always +ve

1 mole A at T_m

ΔH vaporisation

A(l) + heat → A(g) $\Delta H = \Delta H_{\text{vap.}}$ always +ve

1 mole A at Temperature Boiling Point

$$\Delta H_{\text{sub.}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vap.}}$$

If ∴ $\Delta rC_p \rightarrow 0$ $\quad \Delta H_{T_2} = \Delta H_{T_1}$

ΔH transition. (+ve or –ve)

1 mole C(graphite) $\longrightarrow$ 1 mole C(diamond) ΔH = ΔH transition.

ΔH neutralisation

When 1 g of equivalent of strong acid reacts with 1 g equivalent of strong base, energy is always released and enthalpy change for the reaction is always same and is equal to $\Delta H_{\text{neutralisation}}$

∵ Strong Acid (SA) and Strong Base (SB) taken

∴ dissociation energy of acid and base = 0

$$\begin{array}{ccccl} HA\ (SA) & + & BOH\ (SB) & & \\ 1\ \text{gm}-\text{eq.} & & 1\ \text{gm}-\text{eq.} & & \\ \downarrow \text{gives} & & \downarrow \text{gives} & & \\ H^+ & + & OH^- & \longrightarrow & H_2O + 57.3\ \text{kJ/mole} \\ 1\ \text{g}-\text{eq.} & & 1\ \text{g}-\text{eq.} & & (13.7\ \text{KCal/mole}) \\ n_f = 1 & & n_f = 1 & & \end{array}$$

1 g – mole (H^+) 1 g-mole (OH^-) = 1 Mole H_2O

$\Delta H_{\text{neut.}} = -57.3$ kJ/mole.

Case of weak acid and weak base

Weak acid and weak base do not dissociate completely into respective ions and some amount of heat is consumed in dissociation of weak acid and weak base. Hence,

$$|\Delta H_{\text{neut.}}| < 57.3\ \text{kJ/mole}$$

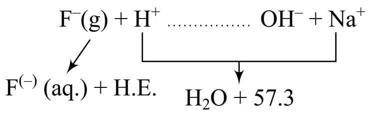
$$\begin{array}{ccccl} HA & + & BOH & & \\ WA & & WB & & \\ 1\ \text{g eq.} & & 1\ \text{g-eq.} & & \\ + \downarrow x\ \text{kJ} & + & \downarrow y\ \text{kJ} & & \\ H^+ & + & OH^- & \longrightarrow & H_2O + 57.3\ \text{kJ/mole} \\ 1\ \text{g-eq.} & & 1\ \text{g-eq.} & & \\ n_f = 1 & & n_f = 1 & & \\ 1\ \text{g-mole} & & 1\ \text{g-mole} & & \end{array}$$

$$\Delta H_{\text{neut.}} = -[57.3 - (x + y)]\text{kJ/mole}$$

Case of HF(WA)

Although, HF is a weak acid still its $|\Delta H_{\text{neut.}}| > 57.3$ kJ/mole with strong base.

$$\begin{array}{ccc} HF & + & NaOH \\ (WA) & & (SB) \\ 1\ \text{g eq.} & & 1\ \text{g eq.} \\ + \downarrow x & & \downarrow \end{array}$$



Since hydration $\propto \dfrac{\text{charge}}{\text{size}}$

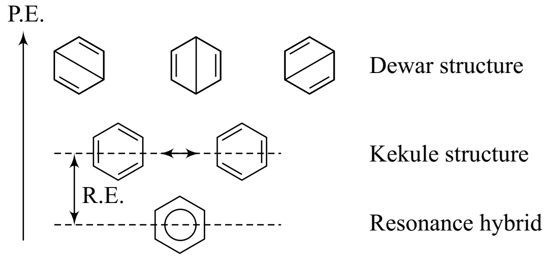
F^- size very small ∴ |HE| > |X|

$$\Delta H_{\text{neut.}} = -[57.3 + \text{H.E.} - x]$$

$$\text{H.E} >> x$$

and Hydration energy (HE) for other acid negligible due to bigger size of anion.

RESONANCE ENERGY (RE)



Resonance energy is defined as difference in energy between most stable *R*.S. (hypothetical) and actual resonance hybrid.

Resonance energy is always negative.

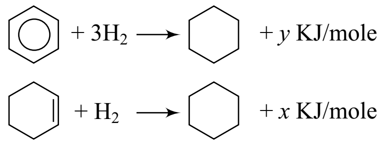
$$\text{R.E.} = (\Delta H_f^o)_{th} \sim (\Delta H_f^o)_{actual}$$
$$= (\Delta H_c^o)_{th} \sim (\Delta H_c^o)_{actual}$$

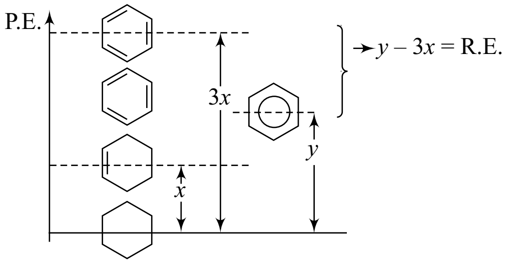
All theortical calculations are done with respect to most stable R.S, (Resonating structure) while actual experimental data are related with actual R.H. (Resonance hybrid)

If R.H. appears on the reactant side then, resonance energy is absorbed otherwise it is released.

From the following observation calculate the R.E. of benzene.

IF





R.E. of benzene = $y - 3x$

Lattice Dissociation Enthalpy: Amount of energy required to break 1 mole ionic crystal into constituent gaseous ion. Always positive

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ $\Delta H = \Delta H_{L.D.E.}$

(1 mole)

$Al_2(SO_4)_3(s) \rightarrow 2Al^{+3}(g) + 3SO_4^{--}(g)$

(1 mole) $\Delta H = \Delta H_{L.D.E. of Al_2(SO_4)_3}$

$$\Delta H_{L.D.E.} \propto \frac{\text{charge}}{\text{size}}$$

$\Delta H_{hydration}$ are of two types

(i) $\Delta H_{hydration}$ for ions

When one mole of gaseous ion is treated with excess water, the energy is always released and enthalpy change is known as $\Delta H_{hyd.}$ always –Ve.

$A^{+n}(g) + aq. \rightarrow A^{+n}(aq.)$ $\Delta H = \Delta H_{hyd}$ of A^{+n}(–ve)

$B^{-m}(g) + aq. \rightarrow B^{-n}(aq.)$ $\Delta H = \Delta H$ hydration of B^{-m}(–ve)

$$|\Delta H_{hyd.}| \propto \frac{\text{charge}}{\text{size}}$$

(ii) $\Delta H_{hydration}$ for molecules

When 1 mole of anhydrous-solid or partially hydrated solid is further hydrated, enthalpy change for the process is known as $\Delta H_{hyd.}$ (may be +ve or –ve)

$CuSO_4$ (anhydrous solid) $\xrightarrow{aq.}$ $CuSO_4 \cdot 2H_2O$

(1 mole)

$CuSO_4 \cdot H_2O(s) \xrightarrow{aq.} CuSO_4 \cdot 5H_2O(s)$

(1 mole)

ΔH solution

When 1 mole of solute is dissolved in large excess of solvent (more than 200 moles) the enthalpy change is known as $\Delta H_{solution}$.

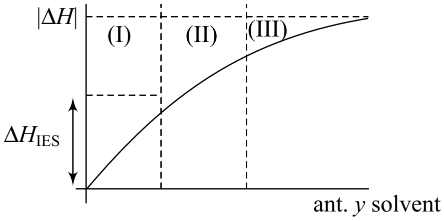
$$1 \text{ mole } A_{(\text{solute of solid/liquid/gas})} \xrightarrow[\text{large (excess)}]{\text{Solvent}} A(\text{solution})$$

$$\Delta H = \Delta H_{solution}$$

At $C \rightarrow 0$ M or infinite dilution.

there is no solute-solute interaction.

$$\Delta H_{IES} \quad A(\text{solute})\ 1 \text{ mole} \xrightarrow[\text{specified Amount.}]{\text{solvent}} \frac{A(\text{solution})}{C_1 M}$$



ΔH dilution

$$\underset{C_1M}{A(\text{solution}-1)} \xrightarrow[\text{(given amount)}]{+\text{solvent}} \underset{C_2M}{A(\text{solution}-2)}$$

$(C_1 > C_2)$ ΔH_{dil^n} of $A_{C_1 \rightarrow C_2}$

$\Delta H_{I.E.}$

$[A(g) + I.E._1 \rightarrow A+(g) + e^-]$ at 0 K

ΔH_{IE} is at temp 'T' K

$$\frac{\Delta H_{I.E.} - I.E.}{T - 0} = (\Delta rCp) = \frac{5}{2}R$$

For monoatomic gaseous atom

$\Delta H_{IE} = I.E. + 5/2RT \Rightarrow \Delta H_{I.E.} = I.E.$

because I.E. >> $\frac{5}{2}RT$

$\Delta H_{E.A.}$

[A(g) + $e^- \rightarrow$ A^-(g) + E.A. (energy released)]

$$\frac{\Delta H_{E.A.} - E.A.}{T - 0} = (\Delta rCp)$$

$$\Delta H_{E.A.} = \underset{\text{(with sign)}}{\underset{\downarrow}{E.A.}} - \frac{5}{2}RT \qquad |\Delta H_{EA}| \simeq |EA|$$

Hess's law

According to Hess's, whether any chemical reaction occurs in one step or more than one step, ΔH is same.

$$\begin{tikzcd} A \arrow[r, "\Delta H_1"] \arrow[d, "\Delta H_3"] & B \\ C \arrow[r, "\Delta H_3"'] & D \arrow[u, "\Delta H_4"'] \end{tikzcd}$$

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

In other words, we can treat that thermochemical equation as algebraic equation.

Solved Examples

1. Any real gas is subjected to change in its state from 10 atm, 5*l* to 3 atm, 2*l*. $\Delta U = 20\ l$ – atm. Calculate ΔH for the process.

Sol. $\Delta H = \Delta U + (P_2V_2 - P_1V_1)$

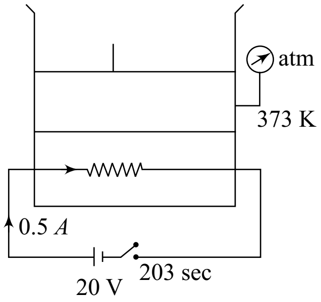
$= 20 + (6 - 50)$

$= -24l$ atm

2. 0.5 A current from a 20 V supply is passed for 203 sec. through a water sample. 0.9 g water vapourises at 1 atm at its boiling point. Calculate ΔE and ΔH for the vapourisation of 1 mole water.

Sol. $H_2O(l) \longrightarrow H_2O(g)$

0.9 g



$W = q \times V$ = Charge × Voltage

$= i \times t \times V = 0.5 \times 203 \times 20$ J

$= 2030$ J $= 2.03$ kJ

For one mole or 18 g water heat supplied = ΔH

$$\Delta H = \frac{2.03}{0.9} \times 18 = 40.6 \text{ KJ/mole}$$

3. 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution temperature rises by 3.0°C. Calculate the enthalpy of neutralization per mol of HCl.

(a) -2.5×102 kJ (b) -1.3×102 kJ
(c) -8.4×101 kJ (d) -6.3×101 kJ

Sol. HCl + NaOH $\longrightarrow$ NaCl + H_2O

for water $C = 4.2$ J/gram

enthalpy change = mCdT = $100 \times 4.2 \times 3 = 1.26$ kJ

enthalpy change for 5 millimole = 1.26 kJ

enthalpy change for 1 mole $\Rightarrow \frac{1.26}{5 \times 10^{-3}}$

$\Rightarrow$ 2.52×102 kJ

4. One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C. If the work done by the gas in the process is 3 kJ, the final temperature will be equal to ($C_V = 20$ J/K mol)

(a) 100 K (b) 450 K (c) 150K (d) 400 K

Sol. **(c)** for adiobatic process $\Delta U = W$ because $q = 0$

$\Rightarrow$ $3000 = C_V(T_2 - T_1)$

$$T_2 - T_1 = \frac{3000}{20}$$

$T_2 = T_1 + 150 = 450$ K

5. Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a constant external pressure of 1 atm. Calculate q, w, ΔU and ΔH. Calculate the corresponding value of all if the above process is carried out reversibly.

Sol. $$W_{irr} = -P_{ext}[V_2 - V_1] = -1\left[\frac{nRT}{P_2} - \frac{nRT}{P_1}\right]$$

$$= -nRT\left[\frac{1}{P_2} - \frac{1}{P_1}\right] = -nRT\left[1 - \frac{P_2}{P_1}\right]$$

$$= -5 \times 8.314 \times 300\left(1 - \frac{1}{4}\right)$$

$W_{irr} = -9.353$ kJ

$W_{rev} = -2.303\ nRT\ 1\log\left(\frac{V_2}{V_1}\right)$

$W_{rev} = -2.303 \times 5 \times 8.314 \times 300 \log 4$

$W_{rev} = -17.29$ kJ

and $\Delta q = \Delta E - W$

at $\Delta T \rightarrow 0$ $\qquad \Delta E \rightarrow 0$ $\qquad \Delta H \rightarrow 0$

$W_{rev} = -q = 17.29$ kJ

6. 1 mole of CO_2 gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.

(a) What is final temperature?
(b) What is work done?
Given $\gamma = 1.33$ and $C_V = 25.08\ \text{J mol}^{-1}\ \text{K}^{-1}$ for CO_2.

Sol. $n_1 = 1$

$$T_1 = 300 \qquad V_2 = 27\ V_1 \qquad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$\left(\frac{T_1}{T_2}\right) = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \qquad T_2 = 300\left(\frac{1}{27}\right)^{\frac{1}{3}}$$

$T_2 = 100$ K

Adiabatic condition $q = 0 \Rightarrow \Delta E = W = nC_V(T_2 - T_1)$

$$W = 1 \times 25 \times -200 \qquad W = -5.000\ \text{kJ/mole}$$

7. A sample of a fluorocarbon was allowed to expand reversibly and adiabatically to twice its volume. In the expansion, the temperature dropped from 298.15 to 248.44 K. Assume the gas behaves perfectly. Estimate the value of C_V.

Sol. Process reversibly adiabatic

$\therefore$ TV^{γ} = constant

$$T_1 = 298.15\ \text{K} \qquad V_2 = 2V_1$$

$$T_2 = 248.44\ \text{K}$$

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$\left(\frac{T_1}{T_2}\right) = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \qquad \left(\frac{298.15}{248.44}\right) = 2^{\gamma-1}$$

$$1.2 = 2^{\gamma-1} \qquad \log 1.2 = \log 2 \cdot (\gamma-1)$$

$$\gamma - 1 = \frac{\log 1.2}{\log 2} \qquad \gamma - 1 = 0.263$$

$$W = nC_V(T_2 - T_1) = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{nR(T_2 - T_1)}{(\gamma - 1)}$$

$$C_V = \left(\frac{R}{\gamma - 1}\right)$$

$$C_V = \frac{8.314}{0.263} \qquad C_V = 31.61$$

8. Two moles of an ideal gas $\left(C_V = \frac{5}{2}R\right)$ was compressed adiabatically against constant pressure of 2 atm which was initially at 350 K and 1 atm pressure. The work involve in the process is equal to?
(a) 250 R (b) 300 R (c) 400 R (d) 500 R

Sol. (d) in irreversible process if final pressure not given means $P_{\text{ext}} = P_{\text{final}} = P_2$

Irreverssible adiabatic process

$$W = -P_{\text{ext}}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right) \qquad P_2 = P_{\text{ext}} = 2\ \text{atm}$$

$$P_1 = 1\ \text{atm} \qquad T_1 = 300\ \text{K}$$

$$W = -(2\ \text{atm})\left[\frac{2(R)\cdot T_2}{2\ \text{atm}} - \frac{2R(350)}{1\ \text{atm}}\right]$$

and $W = 2C_V(T_2 - 350) = 2 \times \frac{5}{2}R\,(T_2 - 350)$

$$5R(T_2 - 350) = (750R - 2RT_2)$$

$$5T_2 - 1750 = 1400 - 2T_2$$

$$7T_2 = 3150 \quad \therefore \quad T_2 = 450\ \text{K}$$

$$W = 2 \times C_V(450 - 350)$$

$$= 2 \times \frac{5}{2}R \times (100) = 500\ R$$

9. The standard enthalpy of formation of water liquid is –285.76 kJ at 298 K. Calculate the value at 373K. The molar heat capacities at constant pressure (C_P) in the given temperature range of $H_2(g)$, $O_2(g)$ and $H_2O(l)$ are respectively 38.83, 29.16 and 75.312 JK^{-1} mol^{-1}.

Sol. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

Use kirchoff equation $\dfrac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta rC_P$

$$\Delta_r C_P = C_{PH_2O(l)} - C_{PH_2(g)} - \frac{1}{2}C_{PO_2(g)}$$

$$= 75.312 - 38.83 - \frac{1}{2} \times 29.16$$

$$\Delta_r C_p = 21.90\ \text{kJ}$$

10. Methane (Considered to be an ideal gas) initially at 25°C and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molar heat capacity with absolute temperature is given by: $C_P = 22.34 + 48.1 \times 10^{-3}\ T$. where C_P is in JK^{-1} mol^{-1}. Calculate molar (a) ΔH (b) ΔU.

Sol. $C_P = 22.34 + 48.1 \times 10^{-3}\ T \qquad \text{JK}^{-1}\ \text{mol}^{-1}$

$$\Delta H = \int^{n=1} nC_p dT = \int_{T_1}^{T_2} (22.34 + 48.1 \times 10^{-3}T)$$

$$\Delta H = 22.34 \times 298 + \frac{48.1 \times 10^{-3} \times 298 \times 3}{2} \times 298$$

$$\Delta H = 13.064\ \text{kJ/mole}$$

$$W = -P(V_2 - V_1) = -nR(T_2 - T_1)$$

$$W = -2477\ \text{J} = -2.477\ \text{kJ}$$

$$\Delta E = 13.064 - 2.477$$

$$\Delta E = 10.587\ \text{kJ}$$

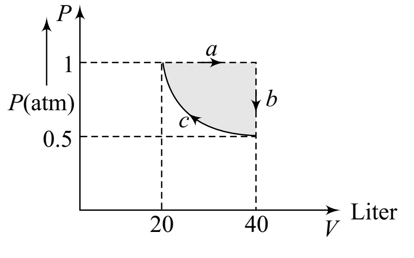
11. One mole of NaCl(s) on melting absorbed 30.5 kJ of heat and its entropy increased by 28.8 JK^{-1}. What is the melting point of sodium chloride?

Sol. $\Delta S_f = 28.8$ J/K $\qquad \Delta H_f = 30.5$ kJ

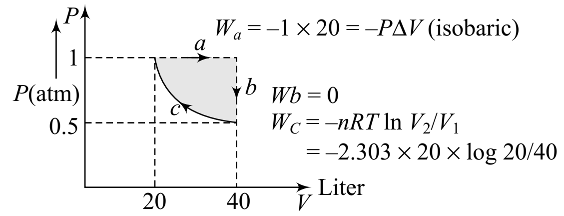
$$\Delta S_f = \frac{\Delta H_f}{T_{\text{mp}}}$$

$$\therefore \quad T_{\text{mp}} = \frac{30.5 \times 10^3}{28.8} = 1059\ \text{K}$$

12. Find W_a, W_b and W_c and total work from given graph



Sol.



$$PV = nRT$$

$$nT = \frac{PV}{R} = \frac{.5 \times 40}{R}$$

$$\therefore \quad W_C = -2.303R \times \frac{0.5 \times 40}{R} \log \frac{20}{40}$$

$$= +13.86 \text{ l-atm}$$

$\Delta E = \Delta H = \Delta S = \Delta G = 0$ for entire cycle

$$\Rightarrow \quad \Delta E = q + w$$

$$q = -w = W_T$$

$$R = 8.314 \text{ J/mol} - \text{K}$$

$$= 2 \text{ cal/mol} - \text{K}$$

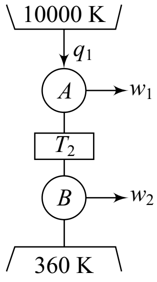
$$= 0.082 \frac{l - \text{atm}}{\text{mol} - \text{K}}$$

$$\Rightarrow \quad 1l - \text{atm} = 101.3 \text{ J} = \frac{101.3}{4.18} \text{Cal}$$

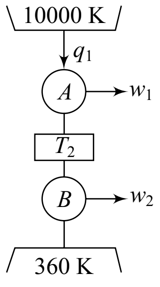
$$W_T = W_a + W_b + W_c \quad (l - \text{atm})$$

$$-20 + 13.86 = -6.14l - \text{atm}$$

13. From given figure, if $\eta_A = \eta_B$ find T_2



Sol. If



$$\eta_A = 1 - \frac{T_2}{10000}$$

$$\eta_B = 1 - \frac{360}{T_2}$$

If $\eta_A = \eta_B$

T_2 can be calculated as

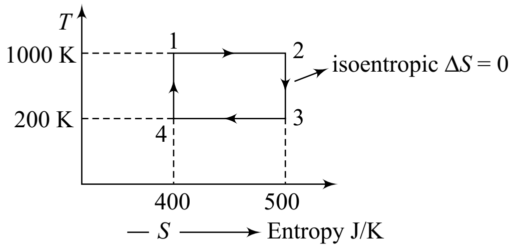
$$1 - \frac{T_2}{10000} = 1 - \frac{360}{T_2}$$

$$\frac{10000 - T_2}{10000} = \frac{T_2 - 360}{T_2}$$

$$10000T_2 - (T_2)^2 = 10000T_2 - 360 \times 10^4$$

$$T_2 = 1897.36 \text{ K} + (T_2)^2 = +360 \times 10^4$$

14. A Carnot cycle is plotted on the following T-S curve.



Calculate the following:

1. Heat absorbed from the source.
2. Heat released to the sink
3. Work done in one cycle
4. Efficiency of the cycle
5. How many cycles per second will be required to perform in order to illuminate 10^4 bulbs of 40 W each.

Sol. 1. $\Delta S = \frac{q_{\text{rev}}}{T}$

$$q_1 = \Delta S \times T_1 = 100 \times 1000 = 10^5 \text{ J}$$

2. $q_2 = \Delta S \times T_2 = -100 \times 200 = -0.2 \times 10^5$ J
3. $W = -0.8 \times 10^5 \text{ J} \Rightarrow q_1 = q_2 + W$
4. $\eta = \frac{W}{q_1} = \frac{0.8 \times 10^5}{10^5} \times 100 = 80\%$
5. Energy required per second = 40×10^4 J/sec

   $= (P \times t) \times$ No of bulb

   $\Rightarrow \quad 4 \times 10^4 = x \times 0.8 \times 10^5$

   $\Rightarrow \quad x = 5$ cycle sec^{-1}

15. The entropy change when two moles of ideal monoatomic gas is heated from 200°C to 300°C reversibly and isochorically?

(a) $\frac{3}{2}R \ln\left(\frac{300}{200}\right)$ (b) $\frac{5}{2}R \ln\left(\frac{573}{273}\right)$

(c) $3R \ln\left(\frac{573}{473}\right)$ (d) $\frac{3}{2}R \ln\left(\frac{573}{473}\right)$

Sol. (c) $\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right)$ for isochoric change.

$$\Delta S = 2 \times \left(\frac{3}{2}R\right) \ln\left(\frac{573}{473}\right)$$

$$\Delta S = 3R\left(\frac{573}{473}\right)$$

16. When two equal sized pieces of the same metal at different temperatures T_h (hot piece) and T_c (cold piece) are brought into thermal contact and isolated from its surrounding. The total change in entropy of system is given by? [C_v (J/K) = heat capacity of metal]

(a) $C_v \ln \dfrac{T_c + T_h}{2T_c}$ (b) $C_v \ln \dfrac{T_2}{T_1}$

(c) $C_v \ln \dfrac{(T_c + T_h)^2}{2T_h \cdot T_c}$ (d) $C_v \ln \dfrac{(T_c + T_h)^2}{4T_h \cdot T_c}$

Sol. **(d)** The net heat absorbed by hot and cold body is equal to zero.

$$q_h + q_c = 0$$

Let C_V is the total heat capacity of hot and cold body.

$$C_V(T_f - T_C) + C_V(T_f - T_h) = 0$$
$$= C_V T_f - C_V T_C + C_V T_f - C_V T_h$$
$$= 2C_V T_f = C_V[T_h + T_C]$$
$$\Rightarrow \quad T_f = \frac{T_h + T_C}{2}$$

Entropy change

$$\Delta S_{\text{Total}} = \Delta S_{\text{hot body}} + \Delta S_{\text{cold body}}$$
$$\Delta S_{\text{hot body}} = C_V \cdot \ln\left(\frac{T_f}{T_h}\right)$$
$$\Delta S_{\text{cold body}} = C_V \cdot \ln\left(\frac{T_f}{T_C}\right)$$
$$\Delta S_{\text{Total}} = C_V\left(\ln\frac{T_f}{T_h} + \ln\frac{T_f}{T_C}\right)$$
$$= C_V\left(\ln\frac{T_f^2}{T_h \cdot T_C}\right)$$
$$\Delta S_{\text{Total}} = C_V \ln\left[\frac{(T_f + T_C)^2}{4T_h \cdot T_C}\right]$$

OR

$$\Delta S_{\text{Total}} = \Delta S_{\text{I}} + \Delta S_{\text{II}}$$
$$= C_V \int_{Th}^{\frac{T_h+T_C}{2}} \frac{1}{T} dT + C_V \int_{T_C}^{\frac{T_h+T_C}{2}} \frac{1}{T} dT$$
$$= C_V\left[\ln\frac{\frac{T_h+T_C}{2}}{T_h} + \ln\frac{\frac{T_h+T_C}{2}}{T_C}\right]$$
$$= C_V\left[\ln\frac{\left(\frac{T_h+T_C}{2}\right)^2}{T_h \times T_C}\right]$$

17. For the reaction at 300 K

$$A(g) + B(g) \longrightarrow C(g)$$

$\Delta E = -3.0$ kcal; $\Delta S = -10.0$ cal/K value of ΔG is?

(a) –600 cal (b) –6600 cal

(c) –6000 cal (d) None

Sol. **(a)** $\Delta H = \Delta E + \Delta n_g RT$

$$= -3000 + [1 - 2] \times 2 \times 300$$
$$= -3600 \text{ cal}$$
$$\Delta G = \Delta H - T\Delta S = -3600 - 300 \times (-10)$$
$$= -600 \text{ cal}$$

18. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure?

(a) 80 cal (b) 540 cal (c) 620 cal (d) zero

Sol. **(d)** $H_2O(l) \longrightarrow H_2O(g)$

373 K 373 K

1 atm 1 atm

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T}$$
$$\Delta G = \Delta H_f - \Delta H_i = 0$$

19. If $PH_3(g) \longrightarrow P(g) + 3H(g)$ $\Delta H = 954$ kJ

$P_2H_4(g) \longrightarrow 2P(g) + 4H(g)$ $\Delta H = 1485$ kJ

find P-*P* bond energy

Sol. $E_{\text{P–H}} = \dfrac{954}{3} = 318$ KJ

because in PH_3(g) 3P-H bond present

$$E_{P-P} + 4 \times 318 = 1485 = E_{P-P} + 4E_{P-H}$$
$$E_{P-P} = 1485 - 1272$$
$$= 213 \text{ kJ}$$

20. Compute Δ_rG for the reaction

H_2O (l, 1 atm, 323 K) → H_2O (g, 1 atm, 323 K)

Given that Δ_{vap}H at 373 K = 40.639 kJ mol^{-1}, $C_P(H_2O$, l) = 75.312 J K^{-1} mol^{-1},

$C_P(H_2O$, g) = 33.305 J K^{-1} mol^{-1}.

