

$$4. v = \frac{2\pi z e^2}{nh} = \frac{2.18 \times 10^6 \times z}{n} \text{ m/s}$$

$$5. \text{ Revolutions per sec} = f = v / 2\pi r = \frac{0.657 \times Z^2 \times 10^{16}}{n^3}$$

$$6. \text{ Time taken for one revolution} = 2\pi r / v = \frac{1.52 \times 10^{-16} \times n^3}{Z^2}$$

$$7. E_n = \text{K.E.} + \text{P.E.} = -\text{K.E.} = \frac{1}{2} \text{P.E.}$$

$$8. \text{P.E.} = -2\text{K.E.}$$

$$9. \text{T.E.} = -\text{K.E.}$$

$$10. \text{K.E.} = \frac{1}{2} mv^2, \text{P.E.} = -\frac{1}{4\pi\epsilon_0} \frac{ze^2}{r}$$

De-Broglie wavelength :

$$\lambda = \frac{h}{mc} = \frac{h}{p} \text{ (for photon)}$$

If a charged particle Q is accelerated through potential difference V from rest then de-broglie wavelength is

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(\text{K.E.})}} = \frac{h}{\sqrt{2mQV}}$$

The circumference of the n^{th} orbit is equal to n times the wavelength of the electron.

$$\sqrt{2\pi r_n} = n\lambda.$$

Energy of photon on the basis of Einstein's mass energy relationship

$$E = mc^2 \quad \text{or} \quad \lambda = \frac{h}{mc}$$

$$\sqrt{m} = \text{dynamic mass} = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

m_0 = rest mass of particle, v = velocity of particle, C = speed of light

If velocity of particle is zero then :

dynamic mass = rest mass

Rest mass of photon is zero that means photon is never at rest

$$\lambda = \frac{h}{\sqrt{2m(\text{K.E.})}} = \frac{h}{\sqrt{2m(qV)}}$$

If an electron is accelerated through a potential difference of 'V' volt from rest then :

$$\Rightarrow \lambda = \frac{h}{\sqrt{2m_e(eV)}} \Rightarrow \lambda = \left(\frac{150}{V}\right)^{1/2} \text{ Å} \Rightarrow \lambda = \frac{12.3}{\sqrt{V}} \text{ Å} \quad V \text{ in volt}$$

Line Spectrum of Hydrogen :

$$\text{Energy of emitted photon} = (\Delta E)_{n_2 \rightarrow n_1} = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Wavelength of emitted photon

$$\frac{1}{\lambda} = \frac{(13.6)Z^2}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{\lambda} = \bar{v} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Wave number

$$R = \text{Rydberg constant} = 1.09678 \times 10^7 \text{ m}^{-1}; R \approx 1.1 \times 10^7 \text{ m}^{-1}; R = \frac{13.6 \text{ eV}}{hc}; R \text{ ch} = 13.6 \text{ eV}$$

The wavelength of marginal line = $\frac{n_1^2}{R_H}$ for all series.
 $\infty \rightarrow$

No. of photons emitted by a sample of H atom

- If an electron is in any higher state n and makes a transition to ground state, then total no. of different

$$\boxed{\text{photons emitted is equal to } \frac{n \times (n-1)}{2}}$$

- If an electron is in any higher state n and makes a transition to another excited state, then total no. of

$$\boxed{\text{different photons emitted is equal to } \frac{\Delta n(\Delta n + 1)}{2}}$$

Note In case of single isolated atom if electron make transition from n^{th} state to the ground state then max. number of spectral lines observe = $(n - 1)$

Heisenberg's uncertainty principle :

$$\boxed{\Delta x \cdot \Delta p > \frac{h}{4\pi} \quad \text{or} \quad m \Delta x \cdot \Delta v \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}}$$

where, Δx = uncertainty in position ; Δp = uncertainty in momentum

h = Planck's constant ; m = mass of the particle ; Δv = uncertainty in velocity

Quantum Numbers :

- * Principal quantum number (n) = 1, 2, 3, 4 to ∞ .
- * Number of subshell present in n^{th} shell = n
- * Number of orbitals present in n^{th} shell = n^2 .
- * The maximum number of electrons which can be present in a principal energy shell is equal to $2n^2$.
- * Orbital angular momentum of electron in any orbit = $\frac{nh}{2\pi}$.
- * Azimuthal quantum number (ℓ) = 0, 1, to $(n - 1)$.
- * Number of orbitals in a subshell = $2\ell + 1$

* Maximum number of electrons in particular subshell = $2 \times (2\ell + 1)$

Orbital angular momentum $L = \frac{\hbar}{2\pi} \sqrt{\ell(\ell+1)} = \hbar \sqrt{\ell(\ell+1)}$ $\left[\hbar = \frac{h}{2\pi} \right]$

* m (magnetic quantum no.) can have values from $-\ell$ to $+\ell$ including zero, i.e., total $(2\ell + 1)$ values.

Spin magnetic moment $\mu_s = \frac{e\hbar}{2\pi mc} \sqrt{s(s+1)}$ or $\mu = \sqrt{n(n+2)}$ B.M. (n = no. of unpaired electrons)

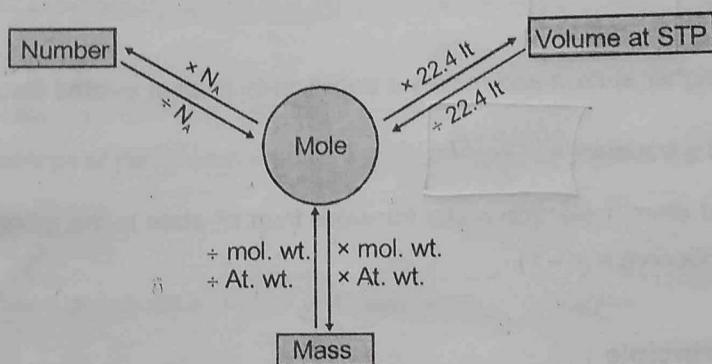
It represents the value of spin angular momentum which is equal to $\frac{\hbar}{2\pi} \sqrt{s(s+1)}$

Maximum spin of atom = $\frac{1}{2} \times$ No. of unpaired electron.

STOICHIOMETRY

Relative atomic mass (R.A.M) = $\frac{\text{Mass of one atom of an element}}{\frac{1}{12} \times \text{mass of one carbon atom}} = \text{Total Number of nucleons}$

Y-map



DENSITY :

$$\text{Specific gravity} = \frac{\text{density of the substance}}{\text{density of water at } 4^\circ\text{C}}$$

For gases :

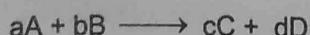
$$\text{Absolute density (mass/volume)} = \frac{\text{Molar mass of the gas}}{\text{Molar volume of the gas}} \Rightarrow \rho = \frac{PM}{RT}$$

$$\text{Vapour density} \quad V.D. = \frac{d_{\text{gas}}}{d_{\text{H}_2}} = \frac{PM_{\text{gas}/RT}}{PM_{\text{H}_2/RT}} = \frac{M_{\text{gas}}}{M_{\text{H}_2}} = \frac{M_{\text{gas}}}{2} \quad [\text{At same pressure and temp. condition}]$$

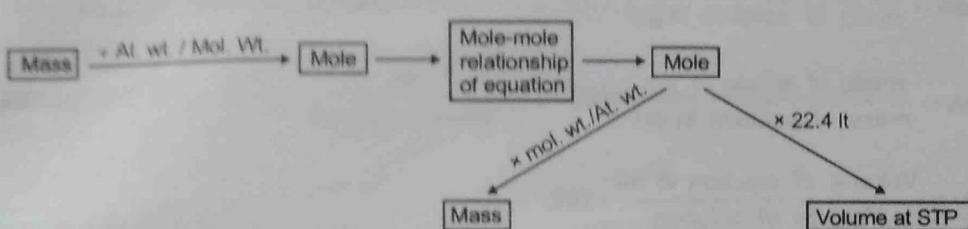
$$M_{\text{gas}} = 2 \text{ V.D.}$$

Mole-mole analysis :

For any general balance chemical equation like



$$\frac{\text{Mole of A reacted}}{a} = \frac{\text{moles of B reacted}}{b} = \frac{\text{moles of C reacted}}{c} = \frac{\text{moles of D reacted}}{d}$$



CONCENTRATION TERMS :

MOLARITY (M) :

$$\text{Molarity of solution} = \frac{\text{number of moles}}{\text{volume of solution in litre}}$$

$$\therefore \text{Molarity (M)} = \frac{w \times 1000}{(\text{Mol. wt of solute}) \times V_{\text{in ml}}}$$

$$\text{Number of millimoles} = \frac{\text{mass of solute}}{(\text{Mol. wt. of solute})} \times 1000 = (\text{Molarity of solution} \times V_{\text{in ml}})$$

$$\text{Molarity} \propto \frac{1}{\text{temperature}} \propto \frac{1}{\text{volume}}$$

Molarity of solution may also given as :

$$\frac{\text{Number of millimole of solute}}{\text{Total volume of solution in ml}}$$

- (i) If a particulars solution having volume V_1 and molarity = M_1 , is diluted to V_2 mL the

$$M_1 V_1 = M_2 V_2$$

M_2 : Resultant molarity

- (ii) If a solution having volume V_1 and molarity M_1 , is mixed with another solution of same solute having

volume V_2 mL & molarity M_2

$$\text{then } M_1 V_1 + M_2 V_2 = M_R (V_1 + V_2)$$

M_R = Resultant molarity

$$= \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

MOLALITY (m) :

$$\text{molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in gram}} \times 1000 = 1000 w_1 / M_1 w_2$$

MOLE FRACTION (x) :

$$\therefore \text{Mole fraction of solute (}x_1\text{)} = \frac{n}{n+N}$$

$$\therefore \text{Mole fraction of solvent (}x_2\text{)} = \frac{N}{n+N}$$

$$x_1 + x_2 = 1$$

(where $n \rightarrow$ mole of solute, $N \rightarrow$ mole of solvent)

% CALCULATION :

$$(i) \quad \% \text{ w/w} = \frac{\text{mass of solute in gm}}{\text{mass of solution in gm}} \times 100$$

$$(ii) \quad \% \text{ w/v} = \frac{\text{mass of solute in gm}}{\text{mass of solution in ml}} \times 100$$

$$(iii) \quad \% \text{ v/v} = \frac{\text{Volume of solution in ml}}{\text{Volume of solution}} \times 100$$

Derive the following conversion :

$$1. \quad \text{Mole fraction of solute into molarity of solution } M = \frac{x_2 \rho \times 1000}{x_1 M_1 + M_2 x_2}$$

$$2. \quad \text{Molarity into mole fraction } x_2 = \frac{M M_1 \times 1000}{\rho \times 1000 - M M_2}$$

$$3. \quad \text{Mole fraction into molality } m = \frac{x_2 \times 1000}{x_1 M_1}$$

$$4. \quad \text{Molality into mole fraction } x_2 = \frac{m M_1}{1000 + m M_1}$$

$$5. \quad \text{Molality into molarity } M = \frac{m \rho \times 1000}{1000 + m M_2}$$

$$6. \quad \text{Molarity into Molality } m = \frac{M \times 1000}{1000 \rho - M M_2}$$