Sol. $\Delta_r C_p = 33.305 - 75.312 = -42.007$ J/K mole

$$\Delta_r S_{323} = \frac{\Delta H}{T} = \frac{40639}{323} = 108.95 \text{ J/K mole}$$
$$d(\Delta_r S) = \frac{\Delta_r C_p dT}{T}$$
$$\Delta_r S_{373} - \Delta_r S_{323} = \Delta_r C_p \ln\frac{T_2}{T_1}$$
$$\Delta_r S_{373} = 108.95 - \left(-42.007 \ln\frac{373}{323}\right)$$
$$= 115 \text{ J/K mole}$$
$$d(\Delta_r H) = \Delta_r C_p dT$$
$$\Delta_r H_{373} - \Delta_r H_{323} = -42.007\ (50)$$
$$\Delta_r H_{373} = 42739.35 \text{ J/mole}$$
$$\Delta_r G_{323} = 42739.35 - 323\ (115)$$
$$= 5594.35 \text{ J} = 5.59 \text{ kJ/mole}$$

21. Enthalpy of neutralisation of HCl by NaOH is –57.32 kJ mol^{-1} and by NH_4OH is –51.34 kJ mol^{-1}. Calculate the enthalpy of dissociation of NH_4OH.

Sol. See $\Delta H_{\text{neutralization}}$ case of weak acid and weak base.

$$\Delta H_{\text{neut}} = -[57.34 - (x + y)] \quad \begin{bmatrix} x = 0 \text{ for strong acid} \\ y = 0 \text{ for strong base} \end{bmatrix}$$
$$-51.32 = -57.34 + y$$
$$y = 5.98 \text{ kJ mol}^{-1}$$

OR

$$H^+(aq) + NH_4OH(aq) \rightarrow NH_4^+(aq) + H_2O(l)$$
$$\Delta_r H = -51.34 \text{ kJ mol}^{-1}$$

we may consider neutralisation in two steps:

(i) ionisation

$$NH_4OH(aq) \rightarrow NH_4^+(aq) + OH^-(aq)\ \Delta_r H_1?$$

(ii) neutralisation

$H^+ (aq) + OH^-(aq) \rightarrow H_2O(l)$

$$\Delta_rH_2 = -57.32 \text{ kJ mol}^{-1}$$

Thus, $\Delta_rH = \Delta_rH_1 + \Delta_rH_2$

Therefore,

$$\Delta_rH_1 = \Delta_rH - \Delta_rH_2$$
$$= -51.34 + 57.32 = 5.98 \text{ kJ/mol}^{-1}$$

22. Calculate $\Delta_rH°$ for the reaction

$Ag^+(aq) + Cl^-(aq) = AgCl\ (s)$ at 25°C.

Given:

$\Delta_fH° (Ag^+, aq) = 105.58 \text{ kJ mol}^{-1}$,

$\Delta_fH° (Cl^-, aq) = -167.16 \text{ kJ mol}^{-1}$ and

$\Delta_fH° (AgCl, s) = -127.07 \text{ kJ mol}^{-1}$

Sol. For the reaction

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

we have,

$$\Delta_rH° = \Delta_fH° (AgCl, s) - \Delta_fH° (Ag^+, aq) - \Delta_fH° (Cl^-, aq)$$
$$= [-127.07 - 105.58 - (-167.16)]$$
$$= -65.49 \text{ kJ mol}^{-1}$$

23. The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are –2839.2, –2275.2 and –5536 kJ mol^{-1} respectively. Calculate the resonance energy of benzene, compared with Kekule structure. The bond enthalpy of C – H bond is given as equal to 410.87 kJ mol^{-1}.

Sol. Bond enthalpy of *C – C* bond

= Enthalpy required to break C_2H_6 into gaseous atoms –6 × bond enthalpy of C – H bond

$= 2839.2 \text{ kJ mol}^{-1} - 6 \times 410.87 \text{ kJ mol}^{-1}$

$= 373.98 \text{ kJ mol}^{-1}$

Bond enthalpy of C = C bond = Enthalpy requried to break C_2H_4 into gaseous atoms –4 × bond enthalpy of C – H bond

$= 2275.2 \text{ kJ mol}^{-1} - 4 \times 410.87 \text{ kJ mol}^{-1}$

$= 631.72 \text{ kJ mol}^{-1}$

For the formation of benzene having Kekule structure, we have to form 3 C – C bonds, 3 C = C bonds and 6 C – H bonds for which enthalpy released is

$[3(-373.98) + 3(-631.72) + 6(-410.87)]$

$= -5482.32 \text{ kJ mol}^{-1}$

But the given value of Δ_fH is

Δ_fH (actual) $= -5536 \text{ kJ mol}^{-1}$

Hence resonance energy compared to Kekule structure

$= \Delta_fH$ (actual) – Δ_fH (Kekule structure)

$= (-5536 + 5482.32)$

$= -53.68 \text{ kJ mol}^{-1}$

24. Using bond enthalpy data given below, estimate enthalpy of formation of acetic acid.

Bond	Bond enthalpies
C – H	413.38 kJ mol^{-1}
C – C	347.69 kJ mol^{-1}
C = O	728.02 kJ mol^{-1}
C – O	351.46 kJ mol^{-1}
O – H	462.75 kJ mol^{-1}

Enthalpy of atomisation

C	718.39 kJ atom^{-1}
H	217.94 kJ atom^{-1}
O	247.52 kJ atom^{-1}

The observed $\Delta_fH°$ for acetic acid is –438.15 kJ mol^{-1}. Compute the resonance energy of acetic acid.

Sol. The desired reaction for the formation of CH_3COOH is

$2C(s) + 2H_2(g) + O_2(g) \rightarrow CH_3COOH(l)$

$\Delta_rH° = -3 \times 413.38 - 1 \times 347.69 - 728.02 - 351.46 - 462.75 + 2 \times 718.39 + 4 \times 217.94 + 2 \times 247.52$

$= -326.48 \text{ kJ mol}^{-1}$

Resonance energy $= \Delta H°_{observed} - \Delta H°_{theoretical}$

$= -438.15 + 326.48$

$= -111.67 \text{ kJ mol}^{-1}$

25. A gas mixture 3.67 L in volume contain C_2H_4 and CH_4 is proportion of 2: 1 by moles and is at 25°C and 1 atm. If the ΔH_C (C_2H_4) and ΔH_C (CH_4) are –1400 and –900 kJ/mol find heat evolved on burning this mixture:

(a) 20.91 kJ (b) 50.88 kJ
(c) 185 kJ (d) 160 kJ

Sol. (c) $n_{C_2H_4} = \dfrac{PV}{RT}$

$$V_{C_2H_4} = \frac{2}{3} \times 3.67 \qquad V_{CH_4} = \frac{1}{3} \times 3.67$$

$$n_{C_2H_4} = \frac{1 \times 2 \times 3.67}{0.082 \times 3 \times 298} \qquad n_{CH_4} = \frac{3.67}{3 \times 0.082 \times 298}$$

$$\text{Heat evolved} = \frac{2 \times 3.67}{3 \times 0.082 \times 298} \times (1400)$$

$$\text{Heat evolved} = \frac{3.67}{3 \times 0.082 \times 298} \times 900$$

Total heat evolved from mixture = 140 + 45 = 185 kJ

26. The bond dissociation energy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. The enthalpy of formation for HCl gas will be

(a) –44.0 kcal (b) –22.0 kcal
(c) 22.0 kcal (d) 44.0 kcal

Sol. (b) $\dfrac{1}{2}H_2 + \dfrac{1}{2}Cl_2 \longrightarrow HCl$

$(\Delta H_f)_{HCl} = 52 + 29 - 103 = -22$ kcal

27. Determine $\Delta H°$ of the following reaction using the listed heats of formation:

$4HNO_3(l) + P_4O_{10}(s) \rightarrow 2N_2O_5(s) + 4HPO_3(s)$

$\Delta H°_f\ HNO_3(l) = -174.1$ kJ/mole

$\Delta H°_f\ N_2O_5(s) = -43.1$ kJ/mole

$\Delta H°_f\ P_4O_{10}(s) = -2984.0$ kJ/mole

$\Delta H°_f\ HPO_3(s) = -948.5$ kJ/mole

(a) –176.3 (b) –199.8

(c) +276.2 (d) –242.4

Sol. **(b)** $\Delta_r H = [2(\Delta H_f)_{N_2O_5} + 4(\Delta H_f)_{HPO_3} - 4(\Delta H_f)_{HNO_3} - (\Delta H_f)_{P_4O_{10}}]$

$\Delta H_r = [2(-43.1) + 4(-948.5) - 4(-174.1) - (-2984.0)]$
$= -199.8$

28. Use the given bond enthalpy data to estimate the ΔH^o (kJ) for the following reaction:
($C - H = 414$ kJ, $H - Cl = 431$ kJ, $Cl - Cl = 243$ kJ, $C - Cl = 331$ kJ).

$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(g) + 4HCl(g)$

(a) 620 (b) 330 (c) 420 (d) 105

Sol. **(c)** $\Delta_r H^o = \Sigma(BDE)_R - \Sigma(BDE)_P$

$\Delta_r H^o = [4\Delta H_{C\text{-}H} + 4\Delta H_{Cl\text{-}Cl} - 4\Delta H_{C\text{-}Cl} - 4\Delta H_{H\text{-}Cl}]$

$= [4 \times 414 + 4 \times 243 - 4 \times 331 - 4 \times 43]$

$\Delta_r H^o = -420$ kJ

29. For which of the following change $\Delta H \neq \Delta E$?

(a) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$

(b) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

(c) $C(s) + O_2(g) \longrightarrow CO_2(g)$

(d) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Sol. **(d)** Since, $\Delta H = \Delta E + \Delta n_g RT$

For $\Delta n_g = 0,$ $\Delta H = \Delta E$

$\Delta n_g \neq 0,$ $\Delta H \neq \Delta E$

30. 4 grams of sodium hydroxide pellets were dissolved in 100 cm^3 of water. The temperature before adding the sodium hydroxide pellets was 25°C, and after adding the pellets it was 35°C. Calculate the enthalpy change in kJ/mole of the reaction (Specific heat capacity of water = 4.2 J/K/g)

(a) 42 kJ/mole (b) 4.2 kJ/mole

(c) 4200 kJ/mole (d) none

Sol. **(a)** Heat evolve $= mC_V\Delta T = 100 \times 4.2 \times 10 = 4.2$ kJ
for 0.1 mole the enthalpy change = 4.2 kJ
for 1 mole the enthalpy change = 42 kJ

Exercise

LEVEL I

1. What is the change in internal energy ΔU, for a system that does 70 J of work as it absorbs 45 J of heat?

(a) 115 J (b) 25 J (c) –25 J (d) –115 J

2. If the internal energy of an ideal gas decreases by the same amount as the work done by the system, the process is

(a) cyclic (b) isothermal

(c) adiabatic (d) isolated

3. When 1 mol gas is heated at constant volume, temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which of the following statements is correct?

(a) $q = W = 500$ J, $\Delta U = 0$

(b) $q = \Delta U = 500$ J, $W = 0$

(c) $q = W = 500$ J, $\Delta U = 0$

(d) $\Delta U = 0, q = W = -500$ J,

4. Internal energy does not include

(a) vibrational energy

(b) rotational energy

(c) nuclear energy

(d) energy arising by gravitational pull

5. Which one of the following quantity is dependent on path?

(a) molar internal energy

(b) volume

(c) w

(d) $q + w$

6. For a monatomic gas, the value of the ratio of $C_{p.m}$ and $C_{v.m}$ is

(a) $\frac{5}{3}$ (b) $\frac{7}{5}$ (c) $\frac{9}{7}$ (d) $\frac{9}{11}$

7. Two moles of an ideal monoatomic gas are allowed to expand adiabatically and reversibly from 300 K and 200 K. The work done in the system is ($C_v = 12.5$ J/K/mol)

(a) –12.5 kJ (b) –2.5 kJ

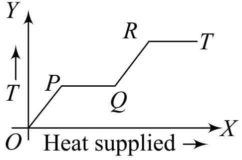
(c) –6.25 kJ (d) 500 kJ

8. The difference between heats of reaction at constatnt pressure and constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25° in kJ mol^{-1} is:

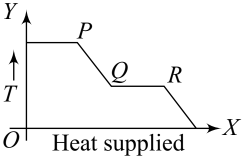
(a) –7.43 (b) +3.72 (c) –3.72 (d) +7.43

9. A block of ice at –10°C is slowly heated and converted into steam at 100°C. Which of the following curves represents the phenomenon qualitatively?

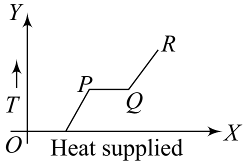
(a)



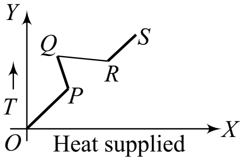
(b)



(c)



(d)



10. If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at

1 bar and 100°C is 41kJ mol^{-1}. Calculate the internal energy change, when 1 mol of water is vapourised at 1 bar pressure and 100°C.

(a) 37.904 kJ mol^{-1} (b) 41.00 kJ mol^{-1}
(c) 44.00 kJ mol^{-1} (d) 39.67 kJ mol^{-1}

11. The reaction of Cyanamide, $NH_2CN(s)$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate the enthalpy change for the reaction at 298 K.

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

(a) –702.5 (b) –741.5 (c) 523 (d) –523

12. Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminum from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

(a) 0.09 kJ (b) 2.71 kJ
(c) 1.09 kJ (d) –2.07 kJ

13. Which of the following has maximum internal energy at 298 K?

(a) Helium gas (b) Oxygen gas
(c) Ozone gas (d) Equal

14. 0.410 mol of a monoatomic gas fills a $1 dm^3$ container to a pressure of 1.013 MPa. It is expanded reversibly and adiabatically until a pressure of 0.1013 MPa is reached. Which is correct?

(a) $T_2 = 421.28$ K (b) $W = -923.7$ J
(c) $T_2 = 280$ K (d) $W = -12$ J

15. Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

(a) –397kJ (b) –315 kJ
(c) +207 kJ (d) –105 kJ

16. Given: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta rH° = -92.4$ kJ mol^{-1}

What is the standard enthalpy of formation of NH_3 gas?

(a) –11.7 (b) –46.2 (c) 32.5 (d) –52.3

17. The equilibrium constant for a reaction is 10. What will be the value of ΔG°?

($R = 8.314$ JK^{-1} mol^{-1}, $T = 300$ K)

(a) –1.24 kJ/mol (b) –5.744 kJ/mol
(c) +1.27 kJ/mol (d) –1.27 kJ /mol

18. ΔH_{vap} for water is 40.73 kJ mol^{-1} and ΔS_{vap} is 109 JK^{-1} mol^{-1}. The temperature at which water is in equilibrium with water vapours is

(a) 100.67°C (b) 260.87 K
(c) 128.69 K (d) 460 K

19. Molar heat capacity of water in equilibrium with ice at constant pressure is

(a) Zero (b) Infinity
(c) 40.45 kJ K^{-1} mol^{-1} (d) 75.48 kJ K^{-1} mol^{-1}

20. A vessel contains 100 L of a liquid *x*. Heat is supplied to the liquid in such a fashion that, Heat given = change in enthalpy. The volume of the liquid increases by 2 L. If the external pressure is one atm, and 202.6 J of heat were supplied then, [$U \rightarrow$ total internal energy] 1 atm L = 101.3 J

(a) $\Delta U = 0$, $\Delta H = 0$
(b) $\Delta U = +202.6$ J, $\Delta H = +202.6$ J
(c) $\Delta U = -202.6$ J, $\Delta H = -202.6$ J
(d) $\Delta U = 0$, $\Delta H = +202.6$ J

21. 1 mole of an ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in J K^{-1} mol^{-1}).

(a) 19.15 (b) –19.15 (c) 4.7 (d) Zero

22. What is the heat of formation of CS_2, if heat of combustion of C, S and CS_2 are “*x*, *y* and *z*” kJ mol^{-1}?

(a) $2y - x + z$ (b) $x - 2y + z$
(c) $x + 2y - z$ (d) $x + y + z$

23. The amount of heat released when 100 mL of $\frac{N}{10} H_2SO_4$ is mixed with 150 mL of $\frac{N}{10}$ NaOH solution is

(a) 5.73 kJ (b) 57.3 kJ (c) 57.3 J (d) 573 J

24. A sample of oxygen gas expands its volume from 3 L to 5 litre against a constant pressure of 3 atm. If the work done during expansion be used to heat 10 mole of water initially present at 290 K, its final temperature will be

(a) 296.0 K (b) 290.8 K
(c) 298.0 K (d) 285 K

25. Using the following information calculate the heat of formation of NaOH in kJ mol^{-1}.

$2\ Na(s) + 2\ H_2O(l) \rightarrow 2\ NaOH(s) + H_2(g)$
$\Delta H° = -\ 281.9$ kJ
$\Delta H°_f\ H_2O(l) = -285.8$ kJ/mole

(a) – 141.6 (b) – 712.6
(c) – 426.8 (d) – 650.4

26. A monoatomic gas X and a diatomic gas Y, both initially at the same temperature and pressure are compresed adiabatically from a volume V to V/2, which gas will be at higher temperature?

(a) X (b) Y
(c) Both are same (d) Cannot say

27. Heat of neutralisation of oxalic acid is –53.35 kJ mol^{-1} using NaOH. Hence ΔH of $H_2C_2O_4 \rightleftharpoons C_2O_4^{2-} + 2H^+$

(a) 5.88 kJ (b) –5.88 kJ
(c) –13.7 kcal (d) 7.9 kJ

28. The standard heat of formation values of $SF_6(g)$, S(g) and F(g) are –1100, 275 and 80 kJ mol^{-1}: respectively. Then the average S — F bond energy in SF_6 is

(a) 52.5 kJ mol^{-1} (b) 320 kJ mol^{-1}
(c) 309 kJ mol^{-1} (d) 280 kJ mol^{-1}

29. One mole of an ideal diatomic gas ($C_V = 5$ cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. The entropy change of the process can be expressed as ($R = 2$ calories/mol/K):

(a) $3 \ln \frac{298}{373} + 2 \ln 10$ (b) $5 \ln \frac{373}{298} + 2 \ln 10$

(c) $7 \ln \frac{373}{298} + 2 \ln$ (d) $5 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$

30. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state, is $\Delta H = -401.7$ J mol^{-1} for the transition. Assume the surrounding to be an ice-water both at 0°C.
(a) -1.09 JK^{-1} (b) 1.47 JK^{-1}
(c) 0.38 JK^{-1} (d) None of these

31. The maximum efficiency of a heat engine operating between 100°C and 25°C is
(a) 20% (b) 22.2% (c) 25% (d) None

32. A heat engine operating between 227°C and 27°C absorbs 2 kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is?
(a) 0.4 kcal (b) 0.8 kcal (c) 4 kcal (d) 8 kcal

33. At a particular temperature
$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$; $\Delta H = -57.1$ kJ. The approximate heat evolved when 400 mL of 0.2 M H_2SO_4 is mixed with 600 mL of 0.1 M KOH solution will be
(a) 3.426 kJ (b) 13.7 kJ
(c) 5.2 kJ (d) 55 kJ

34. When a monoatomic gas undergoes an adiabatic process, its temperature and volume are related by the equation TV^n = constant, the value of n will be
(a) 1.33 (b) 0.33 (c) 2.33 (d) 1

35. Molar heat capacity of water at constant pressure P is 75 J K^{-1}. When 1 kJ of heat is supplied to 100 g of water which is free to expand, the increasing temperature of water is
(a) 1.2 K (b) 2.4 K (c) 4.4 K (d) 6.6 K

36. The $\Delta_r H^\circ$ for $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is

$\Delta H_f\, CO_2(g) = -393.5$ kJ mol^{-1}

$\Delta H_f\, CO(g) = -110.5$ kJ mol^{-1}

$\Delta H_f\, H_2O(g) = -241.8$ kJ mol^{-1}

(a) $+524.1$ kJ mol^{-1} (b) $+41.2$ kJ mol^{-1}
(c) -262.5 kJ mol^{-1} (d) -41.2 kJ mol^{-1}

37. One mole of ice is converted into water at 273 K. The entropies of $H_2O(s)$ and $H_2O(l)$ are 38.20 and 60.01 J mol^{-1} K^{-1} respectively. The enthalpy change for the conversion is
(a) 59.54 J mol^{-1} (b) 5954 J mol^{-1}
(c) 594.5 J mol^{-1} (d) 320.6 J mol^{-1}

38. An ideal gas expands in volume from 10^{-3} m^3 to 10^{-2} m^3 at 300 K against a constant pressure of 10^5 N m^{-2}. The work done is
(a) 900 kJ (b) -900 kJ (c) 270 kJ (d) -900 J

39. For a reversible process at $T = 300$ K, the volume of 2 moles of ideal gas is increased from 1 L to 10 L, the ΔH for isothermal change is
(a) 11.47 J (b) 4.98 kJ (c) 0 (d) 11.47 kJ

40. Enthalpies of formation of CO(g), $CO_2(g)$, $N_2O(g)$ and $N_2O_4(g)$ are -110, -393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:

$$N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$$

(a) -778 kJ (b) -573 kJ (c) -105 kJ (d) $+877$ kJ

41. Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l);$$

$$\Delta_r H^\circ = -726 \text{ kJ mol}^{-1} \quad (1)$$

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g);\ \Delta H_f^\circ = -393 \text{ kJ mol}^{-1} \quad (2)$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\ \Delta H_f^\circ = -286 \text{ kJ mol}^{-1} \quad (3)$$

(a) -239 kJ mol^{-1} (b) -127 kJ mol^{-1}
(c) $+57$ kJ mol^{-1} (d) -55 kJ mol^{-1}

42. For the reaction,

$$2A(g) + B(g) \rightarrow 2D(g)$$

$$\Delta U^\circ = -10.5 \text{ kJ and } \Delta S^\circ = -44.1 \text{ JK}^{-1}$$

Calculate ΔG° for the reaction at 300 K.
(a) 0.164 kJ (b) 0.236 kJ
(c) 0.017 kJ (d) 0.0019 kJ

43. Calculate $\Delta_r G^\circ$ for conversion of oxygen to ozone, $3/2O_2(g) \rightleftharpoons O_3(g)$ at 298 K. If K_P for this conversion is 2.47×10^{-29}.
(a) 152 kJ mol^{-1} (b) 163 kJ mol^{-1}
(c) 121 kJ mol^{-1} (d) 174 kJ mol^{-1}

44. For the gas - phase decomposition,

$$PCl_5(g) \overset{\Delta}{\rightleftharpoons} PCl_3(g) + Cl_2(g):$$

(a) $\Delta H < 0, \Delta S < 0$ (b) $\Delta H > 0, \Delta S > 0$
(c) $\Delta H > 0, \Delta S < 0$ (d) $\Delta H < 0, \Delta S > 0$

45. A reaction has ΔH = -33 kJ and ΔS = -58 J/K. This reaction would be
(a) spontaneous at all temperature
(b) non-spontaneous at all temperature
(c) spontaneous above a certain temperature only
(d) spontaneous below a certain temperature only

46. Calculate the work obtained in 1000 cycles of a reversible engine operating between 1000 K and 300 K if heat absorbed at the higher temperature is 2.1 kJ $cycle^{-1}$. If this engine operates in the reverse direction, how much of work is needed to transfer 2.1 kJ of heat from the sink (300 K)?
(a) 1.470 kJ (b) 4.9 kJ
(c) 10.8 kJ (d) 62 kJ

47. For the given heat of reaction,
(i) $C(s) + O_2(g) \longrightarrow CO_2(g) + 97$ kcal
(ii) $CO_2(g) + C(s) \longrightarrow 2CO(g) - 39$ kcal
The heat of combustion of CO(g) is
(a) 68 kcal (b) -68 kcal
(c) $+48$ kcal (d) -48 kcal

48. The heat of combustion of sucrose, ($C_{12}H_{22}O_{11}(s)$) at constant volume is -1348.9 kcal mol^{-1} at 25°C, then the heat of reaction at constant pressure, when steam is produced, is
(a) -1348.9 kcal (b) $+1342.344$ kcal
(c) $+1250$ kcal (d) -1250 kcal

49. For the given reaction

$$H_2(g) + F_2(g) \longrightarrow 2HF(g) \quad \Delta H^\circ = -124 \text{ kcal}$$

$H_2(g) \longrightarrow 2H(g) \Delta H° = 104$ kcal

$F_2(g) \longrightarrow 2F(g)\ \Delta H° = 37.8$ kcal

then the value of ΔH° for
$H(g) + F(g) \longrightarrow HF(g)$ is

(a) 142 kcal (b) –132.9 kcal
(c) 132 kcal (d) 134 kcal

50. At constant temperature and pressure which one of the following statements is correct for the reaction?

$CO(g) + 1/2O_2(g) \longrightarrow CO_2(g)$

(a) $\Delta H = \Delta E$
(b) $\Delta H < \Delta E$
(c) $\Delta H > \Delta E$
(d) ΔH is independent physical state of reactant

51. The heats of combustion of yellow phosphorus and red phosphorous are –9.19 kJ an –8.78 kJ respectively, then heat of transition of yellow phosphorous to red phosphorous is

(a) –17.97 kJ (b) +0.41 kJ
(c) +17.97 kJ (d) –0.41 kJ

52. For the reaction,
$C_7H_8(l) + 9O_2(g) \rightarrow 7CO_2(g) + 4H_2O(l)$, the calculated heat of reaction is 232 kJ/mol and observed heat of reaction is 50.4 kJ/mol, then the resonance energy is

(a) –182.2 kJ/mol (b) +182.2 kJ/mol
(c) 172 kJ/mol (d) –172 kJ/mol

53. The heat of transition for $C_{Diamond} \rightarrow C_{Amorphus}$ from the following is

$C_{Diamond} + O_2(g) \longrightarrow CO_2(g)$ ΔH = –94.3 kcal
$C_{Amorphus} + O_2(g) \longrightarrow CO_2(g)$ ΔH = –97.6 kcal

(a) 3.3 kJ/mol (b) 3.3 kcal/mol
(c) –3.3 kJ/mol (d) –3.3 kcal/mol

54. The heat of neutralisation of HCl by NaOH is –55.9 kJmol^{-1}. If the heat of neutralisation of HCN by NaOH is –12.1 kJ/mol, the energy of dissociation of HCN is

(a) –43.8 kJ (b) 43.8 kJ
(c) 68 kJ (d) –68 kJ

55. Heat of neutralisation of a strong acid by a strong base is equal to ΔH of

(a) $H^+ + OH^- \rightarrow H_2O$
(b) $H_2O + H^+ \rightarrow H_3O^+$
(c) $2H_2O + O_2 = 2H_2O$
(d) $CH_3COOH + NaOH = CH_3COONa + H_2O$

56. For which change ΔH ≠ ΔE?

(a) Sucrose + $H_2O(l) \rightleftharpoons$ glucose + fructose
(b) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$
(c) $C(s) + O_2(g) \rightarrow CO_2(g)$
(d) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

57. The amount of heat evolved when one mole of H_2SO_4 reacts with two mole of NaOH is

(a) 13.7 kcal (b) Less than 13.7 kcal
(c) More than 13.7 kcal (d) Cannot say

58. The heats of neutralisation of four acids A, B, C, D are –13.7, –9.4, –11.2 and –12.4 kcal respectively when they are neutralised by a common base. The acidic character obeys which of the following order?

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

59. In C_2H_4 energy of formation of (C + C) and (C – C) are –145 kJ/mol and –80 kJ/mol respectively. What is the enthalpy change when ethylene polymerises to form polythene?

(a) +650 kJ/mol (b) +65 kJ/mol
(c) –650 kJ/mol (d) –65 kJ/mol

60. For the reaction shown, which is closest to the value of ΔH?

$2Cr^{+3}(aq) + 3Ni(s) \rightarrow 2Cr(s) + 3Ni^{+2}(aq)$

ΔH_f^0 of $Cr^{+3}_{(aq)}$ and $Ni^{+2}_{(aq)}$ are –143 and –54 kJ/mol

(a) 124 kJ (b) 89 kJ
(c) –89 kJ (d) –124 kJ

61. If bond enthalipies of N ≡ N, H–H and N–H are *x*, *y* and *z* kJ/mol respectively. Then enthalpy of formation of NH_3 is

(a) $x + 3y - 6z$ (b) $\frac{x}{2} + \frac{3y}{2} - 3z$
(c) $3z - \frac{x}{2} - \frac{3y}{2}$ (d) $6z - x^2 - 3y$

62. When a certain amount of ethylene was burnt 6226 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ, the volume of air (at NTP) that entered in the reaction is

(a) 296.5 litre (b) 1482.5 litre
(c) 6226 × 22.4 L (d) 22.4 L

63. If, $H_2(g) + Cl_2(g) \rightarrow 2HCl$; $\Delta H° = -44$ kcal
$2Na(s) + 2HCl(g) \rightarrow 2NaCl(s) + H_2(g)$;
$\Delta H = -152$ kcal
then, ΔH for $2Na + Cl_2 \longrightarrow 2NaCl$ is

(a) 108 kcal (b) –196 kcal
(c) –98 kcal (d) 54 kcal

64. Use the given standard enthalpies of formation to determine the heat of reaction of the following reaction:

$TiCl_4(g) + 2H_2O(g) \rightarrow TiO_2(g) + 4HCl(g)$

$\Delta H°_f TiCl_4(g) = -763.2$ kJ/mole

$\Delta H°_f TiO_2(g) = -944.7$ kJ/mole

$\Delta H°_f H_2O(g) = -241.8$ kJ/mole

$\Delta H°_f HCl(g) = -92.3$ kJ/mole

(a) –278.1 (b) +369.2 (c) +67.1 (d) –67.1

65. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are –394 kJ/mole and –285.8 kJ/mole respectively. Using the data for the following combustion reaction, calculate the heat of formation of $C_3H_8(g)$.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
$\Delta H° = -2221.6$ kJ

(a) 212.2 (b) –143.3 (c) 185.4 (d) –103.6

66. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are –394 kJ/mole and –285.8 kJ/mole respectively. Using the data for the following combustion reaction, calculate the heat of formation of $C_2H_2(g)$ in kJ mol^{-1}.

$$2\,C_2H_2(g) + 5\,O_2(g) \rightarrow 4\,CO_2(g) + 2\,H_2O(l)$$

$$\Delta H^o = -2601 \text{ kJ}$$

(a) –238.6 (b) 253.2 (c) 238.7 (d) 226.7

LEVEL II

1. Given that
$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$, $\Delta H = -115.4$ kcal, the bond energy of H - H and O = O bond respectively is 104 kcal and 119 kcal, then the O – H bond energy in water vapour is

(a) 110.6 kcal/mol (b) – 110.6 kcal
(c) 105 kcal/mol (d) – 105 kcal

2. The piece of zinc at a temperature of 20.0°C weighing 65.38 g is dropped into 180 g of boiling water (T = 100°C). The specific heat of zinc is 0.400 J g^{-1} °C^{-1} and that of water is 4.20 J g^{-1} °C^{-1}. What is the final common temperature reached by both the zinc and water?

(a) 97.3°C (b) 33.4°C
(c) 80.1°C (d) 60.0°C

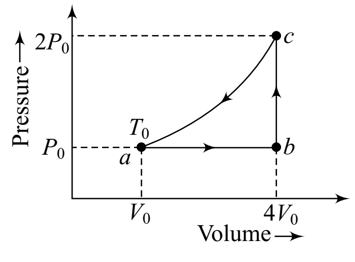
3. How much heat, in joules, must be added to 0.250 mol of Ar(g) to raise its temperature from 20°C to 36.0°C at constant pressure?

(a) 50.0 (b) 83.2 (c) 187 (d) 200

4. In thermodynamics, a process is called reversible when

(a) surroundings and system change into each other.
(b) there is no boundary between system and surroundings.
(c) the surrounding are always in equilibrium with the system.
(d) the system changes into the surroundings spontaneously.

5. One mole of an ideal monoatomic gas is caused to go through the cycle as shown in figure. Then the change in the internal energy in expanding the gas from a to c along the path abc is



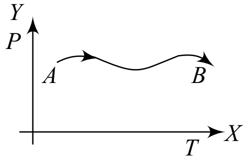
(a) $3P_0V_0$ (b) $6RT_0$
(c) $4.5RT_0$ (d) $10.5RT_0$

6. One mole of an ideal monoatomic gas at temperature T and volume 1 L expands to 2 L against a constant external pressure of one atm under adiabatic conditions, then final temperature of gas will be

(a) $T + \dfrac{2}{3 \times 0.0821}$ (b) $T - \dfrac{2}{3 \times 0.0821}$

(c) $\dfrac{T}{2^{5/3-1}}$ (d) $\dfrac{T}{2^{5/3+1}}$

7. The P–T graph as given below was observed for a process of an ideal gas, which of the following statement is true?



(a) w = +ve, ΔH = +ve (b) w = –ve, ΔH = –ve
(c) w = –ve, ΔH = +ve (d) w = +ve, ΔH = –ve

8. How much energy must be supplied to change 36 g of ice at 0°C to water at room temperature 25°C. Data for water, H_2O $\Delta H^o_{\text{fusion}} = 6.01$ kJ $mol^{-1}C_{p.\text{liquid}} = 4.18$ $J.K^{-1}$ g^{-1}

(a) 12 kJ (b) 15.78 kJ (c) 19 kJ (d) 16 kJ

9. One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is
(R = 0.082 L atm mol^{-1} K^{-1} = 8.3 mol^{-1} K^{-1})

(a) 0 (b) Rln(24.6)
(c) Rln (2490) (d) Rln(24.6)

10. The enthalpy change for a given reaction at 298 K is $-x$ J mol^{-1} (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature

(a) can be negative but numerically larger than $\dfrac{x}{298}$.
(b) can be negative but numerically smaller than $\dfrac{x}{298}$.
(c) cannot be negative.
(d) cannot be positive.

11. If ΔG = –177 K cal for reaction (1)

$$2Fe(s) + \frac{3}{2}O_2\,(g) \longrightarrow Fe_2O_3(s)$$

and ΔG = –19 K cal for reaction (2)

$$4Fe_2O_3(s) + Fe(s) \longrightarrow 3Fe_3O_4(s)$$

What is the Gibbs free energy of formation of Fe_3O_4?

(a) $+\,229.6\dfrac{\text{k cal}}{\text{mol}}$ (b) $-242.3\dfrac{\text{k cal}}{\text{mol}}$

(c) $-727\dfrac{\text{k cal}}{\text{mol}}$ (d) $-229.6\dfrac{\text{k cal}}{\text{mol}}$

12. Given the following data:

Substance	**ΔH°_f (kJ/mol)**	**S° (J/mol K)**
FeO (s)	–266.3	57.49
C(Graphite)	0	5.74
Fe(s)	0	27.28
CO(g)	–110.5	197.6

Determine at what temperature the following reaction is spontaneous?

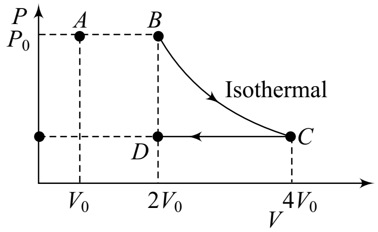
$FeO(s) + C(graphite) \longrightarrow Fe(s) + CO(g)$

(a) 298 K
(b) 668 K
(c) 966 K
(d) ΔG° is positive, hence the reaction will never be spontaneous

13. Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV) Intensive properties are:

(a) I, II (b) I, II, III
(c) I, III, IV (d) all of these

14. q, w, ΔE and ΔH for the following process ABCD for a monoatomic gas are:



(a) $w = -2P_0V_0 \ln 2$, $q = 2P_0V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 0$
(b) $w = -2P_0V_0 \ln 2$, $q = 2P_0V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 2P_0V_0 \ln 2$
(c) $w = -P_0V_0 (1+\ln 2)$, $q = P_0V_0 (1 + \ln 2)$, $\Delta E = 0$, $\Delta H = 0$
(d) $w = -P_0V_0 \ln 2$, $q = P_0V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 0$

15. One mole of a real gas is subjected to heating at constant volume from (P_1, V_1, T_1) state to (P_2, V_1, T_2) state. Then it is subjected to irreversible adiabatic compression against constant external pressure P_3 atm till system reaches final state (P_3, V_2, T_3). If the constant volume molar heat capacity of real gas is Cv, find out correct expression for ΔH from state 1 to state 3.

(a) $Cv(T_3 - T_1) + (P_3V_1 - P_1V_1)$
(b) $Cv(T_2 - T_1) + (P_3V_2 - P_1V_1)$
(c) $Cv(T_2 - T_1) + (P_3V_1 - P_1V_1)$
(d) $Cp(T_2 - T_1) + (P_3V_1 - P_1V_1)$

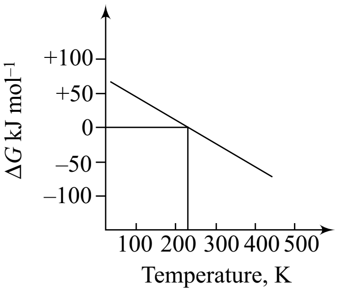
16. A system is changed from an initial state to a final state by a manner such that $\Delta H = q$. If the same change from the initial state to the final state were made by a different path, which of the following statements are correct?

(a) ΔH remain the same.
(b) ΔH will depend upon the type of path.
(c) Heat exchanged q will be same if the path is isobaric.
(d) Heat exchanged q will be different if the path is not isobaric.

17. For which of the following reactions. ΔS will the maximum?

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(c) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
(d) $2HI(g) \rightleftharpoons H_2(g) + I_2(s)$

18. What can be concluded about the values of ΔH and ΔS from this graph?



(a) $\Delta H > 0, \Delta S > 0$ (b) $\Delta H > 0, \Delta S < 0$
(c) $\Delta H < 0, \Delta S > 0$ (d) $\Delta H < 0, \Delta S < 0$

19. What amount of heat energy (kJ) is released in the combustion of 12.0 g of C_3H_4?

(Atomic weights: C = 12.01, H = 1.008, O = 16.00).

$C_3H_4(g) + 4O_2(g) \rightarrow 3CO_2(g) + 2H_2O(l)$

$\Delta H^\circ = -1939.1$ kJ

(a) 725 (b) 504 (c) 783 (d) 581

20. The standard enthalpy of formation of propene, C_3H_6, is +20.6 kJ/mole. Calculate the heat of combustion of C_3H_6. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are –394 kJ/mole and –285.8 kJ/mole respectively.

(a) 1721.2 (b) –1939.1 (c) 2060.0 (d) 2221.6

21. The fat, glyceryl trioleate, is metabolised via the following reaction. Given the enthalpies of formation, calculate the energy (kJ) liberated when 1.00 g of this fat reacts.

(Atomic weights: C = 12.01, H = 1.008, O = 16.00).

$C_{57}H_{104}O_6(s) + 80O_2(g) \rightarrow 57CO_2(g) + 52H_2O(l)$

ΔH° $C_{57}H_{107}O_6 = -70870$ kJ/mole

ΔH° $H_2O(l) = -285.8$ kJ/mole

ΔH° $CO_2(g) = -393.5$ kJ/mole

(a) 40.4 (b) 33.57 (c) 37.98 (d) 42.6

22. Using the enthalpies of formation, calculate the energy (kJ) released when 3.00 g of $NH_3(g)$ reacts according to the following equation:

(Atomic weights: B = 10.81, O = 16.00, H = 1.008).

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

ΔH° $NH_3(g) = -46.1$ kJ/mole

ΔH° $NO(g) = +90.2$ kJ/mole

ΔH° $H_2O(g) = -241.8$ kJ/mole

(a) 34.3 (b) 30.8 (c) 39.9 (d) 42.6

23. A sheet of 15.0 g of gold at 25.0°C is placed on a 30.0 g sheet of copper at 45.0°C. What is the final temperature of the two metals assuming that no heat is lost to the surroundings. The specific heats of gold and copper are 0.129 J/g°C and 0.385 J/g°C respectively.

(a) 42.1 (b) 40.1 (c) 41.1 (d) 43.4

24. Calculate the heat of combustion (kJ) of propane, C_3H_8 using the listed standard enthapy of reaction data:

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$ $\quad \Delta H^o/kJ = -103.8$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^o/kJ = -393.5$

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$ $\quad \Delta H^o/kJ = -241.8$

(a) –2043.9 (b) –1532.9
(c) –1021.9 (d) –739.1

25. Calculate the value of $\Delta H^o/kJ$ for the following reaction using the listed thermochemical equations:

$2C(s) + H_2(g) \rightarrow C_2H_2(g)$

$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$ $\quad \Delta H^o/kJ = -2600$ kJ

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^o/kJ = -390$ kJ

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\quad \Delta H^o/kJ = -572$ kJ

(a) +184 (b) +214 (c) +202 (d) +234

26. Use the given standard enthalpies of formation to determine the heat of reaction of the following reaction:

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

$\Delta H_f^o C_2H_5OH(l) = -277.7$ kJ/mole

$\Delta H_f^o CO_2(g) = -393.5$ kJ/mole

$\Delta H_f^o H_2O(g) = -241.8$ kJ/mole

(a) –1456.3 (b) –1234.7
(c) –1034.0 (d) –1119.4

27. Calculate ΔH°/kJ for the following reaction using the listed standard enthapy of reaction data:

$2N_2(g) + 5O_2(g) \rightarrow 2N_2O_5(s)$

$N_2(g) + 3O_2(g) + H_2(g) \rightarrow 2HNO_3(aq)$ $\quad \Delta H^o/kJ = -414.0$

$N_2O_5(s) + H_2O(l) \rightarrow 2HNO_3(aq)$ $\quad \Delta H^o/kJ = -86.0$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\quad \Delta H^o/kJ = -571.6$

(a) –84.4 (b) –243.6 (c) –71.2 (d) –121.8

28. Determine $\Delta H^o/kJ$ for the following reaction using the listed enthalpies of reaction:

$4CO(g) + 8H_2(g) \rightarrow 3CH_4(g) + CO_2(g) + 2H_2O(l)$

$C(\text{graphite}) + 1/2O_2(g) \rightarrow CO(g)$ $\quad \Delta H^o/kJ = -110.5$ kJ

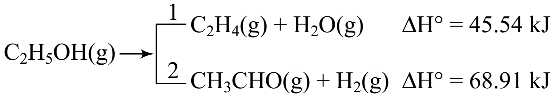
$CO(g) + 1/2O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^o/kJ = -282.9$ kJ

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ $\quad \Delta H^o/kJ = -285.8$ kJ

$C(\text{graphite}) + 2H_2(g) \rightarrow CH_4(g)$ $\quad \Delta H^o/kJ = -74.8$ kJ

(a) –622.4 (b) –686.2 (c) –747.5 (d) –653.5

29. Ethanol undergoes decomposition to form two sets of products?



$$C_2H_5OH(g) \rightarrow \begin{cases} \xrightarrow{1} C_2H_4(g) + H_2O(g) & \Delta H^\circ = 45.54 \text{ kJ} \\ \xrightarrow{2} CH_3CHO(g) + H_2(g) & \Delta H^\circ = 68.91 \text{ kJ} \end{cases}$$

if the molar ratio of C_2H_4 to CH_3CHO is 8: 1 in a set of product gases, then the energy involved in the decomposition of 1 mole of ethanol is

(a) 65.98 kJ (b) 48.137 kJ
(c) 48.46 kJ (d) 57.22 kJ

30. Reactions involving gold have been of particular interest to a chemist. Consider the following reactions:

$Au(OH)_3 + 4HCl \longrightarrow HAuCl_4 + 3H_2O,$ $\quad \Delta H = -28$ kcal

$Au(OH)_3 + 4HBr \longrightarrow HAuBr_4 + 3H_2O,$ $\quad \Delta H = -36.8$ kcal

In an experiment there was an absorption of 0.44 kcal when one mole of $HAuBr_4$ was mixed with 4 moles of HCl. What is the percentage conversion of $HAuBr_4$ into $HAuCl_4$?

(a) 0.5 % (b) 0.6 %
(c) 5 % (d) 50%

LEVEL III

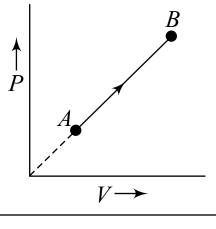
1. Match the following:

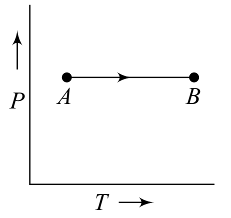
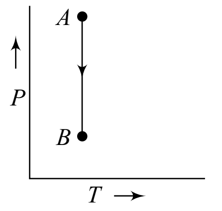
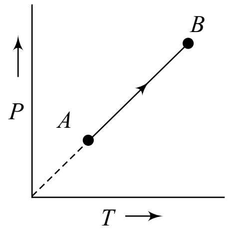
Column I		Column II	
(A)	H_2O (*l*, 1 atm, 263 K) → H_2O (S, 1 atm, 263 K)	(*P*)	$\Delta_r G > 0$
(B)	H_2O (*l*, 1 atm, 363 K) → H_2O (g, 1 atm, 363 K)	(Q)	$\Delta_r S > 0$
(C)	H_2O (*l*, 1 atm, 373 K) → H_2O (g, 1 atm, 373 K)	(*R*)	$\Delta_r H < 0$
(D)	H_2O (S, 1 atm, 373 K) → H_2O (*l*, 1 atm, 373 K)	(S)	$\Delta_r E > 0$

2. Match the following:

Column I		Column II	
(A)	Endothermic reactions	(*P*)	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$
(B)	Exothermic reaction	(Q)	$NH_3(g) \rightarrow N(g) + 3H(g)$
(C)	$\lvert\Delta H\rvert = \lvert\Delta E\rvert$	(*R*)	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
(D)	$\lvert\Delta H\rvert \neq \lvert\Delta E\rvert$	(S)	$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$

3. Match the following:

Column I		Column II	
(A)		(*P*)	Temperature is increasing

(B)		(Q)	Isotherm
(C)		(*R*)	Isochoric
(D)		(S)	Pressure is increasing

4. **Match the following:**

Column I		Column II	
(A)	$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	(*P*)	Standard enthalpy of formation of CO_2
(B)	$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$	(Q)	Enthalpy of reaction
(C)	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	(*R*)	Enthalpy of combustion of CO (g)
(D)	$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$	(S)	Standard enthalpy of formation of $H_2O(l)$

5. **Match the following:**

Column I		Column II	
A.	Isothermal process	***P.***	$q = \Delta U$
B.	Adiabatic process	Q.	$w = -P \times \Delta V$
C.	Isobaric process	***R.***	$w = \Delta U$
D.	Isochoric process	**S.**	$w = -n\,RT \ln V_2/V_1)$

Comprehension 1 (Questions 6 to 8)

The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present .The bond energy of N—H bond in NH_3 is equal to one-third of the energy of dissociation of NH_3 because there are three N-H bonds and those of *C*—H bond in CH_4 is equal to one-fourth of the energy of dissociation of CH_4. Heat of a reaction = Bond energy of reactants - Bond energy of products.

6. The enthalpy changes for the reaction
   $H_2O(g) \longrightarrow H(g) + OH(g)$ and
   $OH(g) \longrightarrow O(g) + H(g)$ are 501.87 kJ mol^{-1}
   and 423.38 kJ mol^{-1}. The bond enthalpy of O–H bond is
   (a) –462.625 kJ mol^{-1} (b) 462.625 kJ mol^{-1}
   (c) –713.54 kJ mol^{-1} (d) 713.54 kJ mol^{-1}
7. In which of the following , the bond enthalpy and bond dissociation enthalpy are identical?
   (a) H– H bond enthalpy in H_2 (g)
   (b) O–H bond ehthalpy in H_2O (g)
   (c) *C*– H bond enthalpy in $CH_4(g)$
   (d) N– H bond enthalpy in NH_3 (g)
8. Find the bond enthalpy of S–S bond from the following data:
   $C_2H_5 - S–C_2H_5$ (g) $\Delta H_f^o = -147.23$ kJ mol^{-1}
   $C_2H_5 - S–S–C_2H_5$ (g) $\Delta H_f^o = -201.92$ kJ mol^{-1}
   S (g) $\Delta H_f^o = 222.80$ kJ mol^{-1}
   (a) –277.49 kJ mol^{-1} (b) 277.49 kJ mol^{-1}
   (c) –349.15 kJ mol^{-1} (d) 349.15 kJ mol^{-1}

Comprehension 2 (Questions 9 to 11)

Two vessels *A* and *B* are connected via a stopcock. The vessel *A* is filled with a gas at a certain pressure and the vessel *B* is completely evacuated. The entire assembly is immersed in a large vat of water and is allowed to come to thermal equilibrium with the water. The stopcock is opened and the gas is allowed to expand till both the vessels are uniformly occupied. After sometime when the vessel has again come to thermal equilibrium, temperature of the water is recorded. The result shows that the temperature of water after the experiment is the same as that before.

9. For the expansion referred to above, which of the following is true?
   (a) $du = 0$ (b) $du > 0$ (c) $du < 0$ (d) $dq > 0$
10. Taking '*u*' as a function of *T* and *V*, under the given conditions of the experiment. Choose the correct statement.
    (a) The change in energy of a gas with change of volume at constant temperature is a positive quantity.
    (b) The energy of the gas is a function of temperature only.
    (c) The change in energy of a gas with change of volume at constant temperature is a negative quantity.
    (d) The result is applicable to both ideal and real gases.
11. The expansion that occurred is
    (a) isothermal reversible expansion
    (c) isothermal irreversible expansion
    (c) adiabatic reversible expansion
    (d) isothermal free expansion

Comprehension 3(Questions 12 to 16)

Standard Gibb's energy of reaction ($\Delta_r G°$) at a certain temperature can be computed as $\Delta_r G° = \Delta_r H° - T.\ \Delta_r S°$ and the change in the value of $\Delta_r H°$ and $\Delta_r S°$ for a reaction with temperature can be computed as follows:

$$\Delta_r H^o_{T_2} - \Delta_r H^o_{T_1} = \Delta_r C^o_p (T_2 - T_1)$$

$$\Delta_r S^o_{T_2} - \Delta_r S^o_{T_1} = \Delta_r C^o_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta_r G° = \Delta_r H° - T \cdot \Delta_r S° \quad \text{and by} \quad \Delta_r G° = -RT \ln K_{eq.}$$

Consider the following reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Given:

$\Delta_f H°$ $(CH_3OH, g) = -201$ kJ/mol ;

$\Delta_f H°$ $(CO, g) = -114$ kJ/mol

$S°(CH_3OH, g) = 240$ J/K–mol ; $S°(H_2, g) = 29\ JK^{-1}\ mol^{-1}$

$S°(CO, g) = 198$ J/mol–K ; $C^o_{p,m}(H_2) = 28.8$ J/mol–K

$C^o_{p,m}(CO) = 29.4$ J/mol–K ; $C^o_{p,m}(CH_3OH) = 44$ J/mol–K

and $\ln\left(\frac{320}{300}\right) = 0.06$, all data at 300 K

12. $\Delta_r S°$ at 300 K for the reaction is
(a) 152.6 J/K–mol (b) 181.6 J/K–mol
(c) –16 J/K–mol (d) none of these

13. $\Delta_r H°$ at 300 K for the reaction is
(a) –87 kJ/mol (b) 87 kJ/mol
(c) –315 kJ/mol (d) –288 kJ/mol

14. $\Delta rS°$ at 320 K is
(a) 155.18 J/mol–K (b) 150.02 J/mol–K
(c) 172 J/mol–K (d) none of these

15. $\Delta rH°$ at 320 K is
(a) –288.86 kJ/mol (b) –289.1 kJ/mol
(c) –87.86 kJ/mol (d) none of these

16. $\Delta rG°$ at 320 K is
(a) –48295.2 kJ/mol (b) –240.85 kJ/mol
(c) 240.85 kJ/mol (d) –83.56 kJ/mol

Comprehension 4(Questions 17 to 20)

The industrial preparation of a polymer, PTFE, is based on the synthesis of the monomer $CF_2 = CF_2$, which is produced according to reaction (i) below.

$$2CHClF_2(g) \longrightarrow CF_2 = CF_2(g) + 2HCl \qquad \text{(i)}$$

The monomer $CF_2 = CF_2$ is also obtained by reaction (ii) below:

$$2CHF_3(g) \longrightarrow CF_2 = CF_2(g) + 2HF(g)\ ;\ \Delta H = 198.1\text{kJ/mol} \qquad \text{(ii)}$$

Consider the information below to answer the questions:

Compound	**ΔH$_f$**	**MoleculeX–X**	**Δ(X–X)**
HCl(g)	–92.3	F–F	154.7
$CHClF_2(g)$	–485.2	Cl–Cl	246.7
$CF_2 = CF_2(g)$	–658.3		
CF_4	–679.6		
CCl_4	–106.6		

17. The enthalpy change for reaction (i).
(a) 100.23 kJ/mol (b) 127.5 kJ/mol
(c) –127.5 kJ/mol (d) –100.23 kJ/mol

18. (i) Use the expressions
$CX_4(g) \longrightarrow C(s) + 2X_2(g)\ \Delta H = -\Delta H_f$
$C(s) \longrightarrow C(g)\ ;\ \Delta H = 718$ kJ/mol and
$2X_2(g) \longrightarrow 4X(g)\ ;\ \Delta H = 2\Delta(X - X)$
where X = F,Cl, to the enthalpy change for the two processes

$$CX_4(g) \longrightarrow C(g) + 4X(g)$$

What is the average C–X bond energies for the species $CX_4(g)$ (where X = F, Cl).
(a) 329.5 kJ/mol, 426.75 kJ/mol
(b) 426.75 kJ/mol, 329.5 kJ/mol
(c) –329.5 kJ/mol, –426.75 kJ/mol
(d) –426.75 kJ/mol, –329.5 kJ/mol

19. Given that the C–H bond energy is 416.1 kJ/mol, the order of relative chemical reactivities of C–H, C–F, and C–Cl bonds.
(a) C – H > C – Cl > C – F
(b) C – F > C – Cl > C – H
(c) C – Cl > C – H > C – F
(d) C – Cl > C – F > C – H

Multiple Correct Type Questions

20. A 0.138 g sample of solid magnesium (molar mass = 24.30 g mol^{-1}) is burned in a constant volume bomb calorimeter that has a heat capacity of 1.77 kJ/°C. The calorimeter contains 300 mL of water (density 1g mL^{-1}) and its temperature is raised by 1.126°C . Which of the following is/are correct?
(a) $q_{combustion} = -3.405$ kJ
(b) $\Delta U = -599.5$ kJ/mol
(c) $\Delta H = -602.08$ kJ/mol
(d) $\Delta H = -300$ kJ/mol

21. By how much does the entropy of 3 mol of an ideal gas change in going from a pressure of 2 bar to a pressure of 1 bar, without any change in temperature. If the surroundings too are at 1 bar pressure and 300 K, and the expansion is against the constant external pressure of the surroundings.
(a) $q = (12.47\ JK^{-1})T$ (b) $\Delta S_{surr} = -12.47\ JK^{-1}$
(c) $\Delta S_{Total} = +ve$ (d) $\Delta S_{Total} = -ve$

22. For which of the following processes, total entropy of universe increases?
(a) Melting one mole of ice to water at 0°C.
(b) Freezing one mole of water to ice at 0°C.
(c) Freezing one mole of water to ice at – 10°C.
(d) Melting one mole of ice at 10°C into water.

23. One mole of helium is mixed with 2 mol of neon, both at the same temperature and pressure. Calculate ΔS for this process if the total volume remains constant.
(a) $\Delta S_{He} = 9.136\ JK^{-1}$ (b) $\Delta S_{Ne} = 5.743\ JK^{-1}$
(c) $\Delta S_{mix} = 15.879\ JK^{-1}$ (d) $\Delta S_{He} = 2.6\ JK^{-1}$

24. 20 g of N_2 at 300 K is compressed reversibly and adiabatically from 20 dm^3 to 10 dm^3 . Which of the following is/are correct?

(a) $T_2 = 396$ K (b) $\Delta U = 1424.69$ J
(c) $\Delta H = 1994.56$ J (d) $T_2 = 200$ K

Integer and Subjective Type Questions

25. The enthalpy change involved in the oxidation of glucose is –2880 kJ mol^{-1}. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk 1 km, what is the maximum distance in km that a person will be able to walk after eating 125 g of glucose?