M_1 and M_2 are molar masses of solvent and solute. ρ is density of solution (gm/mL)

M = Molarity (mole/lit.), m = Molality (mole/kg), x_1 = Mole fraction of solvent, x_2 = Mole fraction of solute

AVERAGE/ MEAN ATOMIC MASS :

$$A_x = \frac{a_1 x_1 + a_2 x_2 + \dots + a_n x_n}{100}$$

MEAN MOLAR MASS OR MOLECULAR MASS:

$$M_{\text{avg.}} = \frac{n_1 M_1 + n_2 M_2 + \dots + n_n M_n}{n_1 + n_2 + \dots + n_n} \quad \text{or} \quad M_{\text{avg.}} = \frac{\sum_{j=1}^{j=n} n_j M_j}{\sum_{j=1}^{j=n} n_j}$$

CALCULATION OF INDIVIDUAL OXIDATION NUMBER :

Formula : Oxidation Number = number of electrons in the valence shell – number of electrons left after bonding

CONCEPT OF EQUIVALENT WEIGHT/MASS :

For elements, equivalent weight (E) = $\frac{\text{Atomic weight}}{\text{Valency-factor}}$

For acid/base, $E = \frac{M}{\text{Basicity / Acidity}}$ Where M = Molar mass

For O.A/R.A., $E = \frac{M}{\text{no. of moles of } e^- \text{ gained/lost}}$

Equivalent weight (E) = $\frac{\text{Atomic or molecular weight}}{\text{v.f.}}$ (v.f. = valency factor)

Concept of number of equivalents :

No. of equivalents of solute = $\frac{Wt}{\text{Eq. wt.}} = \frac{W}{E} = \frac{W}{M/n}$

No. of equivalents of solute = No. of moles of solute \times v.f.

NORMALITY (N) :

Normality (N) = $\frac{\text{Number of equivalents of solute}}{\text{Volume of solution (in litres)}}$

Number of equivalents of solute = $\frac{\text{Weight of solute}}{\text{Equivalent mass of solute}} = \frac{w}{E}$

$\therefore N = \frac{w}{E} \times \frac{1000}{V(\text{in ml})}$

$\therefore \text{Number of equivalents of solute} = \frac{w}{E} = N \times V (\text{in litre})$

Normality = Molarity \times v.f.

Dilution Law $N_1 V_1 = N_2 V_2$

For two solution, of same solute when mixed, new normality is given as :

$$N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

CALCULATION OF VALENCY FACTOR :

For Acid-Base Reaction :

n-factor of acid = basicity = no. of H⁺ ion(s) furnished per molecule of the acid.

n-factor of base = acidity = no. of OH⁻ ion(s) furnished by the base per molecule.

LAW OF EQUIVALENCE :

For an acid base reaction :

At equivalence point, equivalent of Acid = equivalent base.

For a redox reaction :

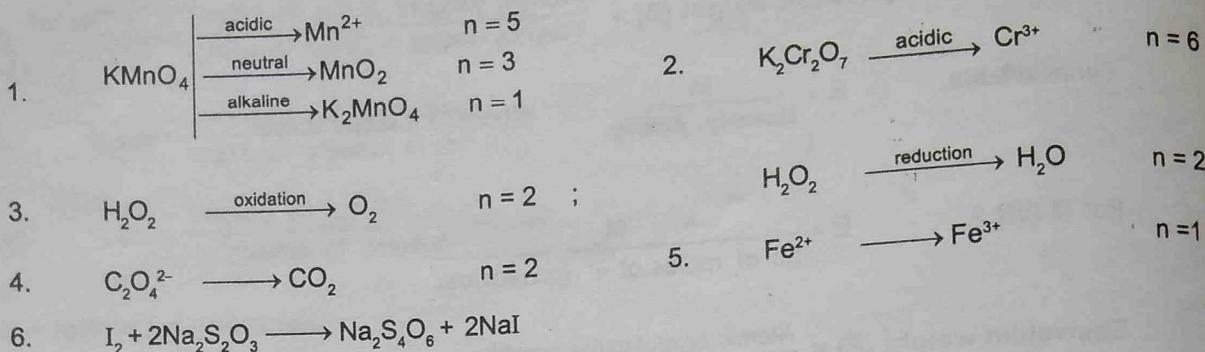
At equivalence point, equivalent of oxidising agent = equivalent of reducing agent.

At equivalence point :

$$\begin{aligned} N_1 V_1 &= N_2 V_2 \\ n_1 M_1 V_1 &= n_2 M_2 V_2 \end{aligned}$$

Compendium (Chemistry)

Some important Oxidising /Reducing agents and their reaction products:

VOLUME STRENGTH OF H_2O_2 :

20V H_2O_2 means one litre of this sample of H_2O_2 on decomposition gives 20 lt. of O_2 gas at S.T.P.

$$\text{Normality of } \text{H}_2\text{O}_2 (\text{N}) = \frac{\text{Volume, strength of } \text{H}_2\text{O}_2}{5.6}$$

$$\text{Molarity of } \text{H}_2\text{O}_2 (\text{M}) = \frac{\text{Volume strength of } \text{H}_2\text{O}_2}{11.2}$$

MEASUREMENT OF HARDNESS : Hardness is measured in terms of ppm (parts per million) of CaCO_3 or equivalent to it. Hardness in ppm = $\frac{\text{mass of } \text{CaCO}_3}{\text{Total mass of water}} \times 10^6$

STRENGTH OF OLEUM :

Oleum is SO_3 dissolved in 100% H_2SO_4 . Sometimes, oleum is reported as more than 100% by weight, say y% (where $y > 100$). This means that $(y - 100)$ grams of water, when added to 100 g of given oleum sample, will combine with all the free SO_3 in the oleum to give 100% sulphuric acid.

Hence weight % of free SO_3 in oleum = $80(y - 100)/18$

CALCULATION OF AVAILABLE CHLORINE FROM A SAMPLE OF BLEACHING POWDER :

$$\% \text{ of } \text{Cl}_2 = \frac{3.55 \times x \times V(\text{mL})}{W(\text{g})} \quad \text{where } x = \text{molarity of hypo solution and } v = \text{mL. of hypo solution used in titration.}$$

W = Weight of bleaching powder sample in gram.

GASEOUS STATE

TEMPERATURE SCALE :

$$\frac{\text{C} - \text{O}}{100 - 0} = \frac{\text{K} - 273}{373 - 273} = \frac{\text{F} - 32}{212 - 32} = \frac{\text{R} - \text{R(O)}}{\text{R}(100) - \text{R(O)}} \quad \text{where R = Temp. on unknown scale.}$$

BOYLE'S LAW AND MEASUREMENT OF PRESSURE :

At constant temperature, $V \propto \frac{1}{P}$

$$P_1 V_1 = P_2 V_2$$

CHARLES LAW :

At constant pressure, $V \propto T$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

GAY-LUSSAC'S LAW :

At constant volume, $P \propto T$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow \text{temp on absolute scale}$$

EQUATION OF STATE :

Combining all the relations

$$\frac{PV}{T} = \text{constant (dependent on amount of the gas (n))}, \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

IDEAL GAS EQUATION :

$$PV = nRT$$

$$PV = \frac{w}{m} RT \text{ or } P = \frac{d}{m} RT \text{ or } Pm = dRT$$

m = molecular mass of the gas

DALTON'S LAW OF PARTIAL PRESSURE :

$$P_1 = \frac{n_1 RT}{v}, \quad P_2 = \frac{n_2 RT}{v}, \quad P_3 = \frac{n_3 RT}{v} \text{ and so on.}$$

$$\text{Total pressure} = P_1 + P_2 + P_3 + \dots$$

Partial pressure = mole fraction \times Total pressure.

Amagat's law of partial volume :

$$V = V_1 + V_2 + V_3 + \dots$$

AVERAGE MOLECULAR MASS OF GASEOUS MIXTURE :

$$M_{\text{mix}} = \frac{\text{Total mass of mixture}}{\text{Total no. of moles in mixture}} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3}$$

GRAHAM'S LAW :

$$\text{Rate of diffusion } r \propto \frac{1}{\sqrt{d}}; \quad d = \text{density of gas}$$

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \sqrt{\frac{V \cdot D_2}{V \cdot D_1}} \quad \text{V.D is vapour density}$$

$$r = \text{volume flow rate} = \frac{dV_{\text{out}}}{dt}; \quad r = \text{mole flow rate} = \frac{dn_{\text{out}}}{dt}$$

$$r = \text{distance travelled by gaseous molecule per unit time} = \frac{dx}{dt}$$

General form of the graham's law of diffusion

$$\text{rate} \propto \frac{P}{\sqrt{TM}} A$$

P – Pressure, A – cross section area of hole, T – Temp., M – mol. wt.

KINETIC THEORY OF GASES :

$$PV = \frac{1}{3} mN \overline{U^2} \quad \text{Kinetic equation of gases}$$

where $\overline{U^2}$ is mean square speed

$$\text{Average K.E.} = \frac{3}{2} kT \quad (\text{only dependent on temperature not on nature of the gas.}) \quad (a)$$

k = Boltzman constant.

$$\text{Average K.E. for one mole} = N_A \left(\frac{1}{2} m \overline{U^2} \right) = \frac{3}{2} k N_A T = \frac{3}{2} RT \quad (b)$$

Root mean square speed

$$U_{\text{rms}} = \sqrt{\overline{U^2}} = \sqrt{\frac{U_1^2 + U_2^2 + U_3^2 + \dots + U_N^2}{N}} = \sqrt{\frac{3kT}{m}} \quad (c)$$

$$U_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad \text{molar mass must be in kg/mole.}$$

Average speed

$$U_{\text{av}} = \frac{U_1 + U_2 + U_3 + \dots + U_N}{N}$$

$$U_{\text{avg.}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}} \quad K \text{ is Boltzman constant}$$

Most probable speed

$$U_{\text{MPS}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2kT}{m}}$$

It is the speed possessed by maximum no. of molecules.

REAL GASES :

$$Z = \frac{(PV)_{\text{real}}}{(PV)_{\text{ideal}}} \Rightarrow Z = \frac{PV}{nRT} = \frac{PV_m}{RT} \Rightarrow Z = \frac{V_m}{V_{m \text{ ideal}}}$$

Conclusions :

$Z = 1$ for ideal gas ,

$Z > 1$ at all pressure for He/H₂

$Z < 1$ at low pressure (for all other gases) ,

$Z > 1$ at high pressure (for all other gases)

$$b \rightarrow \text{excluded volume per mole of gas} = N_A 4 \left\{ \frac{4}{3} \pi r^3 \right\}$$

for n moles excluded volume = nb

$$V_i = V - nb \quad \text{volume correction}$$

Vander waal's equation is

$$\left(P + \frac{an^2}{v^2} \right) (v - nb) = nRT$$

VERIFICATION OF VANDER WAAL'S EQUATIONS :

$$\left(P + \frac{a}{V_m^2} \right) (V - b) = RT$$

(a) At low pressure (at separate temp.)

$$\left(P + \frac{a}{V_m^2} \right) V_m = RT, \quad Z = 1 - \frac{a}{V_m RT} \quad Z < 1$$

(b) At high pressure (moderate temp.)