26. Calculate the enthalpy change in kcal when infinitely dilute solutions of $CaCl_2$ and Na_2CO_3 are mixed. ΔH_f^o for Ca^{2+}(aq.), CO_3^{2-} and $CaCO_3$(s) are –129.80, –161.65 and –288.45 kcal mol^{-1} respectively.

27. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Calculate the fuel value in kcal per cm^3 of the mixture. Heats of formation and densities are as follows:

$$H_{f(Al_2O_3)} = –399 \text{ kcal mol}^{-1};$$

$$H_{f(Fe_2O_3)} = –195.92 \text{ kcal mol}^{-1}$$

Density of F_2O_3 = 5.2 g/cm^3; Density of Al = 2.7 g/cm^3.

28. Calculate the entropy change for the following reversible process at 13°C.

$$\underset{\text{1 mol at 1 atm}}{\alpha - \text{Tin}} \rightleftharpoons \underset{\text{1 mol at 1 atm}}{\beta - \text{Tin}} \;\; (\Delta H_{trans} = 2288 \text{ J mol}^{-1})$$

29. Heat of neutralisation between HCl and NaOH is –13.7 k. cal. If heat of neutralisation between CH_3 COOH and NaOH is –11.7 k. cal. Calculate heat of ionisation of CH_3COOH in kcal.

30. A gas occupies 2 L at STP. It is provided 58.63 J heat so that its volume becomes 2.5 L at 1 atm. Calculate change in its internal energy in Joule.

31. A sample of ideal gas ($\gamma = 1.4$) is heated at constant pressure. If an amount of 85 J of heat is supplied to gas, find ΔU in Joule.

32. Calculate the free energy change in kJ when 1 mole of NaCl is dissolved in water at 298 K. Given,

(a) Lattice energy of NaCl = 778 kJ mol^{-1}
(b) Hydration energy of NaCl = –775 kJ/mol^{-1}
(c) Entropy change at 300 K = 40 J mol^{-1}

33. Calculate the maximum work done in kJ expanding 16 g of oxygen at 300 K and occupying a volume of 5dm^3 isothermally until the volume becomes 25dm^3 .

34. What is the entropy change for the conversion of 1 g of ice to water at 167 K and one atmospheric pressure? [ΔH_{fusion} = 6.025 kJ mol^{-1}].

35. At 300 K, the standard enthalpies of formation of C_6H_5COOH(s), CO_2(g) and H_2O(l) are –408, –393 and –286 kJ/ mol respectively. Calculate the heat of combustion of benzoic acid at

(i) constant pressure (ii) constant volume

36. The heat of combustion of glycogen is about 480 kJ/mol of carbon. Assume that average heat loss by an adult male is 150 watt. If we were to assume that all the heat comes from oxidation of glycogen, how many units of glycogen (1mole carbon per unit) must be oxidised per day to provide for this heat loss?

37. Calculate ΔH_f^o for chloride ion from the following data:

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g);\ \Delta H_f^o = -92.4 \text{ kJ}$$

$$HCl(g) + nH_2O \longrightarrow H^+_{(aq)} + Cl^-_{(aq)};\ \Delta H^o = -74.8 \text{ kJ}$$

$$\Delta H_f^o H^+_{(Aq)} = 0.0 \text{ kJ}$$

38. A constant pressure calorimeter consists of an insulated beaker of mass 92 g made up of glass with heat capacity 0.75 J/K/g. The beaker contains 100 mL of 1 M HCl of 22.6°C to which 100 mL 1M NaOH at 23.4°C is added. The final temperature after the reaction is complete is 29.3°C. What is ΔH in kJ/mole for this neutralisation reaction? Assume that the heat capacities of all solutions are equal to that of same volumes of water.

39. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are –241, – 3800 and – 3920 kJ/mole respectively. Calculate the heat of hydrogenation of cyclohexene.

40. Calculate enthalpy change of the following reaction:

$$H_2C = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$$

The bond energy of $C-H$, $C-C$, $C=C$, $H-H$ are 414, 347, 615 and 435 kJ/ mol respectively.

41. For the reaction, $N_2(g) + 3H_2(g) \longrightarrow (2NH_3(g)$; $\Delta H = –95.4$ kJ and $\Delta S = –198.3$ J/K. Calculate the maximum temperature at which the reaction will proceed in forward direction.

42. Assume that for a domestic hot water supply 150 kg of water per day must be heated from 10°C to 65°C and gaseous fuel propane C_3H_8 is used for this purpose. What moles and volume of propane (in litre at STP) would have to be used for heating domestic water. ΔH for combustion of propane is –2050 kJ/ mol and specific heat of water is 4.184 × 10^{-3} kJ/g.

43. A gas expands from 3 dm^3 to 5 dm^3 against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mole of water of temperature 290 K. Calculate ($\Delta T \times 10$) of water. Specific heat of water = 4.184 J/ g/K.

44. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane:

(i) $2B(s) + \left(\frac{3}{2}\right)O_2(g) \longrightarrow B_2O_3(s);\ \Delta H = –1273$ kJ/mol

(ii) $H_2(g) + \left(\frac{1}{2}\right)O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -286$ kJ/mol

(iii) $H_2O(l) \longrightarrow H_2O(g)$; $\Delta H = 44$ kJ/mol

(iv) $2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$; $\Delta H = 36$ kJ/mol

45. By using the following data draw an appropriate energy cycle & calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion.
Comment on the difference in their values.
* enthalpy change of solution of NaCl(s) = – 2 kJ/mol.
* enthalpy change of solution of NaI(s) = + 2 kJ/mol.
* enthalpy change of hydration of Na^+ (g) = –390 kJ/mol.
* lattice energy of NaCl = – 772 kJ/mol.
* lattice energy of NaI = – 699 kJ/mol.

46. The gas is cooled and loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J which is exchanged with the surroundings. Find the value of ΔE?

47. The enthalpy of combustion of glucose is –2808 kJ mol^{-1} at 25°C. How many grams of glucose do you need to consume [Assume weight = 62.5 kg].
(a) To climb a flight of stairs rising through 3 m.
(b) To climb a mountain of altitude 3000 m?
Assume that 25% of enthalpy can be converted to useful work.

48. What is ΔE when 2.0 mole of liquid water vaporises at 100°C? The heat of vaporisation, of water at 100°C is 40.66 kJ mol^{-1}.

49. If 1.0 kcal of heat is added to 1.2 L of O_2 in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔE and ΔH of the process.

50. When the following reaction was carried out in a bomb calorimeter, ΔE is found to be –742.7 kJ/mol of NH_2CN (s) at 298 K.

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

Calculate ΔH_{298} for the reaction.

51. When 1 mole of ice melt at 0°C and at constant pressure of 1 atm. 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 L and 0.0180 L respectively. Calculate ΔE for the reaction.

52. Water expands when it freezes. Determine amount of work in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.

53. One mole of solid Zn is placed in excess of dilute H_2SO_4 at 27°C in a cylinder fitted with a piston. Find the value of ΔE, q and w for the process if the area of piston is 500 cm^2 and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 kJ.

$$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$$

54. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C?

55. Oxygen is heated from 300 K to 600 K at a constant pressure of 1 bar. What is the increases in molar entropy? The molar heat capacity in JK^{-1} mol^{-1} for the O_2 is.

$$C_P = 25.5 + 13.6 \times 10^{-3}\, T - 42.5 \times 10^{-7}\, T^2$$

56. Calculate the free energy change at 298 K for the reaction:
$Br_2(l) + Cl_2(g) \longrightarrow 2BrCl(g)$. For the reaction ΔH° = 29.3 kJ and the entropies of $Br_2(l)$, $Cl_2(g)$ and BrCl(g) at the 298 K are 152.3, 223.0, 239.7 J mol^{-1} K^{-1} respectively.

57. Using the date given below, establish that the vaporisation of $CCl_4(l)$ at 298K to produce $CCl_4(g)$ at 1 atm pressure occur spontaneously or not.
Given: CCl_4 (l, 1 atm) $\longrightarrow$ CCl_4 (g, 1 atm) ;
ΔS° = 94.98 JK^{-1} mol^{-1}
$\Delta H°_f$ (CCl_4, g) = –106.7 kJ mol^{-1} and $\Delta H°_f$(CCl_4, l) = –139.3 kJ mol^{-1}

58. The increase in entropy of 1 kg of ice at 200 K which is heated to 400 K (super heated steam) at constant atmospheric pressure, will be what?
Given that C_p (ice) = 2.09×10^3 J/kg degree ; C_p(water) = 4.18×10^3 J/kg degree
C_p(steam) = 2.09×10^3 J/kg degree ; L_f (C, 273 K) = 3.34×10^5 J/kg ;
L_v (water, 273 K) = 22.6×10^5 J/kg

59. Calculate workdone in adiabatic compression of one mole of an ideal gas (monoatomic) from an initial pressure of 1 atm to final pressure of 2 atm. Initial temperature = 300 K.
(a) If process is carried out reversibly.
(b) If process is carried out irreversible against 2 atm external pressure.
(c) The final volume reached by gas in two cases.

60. 20.0 dm^3 of an ideal gas (diatomic $C_{v,m} = 5\,R/2$) at 673 K and 0.7 MPa expands until pressure of the gas is 0.2 MPa. Calculate q, w, ΔU and ΔH for the process if the expansion is
(i) isothermal and reversible.
(ii) adiabatic and reversible.
(iii) isothermal and adiabatic.
(iv) against 0.2 MPa and adiabatic.
(v) against 0.2 MPa and isothermal.

61. One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of ΔS_{total} under the following conditions:
(i) Expansion is carried out reversibly.
(ii) Expansion is carried out irreversibly where 836.6 J of heat is less absorbed than in (i)
(iii) Expansion is free.

62. 10 g of neon initially at a pressure of 506.625 kPa and temperature of 473 K expand adiabatically to a pressure of 202.65 kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion:

(i) Expansion is carried out reversibly.
(ii) Expansion occurs against a constant external pressure of 202.65 kPa.
(iii) Expansion is free expansion.

63. Pressure over 1000 mL of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate ΔU and ΔH of the process, assuming linear variation of volume with pressure. (Use 1 L-atm = 100 J)

64. One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate ΔS_{system}, ΔS_{surr}, and ΔS_{total}

(i) when the process is carried out reversibly.
(ii) when the process is carried out irreversibly (one step).

65. Fixed amount of an ideal gas contained in a sealed rigid vessel (V = 24.6 L) at 1.0 bar is heated reversibly from 27°C to 127°C. Determine change in Gibb's energy (in Joule) if entropy of gas $S = 10 + 10^{-2}\,T$ (J/K).

66. A 32 g sample of CH_4 gas initially at 101.325 kPa and 300 K is heated to 550 K. $C_{P,m}/JK^{-1}\,mol^{-1} = 12.552 + 8.368 \times 10^{-2}\,T/K$. Assuming CH_4 behaves ideally, compute w, q, ΔU and ΔH for (a) an isobaric reversible process and (b) an isochoric reversible process.

67. At 298 K, $\Delta H^{o}_{\text{combustion}}$ (sucrose) = – 5737 kJ/mol and $\Delta G^{o}_{\text{combustion}}$ (sucrose) = –6333 kJ/mol. Estimate additional non-PV work that is obtained by raising temperature to 310 K. Assume $\Delta_r C_P = 0$ for this temperature change.

68. During 200J work done on the system, 140 J of heat is given out. Calculate the change in internal energy.

69. A gas absorbs 200 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 L. Calculate the change in internal energy.

70. Two litre of N_2 at 0°C and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.

71. The enthalpy of vaporisation of liquid diethyl ether – $(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35.0°*C*). Calculate ΔS for conversion of: (a) liquid to vapour, and (b) vapour to liquid at 35°*C*.

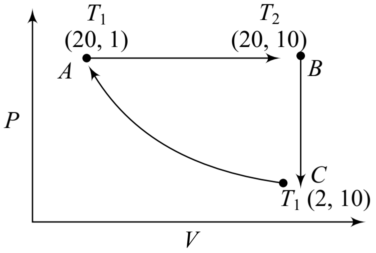
72. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 25°*C*. Lattice energy of NaCl = 777.8 kJ mol^{-1} ; ΔS for dissolution = 0.043 kJ mol^{-1} and hydration energy of NaCl = –774.1 kJ mol^{-1}.

73. The equilibrium constant for the reaction given below is 2.0×10^{-7} at 300 K. Calculate the standard free energy change for the reaction;

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Also, calculate the standard entropy change if $\Delta H^{o} = 28.40$ kJ mol^{-1}.

74. One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps:



(CA) Isothermal compression from 2 atm and 10 L to 20 atm and 1 L.

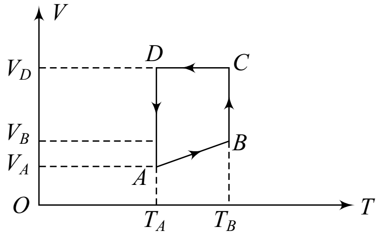
(AB) Isobaric expansion to return the gas to the original volume of 10 L with *T* going from T_1 to T_2.

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

The steps are shown schematically in the figure shown.

(a) Calculate T_1 and T_2.
(b) Calculate ΔE, q and w in calories, for the cycle.

75. A monoatomic ideal gas of two moles is taken through a cyclic process starting from A as shown in figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at *A* is 27°C, calculate



(a) the temperature of the gas at point *B*.
(b) Total Heat absorbed or released by the gas in cyclic process.
(c) the total work done by the gas during complete cycle.

76. Calculate the work done when 50 g of iron reacts with hydrochloric acid in

(i) a closed vessel of fixed volume.
(ii) an open beaker at 25°C.

77. The internal energy change in the conversion of 1.0 mole of the calcite form of $CaCO_3$ to the aragonite form is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively.

78. For a reaction $M_2O(s) \rightarrow 2M(s) + \frac{1}{2}O_2(g)$; $\Delta H = 30$ kJ mol^{-1} and $\Delta S = 0.07$ kJ K^{-1} mol^{-1} at 1 atm. Calculate up to which temperature, the reaction would not be spontaneous.

79. Predict whether the entropy change of the system in each of the following process is positive or negative.

(a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

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

(c) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

(d) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

(e) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

(f) Cooling of $N_2(g)$ from 20°C to –50°C

80. Calculate the boiling point of bromine from the following data:
ΔH^o and ΔS^o values of $Br_2(l) \rightarrow Br_2(g)$ are 30.91 kJ/mole and 93.2 J/mol. K respectively. Assume that ΔH and ΔS do not vary with temperature.

81. The efficiency of the Carnot engine is 1/6. On decreasing the temperature of the sink by 65K, the efficiency increases to 1/3. Find the temperature of the source and the sink.

82. (a) One mole of an ideal gas expands isothermally and reversible at 25°*C* from a volume of 10 L to a volume of 20 L.

(i) What is the change in entropy of the gas?

(ii) How much work is done by the gas?

(iii) What is *q*(surroundings)?

(iv) What is the change in the entropy of the surroundings?

(v) What is the change in the entropy of the system plus the surroundings?

(b) Also answer the questions (i) to (v) if the expansion of the gas occurs irreversibly by simply opening a stopcock and allowing the gas to rush into an evacuated bulb of 10-L volume.

83. The molar heat of formation of $NH_4NO_{3(s)}$ is –367.54 kJ and those of $N_2O(g)$, $H_2O(l)$ are 81.46 and –285.8 kJ respectively at 25°C and 1 atmosphere pressure. Calculate ΔH and ΔE of the reaction

$$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(l)}$$

84. Given the following standard molar enthalpies: ΔH_f^o of CH_3CN (g) = 88 kJ/mol, ΔH_f^o of C_2H_6 = – 84 kJ/mol, $\Delta H^o_{\text{Sublimation}}$ of C(gr) = 717 kJ/mol, bond dissociation energy of N_2 (g) and H_2 (g) are 946 and 436 kJ/mole respectively, B.E. (C—H) = 410 kJ/mol. Determine C—C and C≡N bond energies.

85. The heats of combustion of $C_2H_{4(g)}$, $C_2H_{6(g)}$ and $H_{2(g)}$ are –1409.5, –1558.3 and –285.6 kJ respectively. Calculate heat of hydrogenation of ethylene.

86. ΔH for combustion of ethane and ethyne are –341.1 and –310.0 kcal respectively. Which is the better gas welder and why?

87. The heat of formation of methane is –17.9 kcal. If the heats of atomisation of carbon and hydrogen are 170.9 and 52.1 kcal per mole, calculate the C–H bond energy in methane.

88. Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies:
C–C = 83 kcal, C=C = 140 kcal, C–H = 99 kcal
Heat of atomisation of *C* = 170.9 kcal
Heat of atomisation of H = 52.1 kcal

89. At 25° *C*, 1 mole $MgSO_4$ was dissolved in water. The heat evolved was found to be 91.211 kJ. One mole of $MgSO_4 . 7H_2O$ on dissolution gives a solution of the same composition accompained by an absorption of 13.807 kJ. Find the enthalpy of hydration, i.e., ΔH for the reaciton,

$$MgSO_4(s) + 7H_2O(l) \rightarrow MgSO_4 . 7H_2O(s)$$

Given that

(i) $MgSO_4\ (s) + aq \rightarrow MgSO_4\ (aq)$ $\Delta_rH_1 = -91.211$ kJ mol^{-1}

(ii) $MgSO_4 . 7H_2O\ (s) + aq \rightarrow MgSO_4\ (aq)$ $\Delta_rH_2 = +13.807$ kJ mol^{-1}

90. The specific heats of iodine vapour and solid are 0.031 and 0.055 cal/g respectively. If heats of sublimation of iodine is 24 cal/g at 200°C, what is its value at 250°*C*?

91. When 2 moles of C_2H_6 are completely burnt 3120 kJ of heat is liberated. Calculate the heat of formation, ΔH_f^o for C_2H_6. Give ΔH_f^o for $CO_2(g)$ and $H_2O(l)$ are –395 and –286 kJ respectively.

92. The heat of solution of anhydrous $CuSO_4$ is –15.9 kcal and that of $CuSO_4.5H_2O$ is 2.8 kcal. Calculate the heat of hydration of $CuSO_4$.

93. A swimmer breaths 20 times in one minute when swimming and inhale 200 mL of air in one breath. Inhalded air contain 20% O_2 by volume and exhaled air contain 10% O_2 by volume. If all oxygen are consumed in combustion of glucose in the body and 25% of energy obtained from combustion is available for muscular work. Determine the maximum distance this swimmer can swim in one hour if 100 kJ energy is required for 1.0 km swimming. Standard molar enthalpy of combustion of glucose is –2880 kJ/mol and body temperature is 37°C.

94. If the enthalpy of formation of HCl (g) and Cl^- (aq) are –92.3 kJ/mole and –167.44 kJ/mol, find the enthalpy of solution of hydrogen chloride gas.

95. When 1.0 g of fructose $C_6H_{12}O_6(s)$ is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter water increases by 1.56°C. If the heat capacity of the calorimeter and its contents is 10.0 kJ/°C. Calculate the enthalpy of combustion of fructose at 298 K.

96. Consider the following thermodynamic data:
Enthalpy of formation of CaC_2 (s) = – 60 kJ/mol;
Enthalpy of sublimation of Ca (s) = 179 kJ/mol;
Enthalpy of sublimation of C (s) = 718 kJ/mol;
First ionization energy of Ca (g) = 590 kJ/mol;
Second ionization energy of Ca (g) = 1143 kJ/mol;

Bond energy of C_2 (g) = 614 kJ/mol;
First electron affinity of C_2 (g) = –315 kJ/mol;
Second electron affinity of C_2 (g) = +410 kJ/mol;
Draw a clear Born-Haber cycle and determine lattice energy of CaC_2 (s).

97. The enthalpy change for the following process at 25°C and under constant pressure at 1 atm are as follows:
$CH_4(g) \longrightarrow C(g) + 4H(g) \quad \Delta_r H = 396$ kcal/mole
$C_2H_6(g) \longrightarrow 2C(g) + 6H(g) \quad \Delta_r H = 676$ kcal/mole
Calculate *C–C* bond energy in C_2H_6 and heat of formation of $C_2H_6(g)$
Given: $\Delta_{sub}\, C(s) = 171.8$ kcal/mole
B.E. (H–H) = 104.1 kcal/mole

98. Cesium chloride is formed according to the following equation:

$$Cs(s) + 0.5Cl_2(g) \longrightarrow CsCl(s).$$

The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionisation energy of Cs and electron affinity of chlorine are 81.2, 243.0, 375.7 and –348.3 kJ mol^{-1}. The energy change involved in the formation of CsCl is –388.6 kJ mol^{-1}. Calculate the lattice energy of CsCl.

99. The enthalpy of formation of ethane, ethylene and benzene from the gaseous atom are –2839.2, –2275.2 and –5506 kJ mol^{-1} respectively. Calculate the resonance energy of benzene. The bond enthalpy ofC–H bond is given as equal to +410.87 kJ/mol.

100. Determine resonance energy of benzene [C_6H_6 (l)] from the following information :
ΔH^o_f of C_6H_6 (l) = + 49 kJ ;
ΔH^o_f of C_2H_2(g) =+75 kJ ΔH^o_v of C_6H_6 (l) = + 45 kJ
B.E.C ≡ C (930 kJ/mol) ; C = C (615 kJ/mol) ;
C — C (348 kJ/mol)

101. A bomb containing 5.4g of Al and 15.97g of Fe_2O_3 is placed in an ice calorimeter containing initially 8 kg of ice and 8 kg of water. The reaction $2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$ is set off by remote control and it is then observed that the calorimeter contains 7.746 kg of ice and 8.254 kg of water. Find the ΔH for the above reaction.

ΔH_{fusion} (ice) = 1.436 kcal/mole

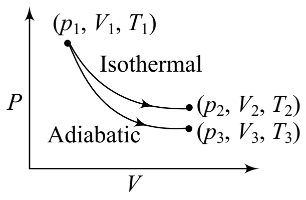
102. The heat of combustion of formaldehyde(g) is –134 kcal $mole^{-1}$ and the heat of combustion of paraformaldehyde(s) is –122 kcal per (1/n) $(CH_2O)_n$. Calculate the heat of polymerisation of formaldehyde to paraformaldehyde.

103. For the reaction cis-2-butene → trans-2-butene and cis-2-butene → 1-butene, ΔH = – 950 and + 1771 cal/mol respectively. The heat of combustion of 1-butene is –649.8 kcal/mol. Determine the heat of combustion of trans-2-butene. Also calculate the bond energy of *C*=*C* bond in trans-2-butene. Given B.E of *C* = O = 196, O—H = 110, O = O = 118, *C*—*C* = 80 and *C*—H = 98 kcal/mol respectively. $\Delta H_v(H_2O)$ = 11 kcal/mol.

104. Using the data (all values are in kJ/mol at 25°C) given below :
(i) Enthalpy of polymerization of ethylene = – 72.
(ii) Enthalpy of formation of benzene (l) = 49
(iii) Enthalpy of vaporization of benzene (l) = 30
(iv) Resonance energy of benzene (l) = – 152
(v) Heat of formation of gaseous atoms from the elements in their standard states H = 218, C = 715. Average bond energy of C—H = 415. Calculate the B.E. of C—C and C= C.

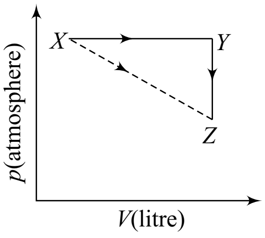
PREVIOUS YEARS' QUESTIONS OF JEE (MAIN AND ADVANCED)

1. The reversible expansion ob an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct? **[2012]**



(a) $T_1 = T_2$
(b) $T_3 > T_1$
(c) $W_{isothermal} > W_{adiabatic}$
(d) $\Delta U_{isothermal} > \Delta U_{adiabatic}$

2. For an ideal gas, consider only *P-V* work in going from initial state *X* to the final state *Z*. The final state *Z* can be reached by either of the two paths shown in the figure. **[2012]**
[Take Δ*S* as change in entropy and *W* as work done]
Which of the following choice(s) is (are) correct?

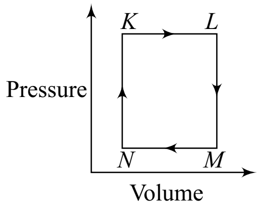


(a) $\Delta S_{X \to Z} = \Delta S_{X \to Y} + \Delta S_{Y \to Z}$
(b) $W_{X \to Z} = W_{X \to Y} + W_{Y \to Z}$
(c) $W_{X \to Z \to Z} = W_{X \to Y}$
(d) $\Delta S_{X \to Y \to Z} = \Delta S_{X \to Y}$

3. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C ≡ C bond in C_2H_2. That energy is (take the bond energy of a C – H bond as 350 kJ mol^{-1}) **[2012]**
$2C(s) + H_2(g) \longrightarrow C_2H_2(g); \; \Delta H = 225$ kJ mol^{-1}
$2C(s) \longrightarrow 2C(g); \quad \Delta H = 1410$ kJ mol^{-1}
$H_2(g) \longrightarrow 2H(g); \quad \Delta H = 330$ kJ mol^{-1}
(a) 1165 (b) 837 (c) 865 (d) 815

(Passage From Q. No. 4 to Q. No. 5)

A fixed mass *m* of a gas is subjected to transformation of states from *K* to *L* to *M* to *N* and back to *K* as shown in the figure. **[2013 Adv.]**



4. The pair of isochoric processes among the transformation of states is

(a) K to L and L to M (b) L to M and N to K
(c) L to M and M to N (d) M to N and N to K

5. The succeeding operations that enable this transformation of states are

(a) heating, cooling, heating, cooling
(b) cooling, heating, cooling, heating
(c) heating, cooling, cooling, heating
(d) cooling, heating, heating, cooling

6. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are) **[2013 Adv.]**

(a) ΔG is positive (b) ΔS_{system} is positive
(c) $\Delta S_{\text{surrounding}} = 0$ (d) $\Delta H = 0$

7. A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be **[2013 Main]**

($R = 8.314$ J/mol K, ln 7.5 = 2.01)

(a) $q = +208$ J, $W = -208$ J
(b) $q = -208$ J, $W = -208$ J
(c) $q = -208$ J, $W = +208$ J
(d) $q = +208$ J, $W = +208$ J

8. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25°C are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is **[2013 Adv.]**

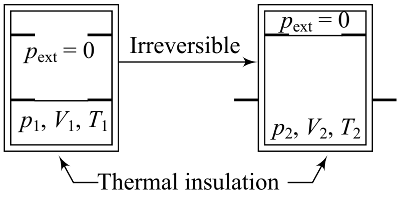
(a) +2900 kJ (b) –2900 kJ
(c) –16.11 kJ (d) +16.11 kJ

9. For the complete combustion of ethanol, **[2014 Main]** $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the enthalpy of combustion, $\Delta_C H$, for the reaction will be ($R = 8.314$ J K^{-1} mol^{-1})

(a) –13.66 kJ mol^{-1} (b) –1361.95 kJ mol^{-1}
(c) –1460.50 kJ mol^{-1} (d) –1350.50 kJ mol^{-1}

10. An ideal gas in thermally insulated vessel at internal pressure = p_1, volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram.

The final internal pressure, volume and absolute temperature of the gas are p_2, V_2 and T_2, respectively. For this expansion **[2014 Adv.]**



(a) $q = 0$ (b) $T_2 = T_1$
(c) $p_2V_2 = p_1V_1$ (d) $p_2V_2^{\gamma} = p_1V_1^{\gamma}$

11. For the process, $H_2O(l) \longrightarrow H_2O(g)$ **[2014 Adv.]** at $T = 100$°C and 1 atmosphere pressure, the correct choice is

(a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} > 0$
(b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} < 0$
(c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surrounding}} > 0$
(d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surrounding}} < 0$

12. The following reaction is performed at 298K. **[2015 Main]**

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K? $K_P = 1.6 \times 10^{12}$

(a) $R(298)$ In $(1.6 \times 10^{12}) - 86600$
(b) $86600 + R(298)\ \ln (1.6 \times 10^{12})$
(c) $86600 - \dfrac{\ln (1.6 \times 10^{12})}{R(298)}$
(d) $0.5[2 \times 86600 - R(298)\ \ln (1.6 \times 10^{12})]$

Answer Key

LEVEL I

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

51. (d) 52. (a) 53. (b) 54. (b) 55. (a) 56. (d) 57. (c) 58. (b) 59. (b) 60. (a)
61. (b) 62. (b) 63. (b) 64. (d) 65. (d) 66. (d)

LEVEL II

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

LEVEL III

1. (A) → R; (B) → P, Q, S; (C) → Q, S; (D) → Q, S 2. [(A) → Q; (B) → P, R, S; (C) → S; (D) → P, Q, R]
3. [(A) → P, S; (B) → P; (C) → Q; (D) → P, R, S] 4. [(A) → R, Q; (B) → P, Q; (C) → S, Q; (D) → Q]
5. [(A) → S; (B) → R; (C) → Q; (D) → P]
6. (b) 7. (a) 8. (b) 9. (a) 10. (a) 11. (d) 12. (c) 13. (a) 14. (d) 15. (c)
16. (d) 17. (b) 18. (b) 19. (c) 20. (a, b, c) 21. (a, b, c) 22. (c, d) 23. (a, b, c)
24. (a, b, c) 25. (5) 26. (3) 27. (4) 28. (8) 29. (2) 30. (8) 31. (55) 32. (–9) 33. (–2)
34. (2) 35. (i) –3201 kJ, (ii) –3199.75 kJ 36. (27) 37. (–167.2 kJ) 38. (–57) 39. (–121) 40. (–125)
41. (481) 42. (377) 43. (8) 44. (–2035 kJ) 45. (–384 KJ, –307 KJ) 46. (–45 J)
47. (0.4807 g), (0.4807 kg) 48. (75.118 kJ) 49. (0.993 kcal) 50. (–741.46 KJ)
51. (1440.03877 Cal) 52. (10.13 J) 53. (–36.5 KJ, –2.5 KJ, –39.03 KJ) 54. (–3.988 kJ)
55. (20.618 kJ) 56. (–1721.8 J) 57. (Non spontenous) 58. (9383.4 J/°C)
59. (a) 1195.37 J, (b) 1496.52 J, (c) 16.25 L and 17.24 L 60. See solution 61. (i) 0, (ii) 2.807 J/K, (iii) 2.807 J/K
62. (i) 0,0 (ii) 0.957 J/K, 0.957 J/K (iii) 3.81 J/K, 3.81 J/K 63. ($\Delta U = 501$ J & $\Delta H = 99.5$ kJ)
64. (i) $\left(0, -\frac{3}{2}R\ln 10, -\frac{3}{2}R\ln 10\right)$ (ii) $\left(\frac{3}{2}R\ln 10, -\frac{3}{2}R\,(0.9), \frac{3}{2}R(1.402)\right)$ 65. (– 530 J)
66. (a) ($W = –4.15$ kJ, $q = \Delta H = 24.04$ kJ, $\Delta U = 19.9$ kJ) (b) ($W = 0$, $q = \Delta U = 19.9$ kJ, $\Delta H = 24.04$ kJ)
67. (24 kJ/mole) 68. (+60 J) 69. (+124.025 J) 70. (–810.4 joule)
71. (a) (+84.41 JK^{-1} mol^{-1}) (b) (–84.41 JK^{-1} mol^{-1}) 72. (–9.114 kJ mol^{-1}) 73. (–33.6 JK^{-1})
74. (a) (243.6 K, 2436 K (b) ($\Delta E = 0$; $q = 3262.88$ cal; $w = –3262.88$ cal)
75. (a) (600 K); (b) (–1200 cal); (c) (1200 cal) 76. (–2212.22 J) 77. (209.72 J)
78. ($T < 428.57$ K) 79. ((a) positive (b) negative (c) impossible to predict (d) negative (e) negative (f) negative
80. (331.6 K) 81. (390 K, 325 K)
82. (a) (i) 5.76 J/K (ii) –1718 J (iii) 1718 J (iv) –5.76 J/K (v) 0 (b) (i) 5.76 J/K (ii) 0 (iii) 0 (iv) 0 (v) –5.76 J/K
83. (–122.6 kJ, –125.077 kJ) 84. (366 KJ, 877 KJ) 85. (136.8 KJ) 86. (C_2H_2)
87. (+99.3 kcal/mole) 88. (75.0 kcal) 89. (–105.018 kJ mol^{-1}) 90. (22.8 cal/g)
91. (–88 kJ/mol) 92. (–18.7 kcal) 93. (1.132 km) 94. (–75.14 kJ/mol) 95. (–2808 kJ)
96. (– 2889 kJ/mole) 97. (84 kcal) 98. (– 618.6 kJ mol^{-1}) 99. (–23.68 kJ/mol) 100. (–32)
101. (–202.6 kcal) 102. (12 Kcal) 103. (–604079 cal mol^{-1}, 192.91 kcal mol^{-1})
104. (343.66 kJ, 615.33 kJ)

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN & ADVANCED)

1. (a, c, d) 2. (a, c) 3. (d) 4. (b) 5. (c) 6. (b, c, d) 7. (a) 8. (c) 9. (a) 10. (a, b, c)
11. (b) 12. (d)

Hints and Solutions

LEVEL I

1. **(c)** $\Delta U = q + w$
heat absorb (q) = 45 J
since $w = -70$ joule
Work done by the system.
$\Delta U = q + w = 45 - 70 = -25$ J

2. **(c)** Decrease in internal energy = $-\Delta U$
Work done by the system = $-w$
$-\Delta U = -w \Rightarrow \Delta U = w \Rightarrow q = 0$
The process is adiabatic.

3. **(b)** At constant volume $\Delta V = 0$
$\therefore \quad W = -P_{\text{ext}}\,\Delta V = 0$
$\therefore \quad \boxed{\Delta U = q}$ first law

4. **(d)** The energy due to external field is not included in internal energy like gravitational field, earth's magnetic field, etc.

5. **(c)** Heat and work are path dependent, or indefinite quantity.

6. **(a)** For monoatomic ideal gas total degree of freedom = 3
Three translational mode of motion

$$C_V = 3 \times \frac{1}{2}R = \frac{3}{2}R$$

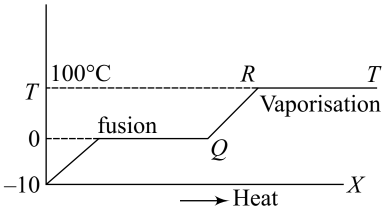
$$C_P = C_V + R = \frac{5}{2}R$$

and $\gamma = \dfrac{C_P}{C_V} = \dfrac{5}{3}$

7. **(b)** Work done in adiabatic process
$\Delta U = W = nC_V\Delta T$
$W = (2)(12.5)(200 - 300)$

8. **(a)** Heat of reaction at constant pressure = ΔH
Heat of reaction at constant volume = ΔE
$\Delta H = \Delta E + \Delta n_g RT$
$\Delta n_g = -3$
$\Delta H - \Delta E = (-3RT)$
$= -3 \times 8.314 \times 298 \times 10^{-3} = -7.431$

9. **(a)** Fusion and vaporisation are example of isothermal processes



$T_f < T_b \qquad PQ - T_f \;\; RT - T_b$

10. **(a)** $\Delta H = \Delta E + \Delta n_g RT$
41 kJ mol^{-1} = ΔE + (1) × 8.3 × 10^{-3} × 373
$\Delta E = 37.904$ kJ mol^{-1}

11. **(b)** $\Delta H = \Delta U + \Delta n_g RT$

$$\Delta H = -742.7 \text{ kJ mol}^{-1} + \left(2 - \frac{3}{2}\right) \times 8.3 \times 10^{-3} \times 298$$
$$= -741.5 \text{ kJ mol}^{-1}$$

12. **(c)** Atomic weight of Al = 27
The heat capacity required to raise the temperature of 27g Al through 1 K is 24 Joules

for 60 g Al = $\dfrac{60 \times 24 \times 20 \times 10^{-3}}{27}$ KJ = 1.066 kJ

13. **(c)** At constant T, the molecule with maximum atoms have greatest internal energy.

14. **(b)** $PV = nRT$

$$1.013 \times 10^6 \times 1 = 0.4 \times 8.314 \times T_1$$
$$T_1 = 304.6 \text{ K}$$
$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$
$$T_2 = 121.28 \text{ K}$$
$$w = \frac{nR}{\gamma - 1}(T_2 - T_1)$$
$$w = -923.7 \text{ J}$$

15. **(b)** Heat of combustion is defined as heat evolved when one mole of compound is completly oxidised in exces of air (or oxygen)

$$\frac{35.2 \times -393.5}{44} = -314.8 \text{ kJ}$$

16. **(b)** Enthalpy of formation of a compound is defined as heat evolved or absorbed in formation of one mole of compound starting from its elemental level

17. **(b)** $\Delta G° = -2.303\, RT \log K_{\text{eq}}$
$= -2.303 \times 8.314 \times 10^{-3} \times 300 \times \log 10$

18. **(a)** $\Delta S_{\text{vapourisation}} = \dfrac{\Delta H_{\text{vapourisation}}}{T_b}$

$\therefore \quad T_b = \dfrac{40.73 \times 10^3}{109}$

19. **(b)** When ice $\rightleftharpoons$ liquid: the process is reversible fusion. The fusion is isothermal process.

$$C = \frac{dq}{dT} = \frac{dq}{0} \to \infty$$

20. **(d)** $\Delta U = q + w$
P = constant since $\Delta H = q_p$
$202.6 = \Delta U + 1$ atm (2 L)
$\Rightarrow \quad \Delta U = 202.6 - 2$(L atm) (101.325 J/L atm)
$\Delta U = 0$

21. **(d)** For reversible adiabatic process $\Delta S = \dfrac{q_{\text{rev}}}{T}$
$q_{\text{rev}} = 0 \Rightarrow \Delta S_{\text{system}} = 0$

22. **(c)** $C + 2S \longrightarrow CS_2 \quad \Delta_r H = ?$

$$\Delta_r H = (\Delta H_{\text{combution}})_R - (\Delta H_{\text{combution}})_P$$

$$\Delta_r H = (x + 2y) - (z)$$

OR

$$C + 2S \rightarrow CS_2 \pm \text{‘}a\text{’ kJ} \qquad a = ?$$

$$C + O_2 \rightarrow CO_2 + x \text{ kJ} \qquad (1)$$

$$S + O_2 \rightarrow SO_2 + y \text{ kJ} \qquad (2)$$

$$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2 + z \text{ kJ} \qquad (3)$$

Equation 2 multiplying with 2, we get

$$2S + 2O_2 \rightarrow 2SO_2 + 2y \text{ kJ} \qquad (4)$$

1 + 4 – 3 we get $C + 2S \rightarrow CS_2 + x + 2y - z$

23. **(d)** The heat of neutralisation is defined as heat evolved only when 1 g equivalent of acid is completely neutralised by 1 g equivalent of base in dilute solution

Number of gram equivalent of H_2SO_4

$$= 100 \times \frac{1}{10} = 10 \text{ meq}$$

Number of gram equivalent of NaOH

$$= 150 \times \frac{1}{10} = 15 \text{ meq}$$

$$\frac{10}{1000} \times 57.3 = 0.573 \text{ kJ}$$

H_2SO_4	+	2NaOH	→	Na_2SO_4	+	$2H_2O$
5 mm		15 mm		—		—
0		5 mm		5 m		10 mm

24. **(b)** Work done in expansion

$$= P \times \Delta V$$

We have 1 L atm = 101.3 J

Work done = 6 × 101.3 J = 607.8 J

Let ΔT be the change in temperature of water

Therefore, $P\Delta V = m \times C \times \Delta T$

$$607.8 = 180 \times 4.18 \times \Delta T$$

$$\Delta T = 0.81 \text{ K}$$

$$T_f = T_1 + \Delta T = 290.8 \text{ K}$$

25. **(c)** $\Delta_r H = [\Sigma V_P(\Delta H_f)_P + \Sigma V_R(\Delta H_f)_P]$

$$\Delta_r H = [2(\Delta H_f)_{\text{NaOH}} - 2(\Delta H_f)_{H_2O}]$$

$$\frac{-281.9}{2} = (\Delta H_f)_{\text{NaOH}} + 285.8$$

$$(\Delta H_f)_{\text{NaOH}} = -426.75 \text{ kJ mol}^{-1}$$

26. **(a)** $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$$\therefore \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = 2^{\gamma-1}$$

Since γ is more for the gas X, the temperature will also be more for it.

27. **(d)** By the definition of heat of neutralisation, we have

$$\frac{1}{2}H_2C_2O_4 + \text{NaOH} \longrightarrow \frac{1}{2}Na_2C_2O_4 + H_2O;$$

$$\Delta H = 53.35 \text{ kJ}$$

or $$\frac{1}{2}H_2C_2O_4 + OH^- \longrightarrow \frac{1}{2}C_2O_4^{2-} + H_2O;$$

$$\Delta H = -53.5 \text{ kJ} \quad \text{(i)}$$

$$H^+ + OH^- \longrightarrow H_2O; \Delta H = -57.3 \text{ kJ} \qquad \text{(ii)}$$

Subtracting Eq. (ii) from Eq. (i), we get

$$\frac{1}{2}H_2C_2O_4 \longrightarrow \frac{1}{2}C_2O_4^{2-} + H^+;\ \Delta H = +3.95$$

$$\therefore \quad H_2C_2O_4 \longrightarrow C_2O_4^{2-} + 2H^+; \quad \Delta H = +7.90$$

28. **(c)**

$$\begin{tikzcd}
\mathrm{S_{(s)}} \arrow[d, "+275"'] & + & \underset{(g)}{\mathrm{3F_2}} \arrow[d, "+6\times 130"] \arrow[r] & \underset{(g)}{\mathrm{SF_6}} \quad \Delta \mathrm{H_f} = -1100\ \mathrm{KJ\ mol^{-1}} \\
\underset{(g)}{\mathrm{S}} & & \underset{(g)}{\mathrm{6F}} \arrow[r] & \mathrm{SF_6} + 1100 \arrow[d, "6\times[\mathrm{E_{S-F}}]"] \\
 & & & {}
\end{tikzcd}$$

Since reactants are not in gaseous state

$$\therefore \quad \Delta H = E_{\text{absorbed}} - E_{\text{released}}$$

$$-1100 = [275 + 6 \times 80] - [6 \times E_{S-F}]$$

Bond energy of S – F = 309 kJ mol^{-1}

29. **(b)** $\Delta S = nC_V \ln \dfrac{T_2}{T_1} + nR \ln\left(\dfrac{V_2}{V_1}\right)$

$$\Delta S = 5 \ln \frac{373}{298} + R \ln\left(\frac{10}{1}\right)$$

30. **(c)** Using $\Delta S_{\text{transition}} = \dfrac{\Delta H_{\text{transition}}}{T_{\text{transition}}}$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{trans}}}{T}$$

$$\Delta S_{\text{trans}} = \frac{-401.7}{368}$$

$$\Delta S_{\text{surr}} = \frac{+401.7}{273}, \because \text{ temperature of ice bath} = 273 \text{ K}$$

$$\Delta S_{\text{total}} = \frac{-401.7}{368} + \frac{401.7}{273}$$

31. **(a)** $\eta = \dfrac{T_1 - T_2}{T_1}$

$$\eta = \frac{373 - 298}{373} = \left(\frac{75}{373}\right)$$

$$\eta \times 100 = \frac{75}{373} \times 100$$

32. **(b)** $\eta = \dfrac{T_1 - T_2}{T_1}$

$$\eta = \frac{500 - 300}{500} = \frac{2}{5}$$

$$\eta = \frac{W}{q_{\text{source}}} \Rightarrow W = (\eta)\,(q_{\text{source}})$$

$$= \left(\frac{2}{5}\right)(2 \text{ kcal}) = 0.8 \text{ kcal}$$

33. **(a)** Number of equivalent of H_2SO_4 taken

$$= \frac{0.2 \times 2 \times 400}{1000} = 0.16$$

Number of equivalent of KOH added

$$= \frac{600 \times 0.1}{1000} = 0.06$$

Number of equivalents of acid and bases which neutralised each other = 0.06

$\therefore$ Heat evolved = 0.06×57.1 kJ = 3.426 kJ

34. **(b)** For adiabatic process; $TV^{\gamma-1}$ = Constant

For monoatomic gas, $\gamma = \frac{4}{3} = 1.33$; $n = 1.33 - 1 = 0.33$

35. **(b)** $q = nC_P\Delta T$

$$1000 = \frac{100}{18} \times 75 \times \Delta T$$

$\Delta T = 2.4$ K

36. **(b)** $\Delta_r H = \Sigma\nu_P(\Delta H_f)_P - \Sigma\nu_R(\Delta H_f)_R$

$= [(-110.5) + (-241.8)] - [-393.5]$ KJ mol^{-1}

$= 41.2$ KJ mol^{-1}

OR

(i) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H_f = -393.5$ kJ mol^{-1}

(ii) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$; $\Delta H_f = -110.5$ kJ mol^{-1}

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$; $\Delta H_f = -241.8$ kJ mol^{-1}

For getting $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$, add (ii) and (iii) and subtract (i).

Thus $-110.5 - 241.8 + 393.5 = 393.5 - 352.3 = 41.2$

37. **(b)** $\Delta G = \Delta H - T\Delta S$.

At equilibrium ; $\Delta G = 0$, so $\Delta H = T\Delta S$

$= 273 \times (60.01 - 38.20) = 5954$ J/mol)

38. **(d)** Work done by a gas $= -P_{ext} \times \Delta V$

$= -10^5(10^{-2} - 10^{-3})$

$= -10^5(0.009) = -900$ J

39. **(c)** For isothermal process $\Delta U = \Delta H = 0$

40. **(a)** Use $\Delta_r H = \Sigma\nu_P(\Delta H_f)_P - \Sigma\nu_R(\Delta H_f)_R$

41. **(a)** $C_{graphite} + 2H_2 + \frac{1}{2}O_2 \rightarrow CH_3OH \quad \Delta H = x$

$x = (2) + 2 \times (3) - (1)$

$= -239$ KJ mol^{-1}

42. **(b)** $\Delta H = \Delta U + \Delta n_g RT$

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

43. **(b)** $\Delta G^0 = -2.303\, RT \log K_p$

$= -2.303 \times 8.314 \times 298 \times \log 2.47 \times 10^{-29}$

$= 163.228$ kJ/mole

44. **(b)** For dissociation reactions

$\Delta H > 0$ and $\Delta n_g > 0 \Rightarrow \Delta_r S > 0$

45. **(d)** $\Delta G = \Delta H - T\Delta S$

$\Delta G = -33000 - [T(-58)]$

$\Delta G = -33000 + 58T$

at $\quad T = 568.96$ K $\quad \Delta G = 0$

spontaneous below 568.96 K temperature.

46. **(a)** $w = q \times \left[\frac{T_1 - T_2}{T_1}\right]$

$$= 2.1 \times \left(\frac{700}{1000}\right) = 1.47 \text{ kJ}$$

47. **(b)** $\underset{(S)}{C} + \underset{(g)}{O_2} \rightarrow \underset{(g)}{CO_2} + 97$ Kcal ...(i)

$\underset{(g)}{CO_2} + \underset{(g)}{C} \rightarrow 2CO - 39$ Kcal ...(ii)

To find $CO + \frac{1}{2}O_2 \rightarrow CO_2 + ?$

Subtracting eq. (ii) from (i)

$-CO_2 + O_2 \rightarrow CO_2 - 2CO + 97 + 39$

$2CO + O_2 \rightarrow 2CO_2 + 136$ Kcal

$\therefore \quad CO + \frac{1}{2}O_2 \rightarrow CO_2 + 68$ Kcal

48. **(a)** The combustion equation of sucrose is

$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(g)$

Here,

Δn_g = sum of gaseous product moles – sum of gaseous reactant moles

$\Delta n_g = 12 + 11 - 12$

As we know,

$\Delta H = \Delta E + \Delta n_g RT$, where ΔH = heat of reaction at constant pressure

ΔE = heat of reaction at constant volume

Here, $\Delta E = -1348.9$ kcal

$R = 2.0$ cal, $T = 25 + 273 = 298$ K

$\therefore \quad \Delta H = (-1348.9 \times 1000) + 11 \times 2 \times 298$

$= -1348900 + 6556 = -1342344$ cal

$= -1342.344$ kcal

49. **(b)** Now for the reaction,

$H_2(g) + F_2(g) \longrightarrow 2HF(g)$;

$\Delta H° = -124$ kcal

$\therefore \quad \Delta H° = \Sigma$B.DE. (ractants) – ΣB.DE. of (products)

or $\quad -124 = \Delta H_{H-H} + \Delta H_{F-F} - 2\Delta H_{H-F}$

$= 104 + 37.8 - 2\Delta H_{H-F}$

$\therefore \quad 2\Delta H^o_{H\text{-}F} = 104 + 37.8 + 124$

$= 265.8$ kcal

Bond energy of H – F $= \frac{265.8}{2} = 132.9$ kcal

$\therefore$ $\Delta H°$ for the given reaction = –132.9 kcal

50. **(b)** As we know, $\Delta H = \Delta E + \Delta n_g RT$

For the reaction,

$CO(g) + 1/2O_2(g) \longrightarrow CO_2(g)$

$\Delta n_g = 1 - (1 + 1/2) = -1/2$

$\therefore \quad \Delta H = \Delta E - 1/2RT$

$\therefore \quad \Delta H < \Delta E$

51. **(d)**

(i) P_4 (yellow) + $5O_2(g) \longrightarrow P_4O_{10} + 9.19$ kJ (1)

(ii) P_4 (red) + $5O_2(g) \longrightarrow P_4O_{10} + 8.78$ kJ (2)

P_4 (yellow) $\rightarrow P_4$ (red) + 0.41 kJ

so, heat of transition of yellow to red phosphorous is –0.41 kJ

52. **(a)** As we know that, resonance energy = ΔH° (observed) – ΔH° (calculated)

$= (50.4 - 232.6)\ \text{kJ/mol} = -182.2\ \text{kJ mol}^{-1}$

53. **(b)** Given

$$C_D + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -94.3\ \text{kcal} \quad (1)$$
$$C_A + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -97.6\ \text{kcal} \quad (2)$$

Subtracting Eq. (2) from Eq. (1):

$$C_{\text{Diamond}} \longrightarrow C_{\text{Amorphous}} \quad \Delta H = 3.3\ \text{kcal}$$

54. **(b)** $\Delta H_N = -[55.9 - (x + y)]$

$-12.1 = -[55.9 - (x + y)]$

$-12.1 = -55.9 + x \qquad \text{Since } y = 0$

$x = 55.9 - 12.9$

$x = +43.8\ \text{kJ}$

55. **(a)** Since heat of neutralisation of strong acid and strong base is equal to the formation of one mole of water, i.e., $NaOH + HCl \rightarrow NaCl + H_2O + Q$

where Q = heat of neutralisation

$\Rightarrow \quad Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^-\ H_2O + Q$

OR $\quad H^+ + OH^- \rightarrow H_2O + Q$

56. **(d)** $\Delta H = \Delta E + \Delta n_g RT$

57. **(c)** $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$;

$\Delta H = 2 \times (-13.7) = -27.4\ \text{kcal}$

58. **(b)** Lower the heat of neutralisation, more is the dissociation energy and weaker is the acid

∴ Correct order of Acidic strength $A > D > C > B$

59. **(b)** One double bond break and one single bond formed per molecule of C_2H_4 in polymerisation

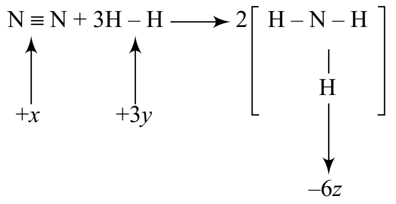
$$n \quad C = C \rightarrow (\text{—C—C—})_n$$
$$\Delta H = \Sigma(\text{B.D.E})_{\text{Reactants}} - \Sigma(\text{B.D.E})_{\text{Products}}$$
$$= +145 - (+80) = 65\ \text{kJ/mol}$$

Note: C – H bonds are common in both reactants and products.

60. **(a)** $\Delta H = 3 \times (-54) - 2(-143) = -162 + 286$

$= 124\ \text{kJ}$

61. **(b)**



$$N \equiv N + 3H - H \longrightarrow 2\left[\begin{array}{c} H - N - H \\ | \\ H \end{array}\right]$$

∴ for the formation of 2 mole NH_3 ΔH
$= E_{\text{absorbed}} - E_{\text{released}}$
$= x + 3y - 6z$

∴ for 1 mole $\Delta H = \dfrac{x}{2} + \dfrac{3}{2}y - 3z$

OR

$$\Delta H = \Sigma(\text{B.D.E})_{\text{Reactants}} - \Sigma(\text{B.D.E})_{\text{Products}}$$

62. **(b)** $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

Thus, V_{O_2} used $= \dfrac{6226 \times 3 \times 22.4}{1411} = 296.5$ litre

$= \dfrac{20}{100} \times$ volume of air

∴ Volume of air = 1482.5 L

63. **(b)** By adding (i) and (ii),

$2Na + Cl_2 \longrightarrow 2NaCl;\ \Delta H = -196\ \text{kcal}$

64. **(d)** $\Delta_r H = [(\Delta H_f)_{TiO_2} + 4(\Delta H_f)_{HCl} - (\Delta H_f)_{TiCl_4} - 2(\Delta H_f)_{H_2O}]$

$\Delta_r H = -944.7 - (4 \times 92.3) + 763.2 + (2 \times 241.8)$

$\Delta_r H = -67.1\ \text{kJ/mole}$

65. **(d)** $\Delta_r H = [\Sigma \nu_P (\Delta H_f)_P - \Sigma \nu_R (\Delta H_f)_R]$

$\Delta_r H = [3(\Delta H_f)_{CO_2} + 4(\Delta H_f)_{H_2O} - (\Delta H_f)C_3H_8]$

$-2221.6 = 3 \times (-394) - 4(285.8) - (\Delta H_f)C_3H_8$

$(\Delta H_f)C_3H_8 = -\ 103.6\ \text{kJ/mole}$

66. **(d)** $\Delta_r H = [\Sigma \nu_P (\Delta H_f)_P - \Sigma \nu_R (\Delta H_f)_R]$

$\Delta_r H = [4(\Delta H_f)_{CO_2} + 2(\Delta H_f)_{H_2O} - 2(\Delta H_f)C_2H_2]$

$-2601 = -\ 4(394) - 2(285.8) - 2(\Delta H_f)\ C_2H_2$

$2(\Delta H_f)C_2H_2 = 226.7$

LEVEL II

1. **(a)** We know that the heat of reaction

$\Delta H = \Sigma\text{B.DE. (reactant)} - \Sigma\text{B.DE. (product)}$

For the reaction,

$2H - H(g) + O = O(g) \longrightarrow 2[H - O - H](g)$

ΔH = –115.4 kcal, B.E. of H – H = 105 kcal; B.E. of O = O = 119 kcal

Since one H_2O molecule contains two O – H bonds

$-\ 115.4 = (2 \times 104) + 119 - 4\ (O - H)$ bond energy

∴ $\quad 4 \times (O - H)$ bond energy $= (2 \times 104) + 119 + 115.4$

i.e., O – H bond energy $= \dfrac{(2 \times 104) + 119 + 115.4}{4} = 110.6\ \text{kcal mol}^{-1}$

2. (a) $m_{Zn} \cdot S_{Zn} \cdot (T_f - T_i) + m_{H2O} \cdot S_{H2O} \cdot (T_f - T_i) = 0$

$(65.38)\,(0.4)\,(T_f - 20°) + 180\ \text{gm}\,(4.20) \times (T_f - 100°) = 0$

$\Rightarrow \quad [(65.38)(0.4) + 180(4.20)] \times T_f$
$= (65.38)(0.4)(20) + (180)(4.20)(100)$

$$T_f = \left[\frac{(65.38)(0.4)(20) + (180)(4.20)(100)}{(65.38)(0.4) + (180)(4.20)}\right] = 97.3°\text{C}$$

3. **(b)** Ar = monoatomic ideal gas $\quad C_V = \dfrac{3}{2}R$

At constant pressure $q = \Delta H = nC_P\Delta T$

$= 0.25 \times \dfrac{5}{2} \times 8.314 \times 16 = 83.2$

4. **(c)** Reversible process-involve infinitesimally small driving force. Hence system and surrounding remains in equilibrium.