V_m will be low

$$P(V_m - b) = RT, \quad Z = \frac{Pb}{RT} + 1 \quad Z > 1$$

(c) At low pressure and very high temperature.

V_m will be very large

$$PV_m = RT \text{ (ideal gas condition)}$$

(d) For H₂ or He $a \approx 0$

$$P(V_m - b) = RT$$

$$\text{so } Z = 1 + \frac{Pb}{RT}$$

Boyle's temp.

$$T_B = \frac{a}{Rb}$$

Critical constants :

$$V_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27Rb}$$

At critical point, the slope of PV curve (slope of isotherm) will be zero

$$\left(\frac{\partial P}{\partial V_m} \right)_{T_c} = 0 \quad \dots \text{(i)}$$

$$\frac{\partial}{\partial V_m} \left(\frac{\partial P}{\partial V_m} \right)_{T_c} = 0 \quad \dots \text{(ii)}$$

at all other point slope will be negative,

Virial Equation of state :

It is a generalised equation of gaseous state and all other equation can be written in the form of virial equation of state.

Z is expressed in power series expansion of P or $\left(\frac{1}{V_m} \right)$

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots$$

B – second virial coefficient, C – third virial coefficient, D – fourth virial coefficient.

Vander waal equation in virial form :

$$Z = \left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots \right) - \frac{a}{V_m RT} = 1 + \frac{1}{V_m} \left(b - \frac{a}{RT} \right) + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots$$

REDUCED EQUATION OF STATE :

$$\left(P_r + \frac{3}{V_r^2} \right) (3V_r - 1) = 8 T_r$$

THERMODYNAMICS & THERMOCHEMISTRY

Thermodynamic process :

1. **Isothermal process :** $T = \text{constant}$
 $dT = 0$
 $\Delta T = 0$
2. **Isochoric process :** $V = \text{constant}$
 $dV = 0$
 $\Delta V = 0$
3. **Isobaric process :** $P = \text{constant}$
 $dP = 0$
 $\Delta P = 0$
4. **Adiabatic process :** $q = 0$
or heat exchange with the surrounding = 0(zero)

IUPAC Sign convention about Heat and Work

Work done on the system = Positive

Work done by the system = Negative

1st Law of Thermodynamics

$$\Delta U = (U_2 - U_1) = q + w$$

ΔE = Calculation for an ideal gas.

For an ideal gas E is a function of temperature only - Also known as Thermodynamics definition of an ideal gas

$$\text{so } \left(\frac{\partial E}{\partial V} \right)_T = 0, \left(\frac{\partial E}{\partial P} \right)_T = 0$$

$$\Delta E = \Delta (\text{Translational KE}) + \Delta (\text{Rotational KE}) + \Delta (\text{Vibrational KE}) + 0 + 0 + 0 \dots$$

Law of equipartition of energy :

$$U/\text{molecule} = f \times \frac{1}{2} kT$$

$$\therefore U/\text{mole} = \frac{f}{2} \times kT \times N_A \quad \Rightarrow U/\text{mole} = \frac{f}{2} RT$$

$$\therefore \text{For } n \text{ moles} = \frac{f}{2} nRT$$

$$U = \frac{f}{2} nRT \quad (\text{only for ideal gas})$$

$$\Delta E = \frac{f}{2} nR (\Delta T)$$

where f = degrees of freedom for that gas. (Translational + Rotational)

$f = 3$ for monoatomic

$= 5$ for diatomic or linear polyatomic

$= 6$ for non-linear polyatomic.

Calculation of heat (q)

Total heat capacity –

$$\oint_T = \frac{\Delta q}{\Delta T} = \frac{dq}{dT} = J/\text{°C}$$

Molar heat capacity –

$$C = \frac{\Delta q}{n\Delta T} = \frac{dq}{n dT} = J \text{ mole}^{-1} \text{ K}^{-1}$$

So. $dq = ncdT$

$$\oint = \int ncdT = nc\Delta T$$

For an ideal gas C_p and C_v are used

$$\oint_{C_p} = \frac{\gamma R}{\gamma - 1} \quad \oint_{C_v} = \frac{R}{\gamma - 1}$$

Specific heat capacity (s) :

$$\oint_s = \frac{\Delta q}{m\Delta T} = \frac{dq}{mdT} = J \text{ gm}^{-1} \text{ K}^{-1}$$

so $dq = msdT$

$$\oint_s = \int dq = \int msdT = ms\Delta T$$

Total heat capacity, molar heat capacity & specific heat capacity of a process on a substance are related as

$$C_T = nC = ms \quad \& \quad C = Ms$$

Where m – mass of substance

M – molar mass of substance

n – no. of moles of the substance

For	isothermal process	$C = \infty$
For	isobaric process	$C = C_p$
For	isochoric process	$C = C_v$
For	adiabatic process	$C = 0$

WORK DONE (w) :

For all processes (Reversible and Irreversible)

$$W_{\text{ext}} = - \int P_{\text{ext}} \cdot dV$$

(a) Isothermal Reversible expansion/compression of an ideal gas.

$$W = -nRT \ln(V_f/V_i)$$

(b) Reversible and irreversible isochoric processes.

$$\text{Since } dV = 0$$

$$\text{So } dW = -P_{\text{ext}} \cdot dV = 0.$$

(c) Reversible isobaric process :Since pressure of gas is defined during whole of the process and hence the process must be reversible
 $P_{\text{gas}} = \text{constant}$

$$W = - \int_{V_i}^{V_f} dV ; \quad W = P(V_f - V_i)$$

(d) Adiabatic reversible expansion : $dQ = 0$ (no heat exchanged b/w system and surrounding)

$$\Rightarrow T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

$$\therefore TV^{\gamma-1} = \text{constant} \quad \text{or} \quad PV^\gamma = \text{constant} \quad P^{1-\gamma} T^\gamma = \text{constant}$$

These formulae are valid only in case of reversible (quasi-static) adiabatic process.

For irreversible process PV^γ is not constant.**REVERSIBLE WORK :**

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} = \frac{nR(T_2 - T_1)}{\gamma - 1}$$

IRREVERSIBLE PROCESS :

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} = \frac{nR(T_2 - T_1)}{\gamma - 1} = nC_v(T_2 - T_1) = -P_{\text{ext}}(V_2 - V_1) \text{ and use } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

(e) Free expansion – Always going to be irreversible and since $P_{\text{ext}} = 0$

$$\text{so } dW = -P_{\text{ext}} \cdot dV = 0$$

$$\text{If no. heat is supplied } q = 0$$

$$\text{then } \Delta E = 0 \quad \text{so} \quad \Delta T = 0.$$

APPLICATION OF Ist LAW

$$\Delta U = \Delta Q + \Delta W$$

$$\Rightarrow$$

$$\Delta W = -P \Delta V$$

$$\therefore \Delta U = \Delta Q - P \Delta V$$

(a) Constant volume process

Heat given at constant volume = change in internal energy

$$\therefore du = (dq)_v$$

$$du = nC_v dT$$

$$C_v = \frac{1}{n} \cdot \frac{du}{dT} = \frac{f}{2} R$$

(b) Constant pressure process :

$H = \text{Enthalpy}$ (state function and extensive property)

$$H = U + PV$$

$$\text{as } dH = dU + d(PV)$$

Heat given at constant pressure = Change in enthalpy

$\therefore dH = (dq)_p$ only at constant pressure.

$$dH = nC_p dT$$

$$C_p = \frac{1}{n} \frac{dH}{dT} = \frac{1}{n} \frac{(dq)_p}{dT}$$

$$\Rightarrow C_p - C_v = R \text{ (only for ideal gas)}$$

$$C_p = C_v + R = \left(\frac{f}{2} + 1\right) R$$

Calculation of ΔH , ΔU , work, heat etc.

Case - I : For an ideal gas undergoing a process.

$$dU = nC_v dT = \frac{f}{2} nRdT$$

$$dH = nC_p dT = \left(\frac{f}{2} + 1\right) nRdT$$

$$W = - \int P_{\text{ext}} dv$$

$$dH = dU + d(PV)$$

$$\Delta H = \Delta U + nR \Delta T$$

$$dU = dQ + dw$$

Case - II : For solids and liquid system :

$$dU = nC_v dT \neq \frac{f}{2} nRdT$$

$$dH = nC_p dT \neq \left(\frac{f}{2} + 1\right) nRT$$

$$W = - \int P_{\text{ext}} dv$$

$$\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$$

$$du = dq + dw$$

Case III : Calculation of q , W , ΔE and ΔH during phase transformations.

Phase transitions generally take place at constant pressure (unless specified) and at constant temperature.

so $\Delta T = 0$

But still ΔH and ΔE are non zero (different from process on an ideal gas)

Because during phase transitions though the kinetic energy of molecules of substance remains same but the potential energy gets modified or changed and since E is summation of all type of energies so $\Delta E \neq 0$.
Also during this phase transition $\Delta(PV) \neq 0$. Hence $\Delta H \neq 0$.

Now to calculate heat – generally latent heats of transitions are given and since process is taking place at constant pressure so $q_p = \Delta H$.

To calculate W use $dW = - P_{\text{ext}} dV$ and then calculate ΔE using 1st law of thermodynamics.

SECOND LAW OF THERMODYNAMICS :

Entropy of the universe is constantly increasing.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \quad \text{for a spontaneous process.}$$

ENTROPY (S) :

$$\Delta S_{\text{system}} = \int_A^B \frac{dq_{\text{rev}}}{T}$$

$$\therefore \Delta S_{\text{sur}} = \frac{1}{T} \int dq_{\text{sur}} = \frac{-q_{\text{surrounding}}}{T}$$

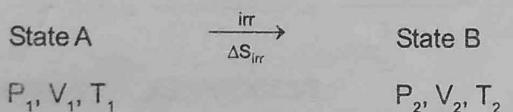
FOR PHASE TRANSFORMATIONS

If T is freezing point, for constant pressure $\Delta S_{\text{fus.}} = \frac{\Delta H_{\text{fus}}}{T}$

for constant volume $\Delta S_{\text{fus.}} = \frac{\Delta U_{\text{fusion}}}{T}$

If T is boiling point, for constant Pressure, $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$

for constant Volume, $\Delta S_{\text{vap}} = \frac{\Delta U_{\text{vap}}}{T}$

ENTROPY CALCULATION FOR AN IDEAL GAS UNDERGOING A PROCESS.

$$\Delta S_{\text{system}} = n c_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad (\text{only for an ideal gas})$$

1. For a reaction entropy change (ΔS) is given by $\Delta S = \sum S_{\text{Products}} - \sum S_{\text{Reactants}}$
2. Entropy of one mole of a substance in pure state at one atmosphere and 25°C is termed as standard entropy, S°
For a reaction in standard state, $A \longrightarrow B$
 $\Delta S^\circ = S_B^\circ - S_A^\circ$
3. Entropy, S, is related to thermodynamic probability, W by the relation :
 $S = k \log_e W$ or $S = 2.303 k \log_{10} W$
where k is Boltzmann's constant.
4. At absolute zero temperature, a solid is supposed to have highly ordered state,
i.e., $W = 1$ and hence $S = 0$, i.e., $\lim_{T \rightarrow 0} S = 0$; This is zeroth law of thermodynamics.