5. **(d)** Temperature at 'a' $= T_0 = \dfrac{PV}{R}$

at (a) $T_0 = \dfrac{P_0V_0}{R} \qquad$ (i)

at (C) $T_C = \dfrac{(2P_0)(4V_0)}{R} = 8T_0$

$$\Delta U = nC_V(T_f - T_i) = \frac{3}{2}R(8T_0 - T_0)$$

$$\boxed{\Delta U = \frac{21RT_0}{2} = 10.5RT_0}$$

6. **(b)** The case of irreversible adiabatic process.

$$W_{\text{irr}} = -P_{\text{ext}}(V_2 - V_1)$$

$$\Rightarrow \quad nC_V(T_2 - T_1) = -P(V_2 - V_1) \qquad n = 1$$

$$C_V = \frac{3}{2}R \qquad T_1 = T$$

$$P_{\text{ext}} = 1 \text{ atm}$$

$$T_2 = \frac{-1(V_2 - V_1)}{1\,C_V} + T = T - \frac{(1\text{ atm})(2\text{L} - 1\text{L})}{\frac{3}{2}(R)}$$

$$T_2 = T - \frac{2(L\text{ atm})}{3 \times 0.0821(L\text{ atm k}^{-1}\text{mole}^{-1})}$$

7. **(c)** $V_B > V_A$ and $T_B > T_A$

$$\Delta H = nC_P(T_B - T_A) > 0$$

$$w = -P_{\text{ext}}(V_B - V_A) < 0$$

8. **(b)** $$\underset{0°\text{C}}{H_2O(s)} \xrightarrow{q_1} \underset{0°\text{C}}{H_2O(l)} \xrightarrow{q_2} \underset{25°\text{C}}{H_2O(l)}$$

$$q_1 = \Delta H_{\text{fusion}}(\text{kJ/mole}) \times \left(\frac{36}{18}\text{mole}\right)$$

$$q_1 = 6.01 \times 2 = 12.02 \text{ kJ}$$

$$q_2 = \text{mC}\Delta T = (36\text{ g})(4.18\text{ J/K g})25$$

$$q_{\text{NET}} = q_1 + q_2 = \left[12.02 + \frac{(36)(25)(4.18)}{1000}\right]\text{kJ}$$

$$= 12.02 + 3.76 = 15.78$$

9. **(b)** Initial pressure $P = \frac{RT}{V}$

$$P = 300\,R = (300 \times 0.0821)\text{ atm}$$

final pressure = 1 atm

final volume; $P_fV_f = P_iV_i$

$$\Rightarrow \quad V_f = \frac{P_iV_i}{P_f} = \left(\frac{(300)R}{1}\right) = 24.6\text{ L}$$

$$\Delta S = nRT\ln\frac{V_2}{V_1} \text{ for isothermal}$$

$$\Delta S = R\ln\left(\frac{24.6}{1}\right)$$

10. (b) For spontaneous reactions $\Delta S_{\text{total}} > 0$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \left(\frac{\Delta H_{\text{Surr}}}{T}\right)$$

$$= \Delta S_{\text{system}} +$$

$$\Delta S_{\text{total}} > 0 \Rightarrow \Delta S_{\text{sys}} + \qquad > 0$$

$$\Delta S_{\text{syst}} >$$

Hence ΔS_{syst} can be negative but numerically smaller than .

11. **(b)** Formation of Fe_3O_4

$$3Fe(s) + 2O_2(g) \longrightarrow Fe_3O_4(s)\ ;\ \Delta G = ?$$

12. **(c)** $T =$

$$\Delta H° = -110 - (-266.3)$$

$$\Delta S° = 197.6 + 27.28 - 5.74 - 57.49$$

Above this temperature, the process becomes spontaneous.

13. **(c)** Intensive property =

pH ∝ concentration = mole/volume

though pH is a dimensionless number and intensive property

EMF = = Intensive property

Boiling point (T_b) = temperature = intensive property

Entropy (s) = = extensive property

14. **(a)** Temperature at $A(T_A)$ =

Since BC curve isothermal

∴

now

$\because \quad T_D - T_A$

$\therefore \quad \Delta U = \Delta H = 0$

15. **(c)**

$\Delta H_T = \Delta H_1 + \Delta H_2$

$\Delta H_1 = \Delta U_1 + (P_2V_1 - P_1V_1)$

$\Delta H_1 = C_V(T_2 - T_1) + (P_2V_1 - P_1V_1)$

$\Delta H_2 = \Delta U_2 + (P_3V_2 - P_2V_1)$

In adiabatic process $\Delta U = W = -P_{ext}(V_f - V_i)$

$\therefore \quad \Delta U_2 = -P_3[V_2 - V_1]$

$\Delta H_2 = -P_3(V_2 - V_1) + (P_3V_2 - P_2V_1)$

$\Delta H_2 = P_3V_1 - P_2V_1$

$\Delta H_T = C_V(T_2 - T_1) + (P_2V_1 - P_1V_1) + P_3V_1 - P_2V_1$

$\Delta H_T = C_V(T_2 - T_1) + P_3V_1 - P_1V_1$

16. **(a)** $\Delta H = q_p$

since *H* is state function ΔH will remain same from both path-isobaric and non-isobaric.

But $q = q_p$ only when path was isobaric.

$\Delta H = q_p$ only for isobaric path.

17. **(b)** Greater the Δn_g greater the value of ΔS.

18. **(a)** $\Delta G = \Delta H - T\Delta S$

$y = C + mX$

$\Rightarrow \quad \Delta H = C$

$m = -\Delta S$

from intercept $C > 0 \Rightarrow \Delta H > 0$

$m < 0 \Rightarrow -\Delta S < 0$

$\Rightarrow \quad \Delta S > 0$

19. **(d)** Heat evolve = $\times 12 = 581.73$

20. (c) $C_3H_6 + \quad O_2 \longrightarrow 3CO_2 + 3H_2O$

here

OR

$C_3H_6 + \quad O_2 \longrightarrow 3CO_2 + 3H_2O$

$3C + 3H_2 \longrightarrow C_3H_6 \quad \Delta H = 20.6$ kJ/mole

$C + O_2 \longrightarrow CO_2 \quad \Delta H = -394$ kJ/mole

$H_2 + \quad O_2 \longrightarrow H_2O \quad \Delta H = -285.8$ kJ/mole

$= [3 \times (-394) - 3(285.8) - 20.6]$

$= -2060$ kJ/mole

21. **(c)**

$\Delta H_C = [52(-285.8) + 57(-393.5) - (-70870)]$

$= -14861.6 - 22429.5 + 70870 = 33578.9$

energy liberated for 1 g fat

$= \qquad = 37.98$ kJ/mole

22. **(c)**

$\Delta_r H = [4(90.2) + 6(-241.8) + 4(46.1)]$

$= 360.8 - 1450.8 + 184.4 = -905.6$

heat released for 3 g = $\times 3 = 39.9$

23. **(a)** Heat lost by copper = heat gain by gold

$30 \times 0.385(318 - T) = 15 \times 0.129\,(T - 298)$

Final temperature $T = 315.1$ K

$T = 42.1°C$

24. **(a)** Applying Hess's law.

25. **(d)** $2\,C_2H_2(g) + 5\,O_2(g) \rightarrow 4\,CO_2(g) + 2\,H_2O(l)$ (i)

ΔH^o/kJ = –2600 kJ

$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^o$/kJ = –390 kJ (ii)

$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l) \quad \Delta H^o$/kJ = –572 kJ (iii)

$\Delta_r H$ for $2C(s) + H_2(g) \rightarrow C_2H_2(g)$ can be calculated by

$\Delta_r H = - \quad (-1300) + 2(-390) + \quad \times (-572)$

$\Delta_r H = 234$

26. **(b)**

$\Delta_r H =$

$\Delta_r H = [2(-393.5) + 3(-241.8) - (-277.7)]$

$\Delta_r H = -1234.7$ kJ/mole

27. **(a)** $N_2(g) + 3\,O_2(g) + H_2(g) \rightarrow 2\,HNO_3(aq)$ (i)

ΔH^o/kJ = –414.0

$N_2O_5(s) + H_2O(l) \rightarrow 2\,HNO_3(aq)$ (ii)

ΔH^o/kJ = –86.0

$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$ (iii)

ΔH^o/kJ = –571.6

$\Delta_r H$ for $2N_2(g) + 5O_2(g) \rightarrow 2N_2O_5\,(s)$ can be calculated by $2 \times (i) - 2 \times (ii) - (iii)$

$\Delta_r H = [2(-414) + 2(86) + 571.6]$

$\Delta_r H = -84.4$ kJ

28. (c)

$\Delta H_r = [3(110.5) - 28.9 + 2(-285.8) + 3(-74.8)]$
$= -747.5$

29. **(b)** $C_2H_5OH \longrightarrow C_2H_4 + H_2O$ ... (i) $\Delta H = 45.54$
$8a$ $8a$
$C_2H_5OH \longrightarrow CH_3CHO + H_2$ ...(ii) $\Delta H = 68.91$
a a
$8a + a = 1$

$a =$

Energy involved in (i) reaction = 45.54 ×

Energy involved in (ii) reaction = 68.91 ×

Total involved in (i) + (ii) are ⇒ 48.137 kJ

30. (c) $HAuBr_4 + 4HCl \longrightarrow HAuCl_4 + 4HBr \quad \Delta H = 8.8$

% conversion = × 100 = 5%

LEVEL III

1. **(A) → *R*; (B) → *P*, Q, S; (C) → Q,S; (D) → Q, S**
2. **[A → Q, (B) → *P*, *R*, S, (C) → S , (D) → *P*, Q, *R*]**
3. **[(A) → *P*, S, (B) → *P*, (C) → Q, (D) → *P*, *R*, S]**
4. **[(A) → *R*, Q; (B) → *P*, Q; (C) → S, Q; (D) → Q]**
5. [**A → S; (B) → *R*; (C) → Q; D → *P***]

Comprehension 1 (Question 6 to 8)

6. **(b)** The enthalpy of dissociation of the O–H bond depends on the molecular species from which H-atom is being separated.
$H_2O(g) \longrightarrow H(g) + OH(g); \Delta H^0 = 501.87$ kJ mol–1
However to break O–H bond in hydroxyl a different quantity of heat (423.38 kJ mol^{-1}) is

B.E. (O – H) =

$= 462.625$ kJ mol^{-1}

7. **(a)** In case of diatomic gaseous molecules, bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction
$H_2(g) \rightarrow 2H(g)$; BE (H – H) = 433.93 kJ mol^{-1}

8. **(b)** $C_2H_2S - SC_2H \rightarrow C_2H_5 - S - C_2H_5 + S\ \Delta H$
S – S bond enthalpy = ΔH

Comprehension 2 (Question 9 to 11)

9. **(a)** The gas exapands against a zero opposing pressure. Since $dw = -P_{ext.} \times V$, it is obvious that the work involved in the expansion in zero.
$du = dq + dw$
Hence $du = dq$
Since there is no change in temperature $dq = 0$
Hence $du = 0$

10. **(a)** $u = f(T, V)$

Since $dT = 0$; $du = 0$

Since $dV \neq 0$, follows that

Since it is a free expansion, it is applicable to only ideal gases.

11. **(d)** If the external pressure is only infinitesimally smaller than the pressure of the gas, the expansion is said to take place reversibly. If, however, the external pressure is much smaller than the gas pressure, the expansion occurs irreversibly. If the external pressure is zero, the expansion is known as free expansion.

Comprehension 3 (Question 12 to 16)

12. **(c)** $\Delta_r S^\circ = S^\circ(CH_3OH, g)$
$- [S^\circ(CO, g) + 2 \times S^\circ(H_2, g)]$
$= 240 - 198 - 29 \times 2 = -16$ J/K–mole

13. **(a)** $\Delta_r H^\circ = \Delta H_f^\circ(CH_3OH, g) - \Delta H_f^\circ(CO, g)$
$= -201 - (114) = -87$ kJ/mol

14. **(d)**

$= 44 - (29.4 + 2 \times 28.8) = -43$ J/K-mol

$= -13.42$ J/K-mol

15. **(c)**

$- (-87) = -43(320 - 300)$

$= -87.86$ kJ/mol

16. **(d)**

$= -87860 - 320(-13.42) = 83565.6$
$\Delta G^o = 83.565$ kJ/mol

Comprehension 4 (Question 17 to 20)

17.

$\Delta_r H =$

$= [-658.3 + 2(-92.3) - 2(-485.2)]$
$= 127.5$ kJ/mole

18. Add Eq. (i), (ii) and (iii)

$CX_4(g) \longrightarrow C(g) + 4X$
$\Delta H = -\Delta H_f + 718 + 2\Delta(X - X)$

If $X = F$, then
$\Delta H = +679.6 + 718 + 2 \times 154.7$
$\Delta H = 1707$

Average bond energy of C – F bond =
= 426.75 kJ/mole

If $X = Cl$, then
$\Delta H = 106.6 + 718 + 2(246.7) = 1318$

Average bond energy of C – Cl bond = 329.5 kJ

19. **(c)** C – Cl bond energy = 329.5
C – H bond energy = 416.1
C – F bond energy = 426.75
Order of reactivity C – Cl > C – H > C – F

20. **(a, b, c)** We have

$q_{\text{water}} = m_{\text{water}} \times S_{\text{water}} \times \Delta T$
$= \{(300\ \text{mL})\ (1\text{g mL}^{-1})\}\ (4.184\ \text{J g}^{-10}\ \text{C}^{-1})\ (1.126°\text{C})$
$= 1413\ \text{J} = 1.413\ \text{kJ}$

$q_{\text{bomb}} = (m_{\text{bomb}} \times S_{\text{bomb}})\ \Delta T = (\text{heat capacity})_{\text{bomb}} \times \Delta T$
$= S_{\text{bomb}}\Delta T$
$= (1.77\ \text{kJ°}\ \text{C}^{-1})\ (1.126°\text{C})$
$= 1.992$ kJ

∴ Total heat released in combution of 0.138 gram Mg at constant volume
$= -(q_{\text{water}} + q_{\text{bomb}})$
$= -(1.413 + 1.992)\ \text{kJ} = -3.405$ kJ

∴ Heat released in the combustion of 1 mole or 24.30 Mg at constant volume.

∴

For the reaction,

$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \qquad \Delta n_g = -1$
$\Delta H = \Delta E + (\Delta n_g)\ RT$
$= -599.60 + (-1)(8.314 \times 10^{-3} \times 298\ \text{K})$
$= (-599.60 - 2.48)\ \text{kJ mol}^{-1} = -602.08\ \text{mol}^{-1}$

21. **(a, b, c)** Entropy change of the gas at constant temperature.

Entropy change of the surroundings.

Since $\Delta T = 0$, therefore $\Delta E = 0$ and according to the first law of thermodynamics. $\Delta E = q + W$

∴

Substituting the values, we get

$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
$= (17.29 - 12.47)\ \text{JK}^{-1}$, which is positive.

Since ΔS_{Total} is positive, the processes is irreversible.

22. **(c, d)** Melting of $H_2O(s)$ at 0°C and 1 atm is a reversible process $\Rightarrow \Delta S_{\text{Total}} = 0$
Vaporisation of $H_2O(l)$ at 373 K is a reversible process $\Delta S_{\text{Total}} = 0$
Below 0°C $[H_2O(s) \longrightarrow H_2O(l)]$ is non spontaneous not feasible.
$H_2O(l) \longrightarrow H_2O(s)$ (freezing) is feasible below 0°C
$H_2O(s) \longrightarrow H_2O(l)$ not feasible below 0°C and feasible above 0°C $\Rightarrow \Delta G$ = negative for melting process $\Rightarrow \Delta S_{\text{Total}}$ increases

23. **(a, b, c)** Both the gases before mixing are at the same temperature and pressure. Since the amount of neon is twice as that of helium, it is obvious that

$V_{\text{Ne}} = 2V_{\text{He}}$

Now the volume of the gas after mixing will be

$V_{\text{total}} = V_{\text{He}} + V_{\text{Ne}} = V_{\text{He}} + 2V_{\text{He}} = 3V_{\text{He}}$

Each of the two gases will suffer entropy change due to the volume change. Thus,

Thus

$\Delta S_{\text{mix}} = \Delta S_{\text{He}} + \Delta S_{\text{Ne}} = 9.136 + 6.743 = 15.879\ \text{JK}^{-1}$

24. **(a, b, c)** Amount of

$T_1 = 300\ \text{K};\ V_1 = 20\ \text{dm}^3;\ V_2 = 10\ \text{dm}^3$

For an adiabatic reversible process

$$T_2V_2^{R/C_{V,m}} = T_1V_1^{R/C_{V,m}} \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Thus,

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{R/C_{V,m}} = (300\text{ K})\left(\frac{20\text{ dm}^3}{10\text{ dm}^3}\right)^{2/5}$$

$$= (300\text{ K})(1.32) = 396\text{ K}$$

Hence,

$$\Delta E = W = nC_V\Delta T = 0.714\times\frac{5}{2}\times 8.314\times 96$$

$$= 1424.69\text{ J}$$

$$\Delta H = nC_P\Delta T = 0.714\times\frac{7}{2}\times 8.314\times 96$$

$$= 1994.56\text{ J}$$

25. **(5)** Energy available for muscular work

$$= \frac{2880\times 25}{100} = 720\text{ kJ/mol.}$$

$\therefore$ energy available for muscular work for 125 grams glucose = $720\times\frac{125}{180}\times\frac{1}{100}$ = 5 km

26. **(3)** On mixing $CaCl_2$ (aq.) and Na_2CO_3

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

Solutions are very dilute and thus, 100% dissociation occurs.

Ca^{2+} (aq.) + $2Cl^-$ (aq.) + $2Na^+$ (aq.) + CO_3^{2-} (aq.) $\longrightarrow$ $CaCO_3$ + $2Na^+$ (aq.) + $2Cl^-$ (aq.)

or Ca^{2+} (aq.) + CO_3^{2-} (aq.) $\longrightarrow CaCO_3(s)$

$$\Delta_r H = [\Sigma\nu_P(\Delta H^o_f)_P] - [\Sigma\nu_R(\Delta H^o_f)_R]$$

$$= \Delta H^o_{f\,CaCO_3} - [\Delta H^o_{f\,ca^{2+}} + \Delta H^o_{f\,CO_3^{2-}}]$$

$\because$ $\Delta_r H$ of a compound

$= \Delta_r H = -288.45 - (-129.80 - 161.65) = 3$ k cal

27. **(4)** The required equation is

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe,\ \Delta H = ?$$

$$\Delta H = \Delta H_{f(\text{products})} - \Delta H_{f(\text{reactants})}$$

$$= [\Delta H_{f(Al_2O_3)} + 2\Delta H_{f(Fe)}]$$

$$- [2\Delta H_{f(Al)} + \Delta H_{f(Fe_2O_3)}]$$

$= (-399 + 2\times 0) - [2\times 0 + (-195.92)]$

$= -399 + 195.92 = -203.8$

At. mass of aluminum = 27, Mol. mass of Fe_2O_3 = 160

$$\therefore\quad \text{Volume} = \frac{160}{5.2} + \frac{2\times 27}{2.7} = 50.77\text{ cm}^3$$

$$\therefore \text{Fuel value per cm}^3 = \frac{-203.08}{50.77} = 4\text{ kcal}$$

28. **(8)** $\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T} = \frac{2288}{286} = 8\text{ JK}^{-1}\text{mol}^{-1}$

29. **(2)** $Q = 13.7 - 11.7 = 2$

30. **(8)** Work done $= -P_{\text{ext}}\times dV = -1\times(2.5 - 2.0)$

$= -0.5$ L – atm

$$= -\frac{0.5\times 1.987\times 4.184}{0.0821} = -50.63\text{ J}$$

Since, Work is carried out at constant P and thus irreversible process.

From first law of thermodynamics

$\Delta E = q + w$

$= 58.63 - 50.63$

$= 8$ J

31. Gas is diatomic as $\gamma = 1.4$, thus, $C_V = \frac{5}{2}R$ and $C_p = \frac{7}{2}R$

and $\Delta H = 85$ J at constant pressure

$\Delta H = nC_P\Delta T$

$$\therefore\quad \Delta T = \frac{85}{nC_p} = \frac{85\times 2}{n\times 7\times R} = \frac{30}{nR}$$

Now, $W = -nR\Delta T = -nR\times\frac{30}{nR} = -30$ J

$\Delta H = \Delta E + nR\Delta T$

$85 = \Delta E + 30$

$\Delta E = 55$ J

32. $\Delta H_{\text{dissolution}} = \Delta H_{(\text{ionization})} + \Delta H_{(\text{hydration})}$

$= 778 - 775 = 3\text{ kJ mol}^{-1} = 3000\text{ J mol}^{-1}$

$\Delta S_{\text{dissolution}} = 40\text{ J mol}^{-1}$

$\Delta G_{(\text{dissolution})} = \Delta H - T\Delta S \Rightarrow 3000 - 300\times 40 = -9000$ J;

$\Delta G = -9$ kJ

33. Reversible work is maximum work.

$$\therefore\quad w = -2.303nRT\log\left(\frac{V_2}{V_1}\right)$$

$$= -2.303\times\frac{16}{32}\times 8.314\times 300\log\frac{25}{5}$$

$= -2.01\times 10^3\text{ J} = -2$ kJ

34. $\Delta H_{\text{fusion}} = 6.025\times 1000\text{ J mol}^{-1}$

$$= \frac{6025}{18}\text{Jg}^{-1} = 334.72\text{ J g}^{-1}$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f} = \frac{334.72}{167K} = 2\text{ JK}^{-1}\text{g}^{-}$$

35. **(i)** –3201 kJ, (ii) –3199.75 kJ

Given,

$7C(s) + 3H_2(g) + O_2(g) \longrightarrow C_6H_5COOH(s);$ $\Delta H^0 = -408$ kJ (i)

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^0 = -393$ kJ (ii)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H^0 = -286$ kJ (iii)

$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l);$

$\Delta H = ?$ (iv)

By (ii) × 7 + (iii) × 3 – (i)

$$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l)$$

$\Delta H^o = [-393\times 7 - 286\times 3 + 408]$

$\therefore$ $\Delta H^o = -3201$ kJ

Also $\Delta H = \Delta E + \Delta n_g RT$

∴ $= 3201 = \Delta E + (-0.5) \times 8.314 \times 10^{-3} \times 300$

∴ $\Delta E = -3201 + 1.2471 = -3199.75$ kJ

36. Total energy required in the day

$$= \frac{150 \times 24 \times 60 \times 60}{1000} \text{kJ (1 W = J/ sec)}$$

= 12960 kJ

Units of glycogen required $= \frac{12960}{476} = 27$

37. Given, $\frac{1}{2}\text{H}_2(\text{g}) + \text{aq.} \longrightarrow \text{H}^+_{(\text{aq})} + e;\quad \Delta H^\circ = 0$ (i)

$$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \longrightarrow \text{HCl(g)};\quad \Delta H^\circ = -92.4 \text{ kJ} \quad \text{(ii)}$$

$$\text{HCl(g)} + n\text{H}_2\text{O(l)} \longrightarrow H^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})};\ \Delta H^0 = -74.8 \text{ kJ} \quad \text{(iii)}$$

Add Eqs. (ii) and (iii)

$$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) + n\text{H}_2\text{O} \longrightarrow \text{H}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})};$$

$\Delta \text{H}^0 = -167.2$ kJ (iv)

Subtract Eq. (i) from (iv)

$$\therefore \quad \frac{1}{2}\text{Cl}_2(\text{g}) + \text{aq.} + e^- \longrightarrow \text{Cl}^-_{(\text{aq})};\quad \Delta H = -167.2 \text{ kJ}$$

Heat of formation for $\text{Cl}^-_{(\text{aq})} = -167.2$ kJ

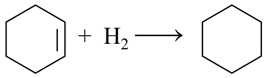
38. Initial average temperature of the acid and base $= \frac{22.6 + 23.4}{2} = 23.0$°C [Since mass same]

Rise in temperature = (29.3 – 23.0) = 6.3°C

Total heat produced = (92 × 0.75 + 200 × 4.184) = (905.8) × 6.3 = 5706.54 J

Enthalpy of neutralisation $= -\frac{5706.54}{100} \times 1000 \times 1$

= – 57065.4 J = – 57 kJ

39. 

$\Delta_r H = ?$

See heat of combution

$$\Delta_r H = [\Sigma v_R (\Delta H_{\text{combution}})_R - \Sigma v_P (\Delta H_{\text{combution}})_P]$$

$$= (-241) + (-3800) - (-3920)$$

$$= -121 \text{ kJ/mole}$$

40. $\Delta H_{\text{reaction}}$ = Bond energy data for the formation of bond + Bond energy data for the dissociation of bond

$= -[1(C-C) + 6(C-\text{H})]$

$+ [1(C=C) + 4(C-\text{H}) + 1(\text{H}-\text{H})]$

$= -347 - 2 \times 414 + 615 + 435$

= – 125 kJ

Enthalpy change for the reaction = –125 kJ

41. $\Delta G = \Delta H - T\Delta S$

For a reaction to be spontaneous, ΔG = –ve

$\Delta H - T\Delta S$ = –ve or $\Delta H > T\Delta S$ or $\frac{\Delta H}{\Delta S} > T$ or

$$\frac{-95.4 \times 10^{+3}}{-198.3} > T \text{ or } 481.0 > T$$

Thus, if temperature of system is lesser than 481 K, the reaction would be spontaneous. At 481 K, the reaction will be in equilibrium. An increase in temperature above 481 K will develop non-spontaneity for the reaction.

42. Heat taken up by water $= mC\Delta T$

$= 150 \times 1000 \times 4.184 \times 10^{-3} \times 55 = 34518$ kJ

∵ 2050 kJ heat is provided by 1 mole C_3H_8

∴ 34518 kJ heat is provided by = 34518/2050

= 16.83 mole of C_3H_8

Volume of C_3H_8 at NTP = 16.83 × 22.4 L

$= 3.77 \times 10^2$ L

43. Work is done aganist constant P ∴ irreversible

$\Delta V = 5 - 3 = 2dm^3 = 2$ L; $P = 3$ atm.