THIRD LAW OF THERMODYNAMICS :

The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

Gibb's free energy (G) : (State function and an extensive property)

$$\begin{aligned} G_{\text{system}} &= H_{\text{system}} - TS_{\text{system}} \\ \Delta G &= \Delta H - T\Delta S \\ \Delta G_{\text{system}} &= \Delta H_{\text{system}} - T\Delta S_{\text{system}} \\ \Delta G_{\text{system}} &= -T\Delta S_{\text{universe}} \end{aligned}$$

Criteria of spontaneity :

- (i) If ΔG_{system} is $(-\text{ve}) < 0$ \Rightarrow process is spontaneous
- (ii) If ΔG_{system} is > 0 \Rightarrow process is non spontaneous
- (iii) If $\Delta G_{\text{system}} = 0$ \Rightarrow system is at equilibrium.

ΔH_{system}	ΔS_{system}	$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$
+ Ve	- Ve	+
- Ve	+ Ve	-
+ Ve	+ Ve	- Ve at high temperature
- Ve	- Ve	+ Ve at high temperature.

Physical interpretation of ΔG :

→ The maximum amount of non-expansional (compression) work which can be performed.

$$\Delta G = dw_{\text{non-exp}} = dH - TdS.$$

$$dw_{\text{non-exp}} = dH - dq.$$

Standard Free Energy Change (ΔG°) :

$$1. \Delta G^\circ = -2.303 RT \log_{10} K$$

2. At equilibrium $\Delta G = 0$.

3. The decrease in free energy $(-\Delta G)$ is given as : $dG = v dp$

$$-\Delta G = W_{\text{net}} = 2.303 nRT \log_{10} \frac{V_2}{V_1}$$

4. ΔG_f° for elemental state = 0

$$5. \Delta G_f^\circ = G_{\text{products}}^\circ - G_{\text{Reactants}}^\circ$$

6. Entropy of mixing (ideal solution)

$$\Delta G_{\text{mix}} = -nRT \sum_{i=1}^k x_i \ln x_i, \Delta H_{\text{mix}} = 0, \Delta S_{\text{mix}} = -nR \sum x_i \ln x_i$$

x_i = mole fraction of i^{th} component.

THERMOCHEMISTRY :

Enthalpy of a substance :

Every substance has a fixed value of enthalpy under any particular state. Through its exact value cannot be calculated but it has some finite fixed value. The enthalpy of one mole of a substance called molar enthalpy in any particular state can be assigned symbol H_m (substance).

○ Change in standard enthalpy $\Delta H^\circ = H_{m,2}^\circ - H_{m,1}^\circ$
 $= \text{heat added at constant pressure.} = C_p \Delta T.$

If $H_{\text{products}} > H_{\text{reactants}}$

→ Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products and if $H_{\text{products}} < H_{\text{reactants}}$

Compendium (Chemistry)

→	Reaction will be exothermic as extra heat content of reactants will be released during the reaction.
	Enthalpy change of a reaction : $\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$
$\Delta H^{\circ}_{\text{reactions}}$	$= H^{\circ}_{\text{products}} - H^{\circ}_{\text{reactants}}$
	= positive - endothermic
	= negative - exothermic

TEMPERATURE DEPENDENCE OF ΔH : (KIRCHOFF'S EQUATION)

- For a constant volume reaction

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_P \cdot dT$$

$$\Delta H_2^{\circ} = \Delta H_1^{\circ} + \Delta C_P (T_2 - T_1)$$

where $\Delta C_P = C_P (\text{products}) - C_P (\text{reactants})$.

e.g. for $aA + bB = cC + dD$; $\Delta C_P = cC_P(C) + dC_P(D) - aC_P(A) - bC_P(B)$

- For a constant volume reaction

$$\Delta E_2^0 = \Delta E_1^0 + \int \Delta C_V \cdot dT$$

$$\Delta E_2^0 = \Delta E_1^0 + \int \Delta C_V \cdot dT$$

ENTHALPY OF FORMATION :

It is not possible to determine the absolute value of the molar enthalpy of a substance. However, based on the following convention, the relative values of standard molar enthalpies of formation of various substances can be built. The standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value. The specified temperature is usually taken as 25 °C.

A few examples are

$$\Delta H_f^{\circ} (\text{O}_2, \text{g}) = 0$$

$$\Delta H_f^{\circ} (\text{C, diamond}) \neq 0$$

$$\Delta H_f^{\circ} (\text{Br}_2, \ell) = 0$$

$$\Delta H_f^{\circ} (\text{S, monoclinic}) \neq 0$$

$$\Delta H_f^{\circ} (\text{P, black}) \neq 0$$

$$\Delta H_f^{\circ} (\text{S, Rhombic}) = 0$$

$$\Delta H_f^{\circ} (\text{P, white}) = 0$$

ENTHALPY OF REACTION FROM ENTHALPIES OF FORMATION:

The enthalpy of reaction can be calculated by

$$\Delta H_r^{\circ} = \sum v_B \Delta H_f^{\circ, \text{products}} - \sum v_B \Delta H_f^{\circ, \text{reactants}} \quad v_B \text{ is the stoichiometric coefficient}$$

above equation holds good for any reaction as the same reference state is used for reactants and products

HESS'S LAW OF CONSTANT HEAT SUMMATION :

The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps.

MEASUREMENT OF ENTHALPY OF COMBUSTION : (In bomb calorimeter).

If total heat capacity of calorimeter and all of its contents = C, rise in temperature = ΔT then heat released

= $q = C\Delta T$ of this heat is because of mass m if substance then due to 1 mole heat released = $\left(\frac{M}{m}\right)q$

= ΔE_c° (constant volume reactions) Now ΔH_c° can be calculated by using $\Delta H_c^{\circ} = \Delta E_c^{\circ} + \Delta n_g RT$. Where Δn_g is the change in stoichiometric number of gaseous species in the balanced chemical equation representing the combustion process.

By convention, the standard enthalpy of formation of $\text{H}^+(\text{aq})$ is taken to be zero.

ESTIMATION OF ENTHALPY OF A REACTION FROM BOND ENTHALPIES :

$$\Delta H = \left(\begin{array}{l} \text{Enthalpy required to} \\ \text{break reactants into} \\ \text{gaseous atoms} \end{array} \right) - \left(\begin{array}{l} \text{Enthalpy released to} \\ \text{form products from the} \\ \text{gaseous atoms} \end{array} \right)$$

RESONANCE ENERGY :

$$\begin{aligned}\Delta H^{\circ}_{\text{resonance}} &= \Delta H^{\circ}_{f, \text{experimental}} - \Delta H^{\circ}_{f, \text{calculated}} \\ &= \Delta H^{\circ}_{c, \text{calculated}} - \Delta H^{\circ}_{c, \text{experimental}}\end{aligned}$$

CHEMICAL EQUILIBRIUM**At equilibrium :**

- (i) Rate of forward reaction = rate of backward reaction
- (ii) Concentration (mole/litre) of reactant and product becomes constant.
- (iii) $\Delta G = 0$.
- (iv) $Q = K_{\text{eq}}$.

EQUILIBRIUM CONSTANT (K) :

$$K = \frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}} = \frac{K_f}{K_b}.$$

Equilibrium constant in terms of concentration (K_c).

$$\frac{K_f}{K_b} = K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Equilibrium constant in terms of partial pressure (K_p).

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

*** Equilibrium constant in terms of mole fraction (K_x).**

$$K_x = \frac{x_C^c x_D^d}{x_A^a x_B^b}$$

*** Relation between K_p & K_c**

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

$$K_p = K_x (P)^{\Delta n}$$

Where P = Total pressure at equilibrium.

$\Delta n = (c + d) - (a + b)$, calculation of Δn involves only gaseous components.

$\Rightarrow \Delta n = \text{sum of the number of moles of gaseous products} - \text{sum of the number of moles of gaseous reactants}$.
 Δn can be positive, negative, zero or even fraction.

O Dependence of K_{eq} on the stoichiometry of the reaction.

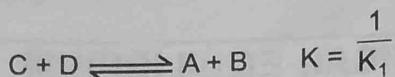
- (a) If two chemical reactions at equilibrium having equilibrium constants K_1 and K_2 are added then the resulting equation has equilibrium constant $K = K_1 \cdot K_2$

		Equilibrium constant
	$A \rightleftharpoons B$	K_1
	$B \rightleftharpoons C$	K_2
On adding	$A \rightleftharpoons C$	$K = K_1 \cdot K_2$

(b) If the reaction having eq. constant K_1 is reversed then resulting equation has eq. constant $\frac{1}{K_1}$

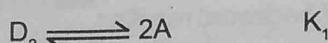


On reversing,



(c) If a chemical reaction having equilibrium constant K_1 is multiplied by a factor n then the resulting equation has equilibrium constant $K = (K_1)^n$, n can be fraction

Eg.



Dependence of K_{eq} on temperature.

Equilibrium constant is only dependent upon the temperature for a given reaction.

It means k_p and k_c will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.

But k_x depends on pressure provided $\Delta n \neq 0$, i.e. even at constant temperature, k_x will undergo a change by the change in total pressure at equilibrium.

* $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]; \Delta H = \text{Enthalpy of reaction}$

If $T_2 > T_1$ then $K_2 > K_1$ provided $\Delta H = +ve$ (endothermic reaction)

$K_2 < K_1$ if $\Delta H = -ve$ (exothermic reaction)

In the above equation, the unit of R and ΔH should be same.

Relation between equilibrium constant & standard free energy change.

$$\Delta G^\circ = -2.303 RT \log K$$

Where $\Delta G^\circ = \text{standard free energy change}$

T = Absolute temperature,

R = universal gas constant.

Significance of value of Equilibrium constant (k) :

How to use neglection in the problem :

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

Case I

If K is large ($k > 10^3$) then product concentration is very very larger than the reactant ($[\text{Product}] \gg [\text{Reactant}]$). Hence concentration of reactant can be neglected with respect to the product. In this case, the reaction is product favourable and equilibrium will be more in forward direction than in backward direction.

Case.II

If K is very small ($K < 10^{-3}$)

[Product] << [Reactant]

Hence concentration of Product can be neglected as compared to the reactant.

In this case, the reaction is reactant favourable.

REACTION QUOTIENT (Q) :

$$\text{The values of expression } Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

at any time during reaction is called reaction quotient

if $Q > K_c$ reaction proceed in backward direction until equilibrium is reached

if $Q < K_c$ reaction will proceed in forward direction until equilibrium is established

if $Q = K_c$ Reaction is at equilibrium

DEGREE OF DISSOCIATION (α) :

α = no. of moles dissociated / initial no. of moles taken

= fraction of moles dissociated out of 1 mole.