∴ $W = -P_{\text{ext}} \cdot \Delta V = -3 \times 2$ litre atm $= -6 \times 101.3$

$= -607.8$ kJ

Now this work is used up in heating water

∴ $W = n \times C \times \Delta T$

$= (10 \times 18) \times 4.184 \times \Delta T = 607.8$

∴ $\Delta T = 0.80$

∴ $\Delta T \times 10 = 8$

44. The concerned chemical reaction is

$\text{B}_2\text{H}_6(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow \text{B}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O(g)}, \Delta H = ?$

The enthalpy change can be calculated in the following way:

Here $\Delta_r H = (\Delta H_C)_{\text{B}_2\text{H}_6}$

$$\Delta_r H = \Sigma v_P (\Delta H^\circ_{\text{f}})_P - \Sigma v_R (\Delta H^\circ_{\text{f}})_R$$

$$\Delta_r H = [\Delta H_{\text{B}_2\text{O}_3(\text{S})} + 3\Delta H_{\text{H}_2\text{O(g)}}] - \Delta H_{\text{B}_2\text{H}_6(\text{S})}$$

$(\because \Delta H^\circ_{\text{f}} \text{ of } \text{O}_2 = 0)$

$\Delta H_{\text{H}_2\text{O(g)}}$ can be obtained by adding $\Delta H_{\text{H}_2\text{O}_{(\text{l})}}$ and $\Delta H_{\text{H}_2\text{O}_{(\text{g})}}$

i.e., $-286 + 44 = -242 \text{ kJ mol}^{-1}$

$\Delta H = [-1273 + 3(-242)] - 36 \text{ kJ mol}^{-1}$

$= -1273 - 726 - 36$

$= -2035 \text{ kJ mol}^{-1}$

45. Given:

$\text{NaCl}_{(\text{s})} + \text{aq} \longrightarrow \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})} \qquad \Delta H = -2$ kJ/mole

$\text{Na}^+_{(\text{g})} + \text{Cl}^-_{(\text{g})} \longrightarrow \text{NaCl(s)} \qquad \Delta H = -772$ kJ/moles

so $\text{Na}^+_{(\text{g})} + \text{Cl}^-_{(\text{g})} + \text{aq.} \longrightarrow \text{Na}^+_{(\text{g})} + \text{Cl}^-_{(\text{aq.})} \quad \Delta H = -774$

and $\text{Na}^+_{(\text{g})} + \text{aq.} \longrightarrow \text{Na}^+_{(\text{aq.})} \qquad \Delta H = -390$

So enthalpy of hydration of Cl^- = –384

Similarly, enthalpy of hydration of I^- = –307

46. $q = -65$ J, $w = 20$ J

$\Delta E = q + w$

$= -65 + 20 = -45$ J

47. (a) $\Delta H_{\text{glucose}} = -2808$ kJ mol

Energy need to climb 3 m = $Mgh = 62.5 \times 10 \times 3$

$\Delta q = 1875$ Joule

Now useful energy from 1 mole of glucose

$= 2808 \times \dfrac{25}{100} = 702$ kJ

⇒ Number of mole of glucose required

$= \dfrac{1875}{702 \times 10^3}$

$= 2.67 \times 10^{-3}$ mole

Grams of glucose = $180 \times 2.67 \times 10^{-3} = 0.4807$ g

(b) Energy need to climb 3000 m = $0.4807 \times 3000/3$ = 0.4807 kg

48. $\Delta H = \Delta E + \Delta n_g RT$

$40.66 \times 2 = \Delta E + 2 \times 8.314 \times 373$

⇒ $\Delta E = (81.32 - 6.202)$ kJ

$\Delta E = 75.118$ kJ

49. $\Delta H = 1$ kcal

$\Delta H = \Delta E + P\Delta V$

$1 \times 10^3 \times 4.18 = \Delta E + 1.013 \times 10^5 \times 3 \times 10^{-3}$

$\Delta E = (4180 - 30.39)$ Joule $= \left(\dfrac{4149.70}{4.18}\right)$ cal

$\Delta E = 0.993$ kcal

50. $NH_4CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$

$\Delta H_{298} = \Delta E + \Delta n_g RT = -742.7 + \dfrac{1}{2} \times \dfrac{8.314 \times 298}{1000}$

$\Delta H_{298} = -741.46$ kJ

51. $\Delta H = 1440$ cal

$\Delta H = \Delta E + P(V_2 - V_1)$

$= \Delta E + 1[0.018 - 0.0196] \times \dfrac{101.3}{4.18}$

$1440 = \Delta E - \dfrac{0.0016 \times 101.3}{4.18}$ Cal

$\Delta E = 1440 + 0.03877$

$= 1440.03877$ Cal

52. $W = -P_{\text{ext}}[V_2 - V_1] = -[1.10 \times 1.0] \times 101.3$ J

$= 10.13$ J

53. $Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$

$q = \Delta H = -36.5$ kJ

$W = -P_{\text{ext}}(V_2 - V_1) = -1 \times \left[\dfrac{500 \times 50}{1000}\right] \times 101.3$ J

$W = -2.53$ kJ

$\therefore \Delta E = q + W \Rightarrow -36.5 - 2.53 = -39.03$ kJ

54. $W = -2.303\, nRT \log\left(\dfrac{P_1}{P_2}\right)$

$= -2.303 \times 1 \times 8.314 \times 298 \log\left(\dfrac{5}{1}\right)$

$W = -3.988$ kJ

55. $\Delta S = \dfrac{nC_p dT}{T}$

$= 1 \times \int \left(\dfrac{25.5}{T} + 13.6 \times 10^{-3} - 42.5 \times 10^{-7} T\right) dT$

$= 2.303 \times 25.5 \log 2 + 13.6 \times 10^{-3} \times 300 - 42.5 \times 10^{-7} \dfrac{(600^2 - 300^2)}{2}$

$\Delta S = 20.618$ kJ

56. $Br_2(l) + Cl_2(g) \longrightarrow 2BrCl(g), \qquad \Delta H° = 29.3$ kJ

$\Delta S_{Br_2(l)} = 152.3$

$\Delta S_{Cl_2(g)} = 223.0$

$\Delta S_{BrCl(g)} = 239.7$ J mol^{-1} K^{-1}

$\Delta_r S = 2 \times 239.7 - 223 - 152.3 = 104.1$

$\Delta_r G = \Delta H - T\Delta_r S$

$= 29300 - 298 \times 104.1 = -1721.8$ J

57. $CCl_4(l) \longrightarrow CCl_4(g)$

$P = 1$ atm

$T = 298$ K $\qquad \Delta S = 94.98$ JK^{-1}

$\Delta_r H = \Sigma \nu_P (\Delta H_f^o)_P - \Sigma \nu_R (\Delta H_f^o)_R$

$= (-106.7 + 139.3)$ kJ

$= 32.6$ kJ/mol

$\Delta_r G = \Delta_r H - T\Delta S$

$\Delta_r G = 32.6 \times 10^3 - 298 \times 94.98$

$\Delta_r G = 4.296$ kJ/mol

positive hence non spontaneous

58. Since entropy and latent heat given in per kg, so mass taken in kg.

Step 1

Ice (200 K) $\longrightarrow$ Ice (273 K)

$\Delta S_1 = m\, C_p \ln \dfrac{T_2}{T_1} = 1 \times 2.09 \times 10^3 \ln \dfrac{273}{200}$

$\Delta S_1 = 650.312$ J/°C

Step 2

Ice (273 K) $\rightleftharpoons$ Water (273 K)

$\Delta S_2 = \dfrac{\Delta H_f}{273} = \dfrac{3.34 \times 10^5}{273} = 1223.44$ J/°C

Step 3

Water (273 K) $\longrightarrow$ Water (373 K)

$\Delta S_3 = 1 \times 4.18 \times 10^3 \ln \dfrac{373}{273} = 1304.6$ J/°C

Step 4

Water (373 K) $\rightleftharpoons$ Steam (373 K)

$\Delta S_4 = \dfrac{\Delta H_v}{373} = \dfrac{22.6 \times 10^5}{373} = 6058.98$ J/°C

Step-5

Steam (373 K) $\longrightarrow$ Steam (400 K)

$\Delta S_5 = 1 \times 2.09 \times 10^3 \ln \dfrac{400}{373} = 146.06$ J/°C

$\Delta S_T = 9383.4$ J/°C

59. $\gamma = \dfrac{5}{3}$, $P_1 = 1$ atm, $T_1 = 300$ K, $P_2 = 2$ atm

(a) PV^{γ} = constant

$P^{1-\gamma}T^{\gamma}$ = constant

$TP^{(1-\gamma)/\gamma}$ = constant

$T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma}$

$T_2 = 300\left(\dfrac{1}{2}\right)^{-2/5} = 395.85$

$$w = \Delta U = n\,C_V dT = 1 \times \frac{3}{2} \times 8.314 \times 95.85$$
$$w = 1195.37 \text{ J}$$
$$V_2 = \frac{nRT_2}{P_2} = 16.25 \text{ L}$$

(b) $\Delta U = w$

$$1 \times 1.5 \times 8.314\,(T_2 - 300) = -P_{\text{ext}}[V_2 - V_1]$$
$$= -2 \times 101.3 \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right)$$
$$(T_2 - 300) = 1.333 \left(300 - \frac{T_2}{2}\right)$$
$$T_2 = 420 \text{ K} \quad \text{and} \quad V_2 = \frac{nRT_2}{P_2} = 17.24 \text{ L}$$
$$w = \Delta U = 1.5 \times 8.314\,(420 - 300)$$
$$w = 1496.52 \text{ J}$$

60. $V_1 = 20$ L, $\gamma = 7/5$, $T_1 = 673$ K,
$P_2 = 0.2$ MPa = 2 atm, $P_1 = 0.7$ MPa = 7 atm

$$n = \frac{P_1V_1}{RT_1} = 2.5$$

(i) $\Delta U = \Delta H = 0$

$$q = -w = nRT \ln\frac{P_1}{P_2} = 2.5 \times 8.314 \times 673 \ln\frac{7}{2}$$
$q = 17.52$ kJ$w = -17.52$ kJ

(ii) $P_1V_1^{\gamma} = P_2V_2^{\gamma}$
$7(20)^{\gamma} = 2(V_2)^{\gamma} \Rightarrow V_2 = (3.5)^{5/7} = 48.92$ L

$$T_2 = \frac{P_2V_2}{nR} = 470.46 \text{ K}$$
$$q = 0,\ w = \Delta U = nC_V[T_2 - T_1]$$
$$= 2.5 \times 2.5 \times 8.314(470.46 - 673) = -10.524 \text{ kJ}$$
$$w = \Delta U = -\ 10.524 \text{ kJ}$$
$$\Delta H = 2.5 \times 3.5 \times 8.314\,(470.46 - 673) = -\ 14.73 \text{ kJ}$$

(iii) $q = w = \Delta U = \Delta H = 0$

(iv) $q = 0,\ \Delta U = w = nC_V[T_2 - T_1] = -P_{\text{ext}}[V_2 - V_1]$

$$2.5 \times 2.5 \times 8.314\,(T_2 - 673)$$
$$= -\ 101.3 \times 2 \times 2.5 \times 0.0821\left(\frac{T_2}{2} - \frac{T_1}{7}\right)$$
$$T_2 - 673 = -\ 0.79\left(\frac{T_2}{2} - 96.142\right)$$
$$T_2 = 536.91 \text{ K}$$
$$w = \Delta U = 2.5 \times 2.5 \times 8.314\,(-136) = -\ 7.1 \text{ kJ}$$
$$\Delta H = 2.5 \times 3.5 \times 8.314\,(-136) = -\ 9.9 \text{ kJ}$$

(v) $\Delta U = \Delta H = 0$

$$V_2 = \frac{nRT}{P_2} = \frac{2.5 \times 0.821 \times 673}{2} = 69 \text{ L}$$
$$w = -P_{\text{ext}}[V_2 - V_1] = -2 \times 49 = -98.13 \text{ L-atm}$$
$$w = -98.13 \times 101.3 = -9940.9 \text{ J}$$
$$w = -\ 9.94 \text{ kJ} \qquad q = -w = 9.94 \text{ kJ}$$

61. (i) The entropy change of the system $\Delta S_{\text{sys.}}$ will be same in all the three process as it is state function.

$$\Delta S_{\text{sys.}} = nR \ln\frac{V_2}{V_1} = 1 \times 8.314 \ln 3 = 9.134 \text{ J/K}$$

For reversible process

$$\Delta S_T = 0$$
$$\Delta S_{\text{surr.}} = -\ \Delta S_{\text{sys.}} = -\ 9.134 \text{ J/K}$$

(ii) $\Delta S_{\text{sys.}} = 9.134$ J/K

$$\Delta S_{\text{surr.}} = \frac{-q_{\text{irrev.}}}{T} = -\left[\frac{q_{\text{rev.}} - 836.6}{298}\right]$$
$$= -\ \Delta S_{\text{sys.}} + 2.807$$
$$\Delta S_T = \Delta S_{\text{sys.}} + (-\Delta S_{\text{sys.}} + 2.807) = 2.807 \text{ J/K}$$

(iii) For free expansion system does not absorb any heat so $q = 0$

$$\Delta S_{\text{sys.}} = 0$$
$$\Delta S_T = \Delta S_{\text{sys.}} = 2.807 \text{ J/K}$$

62. (i) $\Delta S_{\text{sys.}} = 0,\ \Delta S_{\text{surr.}} = 0,\ \Delta S_T = 0$

(ii) $\Delta E = w = n\,C_v\,(T_2 - T_1) = -\ P_{\text{ext}}[V_2 - V_1]$

$$0.5 \times 1.5 \times 8.314\,(T_2 - 473)$$
$$= -101.3 \times 2 \times 0.5 \times 0.0821\left(\frac{T_2}{2} - \frac{473}{5}\right)$$
$$T_2 - 473 = -\ 1.333\left(\frac{T_2}{2} - 94.6\right)$$
$$T_2 = 359.49 \text{ K}$$
$$\Delta S_{\text{sys.}} = n\left[C_p \ln\frac{T_2}{T_1} + R \ln\frac{P_1}{P_2}\right]$$
$$= 0.5\left[2.5 \times 8.314 \ln\frac{359.49}{473} + 8.314 \ln\frac{5}{2}\right]$$
$$\Delta S_{\text{sys.}} = 0.957 \text{ J/K}$$

since no heat is transferred $q = 0$

$$\Delta S_{\text{surr.}} = 0$$
$$\Delta S_T = \Delta S_{\text{sys.}} = 0.957 \text{ J/K}$$

(iii) In free expansion $q = w = \Delta U = 0$
T is constant.

$$\Delta S_{\text{sys.}} = nR \ln\frac{P_1}{P_2} = 0.5 \times 8.314 \times \ln\frac{5}{2} = 3.81 \text{ JK}$$
$$\Delta S_{\text{surr.}} = 0$$
$$\Delta S_T = \Delta S_{\text{sys}} = 3.81 \text{ J/K}$$

63. $P_1 = 1$ atm, $V_1 = 1$ L
$P_2 = 1001$ atm, $V_2 = 0.99$L Let $P = a + bV$
On finding $a = 100001$, $b = -10^5$ so

$$P = (100001 - 10^5\text{V})$$
$$w = -\int PdV = \int_{V_1}^{V_2} (100001 - 10^5\text{V})\,dV$$
$$w = -\ 100001\,(V_2 - V_1) + \frac{10^5}{2}(V_2^2 - V_1^2)$$
$$w = -\ 100001\,(-0.01) + \frac{10^5}{2}(-0.0199)$$
$$= 5.01 \text{ L-atm}$$
$$w = 501 \text{ J} \qquad \Delta U = w = 501 \text{ J}$$
$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$
$$= 501 + (1001 \times 0.99 - 1 \times 1) \times 100 = 99500 \text{ J}$$
$$\Delta H = 99.5 \text{ kJ}$$

64. (i) $\Delta S_{\text{sys.}} = n\, C_v \ln \frac{T_2}{T_1} = 1 \times \frac{3}{2} R \ln \frac{1000}{100} = \frac{3}{2} R \ \ln 10$

$\Delta S_T = 0$ (Reversible process)

$$\Delta S_{\text{surr.}} = -\Delta S_{\text{sys.}} = -\frac{3}{2} R \ln 10$$

(ii) $\Delta S_{\text{sys.}} = \frac{3}{2} R \ln 10$

$w = 0 \qquad \because \quad \Delta V = 0$ for isochoric

$$q = -\Delta E = -\frac{3}{2} R\,(900) = -nC_V \Delta T$$

$$\Delta S_{\text{surr.}} = -\frac{q}{T} = \frac{-3R\,(900)}{2 \times 1000} = -\frac{3}{2} R\,(0.9)$$

$$\Delta S_T = \frac{3}{2} R \ln 10 - \frac{3}{2} R\,(0.9) = \frac{3}{2} R\,(1.402)$$

65. We know

$$G = H - TS = U + PV - TS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$w = 0$, $dV = 0$, $dV = dq = T\,dS$ so

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT \Rightarrow \Delta G = V\Delta P - \int SdT$$

$$VdP = V\,(P_2 - P_1)$$

$$\frac{P_2}{T_2} = \frac{P_1}{T_1} \Rightarrow \frac{P_2}{400} = \frac{1}{300} \Rightarrow P_2 = \frac{4}{3}$$

$$VdP = 24.6\,(4/3 - 1) = 8.2 \text{ L-atm} = 820 \text{ J}$$

$$\int SdT = \int_{T_1}^{T_2} (10 + 0.01T)\, dT$$

$$= 10(T_2 - T_1) + 0.005(T_2{}^2 - T_1{}^2)$$

$$SdT = 10(100) + 0.005\,(400^2 - 300^2) = 1350$$

$$\Delta G = 820 - 1350 = -530 \text{ J}$$

66. (a) $n = 2$

$$V_1 = \frac{2 \times 0.0821 \times 300}{1} = 49.26 \text{ L}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{49.26}{300} = \frac{V_2}{550} \Rightarrow V_2 = 90.31 \text{ L}$$

(i) $w = -P\Delta V = 1(90.31 - 49.26) = -41.05$ L-atm

$w = -41.05 \times 101.3 = -4158.36 \text{ J} = -4.15$ kJ

$$q = \Delta H = \int nC_p dT$$

$$= 2\left[12.552(T_2 - T_1) + \frac{8.368 \times 10^{-3}}{2}(T_2^2 - T_1^2)\right]$$

$$q = \Delta H = 2\left[12.552(250) + \frac{8.368 \times 10^{-2}}{2}(212500)\right]$$

$$q = \Delta H = 24.04 \text{ kJ}$$

$$C_v = C_p - R = 4.238 + 8.368 \times 10^{-2}\ T$$

$$\Delta U = \int nC_v dT = 19.9 \text{ kJ}$$

(b) $w = 0$

Since, $\Delta V = 0$ for isochoric

$$q = \Delta U = 19.9 \text{ kJ}$$

$$\Delta H = \int nC_p dT = 24.04 \text{ kJ}$$

67. At 298 K,

$\Delta G° = -6333$ kJ/mole

$\Delta H° = -5737$ kJ/mole

and $\quad \Delta G° = \Delta H° - T\Delta S°$

so $\quad \Delta S° = 2$ kJ/mole

At 310 K

$\Delta G = -5737 - 2 \times 310 = -6357$ kJ/mole

Additional non-PV work = $|\Delta G - \Delta G°| = 24$ kJ/mole

68. $w = 200$ J; $q = -140$ J;

$\because q = \Delta E + (-w)$; where $-w$ is work done by the system

$\Delta E = q + w$

$\Delta E = -140 + 200 = +60$ J

69. $w = -P_{\text{ext}}\Delta V = -1.5 \times (1.0 - 0.5) = -0.75$ L atm

$= -0.75 \times 101.3 \text{ J} = -75.975$ J

$\because$ 1 L atm = 101.3 J

Now, $\Delta E = 200 - 75.975 = +124.025$ J

70. Since the external pressure is greatly different from the pressure of N_2 and thus, process is irreversible.

$w = -P_{\text{ext}}\,(V_2 - V_1)$

$w = -1 \times (V_2 - V_1)$

Given, $V_1 = 2$ L $\qquad V_2 =?\ T = 273$ K

$P_1 = 5$ atm $\qquad P_2 = 1$ atm

$\therefore \quad P_1V_1 = P_2V_2 \qquad$ for isothermal

$$\therefore \quad V_2 = \frac{2 \times 5}{1} = 10 \text{ L}$$

$\therefore \quad w = -1 \times (10 - 2) = -8$ litre atm $= 8 \times 101.3$ J

$= -810.4$ J

71. (a) $\Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T} = \frac{26 \times 10^3}{308} = +84.41 \text{ JK}^{-1} \text{ mol}^{-1}$

(b) $\Delta S_{\text{cond.}} = \frac{\Delta H_{\text{cond.}}}{T} = -\frac{26 \times 10^3}{308} = -84.41 \text{ JK}^{-1} \text{ mol}^{-1}$

($\because H_{\text{cond}} = -26$ kJ)

72. $\Delta H_{\text{dissolution}}$ = Lattice energy + Hydration energy

$= 777.8 - 774.1 = 3.7 \text{ kJ mol}^{-1}$

Now $\quad \Delta G = \Delta H - T\Delta S$

$= 3.7 - 298 \times 0.043 = 3.7 - 12.814$

$\Delta G = -9.114 \text{ kJ mol}^{-1}$

73. $\Delta G° = -2.303\ RT \log$ Keq

$\Delta G° = -2.303 \times 8.314 \times 300 \log\,[2.0 \times 10^{-7}]$

$= +38479.8 \text{ J mol}^{-1} = +38.48 \text{ kJ mol}^{-1}$

Also, $\Delta G° = \Delta H° - T\Delta S°$

$$\therefore \quad \Delta S° = \frac{\Delta H° - \Delta G°}{T} = \frac{28.40 - 38.48}{300}$$

$= -0.0336 \text{ kJ} = -33.6 \text{ JK}^{-1}$

74. We know,

Path CA – Isothermal compression

Path AB – Isobaric expansion

Path BC – Isochoric change

Let V_i and V_f are initial volume and final volume at respective points,

For temperature T_1 (For C): $\qquad PV = nRT_1$

$2 \times 10 = 1 \times 0.0821 \times T_1$

$\therefore \quad T_1 = 243.60$ K

For temperature T_2 (For C and B): $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

$$\frac{2\times 10}{T_1} = \frac{20\times 10}{T_2}$$

$$\therefore \quad \frac{T_2}{T_1} = 10$$

$$\therefore \quad T_2 = 243.60 \times 10 = 2436.0 \text{ K}$$

Path *CA*: $w = +2.303\, nRT_1 \log \dfrac{V_i}{V_f}$

$$= 2.303 \times 1 \times 2 \times 243.6 \log \frac{10}{1}$$

$$= +1122.02 \text{ cal}$$

$\Delta E = 0$ for isothermal compression; Also $q = w$

Path *AB*: $w = -P(V_f - V_i)$

$$= -20 \times (10 - 1) = -180 \text{ litre atm}$$

$$= \frac{-180 \times 2}{0.0821} = -4384.9 \text{ cal}$$

Path *BC*: $w = -P\,(V_f - V_i) = 0 \qquad (\because V_f - V_i = 0)$

since volume is constant for monoatomic gas heat change at constant volume $= q_v = \Delta E$.

Thus for path BC $\quad q_v = C_v \times n \times \Delta T = \Delta E$

$$\therefore \quad q_v = \frac{3}{2} R \times 1 \times (2436 - 243.6)$$

$$q_v = \frac{3}{2} \times 2 \times 1 \times 2192.4 = 6577.2 \text{ cal}$$

Since process involves cooling

$$\therefore \quad q_v = \Delta E = -6577.2 \text{ cal}$$

Also in path AB, the intenal energy in state A and state C is same. Thus during path AB, an increase in internal energy equivalent of change in internal energy during path BC should take place. Thus ΔE for path AB = +6577.2 cal

Now q for path $AB = \Delta E - w_{AB} = 6577.2 + 4384.9 = 10962.1$ cal

Cycle: $\Delta E = 0$; $q = -w = -[\text{w}_{\text{Path}\,CA} + \text{w}_{\text{Path}\,AB} + \text{w}_{\text{Path}\,BC}]$

$$= -\,[+1122.02 + -4384.9 + 0]$$

$$\therefore \quad q = -w = +3262.88 \text{ cal}$$

75. For the given cyclic process,

$$\frac{V_B}{V_A} = 2, \frac{V_D}{V_A} = 4, T_A = 300 \text{ K}$$

(a) For isobaric process AB

$$\frac{V_A}{T_A} = \frac{V_B}{T_B}$$

$$\therefore \quad T_B = T_A \times \frac{V_B}{V_A} = 300 \times 2 = 600 \text{ K}$$

(b) The following process are there in complete cycle

(i) $A \rightarrow B$ Isobaric expansion

(ii) $B \rightarrow C$ Isothermal expansion

(iii) $C \rightarrow D$ Isochoric compression

(iv) $D \rightarrow$ A Isothermal compression

For (i) $q_{A\rightarrow B} = +n \times C_P \times \Delta T = +2 \times \dfrac{5}{2} \times R \times 300 =$ $+1500 \times 2 = +3000$ cal($R = 2$ cal)

(ii) $q_{B\rightarrow C} = \Delta E - w \qquad (\Delta E = 0)$

$$\therefore \quad q_{B\rightarrow C} = \Delta E - w = +\int P dV = +nRT \ln \frac{V_D}{V_B}$$

$$= +2 \times 2 \times 600 \ln \frac{4}{2} = +1.663 + 10^3 \text{ cal}$$

(iii) $q_{C\rightarrow D} = n \times C_v \times \Delta T = 2 \times \dfrac{3}{2} \times 2 \times -300 =$ -1800 cal

(iv) $q_{D\rightarrow A} = +nRT_A \ln \dfrac{V_A}{V_D} = +2 \times 2 \times 300 \ln \dfrac{1}{4} =$ $-2 \times 2 \times 300 \times 1.386 = -1.663 \times 10^3$ cal

$\therefore \quad Q = q_{A\rightarrow B} + q_{B\rightarrow C} + q_{C\rightarrow D} + q_{D\rightarrow A} =$ $3000 + 1663 - 1800 - 1663 = 1200$ cal

(c) Since the process $ABCDA$ is a cyclic process

$\therefore \quad \Delta E = 0$ or $Q = \Delta E - Q = -w$

or $Q = -1200$ cal

i.e., work done on the system = 1200 cal

76. We know,

(i) Vessel is of fixed volume, hence $\Delta V = 0$.
No work is done, $w = -P_{\text{ext}}\Delta V = 0$

(ii) The H_2 gas formed drives back the atmosphere hence.

$$w = -P_{\text{ext}} \cdot \Delta V = -\Delta n_g RT$$

where n is the number of mole of H_2 gas obtained from n mole of Fe(s).

$$Fe_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq.)} + H_2(g)$$

1 mole $\qquad\qquad$ 1 mole

$$\therefore \quad n = \frac{50}{56} = 0.8929 \text{ mole}$$

$$\therefore \quad w = -0.8929 \times 8.314 \times 298 = -2212.22 \text{ J}$$

The reaction mixture in the given system does 2.212 kJ of work driving back to atmosphere.

77. $\Delta H = \Delta E + P\Delta V$

Given, $\Delta E = +0.21 \text{ kJ mol}^{-1} = 0.21 \times 10^3 \text{ J mol}^{-1}$

$P = 1.0 \times 10^5$ Pa

$\Delta V = V_{(\text{aragonite})} - V_{(\text{Calcite})}$

$$= \left(\frac{100}{2.93} - \frac{100}{2.71}\right) \text{cm}^3 \text{ mol}^{-1} \text{ of } CaCO_3$$

$$= -2.77 \text{ cm}^3 = -2.77 \times 10^{-6} \text{ m}^3$$

$$\therefore \quad \Delta H = 0.21 \times 10^3 - 1 \times 10^5 \times 2.77 \times 10^{-6}$$

$$= 209.72 \text{ J} = 0.20972 \text{ kJ mol}^{-1}$$

78. Given, for the change, $\Delta H = 30 \times 10^3 \text{ J mol}^{-1}$, $\Delta S = 70 \text{ JK}^{-1} \text{ mol}^{-1}$

For a non-spontaneous reaction

$\Delta G = +$ve

Since $\Delta G = \Delta H - T\Delta S$

$\therefore \quad \Delta H - T\Delta S$ should be positive

or $\quad \Delta H > T\Delta S$

$$\text{or} \quad T < \frac{\Delta H}{\Delta S} \Rightarrow T < \frac{30 \times 10^3}{70} \Rightarrow T < 428.57 \text{ K}$$

79. Gaseous substances generally possess more entropy than solids. So whenever the products contain more moles of a gas than the reactants, the entropy change is probably positive. And hence, ΔS is

(a) positive
(b) negative
(c) small, the sign of ΔS is impossible to predict
$\because \quad \Delta n_g = 0$
(d) negative
(e) negative
(f) negative

[**Note:** For a given substance at a given temperature, $S_{gas} > S_{liquid} > S_{solid}$]

80. Consider the process: $Br_2(l) \rightarrow Br_2(g)$

The b.p. of a liquid is the temperature at which the liquid and the pure gas coexist at equilibrium at 1 atm.

$\therefore \quad \Delta G = 0$

As it is given that ΔH and ΔS do not change with temperature

$\Delta H = \Delta H^\circ = 30.91$ kJ

$\Delta S = \Delta S^\circ = 93.2$ J/K $= 0.0932$ kJ/K

We have, $\Delta G = \Delta H - T\Delta S = 0$ at equilibrium

$$\therefore \quad T = \frac{\Delta H}{\Delta S} = \frac{30.91}{0.0932} = 331.6 \text{ K}$$

This is the temperature at which the system is in equilibrium, that is, the BP of bromine.