Note : % dissociation = $\alpha \times 100$

O Observed molecular weight and Observed Vapour Density of the mixture

$$\text{Observed molecular weight of } A_n(g) = \frac{\text{molecular weight of equilibrium mixture}}{\text{total no. of moles}}$$

$$\therefore M_{obs} = \frac{M_{th}}{[1 + (n-1)\alpha]}$$

$$* D = \text{vapour density without dissociation} = \frac{M_{A_n}}{2}$$

$$d = \text{vapour density of mixture} = \text{observed v.d.} = \frac{M_{mix}}{2}$$

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

$$\alpha = \frac{D-d}{(n-1) \times d} = \frac{M_T - M_0}{(n-1)M_0}$$

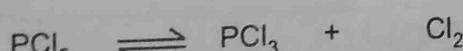
where M_T = Theoretical molecular wt. M_0 = observed molecular wt. or molecular wt. of the mixture at eq.

Note : It is not applicable for $n = 1$ [eg. Dissociation of HI & NO].

Significance of n :

$$n = \frac{\text{sum of stoichiometric coeff of product}}{\text{sum of coeff of reactants}}$$

Ex.



$$K_P = \frac{\alpha^2 \cdot P}{1-\alpha^2} \quad (\text{Remember}).$$

Compendium (Chemistry)**EXTERNAL FACTOR AFFECTING EQUILIBRIUM :****Le Chatelier's Principle:**

If a system at equilibrium is subjected to a disturbance or stress that changes any of the factors that determine the state of equilibrium, the system will react in such a way as to minimize the effect of the disturbance.

EFFECT OF CONCENTRATION :

- * If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction.
- * If the concentration of product is increased then equilibrium shifts in the backward direction.

EFFECT OF VOLUME :

- * If volume is increased pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
- * If volume is increased then, for
 - $\Delta n > 0$ reaction will shift in the forward direction
 - $\Delta n < 0$ reaction will shift in the backward direction
 - $\Delta n = 0$ reaction will not shift.

EFFECT OF PRESSURE :

- * If pressure is increased at equilibrium then reaction will try to decrease the pressure, hence it will shift in the direction in which less no. of moles of gases are formed.

EFFECT OF INERT GAS ADDITION :

- (i) **Constant pressure :** If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed
 - $\Delta n > 0$ reaction will shift in the forward direction
 - $\Delta n < 0$ reaction will shift in the backward direction
 - $\Delta n = 0$ reaction will not shift.
- (ii) **Constant volume :** Inert gas addition has no effect at constant volume.

EFFECT OF TEMPERATURE :

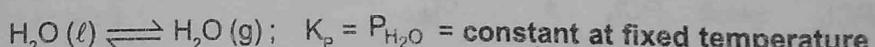
Equilibrium constant is only dependent upon the temperature.

If plot of $\ln K$ vs $\frac{1}{T}$ is plotted then it is a straight line with slope $= -\frac{\Delta H^\circ}{R}$, and intercept $= \frac{\Delta S^\circ}{R}$

- * For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature
- * For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature
- * For $\Delta H > 0$, reaction shifts in the forward direction with increase in temperature
- * For $\Delta H < 0$, reaction shifts in the backward direction with increases in temperature.

○ Vapour Pressure of Liquid :

It is the pressure exerted by the vapour over its liquid when it is in equilibrium with the liquid. Vapour pressure of water is also called **aqueous tension**.



Hence V.P. of liquid is independent of pressure, volume and concentration change.

e.g. at 25°C , vapour pressure of water ≈ 24 mm of Hg

- * **Relative Humidity** =
$$\frac{\text{Partial pressure of H}_2\text{O vapours}}{\text{Vapour pressure of H}_2\text{O at that temp.}}$$

THERMODYNAMICS OF EQUILIBRIUM :

For a general reaction, $mA + nB \rightleftharpoons pC + qD$, ΔG is given by-

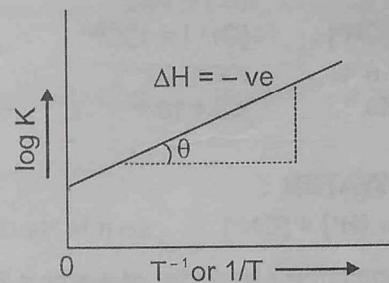
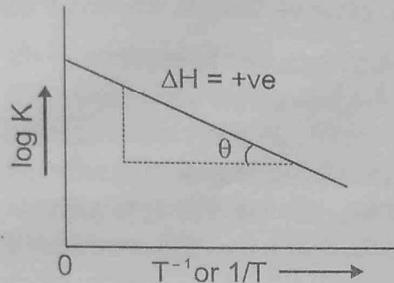
$$\Delta G = \Delta G^\circ + 2.303 RT \log_{10} Q$$

$$\Delta G^\circ = -2.303 RT \log_{10} K$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\log_{10} K = -\frac{\Delta H^\circ}{2.303} \cdot \frac{1}{RT} + \frac{\Delta S^\circ}{2.303R}$$

If plot of $\log K$ vs $\frac{1}{T}$ is plotted then it is a straight line with slope $= -\frac{\Delta H^\circ}{R}$, and intercept $= \frac{\Delta S^\circ}{R}$



$$\text{Slope} = \frac{-\Delta H^\circ}{2.303R} = \tan \theta, \quad \text{y intercept} = \frac{\Delta S^\circ}{2.303R}$$

Vant Hoff equation- $\log\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Note : * ΔH° should be substituted with sign.

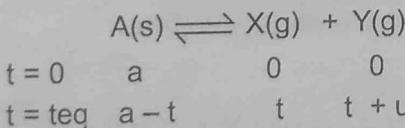
* For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature

* For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature

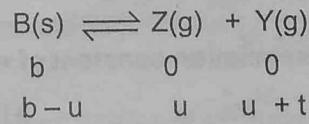
SIMULTANEOUS EQUILIBRIUM :

If in any container there are two or more than two equilibria existing simultaneously involving one or more than one common species. Then in both/all the equilibria the concentration of common species is the total concentration of that species due to all equilibria is taken under concentration.

e.g.



$$K_{C_1} = t(u+t)$$



$$K_{C_2} = (u+t)u$$

IONIC EQUILIBRIUM

OSTWALD DILUTION LAW :

Dissociation constant of weak acid (K_a) , $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[C\alpha][C\alpha]}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$

If $\alpha \ll 1$, then $1 - \alpha \approx 1$ or $K_a = C\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times V}$

$C = \frac{1}{V}$, then $V = 1/C$ (volume of solution in which 1 mole is present) is called dilution, so $K_a = \frac{a^2}{(1-a)V}$

- Similarly for a weak base, $\alpha = \sqrt{\frac{K_b}{C}}$. Higher the value of K_a / K_b , stronger is the acid / base.

Acidity and pH scale :

$\therefore \text{pH} = -\log a_{H^+}$ (where a_{H^+} is the activity of H^+ ions = molar concentration for dilute solution).
Activity of H^+ ions is the concentration of free H^+ ions or H_3O^+ ions in a solution.

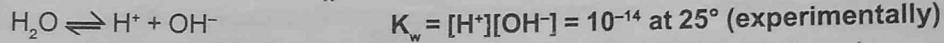
[Note : pH can also be negative or > 14]

$$\begin{aligned}\text{pH} &= -\log [H^+]; & [H^+] &= 10^{-\text{pH}} \\ \text{pOH} &= -\log [OH^-]; & [OH^-] &= 10^{-\text{pOH}} \\ \text{pKa} &= -\log K_a; & K_a &= 10^{-\text{pKa}} \\ \text{pKb} &= -\log K_b; & K_b &= 10^{-\text{pKb}}\end{aligned}$$

PROPERTIES OF WATER :

- In pure water $[H^+] = [OH^-]$ so it is Neutral.
- Molar concentration / Molarity of water = 55.56 M.

3. Ionic product of water (K_w) :



On increasing temp $\Rightarrow K_w$ increases (dissociation of water, is endothermic, so on increasing temperature K_{eq} increases)

Now $\text{pH} = -\log[H^+] = 7$ and $\text{pOH} = -\log[OH^-] = 7$ for water at 25° (exp.)

$\text{pH} = 7 = \text{pOH} \Rightarrow$ neutral

$\text{pH} < 7$ or $\text{pOH} > 7 \Rightarrow$ acidic

$\text{pH} > 7$ or $\text{pOH} < 7 \Rightarrow$ Basic

Note. Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.

4. Degree of dissociation of water :

$$H_2O \rightleftharpoons H^+ + OH^- \Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7}\%$$

5. Absolute dissociation constant of water :

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

$$\text{So, } pK_a = pK_b = -\log (1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

Note: For a conjugate acid base pairs

$$K_a \times K_b = [H^+][OH^-] = K_w$$

$$\Rightarrow pK_a + pK_b = pK_w = 14 \quad \text{at } 25^\circ C.$$

Note: pK_a of H_3O^+ ions = -1.74

pK_b of OH^- ions = -1.74.

pH Calculations of Different Types of Solutions :

(a) Strong acid solution :

(i) If concentration is greater than 10^{-6} M

In this case H^+ ions coming from water can be neglected,
so $[H^+] = \text{normality of strong acid solution}$

(ii) If concentration is less than 10^{-6} M

In this case H^+ ions coming from water cannot be neglected and since water is a weak electrolyte so its dissociation equilibrium will be disturbed much more than dissociation equilibrium of strong acid.

So $[H^+] = \text{normality of strong acid} + H^+ \text{ ions coming from water in presence of this strong acid}$

(b) Strong base solution :

Using similar method as in part (a) calculate first $[OH^-]$ and then use $[H^+] \times [OH^-] = 10^{-14}$

(c) pH of mixture of two strong acids :

If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of another strong acid solution of normality N_2 , then

Number of H^+ ions from I-solution = $N_1 V_1$

Number of H^+ ions from II-solution = $N_2 V_2$

If final normality is N and final volume is V , then $NV = N_1 V_1 + N_2 V_2$

[dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[H^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

(d) pH of mixture of two strong bases :

similar to above calculation

$$[OH^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

(e) pH of mixture of a strong acid and a strong base :

There will be neutralisation of the acid and the base, and the solution will be acidic or basic depending on which component has been taken in excess.

If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of a strong base solution of normality N_2 , then

Number of H^+ ions from I-solution = $N_1 V_1$

Number of OH^- ions from II-solution = $N_2 V_2$

$$\text{If } N_1 V_1 > N_2 V_2, \text{ then solution will be acidic in nature and } [H^+] = N = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

$$\text{If } N_2 V_2 > N_1 V_1, \text{ then solution will be basic in nature and } [OH^-] = N = \frac{N_2 V_2 - N_1 V_1}{V_1 + V_2}$$

(f) pH of a weak acid(monoprotic) solution :

$$K_a = \frac{[H^+] [OH^-]}{[HA]} = \frac{C\alpha^2}{1-\alpha}$$

$$\text{if } \alpha \ll 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \quad (\text{is valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$$

$$pH = \frac{1}{2}(pK_a - \log C)$$

On increasing the dilution

$\Rightarrow C \downarrow \Rightarrow \alpha \uparrow$ and $[H^+] \downarrow \Rightarrow pH \uparrow$

** At very low concentration (∞ dilution) weak electrolyte will be almost 100% dissociate, so behave as strong electrolyte.

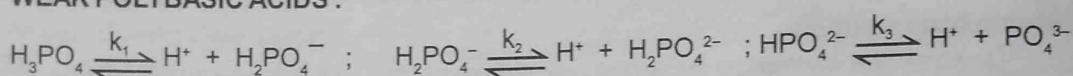
(g) pH of a solution of a polyprotic weak acid :

$$[H^+]_T = c\alpha_1 + c\alpha_1\alpha_2 + c\alpha_1\alpha_2\alpha_3 \approx c\alpha_1.$$

[Generally, $K_{a_3} \ll K_{a_2} \ll K_{a_1}$, α_2 and α_3 can be neglected].

$$pH = \frac{1}{2}(pK_{a_1} - \log C).$$

WEAK POLYBASIC ACIDS :



The relative value of these constant is, $k_1 > k_2 > k_3$

RELATIVE STRENGTH OF TWO ACIDS :

$$\frac{[H^+] \text{ furnished by I acid}}{[H^+] \text{ furnished by II acid}} = \frac{c_1\alpha_1}{c_2\alpha_2} = \sqrt{\frac{k_{a_1}c_1}{k_{a_2}c_2}}$$

If acids are highly strong, the relative strength = $\frac{k_{a_1}}{k_{a_2}}$.

(h) pH of a mixture of two weak acid (both monoprotic) solutions :

Let the acid are HA_1 & HA_2 and their final concentrations are C_1 & C_2 respectively, then

$$\text{Generally, } (\alpha_1 \ll 1) \text{ and } (\alpha_2 \ll 1) \Rightarrow \frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^+] = C_1\alpha_1 + C_2\alpha_2 \Rightarrow [H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

$$\text{So, } [H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$$

** If water is again considered third weak acid in solution of two weak acid then

$$[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2 + K_w}$$

$$C_w K_{aw} = 10^{-14} = K_w$$

$$[H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2} + 10^{-14}}$$

(i) pH of a mixture of weak acid (monoprotic) and a strong acid solution :

If $[SA] = C_1$ and $[WA] = C_2$, then $[H^+]$ from SA = C_1 and $[H^+]$ from WA = C_2
Let HA is a weak acid.

$$\text{Generally, } \alpha \ll 1. \quad \text{Therefore, } K_a \approx (C_2\alpha + C_1)\alpha$$

$$[H^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_a \cdot C_2}}{2}$$

** If a strong acid of low conc is added in water then $[H^+]$ of solution can be calculated as

$$[H^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_w}}{2}$$

O SALT HYDROLYSIS :

Salt of	Type of hydrolysis	k_h	h	pH
(a) weak acid & strong base	anionic	$\frac{k_w}{k_a}$	$\sqrt{\frac{k_w}{k_a c}}$	$7 + \frac{1}{2} p k_a + \frac{1}{2} \log c$
(b) strong acid & weak base	cationic	$\frac{k_w}{k_b}$	$\sqrt{\frac{k_w}{k_b c}}$	$7 - \frac{1}{2} p k_b - \frac{1}{2} \log c$
(c) weak acid & weak base	both	$\frac{k_w}{k_a k_b}$	$\sqrt{\frac{k_w}{k_a k_b}}$	$7 + \frac{1}{2} p k_a - \frac{1}{2} p k_b$
(d) Strong acid & strong base	-----do not hydrolysed-----			pH = 7

Hydrolysis of polyvalent anions or cations

For $[Na_3PO_4] = C$.

$$K_{a1} \times K_{a3} = K_w$$

$$K_{a2} \times K_{a1} = K_w$$

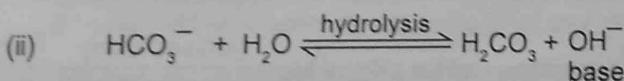
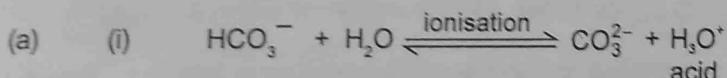
$$K_{a3} \times K_{h1} = K_w$$

Generally pH is calculated only using the first step Hydrolysis

$$K_{h1} = \frac{Ch^2}{1-h} \approx Ch^2$$

$$h = \sqrt{\frac{K_{h1}}{C}} \Rightarrow [OH^-] = ch = \sqrt{K_{h1} \times C} \Rightarrow [H^+] = \sqrt{\frac{K_w \times K_{a3}}{C}}$$

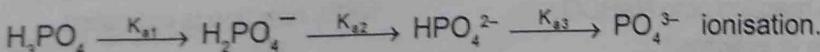
$$\text{So } pH = \frac{1}{2}[pK_w + pK_{a3} + \log C]$$

Hydrolysis of Amphiprotic Anion. (Cation is not Hydrolysed e.g. $NaHCO_3$, $NaHS$, etc.)

$$pH(HCO_3^-) = \left(\frac{pK_{a1} + pK_{a2}}{2} \right)$$

(b) Similarly for $H_2PO_4^-$ and HPO_4^{2-} amphiprotic anions.

$$pH(H_2PO_4^-) = \left(\frac{pK_{a1} + pK_{a2}}{2} \right) \quad \text{and} \quad pH(HPO_4^{2-}) = \left(\frac{pK_{a2} + pK_{a3}}{2} \right)$$



$$\xleftarrow{K_{h1} = \frac{K_w}{K_{a1}}} \xleftarrow{K_{h2} = \frac{K_w}{K_{a2}}} \xleftarrow{K_{h3} = \frac{K_w}{K_{a3}}}$$

Hydrolysis (reverse of ionisation)

The pH of H_3PO_4 = $\frac{1}{2}(pK_{a1} - \log C)$ $\therefore K_{a1} \gg K_{a2} \gg K_{a3}$

$$\text{pH of } \text{NaH}_2\text{PO}_4 = \frac{1}{2} (\text{pK}_{a1} + \text{pK}_{a2})$$

$$\text{pH of } \text{Na}_2\text{HPO}_4 = \frac{1}{2} (\text{pK}_{a2} + \text{pK}_{a3}) \quad \therefore \text{sec ionisation can neglect}$$

$$\text{pH of } \text{Na}_3\text{PO}_4 = \frac{1}{2} (\text{pKw} + \text{pK}_{a3} + \log C) \quad \therefore \text{Sec hydrolysis can neglect.}$$

BUFFER SOLUTION :

(a) **Acidic Buffer** : e.g. CH_3COOH and CH_3COONa . (weak acid and salt of its conjugate base).

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad [\text{Henderson's equation}]$$

(b) **Basic Buffer** : e.g. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$. (weak base and salt of its conjugate acid).

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Buffer capacity (index) :

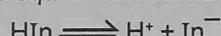
It is the ratio of the small amount of acid or base added to the change in pH caused in the buffer.

$$\text{Buffer capacity} = \frac{\text{Total no. of moles of acid /base added per litre}}{\text{Change in pH}}$$

$$\text{Buffer capacity} = \frac{dx}{d\Delta\text{pH}} = 2.303 \frac{(a+x)(b-x)}{a+b}$$

INDICATOR :

There is equilibrium between the ionised and unionised form of an acid indicator (HIn)



$$\therefore K_{\text{HIn}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad [K_{\text{HIn}} = \text{indicator constant or dissociation constant of indicator}]$$

$$\text{or} \quad [\text{H}^+] = K_{\text{HIn}} \times \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$\therefore \text{pH} = \text{pK}_{\text{HIn}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} \quad \Rightarrow \quad \text{pH} = \text{pK}_{\text{HIn}} + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

SIGNIFICANCE OF INDICATORS :

☞ Extent of reaction of different bases with acid (HCl) using two indicators :

	Phenolphthalein	Methyl Orange
NaOH	100% reaction is indicated $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$	100% reaction is indicated $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
Na_2CO_3	50% reaction upto NaHCO_3 stage is indicated $\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl}$	100% reaction is indicated $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$
NaHCO_3	No reaction is indicated $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$	100% reaction is indicated $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$

- ISOELECTRIC POINT :** of amino acid is the point when the net charge is equal to zero :

⇒ At isoelectric point, [Anionic form] = [Cationic form]

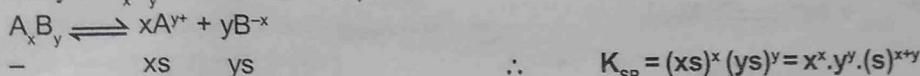
$$[\text{H}^+] = \sqrt{K_{a1} K_{a2}}$$

$$\text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2}$$

SOLUBILITY PRODUCT :

- Simple Solubility in water :**

The solubility of A_xB_y in water is 's' M, then



CONDITION FOR PRECIPITATION :

If ionic product $K_{I.P} > K_{sp}$ precipitation occurs,
if $K_{I.P} = K_{sp}$ saturated solution (precipitation just begins or is just prevented).

ELECTROCHEMISTRY

ELECTRODE POTENTIAL

For any electrode → oxidation potential = - Reduction potential

$$E_{cell} = \text{R.P. of cathode} - \text{R.P. of anode}$$

$$E_{cell} = \text{R.P. of cathode} + \text{O.P. of anode}$$

E_{cell} is always a +ve quantity & Anode will be electrode of low R.P

$$E_{cell}^o = \text{SRP of cathode} - \text{SRP of anode.}$$

- Greater the SRP value greater will be oxidising power.**

GIBBS FREE ENERGY CHANGE:

$$\Delta G = -nFE_{cell}$$

$$\Delta G^o = -nFE_{cell}^o$$

where, n → no. e⁻ involved in cell (electrode) reaction

F → Faraday's constant = 96500 C ≈ (96485 C)

= charge on 1 mole of e⁻

$$= (1.6 \times 10^{-19} \text{ C}) \times 6.022 \times 10^{23} = 96500 \text{ C.}$$

Note : 1. E.M.F. is an intensive properties (not dependent on mass or size) so we can not add or subtract.

E^o value of two reaction to calculate E^o of any other reaction.

2. ΔG is an extensive properties we can add or subtract. ΔG value of two reaction.

NERNST EQUATION : (Effect of concentration and temp of an emf of cell)

$$\Rightarrow \Delta G = \Delta G^o + RT \ln Q \quad (\text{where } Q \text{ is reaction quotient})$$

$$\Delta G^o = -RT \ln K_{eq}$$

$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E_{cell}^o - \frac{2.303RT}{nF} \log Q$$

At 298 K

$$E_{cell} = E_{cell}^o - \frac{0.0591}{n} \log Q \quad [\text{At } 298 \text{ K}]$$

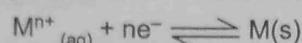
At chemical equilibrium

$$\Delta G = 0 ; E_{\text{cell}}^{\circ} = 0.$$

$$\log K_{\text{eq}} = \frac{nE_{\text{cell}}^{\circ}}{0.0591}.$$

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_{\text{eq}}$$

Note- Nernst equation for an actual reaction



$$E_{\text{RP}} = E_{\text{SRP}}^{\circ} - \frac{0.0591}{n} \log \left(\frac{1}{[\text{M}^{n+}]_{\text{aq}}} \right)$$

For an electrode M(s)/Mⁿ⁺.

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[\text{M}^{n+}]}.$$

CONCENTRATION CELL : A cell in which both the electrodes are made up of same material.