81. We have,

$\eta = \dfrac{T_1 - T_2}{T_1}$, where T_1 and T_2 are the temperatures of sink and source respectively.

$$\therefore \quad \eta = \frac{T_1 - T_2}{T_1} = \frac{1}{6} \quad \text{...(i)}$$

Now the temperature of the sink is reduced by 65 K.

$\therefore$ temperature of the sink $= (T_2 - 65)$

$$\therefore \quad \eta = \frac{T_1 - (T_2 - 65)}{T_1} = \frac{1}{3} \quad \text{...(ii)}$$

On solving Eqs. (i) and (ii), we get,

$T_1 = 325$ K

$T_2 = 390$ K

82. (a) (i) $\Delta S = 2.303 nR \log \dfrac{V_2}{V_1}$

$$= 2.303 \times 1 \times 8.314 \times \log \frac{20}{10} = 5.76 \text{ J/K.}$$

(ii) $w_{rev} = 2.303\, nRT \log \dfrac{V_2}{V_1}$

$$= -2.303 \times 1 \times 8.314 \times 298 \times \log \frac{20}{10}$$
$$= -1718 \text{ J.}$$

(iii) For isothermal process, $\Delta E = 0$ and heat is absorbed by the gas,

$q_{rev} = \Delta E - W = 0 - (-1718) = 1718$ J

$\therefore \quad q_{surr} = 1718$ J. ($\because$ process is reversible)

(iv) $\Delta S_{surr} = \dfrac{1718}{298} = -5.76$ J/K.

As entropy of the system increases by 5.76 J, the entropy of the surroundinig decreases by 5.76 J, since the process is carried out reversible.

(v) $\Delta S_{sys} + \Delta S_{surr} = 0$ ... for reversible process.

(b) (i) $\Delta S = 5.76$ J/K, which is the same as above because S is a state function.

(ii) $w = 0$. ($\because p_{ext} = 0$)

(iii) No heat is exchanged with the surroundings.

(iv) $\Delta S_{surr} = 0$

(v) The entropy of the system plus surroundings increases by 5.76 J/K, as we expect entropy to increases in an irreversible process.

83. We have to find ΔH for

$$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(l)}; \qquad \Delta H = ?$$

$$\Delta_r H = \Sigma \nu_P (\Delta H_f^o)_P - \Sigma \nu_R [\Delta H_f^o]_R$$
$$= \Delta H^o_{f\ N_2O} + 2\Delta H^o_{f\ H_2O} - \Delta H^o_{f\ NH_4NO_3}$$

Given, $\Delta H_{N_2O} = +81.46$ kJ, $\Delta H_{H_2O} = -285.8$ kJ, $\Delta H_{NH_4NO_3} = -367.54$ kJ

$\therefore \quad \Delta H_{reaction} = +81.46 + 2(-285.8) - (-367.54)$

$\Delta H = -122.6$ kJ

Further $\Delta H = \Delta E + \Delta n_g RT$

($\Delta n_g = 1 - 0 = 1$, $R = 8.314$ J and $T = 298$ K)

$\therefore \quad -122.6 \times 10^3 = \Delta E + 1 \times 8.314 \times 298$

$\therefore \quad \Delta E = -125077$ joule

$= -125.077$ kJ

84. Given,

$$2C(s) + \frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \longrightarrow CH_3CN(g) \qquad \Delta H = 88 \quad \text{(i)}$$

$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g) \qquad \Delta H = -84 \quad$ (ii)

$C(s) \longrightarrow C(g) \qquad \Delta H = 717$

$N_2(g) \longrightarrow 2N(g) \qquad \Delta H = 946$

$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = 436$

$B_{C-H} = 410$

from equation (i)

$(2 \times 717 + 1.5 \times 436 + 0.5 \times 946) - (3 \times 410 + B_{C-C} + B_{C\equiv N}) = 88$

$B_{C-C} + B_{C\equiv N} = 1243 \quad$ (iii)

from equation (ii)

$(2 \times 717 + 3 \times 436) - (B_{C-C} + 6 \times 410) = -84$

$B_{C-C} = 366$ kJ/mole from equation (iii)

$B_{C\equiv N} = 877$ kJ/mole

85. $C_2H_4 + H_2 \longrightarrow C_2H_6$

here $\Delta_r H = \Delta H_{hydrogenation}$

$$\therefore \quad \Delta_r H = [\Delta H^o_{combustion}]_R - [\Delta H^o_{combution}]_P$$
$$= [(-1409) + (-285.6)] - [-1558.3]$$
$$= -136.8 \text{ kJ}$$

OR

We have to find

$$C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_{6(g)}\ ; \quad \Delta H = ?$$

Given, $C_2H_{4(g)} + 3O_{2(g)} \longrightarrow 3CO_{2(g)} + 2H_2O_{(g)}\ ;$

$$\Delta H = -1409.5 \text{ kJ} \quad (1)$$

$$C_2H_6 + \frac{7}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)};$$

$$\Delta H = -1558.3 \text{ kJ} \quad ...(2)$$

$$H_2 + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}\ ; \Delta H = -285.6 \text{ kJ} \quad ...(3)$$

Adding Eqs. (1) and (3)

$$C_2H_{4(g)} + \frac{7}{2}O_{2(g)} + H_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}\ ;$$

$$\Delta H = -1695.1 \text{ kJ} \quad ...(4)$$

Subtracting Eq. (2) from (4)

$$C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

$$\Delta H = -1558.3 \text{ kJ} \quad ...(5)$$

$$- \quad - \quad - \quad - \quad +$$

$$C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_{6(g)}\ ;$$

$\Delta H = -136.8$ kJ

∴ heat of hydrogenation of C_2H_4 = 136.8 kJ

86. A better gas welder is one which posses high calorific value, i.e., heat produced by 1 g of fuel.

$\Delta H_{\text{combustion}}$ for $C_2H_6 = -341.1$ kcal

$$\therefore \text{ calorific value} = \frac{-341.1}{30} \text{ kcal/g} = -11.37 \text{ kcal/g}$$

$\Delta H_{\text{combustion}}$ for $C_2H_2 = -310.0$ kcal

$$\therefore \text{ calorific value} = \frac{-310.0}{26} \text{ kcal/g} = -11.92 \text{ kcal/g}$$

∴ C_2H_2 is a better gas welder.

87. Given that

$$C(s) + 2H_2(g) \rightarrow CH_4(g); \Delta H = -17.9 \text{ kcal}$$

Energy change in reactants:

Heat of atomisation of 1 mole of C = 170.9 kcal

Heat of atomisation of 4 moles of H = 4 × 52.1 kcal

Energy change in product:

Heat of formation of 4 moles of C–H bonds = $4 \times x$ kcal.

(where x is the energy of formation of C–H bonds in kcal/mole).

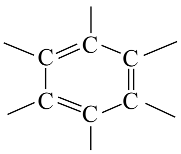
Since the algebraic sum of all the heat changes is equal to the heat of formation of the above given equation, we have

$$170.9 + 4 \times 52.1 + 4x = -17.9;\ x = -99.3 \text{ kcal}$$

Thus the bond energy = +99.3 kcal/mole.

88. We have to calculate ΔH for the reaction

$$6C(s) + 3H_2(g) \rightarrow C_6H_6(g)$$



ΔH = ?

For reactants:

Heat of atomisation of 6 moles of C = 6 × 170.9 kcal

Heat of atomisation of 6 moles of H = 6 × 52.1 kcal

For products:

Heat of formation of 6 moles of C – H bonds = –6 × 99

Heat of formation of 3 moles of C – C bonds = –3 × 83

Heat of formation of 3 moles of C = C bonds = –3 × 140

On adding, we get heat of formation of C_6H_6, i.e.,

$$\Delta H = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140$$
$$= 75.0 \text{ kcal.}$$

89. $MgSO_4 \cdot 7H_2O\ (s) + aq \rightarrow MgSO_4\ (aq) \qquad \Delta_r H_2$
$= +13.807 \text{ kJ mol}^{-1}$ ...(ii)

Equation (i) can be written as follows:

$$MgSO_4(s) + 7H_2O(l) + aq \rightarrow MgSO_4(aq)$$
$$\Delta_r H = -91.211 \text{ kJ mol}^{-1} \quad ...(iii)$$

Equation (iii) – (ii) will give

$$MgSO_4(s) + 7H_2O(l) \rightarrow MgSO_4 \cdot 7H_2O(s)$$
$$\Delta_r H = -91.211 - 13.807 = -105.018 \text{ kJ mol}^{-1}.$$

90. Given, $I_{2(s)} \longrightarrow I_{2(v)}\ ; \qquad \Delta H = 24$ cal/g at 200°C

$$\Delta_r C_P = C_P \text{ of product} - C_P \text{ of reatant}$$
$$= 0.031 - 0.055$$
$$= -0.024 \text{ cal/g}$$

Now $\Delta H_{T_2} - \Delta H_{T_1} = \Delta_r C_P\,(T_2 - T_1)$

$$\Delta H_{T_2} - 24 = -0.024 \times (523 - 473)$$

$$\therefore \quad \Delta H_{T_2} = 24 - 1.2 = 22.8 \text{ cal/g.}$$

91. $C_2H_6 + O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$ 2 mol

for 1 mole $\qquad \Delta H = -\ 1560$ kJ

$$\Delta_r H = \Sigma \nu_P (\Delta H_f^o)_P - \Sigma \nu_R [\Delta H_f^o]_R$$

$$-1560 = 2\,(-395) + 3(286) - (\Delta H_f^o)_{C_2H_6}$$

$$\Delta H^\circ_f = -790 - 858 + 1560 = -\ 88 \text{ kJ/mol}$$

92.

$$\begin{tikzcd} CuSO_4 + 5H_2O \arrow[rr, "\Delta H"] \arrow[dr, "-15.9\ \text{kcal}"'] & & CuSO_4 \cdot 5H_2O \arrow[dl, "+2.8"] \\ & \boxed{CuSO_4(aq.)} & \end{tikzcd}$$

Applying Hess's law $\qquad \Delta H + 2.8 = -15.9$

$\Delta H = -15.9 - 2.8 \qquad \Delta H = -18.7$ kcal

93. O_2 consumed by body in 1 hr.

$= 20 \times 60 \times 200\ (0.2 - 0.1) = 24000$ mL. at 37°C

So, volume at 273 K can be calculated by

$$\frac{V}{273} = \frac{24000}{310}$$

$V = 21135.48$ mL = 0.9435 mole O_2

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

$\Delta H = -2880$ kJ/mol

moles of glucose $\longrightarrow \dfrac{0.9435}{6}$

Heat released = $\dfrac{2880 \times 0.9435}{6}$ = 452.9 kJ

Heat used for muscular work = 452.9 × 0.25 = 113.22 kJ

so distance = 1.132 km

94.

$$\begin{tikzcd}
\frac{1}{2}H_2 + \arrow[d] & \frac{1}{2}Cl_2 \arrow[d, "-167.44"] \arrow[r, "-92.3"] & HCl(g) \arrow[dl, "x"] \\
H^+(aq.) & Cl^-(aq.) &
\end{tikzcd}$$

$-92.30 + x = -167.44$

$x = -75.14$ kJ/mol

95. $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

1.0 g

$\Delta E = mC\Delta T$

$\Delta E = -10 \text{ kJ} \times 1.56 = 15.6$ kJ

Since $\Delta n_g = 0$ $\quad\therefore\quad$ $\Delta H = \Delta E$

for 1 mole = 15.6 × 180 = –2808 kJ

96. $Ca(s) \longrightarrow Ca(g) \longrightarrow Ca^{+1}(g) \longrightarrow Ca^{+2}(g) \to CaC_2(s)$

$2C_{(s)} \longrightarrow 2C_{(g)} \longrightarrow C_{2(g)} \longrightarrow C^-_{2(g)} \longrightarrow C^{-2}_{2(g)}$

$-60 = [179 + 590 + 1143 + 718 \times 2$
$\quad - 614 - 315 + 410 + \text{L.E.}]$

L.E. = –2889 kJ/mole

97.

$$\begin{tikzcd}
2C(g) & + & 6H(g) \arrow[r, "-676"] & C_2H_6(g) \\
2C(s) \arrow[u, "2 \times 171.8"'] & + & 3H_2(g) \arrow[u, "3(104.1)"'] \arrow[ur, "\Delta H_t"'] &
\end{tikzcd}$$

$\Delta_r H = -676 + 343.6 + 312.3 = -676 + 655.9 = 20.1$

4 (C – H) = 396 $\qquad$ (C–C) + 6(99) = 676

C – H = 99 K $\qquad$ (C–C) = 676 –594 = 84

98.

$$\begin{tikzcd}
Cs(s) \arrow[d, "81.2"'] & + & \frac{1}{2}Cl_2(g) \arrow[d, "\frac{1}{2}(243)"] \arrow[r, "-388.6"] & CsCl(s) \\
Cs(g) \arrow[d, "375.7"'] & & Cl \arrow[d, "-348.3"] & \\
Cs^{\oplus}(g) & & Cl^{\ominus}(g) \arrow[uur, dash, "x = LE"'] &
\end{tikzcd}$$

$81.2 + 375.7 + 121.5 - 348.3 + x = -388.5$

$578.4 - 348.3 + 388.5 = -x$

$-x = 966.9 - 348.3$

$x = -618.6 \text{ kJ mol}^{-1}$

99. $2C(g) + 6H(g) \xrightarrow{-2839.2} C_2H_6$

$2C(g) + 4H(g) \xrightarrow{-2275.2} C_2H_4$

$6C(g) + 6H(g) \xrightarrow{-5506} C_6H_6$

(C – C) + 6(C – H) = –2839.2 ⇒ C – C = 373.98

(C = C) + 4(C – H) = –2275.2 ⇒ C = C = 637.72

–6(410.87) + 3(373.98) + 3(631.72) + R.E. = –5506

–5482.3 + RE = 0.5506

R.E. = –23.68 kJ/mol

100. Given,

$6C(s) + 3H_2(g) \longrightarrow C_6H_6(l) \qquad \Delta H = 49$

$C_6H_6(l) \longrightarrow C_6H_6(g) \qquad \Delta H = 45$

so $6C(s) + 3H_2(g) \longrightarrow C_6H_6(g) \qquad \Delta H = 94 \qquad$ (i)

$2C(s) + H_2(g) \longrightarrow C_2H_2(g) \qquad \Delta H = 75 \qquad$ (ii)

(i) – 3 × (ii)

$3C_2H_2(g) \longrightarrow C_6H_6(g) = -131$

$3[B_{C\equiv C} + 2B_{C-H}] - [3B_{C-C} + 3B_{C=C} + 6B_{C-H} - \text{R.E.}] = -131$

$3[B_{C\equiv C} - B_{C-C} - B_{C=C}] + \text{RE} = -131$

R.E. = –131 + 99 = –32

101.

$2Al(s) +$	$Fe_2O_3(s) \longrightarrow$	$Al_2O_3(s) +$	$2Fe(s)$
0.2 mole	0.1 mole	—	—
—	—	0.1	0.2

Since, 0.254 kg ice melted

$\therefore \quad \Delta H = \dfrac{-254 \times 1.436}{18} = 20.26$ kcal

Heat liberated for 0.1 mole = 20.26 kcal

Heat liberated for 1 mole = –202.6 kcal

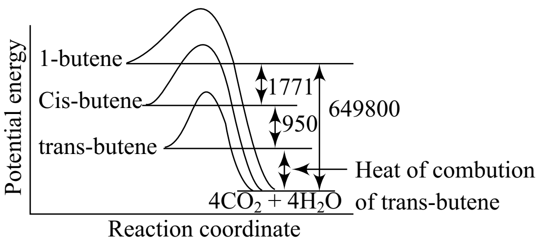
102.

$$\begin{tikzcd}
CH_2{=}O \arrow[r, "\Delta H"] \arrow[d, "-134"] & (CH_2O) \arrow[dl, "-122"] \\
nCO_2 + nH_2O &
\end{tikzcd}$$

Applying Hess law

$\Delta H - 122 = -134 \qquad \Delta H = 12$ Kcal

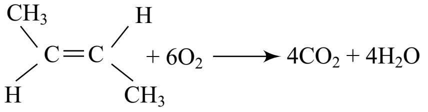
103.



$\therefore$ Heat of combution of trans-2 butene

= –649800 + 1771 + 950

= –604079



$\Delta H_C = \Delta_r H = \Sigma(\text{BDE})_R - \Sigma(\text{BDE})_P = -603.079$

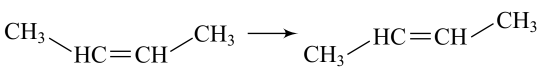
$= [2\,B_{C-C} + B_{C=C} + 8 \times B_{C-H}] + 6 \times B_{O=O}$

$- 8 \times B_{C=O} - 8 \times B_{O-H} = -603.079$

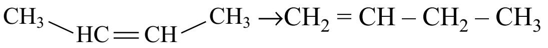
$B_{C=C} = 192.921$ kcal/mole

OR

Given



$\Delta H_1 = -950 \dfrac{\text{cal}}{\text{mole}} = -0.95 \dfrac{\text{k cal}}{\text{mole}} \qquad$ (i)



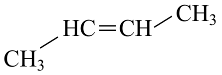
$CH_3-HC=CH-CH_3 \rightarrow CH_2 = CH - CH_2 - CH_3$

$$\Delta H_2 = +1771 \frac{\text{cal}}{\text{mole}} = 1.771 \frac{\text{k cal}}{\text{mole}} \qquad \text{(ii)}$$

$$CH_2 = CH - CH_2 - CH_3 + 6O_2 \longrightarrow 4CO_2 + 4H_2O$$

$$\Delta H_3 = -649.8 \frac{\text{k cal}}{\text{mole}} \qquad \text{(iii)}$$

(ii) + (iii) – (i)



$CH_3-HC=CH-CH_3 + 6O_2 \rightarrow 4CO_2 + 4H_2O(l)$

$$\Delta H = -647.079 \qquad \text{(iv)}$$

$$H_2O(l) \longrightarrow H_2O(g)$$

$$\Delta H_4 = 11 \frac{\text{k cal}}{\text{mole}} \qquad \text{(v)}$$

(iv) + 4 × (v)

$+6CO_2 \rightarrow 4CO_2 + 4H_2O(g)$

$\Delta H = -603.079$

$[2\ B_{C-C} + B_{C=C} + 8\ B_{C-H}]$

$+ 6B_{O=O} - 8\ B_{C=O} - 8B_{O-H} = -603.079$

$= [2\ B_{C-C} + B_{C=C} + 8 \times B_{C-H}] + 6 \times B_{O=O}$

$- 8 \times B_{C=O} - 8 \times B_{O-H} = -603.079$

$B_{C=C} = 192.921$ kcal/mole

104. Given,

$n(CH_2{=}CH_2) \rightarrow (-CH_2-CH_2-)_n \qquad \Delta H = -72$

i.e., $B_{C=C} - 2\ B_{C-C} = -72 \qquad$ (i)

$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(l)} \qquad \Delta H = 49 \qquad$ (ii)

$C_6H_{6(l)} \longrightarrow C_6H_{6(g)} \qquad \Delta H = 30$

R.E. of $C_6H_6 = -152$

$\frac{1}{2}H_2 \longrightarrow H \qquad \Delta H = 218$

$C_{(s)} \longrightarrow C_{(g)} \qquad \Delta H = 715$

$B_{C-H} = 415$ for equation (ii)

$(6 \times 715 + 6 \times 218) - (3B_{C-C} + 3B_{C=C} + 6 \times 415 - RE) = 49$

$B_{C-C} + B_{C=C} = 959 \qquad$ (iii)

from equation (i) and (iii)

$B_{C-C} = 343.66 \qquad B_C = C = 615.33$

PREVIOUS YEARS' QUESTIONS OF JEE (MAIN AND ADVANCED)

1. **(a, c, d)**
   - (a) Since, change of state (p_1, V_1, T_1) to (p_2, V_2, T_2) is isothermal therefore, $T_1 = T_2$.
   - (b) Since, change of state (p_1, V_1, T_1) to (p_3, V_3, T_3) is an adiabatic expansion it brings about cooling of gas, therefore, $T_3 < T_1$.
   - (c) Work done is the area under the curve of p-V diagram. As obvious from the given diagram, magnitude of area under the isothermal curve is greater than the same under adiabatic curve, hence $W_{\text{isothermal}} > W_{\text{adiabatic}}$
   - (d) $\Delta U = nC_v\Delta T$

     In isothermal process, $\Delta U = 0$ as $\Delta T = 0$

     In adiabatic process, $\Delta U = nC_v(T_3 - T_1) < 0$ as $T_3 < T_1$.

     $\Rightarrow \quad \Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

     Note: Here only magnitudes of work is being considered otherwise both works have negative sign.

2. **(a, c)**
   - (a) Entropy is state function, change in entropy in a cyclic process is zero.

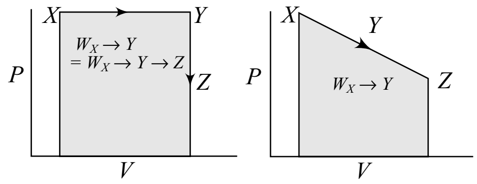
Therefore, $\Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z} + \Delta S_{Z \rightarrow Y} = 0$

$\Rightarrow \quad -\Delta S_{Z \rightarrow X} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z}$

$= \Delta S_{X \rightarrow Z}$

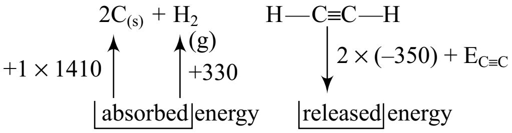
Work is a path function.

Therefore, $W_{X \rightarrow Y \rightarrow Z} = W_{X \rightarrow Y}$. Also, work is the area under the curve on p-V diagram.



As shown above $W_{X \rightarrow Y} + W_{Y \rightarrow Z} = W_{X \rightarrow Y} = W_{X \rightarrow Y \rightarrow Z}$ but not equal to $W_{X \rightarrow Z}$.

3. **(d)**



$\Delta_r H = E_{\text{abs}} - E_{\text{rel}}$

$255 = [1 \times 1410 + 330] - [2 \times 350 + E_{C \equiv C}]$

$\therefore \quad E_{C \equiv C} = 815$ KJ/mole

OR

For calculation of C ≡ C bond energy, we must first calculate dissociation energy of C_2H_2 as

$C_2H_2(g) \longrightarrow 2C(g) + 2H(g) \qquad$ (i)

Using the given bond energies and enthalpies:

$C_2H_2(g) \longrightarrow 2C(g) + 2H(g); \quad \Delta H = -225$ kJ (ii)

$2C(s) \longrightarrow 2C(g); \quad \Delta H = 1410$ kJ (iii)

$H_2(g) \longrightarrow 2H(g) \quad \Delta H = 330$ kJ (iv)

adding Eqs. (ii), (iii) and (iv) gives Eq. (i).

$\Rightarrow \quad C_2H_2(g) \longrightarrow 2C(g) + 2H(g); \quad \Delta H = 1515$ kJ

$\Rightarrow \quad 1515$ kJ $= 2 \times (C - H)$ BE + (C≡C)BE

$= 2 \times 350 + (C \equiv C)$BE

$\Rightarrow \quad (C \equiv C)$BE $= 1515 - 700 = 815$ kJ/mol

(Passage from Q.No. 4 to Q. No. 6)

4. **(b)** $L \rightarrow M$ At constant V – isochoric.

   $N \rightarrow K$

5. **(c)** By Boyle's law at constant temperature $P \propto \frac{1}{V}$

By Charle's law at constant pressure, $V \propto T$
Process taking place at
Constant temperature – isothermal
Constant pressure – isobaric
Constant volume – isochoric
Constant heat – adiabatic

$K \rightarrow L$	At constant P, $V \propto T$	$\therefore$ heating
$L \rightarrow M$	At constant V, $P \propto T$	$\therefore$ cooling
$M \rightarrow N$	At constant p, $V \propto T$	$\therefore$ cooling
$N \rightarrow K$	At constant V, $P \propto T$	$\therefore$ heating

6. **(b, c, d)**
Mixing of solute and solvent is spontaneous process for ideal solution.

$$\Delta H_{\text{mix}} = 0,\ \Delta V_{\text{mix}} = 0 \text{ and } \Delta G_{\text{mix}} < 0$$

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} = 0 - T\Delta S_{\text{mix}}$$

$$\Delta G_{\text{mix}} < 0 \quad \text{and} \quad \Delta S_{\text{mix}} > 0 \quad \therefore \quad \Delta S_{\text{surrounding}} = 0$$

7. **(a)** The process is isothermal expansion, hence

$$q = -W$$

$$\Delta E = 0$$

$$W = -2.303\ nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 0.04 \times 8.314 \times 310 \times \log \frac{335}{50}$$

$$= -208 \text{ J}$$

$$q = +208 \text{ J},\ W = -208 \text{ J}$$

($\because$ Work done by the system)

8. **(c)** $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad \Delta_r H = ?$

$$\Delta_r H = \Delta H_C = \Sigma v_P (\Delta H_f^{o})_P - \Sigma v_R (\Delta H_f^{o})_R$$

$$= [(6 \times (-400) + 6 \times (-300) - (1 \times -1300)]$$

$$= -2400 - 1800 + 1300$$

$$= -2900 \text{ KJ per mole}$$

$$= \frac{-2900}{180} \text{KJ/gram} = -16.11 \text{ KJ/gram}$$

9. **(a)** $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$$\Delta E = -1364.47 \text{ kJ/mol}$$

$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta n_g = -1$$

$$\Delta H = \left(-1364.7 + \frac{-1 \times 8.314 \times 298}{1000}\right) \text{KJ}$$

$$= -1364.47 - 2.4776 = -1366.9476 \text{ kJ/mol}$$

or $\quad = -1366.95$ kJ/mol

10. **(a, b, c) Hint:** This problem includes concept of isothermal adiabatic irreversible expansion.
Process is adiabatic because of the use of thermal insolution therefore, $q = 0$

$$\because \quad p_{\text{ext}} = 0$$

$$w = p_{\text{ext}} \cdot \Delta V = 0 \times \Delta V = 0$$

Internal energy can be written as

$$\Delta E = q + W = 0$$

Because, $\quad \Delta E = nC_V\Delta T$

$$\Delta E = 0$$

$$\therefore \quad \Delta T = 0$$

$$\therefore \quad T_1 = T_2$$

So, in isothermal condition PV = constant whereas PV^{γ} = constant for adiabatic only

11. **(b)** At 100°C and 1 atmosphere pressure,
$H_2O(l) \rightleftharpoons H_2O(g)$ is at equilibrium.
At equilibrium, $\Delta S_{\text{total}} = 0$ = (for reversible process)
and $\quad \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$
As we know during conversion of liquid to gas entropy of system increases, in a similar manner entropy of surrounding decreases.

$$\therefore \quad \Delta S_{\text{system}} > 0 \text{ and } \Delta S_{\text{surrounding}} < 0$$

12. **(d)** For the given reaction,

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Given, $\Delta G_f^{o}(\text{NO}) = 86.6 \text{ kJ/mol}$

$$\Delta G_f^{o}(\text{NO}_2) = ?$$

$$K_p = 1.6 \times 10^{12}$$

Now, we have,

$$\Delta G_f^{o} = 2\Delta G_{f(NO_2)}^{o} - [2\Delta G_{f\,(NO)}^{o} + \Delta G_{f(O_2)}^{o}]$$

$$= -\text{RT} \ln K_p = 2\Delta G_{f(NO_2)}^{o} - [2 \times 86{,}600 + 0]$$

$$\Delta G_{f(NO_2)}^{o} = \frac{1}{2}[2 \times 86600 - R \times 298 \ln (1.6 \times 10^{12})]$$

$$\Delta G_{f(NO_2)}^{o} = 0.5[2 \times 86{,}600 - R \times (298) \ln (1.6 \times 10^{12})]$$