For all concentration cell $E_{\text{cell}}^{\circ} = 0$.

(a) **Electrolyte Concentration Cell :**

Concentration cell in which the electrodes are of same material but they are in contact with the different concentration of their ions

e.g. Zn(s) / Zn²⁺ (c₁) || Zn²⁺(c₂) / Zn(s)

$$E = \frac{0.0591}{2} \log \frac{C_2}{C_1}$$

For spontaneous cell reaction $E_{\text{cell}} > 0 \Rightarrow C_1 < C_2$.
i.e. concentration of anodic compartment < cathodic compartment.

(b) **Electrode Concentration Cell :**

A concentration cell with same gaseous electrodes at different pressure of gases and are in contact with their ions of same concentration.

e.g. Pt, H₂(P₁ atm) / H⁺ (1M) / H₂ (P₂ atm) / Pt

$$E = \frac{0.0591}{2} \log \left(\frac{P_1}{P_2} \right)$$

DIFFERENT TYPES OF ELECTRODES :

1. Metal-Metal ion Electrode M(s)/Mⁿ⁺. $M^{n+} + ne^{-} \longrightarrow M(s)$ $E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$

2. Gas-ion Electrode Pt / H₂(Patm) / H⁺ (XM)

as a reduction electrode $H^{+}(\text{aq}) + e^{-} \longrightarrow \frac{1}{2} H_2 (\text{Patm})$ $E = E^{\circ} - 0.0591 \log \frac{P_{H_2/2}}{[H^{+}]}$

3. Oxidation-reduction Electrode Pt / Fe²⁺, Fe³⁺

as a reduction electrode $Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$

$$E = E^{\circ} - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

4. Metal-Metal insoluble salt Electrode eg. Ag/AgCl, Cl⁻

as a reduction electrode $AgCl(s) + e^{-} \longrightarrow Ag(s) + Cl^{-}$

○ $E_{Cl^-/AgCl/Ag} = E_{Cl^-/AgCl/Ag}^0 - 0.0591 \log [Cl^-]$.

This electrode has a fixed value of reduction potential at a given concentration of anion, hence can be used as a reference electrode.

5. Mercury-Mercuric oxide - Hydroxide ion half cell
 $HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-$

$$E_{OH^-/HgO/Hg} = E_{OH^-/HgO/Hg}^0 - \frac{RT}{F} \ln[OH^-]$$

6. Mercury - Mercurous chloride - chloride ion half cell
 $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^- (aq)$

$$E_{Cl^-/Hg_2Cl_2/Hg} = E_{Cl^-/Hg_2Cl_2/Hg}^0 - \frac{RT}{F} \ln[Cl^-]$$

CALCULATION OF DIFFERENT THERMODYNAMICS FUNCTION OF CELL REACTION

○ $\Delta G = -n F E_{cell}$

○ $S = - \left[\frac{dG}{dT} \right]_p$ (At constant pressure).

○ $\Delta S = - \left[\frac{d(\Delta G)}{dT} \right]_p = nF \left(\frac{d}{dt}(E_{cell}) \right)_p$

○ $\left[\frac{\partial E}{\partial T} \right]_p$ = Temperature coefficient of e.m.f of the cell.

$E = a + bT + CT^2 + \dots$

○ $\Delta H = nF \left[T \left(\frac{\partial E}{\partial T} \right)_p - E \right]$

○ ΔC_p of cell reaction

$$C_p = \frac{dH}{dT}$$

$$\Delta C_p = \frac{d}{dT} (\Delta H)$$

$$\Delta C_p = nFT \frac{d^2E_{cell}}{dT^2}$$

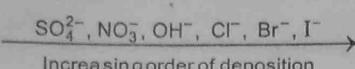
ELECTROLYSIS :

Note : In case two or more types of positive and negative ion are present in solution during electrolysis certain ion are discharged or liberated at the electrode in preference to other. In general in such competition the ion which is stronger oxidising agent (High value of SRP) is discharged first at the cathode.

(a) $K^+, Ca^{+2}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}$.

Increasing order of deposition.

- (b) Similarly the anion which is stronger reducing agent (low value of SRP) is liberated first at the anode.



- ☞ Whenever there are many anions/species which are competing to get oxidised at anode, than species with maximum SOP, will get oxidised perfectly.
- ☞ At cathode, the species with maximum SRP will get reduced.

FARADAY'S LAW OF ELECTROLYSIS :

First Law : The weight of substance deposited or evolved at electrode during electrolysis is directly proportional to the quantity of charge passed through the electrolyte

$$w \propto q \quad w = zq \quad w = Zit \quad Z = \text{Electrochemical equivalent of substance}$$

Second Law : When same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at respective electrodes will be in the proportion of their equivalent weights.

$$W \propto E \quad \frac{W}{E} = \text{constant} \quad \frac{W_1}{E_1} = \frac{W_2}{E_2} = \dots$$

when $W = E$, then charge $q = 96500 \text{ coulomb} = 1 \text{ Faradays}$.

or No of equivalents of substances deposited or evolved

$i = \text{No of faradays of charge (used) in the electrolysis}$

$$\frac{W}{E} = \frac{i \times t \times \text{current efficiency factor}}{96500}$$

$$\text{CURRENT EFFICIENCY} = \frac{\text{actual mass deposited/produced}}{\text{Theoretical mass deposited/produced}} \times 100$$

○ CONDITION FOR SIMULTANEOUS DEPOSITION OF Cu & Fe AT CATHODE

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} - \frac{0.0591}{2} \log \frac{1}{\text{Cu}^{2+}} = E^\circ_{\text{Fe}^{2+}/\text{Fe}} - \frac{0.0591}{2} \log \frac{1}{\text{Fe}^{2+}}$$

Condition for the simultaneous deposition of Cu & Fe on cathode.

SECTION (C) – CONDUCTANCE :

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

Specific conductance or conductivity :

$$(\text{Reciprocal of specific resistance}) \quad K = \frac{1}{\rho} \quad K = \text{specific conductance}$$

Equivalent conductance : The conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution.

$$\lambda_{\text{eq}} = \frac{K \times 1000}{\text{Normality}} \quad \text{unit : } \text{-ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

Molar conductance : The conductance of all the ions produced by ionization of 1 gm mole of an electrolyte when present in v ml solution.

$$\lambda_m = \frac{K \times 1000}{\text{Molarity}} \quad \text{unit : } \text{-ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{specific conductance} = \text{conductance} \times \frac{l}{a}, \quad l = \text{distance between electrodes of conductivity cell}$$

KOHLRAUSCH'S LAW :

Variation of λ_{eq} / λ_M of a solution with concentration :

(i) Strong electrolyte :

These solutions are found to follow Debye-Hückel-Onsager equation at low concentrations.

$$\lambda_M^c = \lambda_M^\infty - b\sqrt{c}$$

(ii) Weak electrolytes :

KOHLRAUSCH LAW : $\lambda_\infty = n_+ \lambda_+^\infty + n_- \lambda_-^\infty$ where λ is the molar conductivity

n_+ = No. of cations obtained after dissociation per formula unit

n_- = No. of anions obtained after dissociation per formula unit

APPLICATION OF KOHLRAUSCH LAW :1. Calculation of λ_M^0 of weak electrolytes :

$$\lambda_M^0 \text{ (CH}_3\text{COOH)} = \lambda_M^0 \text{ (CH}_3\text{COONa)} + \lambda_M^0 \text{ (HCl)} - \lambda_M^0 \text{ (NaCl)}$$

2. To calculate degree of dissociation of a weak electrolyte

$$\alpha = \frac{\lambda_m^c}{\lambda_m^0} ; K_{eq} = \frac{c\alpha^2}{(1-\alpha)}$$

3. Solubility (S) of sparingly soluble salt & their K_{sp}

$$\lambda_M^c = \lambda_M^\infty = \kappa \times \frac{1000}{\text{solubility}}$$

$$K_{sp} = S^2.$$

Note : (i) Conductance of mixture of two electrolytes

$$C_{total} = \sum C_{electrolytes} + C_{water} ; K_{total} = \sum K_{electrolytes} + K_{water}$$

(ii) All the electrolytes will be parallel b/w two electrodes.

(iii) C or K is proportional to concentration of the solution [for any strong electrolyte (100% dissolved)]

○ **IONIC MOBILITY :** It is the distance travelled by the ion per second under the potential gradient of 1 volt per cm. Its unit is $\text{cm}^2 \text{s}^{-1} \text{V}^{-1}$.

Absolute ionic mobility :

Ionic mobility at infinite dilution is called absolute ionic mobility and represented by μ_c^0 or μ_a^0 .
or

Speed of the ion at infinite dilution under unit potential gradient (in $\text{cm}^2 \text{ sec}^{-1} \text{ vol}^{-1}$).

$$\lambda_c^0 \propto \mu_c ; \lambda_a^0 \propto \mu_a$$

$$\lambda_c^0 = F \mu_c^0 ; \lambda_a^0 = F \times \mu_a^0.$$

$$\text{Ionic Mobility } \mu = \frac{v}{(V/\ell)} \xrightarrow{\substack{\text{speed} \\ \text{potential gradient}}}$$

Transport Number :

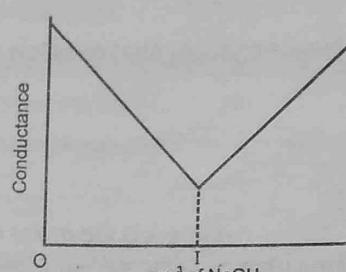
It is the fraction of total current carried by each ion of the electrolyte. Now greater the mobility of the ion larger will be magnitude of current carried by the ion and consequently larger will be its transport number.

$$t_c = \left[\frac{\mu_c}{\mu_c + \mu_a} \right], \quad t_a = \left[\frac{\mu_a}{\mu_a + \mu_c} \right].$$

Where t_c = Transport Number of cation & t_a = Transport Number of anion.

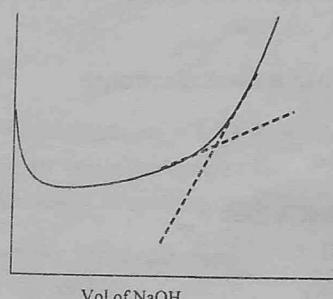
Conductance graphs in some titrations:

1. Strong acid (titrate) + strong base (titrant) : $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

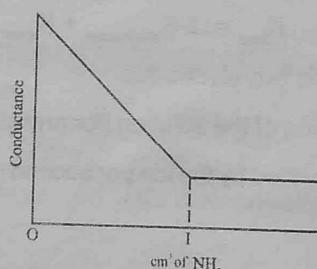


Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

2. Weak acid (titrate) + strong base(NaOH) : $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

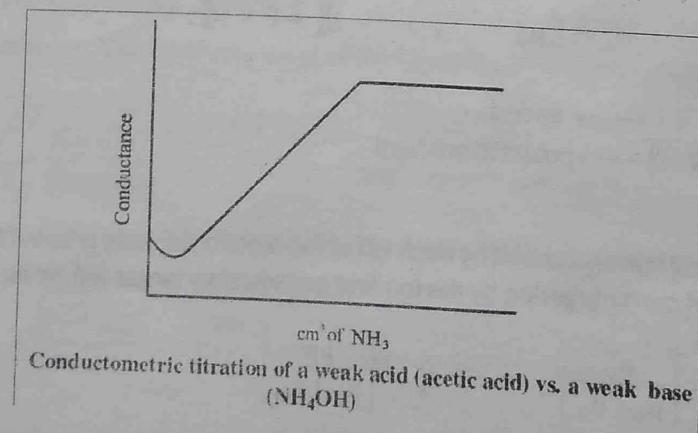


3. Strong acid + weak base : $\text{H}_2\text{SO}_4 + 2 \text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_2\text{SO}_4 + 2 \text{H}_2\text{O}$



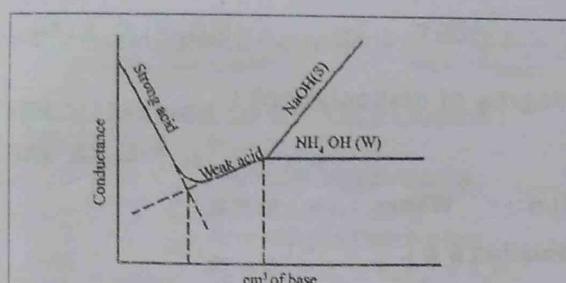
Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)

4. Weak acid with weak base : $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH} \rightarrow \text{CH}_3\text{COONH}_4 + \text{H}_2\text{O}$



Conductometric titration of a weak acid (acetic acid) vs. a weak base (NH_4OH)

5. Mixture of strong acid and weak acid vs strong or weak base :
 (a) $(\text{HCl} + \text{CH}_3\text{COOH}) + \text{NaOH (S)}$ (b) $(\text{HCl} + \text{CH}_3\text{COOH}) + \text{NH}_4\text{OH}$



6 Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH_3COOH) vs. a strong base (NaOH) or a weak base (NH_4OH)

SOLUTION & COLLIGATIVE PROPERTIES

1. OSMOTIC PRESSURE :

$$(i) \quad \pi = \rho gh$$

Where, ρ = density of soln., h = equilibrium height.

$$(ii) \quad \text{Vant - Hoff Formula (For calculation of O.P.)}$$

$$\pi = CST$$

S = ideal soln. constant

$$\pi = atm. \left\{ \begin{array}{l} C - \text{mol/lit.} \\ R - 0.082 \text{ lit.atm. mol}^{-1} \text{ K}^{-1} \\ T - \text{kelvin} \end{array} \right.$$

$$= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (exp value)}$$

= R (ideal gas) constant.

$$\pi = CRT = \frac{n}{V} RT \text{ (just like ideal gas equation)}$$

$$\therefore C = \text{total conc. of all types of particles.} = C_1 + C_2 + C_3 + \dots = \frac{(n_1 + n_2 + n_3 + \dots)}{V}$$

Note : If V_1 mL of C_1 conc. + V_2 mL of C_2 conc. are mixed.

$$\pi = \left(\frac{C_1 V_1 + C_2 V_2}{V_1 + V_2} \right) RT ; \quad \pi = \left(\frac{\pi_1 V_1 + \pi_2 V_2}{RT} \right)$$

Type of solutions :

(a) Isotonic solution – Two solutions having same O.P.

$$\pi_1 = \pi_2 \text{ (at same temp.)}$$

(b) Hyper tonic – If $\pi_1 > \pi_2$. \Rightarrow 1st solution is hypertonic solution w.r.t. 2nd solution.

(c) Hypotonic – 2nd solution is hypotonic w.r.t. 1st solution.

Abnormal Colligative Properties : (In case of association or dissociation)

VANT HOFF CORRECTION FACTOR (i) :

$$i = \frac{\text{exp./observed / actual / abnormal value of colligative property}}{\text{Theoretical value of colligative property}}$$

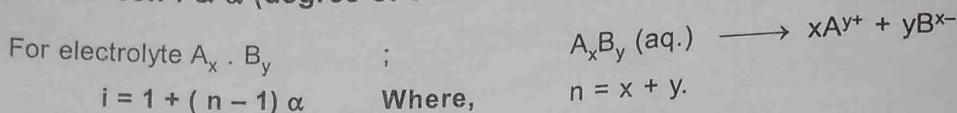
$$= \frac{\text{exp./observed no. of particles / conc.}}{\text{Theoretical no. of particles}} = \frac{\text{observed molality}}{\text{Theoretical molality}}$$

$$= \frac{\text{theoretical molar mass (formula mass)}}{\text{experimental / observed molar mass (apparent molar mass)}}$$

Compendium (Chemistry)

- $i > 1 \Rightarrow$ dissociation.
- $i < 1 \Rightarrow$ association.
- $i = \frac{\pi_{\text{exp.}}}{\pi_{\text{theor.}}} \quad \therefore \pi = iCRT \quad \Rightarrow \quad \pi = (i_1 C_1 + i_2 C_2 + i_3 C_3 \dots) RT$

Relation between i & α (degree of dissociation) :



Relation b/w degree of association β & i .



2. RELATIVE LOWERING OF VAPOUR PRESSURE (RLVP) :

Vapour pressure : $P_{\text{soln.}} < P$

Lowering in VP = $P - P_s = \Delta P$

Relative lowering in vapour pressure $\text{RLVP} = \frac{\Delta P}{P}$

Raoult's law : - (For non-volatile solutes)

Experimentally relative lowering in VP = mole fraction of the non volatile solute in solutions.

$$\text{RLVP} = \frac{P - P_s}{P} = X_{\text{solute}} = \frac{n}{n + N}$$

$$\frac{P - P_s}{P_s} = \frac{n}{N} \quad ; \quad \frac{P - P_s}{P_s} = (\text{molality}) \times \frac{M}{1000} \quad (M = \text{molar mass of solvent})$$

If solute gets associated or dissociated

$$\frac{P - P_s}{P_s} = \frac{i \cdot n}{N} \quad ; \quad \frac{P - P_s}{P_s} = i \times (\text{molality}) \times \frac{M}{1000}$$

- According to Raoult's law

(i) $p_1 = p_1^0 X_1$, where X_1 is the mole fraction of the solvent (liquid). (ii) An alternate form $\rightarrow \frac{p_1^0 - p_1}{p_1^0} = X_2$

- **Ostwald-Walker Method** : Experimental or lab determination of $\frac{\Delta P}{P}$ or $\frac{\Delta P}{P_s}$

Loss of wt of solution containers $\propto P_s$.

Loss of in wt of solvent containers $\propto (P - P_s)$

gain in wt of dehydrating agent $\propto P$.

$$\frac{P - P_s}{P_s} = \frac{\text{loss in wt. of solvent}}{\text{loss in wt. of solution}} \Rightarrow \frac{P - P_s}{P} = \frac{\text{loss in wt. of solvent}}{\text{gain in wt. of dehydrating agent}}$$

3. ELEVATION IN BOILING POINT :

$$\Delta T_b = i \times K_b m$$

$$K_b = \frac{RT_b^2}{1000 \times L_{\text{vap}}} \quad \text{or} \quad K_b = \frac{RT_b^2 M}{1000 \times \Delta H_{\text{vap}}} \quad \therefore \quad L_{\text{vap}} - \text{is cal/gm or J/gm}$$

$R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ or $8.314 \text{ J} \dots$

T_b = b.p. of liq. (in kelvin) ; $K_b = K \text{ kg mol}^{-1}$

$$\Delta H_{\text{vap}} - \text{molar enthalpy of vaporisation.} \quad L_{\text{vap}} = \left(\frac{\Delta H_{\text{vap}}}{M} \right)$$

4. DEPRESSION IN FREEZING POINT :

$$\therefore \Delta T_f = i \times K_f \cdot m.$$

$$K_f = \text{molal depression constant} = \frac{RT_f^2}{1000 \times L_{\text{fusion}}} = \frac{RT_f^2 M}{1000 \times \Delta H_{\text{fusion}}}$$

RAOULT'S LAW FOR BINARY (IDEAL) MIXTURE OF VOLATILE LIQUIDS :

$$P_A = X_A P_A^\circ$$

if $P_A^\circ > X_B$

$$P_B = X_B P_B^\circ$$

∴ A is more volatile than B

∴ B.P. of A < B.P. of B

∴ According to Dalton's law

$$P_T = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$

X_A' = mole fraction of A in vapour above the liquid / solution.

X_B' = mole fraction of B

$$P_A = X_A P_A^\circ = X_A' P_T$$

$$P_B = X_B P_B^\circ = X_B' P_T$$

$$\frac{1}{P_T} = \frac{X_A'}{P_A^\circ} + \frac{X_B'}{P_B^\circ}$$

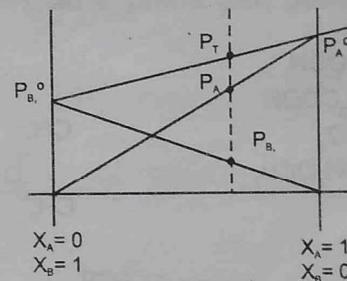
Graphical Representation :

$$P_A = X_A P_A^\circ \quad \& \quad P_B = X_B P_B^\circ$$

$$P_T = X_A P_A^\circ + X_B P_B^\circ$$

$$P_T = X_A P_A^\circ + (1 - X_A) P_B^\circ = (P_A^\circ - P_B^\circ) X_A + P_B^\circ$$

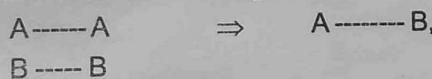
$$P_T = (1 - X_B) P_A^\circ + X_B P_B^\circ = (P_B^\circ - P_A^\circ) X_B + P_A^\circ$$



A more volatile than B $P_A^\circ > P_B^\circ$

Ideal solutions (mixtures) :

1. The mixtures which follow Raoult's law at all temp. & at all compositions will be known as ideal mixture/ideal solution.
2. Ideal solution will be obtained only when the forces of attraction b/w the liq. Molecules are exactly of same nature & almost of same magnitude



$$3. \Delta H_{\text{mix}} = 0$$

$$4. \Delta V_{\text{mix}} = 0$$

$$5. \Delta S_{\text{mix}} = + \text{ve as for process to proceed}$$

$$6. \Delta G_{\text{mix}} = - \text{ve}$$

eg. (1) Benzene + Toluene.

(2) Hexane + heptane.

(3) $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{I}$.

Non - Ideal solutions : Which do not obey Raoult's law.

(a) Positive deviation :-

$$(i) P_{T,\text{exp}} > (X_A P_A^\circ + X_B P_B^\circ)$$

$$(ii) \begin{array}{c} \text{A} \cdots \text{A} \\ \text{B} \cdots \text{B} \end{array} > \begin{array}{c} \text{A} \cdots \text{B}, \\ \text{B} \cdots \text{A} \end{array}$$

↓

Weaker force of attraction

$$(iii) \Delta H_{\text{mix}} = + \text{ve energy absorbed}$$

$$(iv) \Delta V_{\text{mix}} = + \text{ve } (1\text{L} + 1\text{L} > 2\text{L})$$

$$(v) \Delta S_{\text{mix}} = + \text{ve}$$

$$(vi) \Delta G_{\text{mix}} = - \text{ve}$$

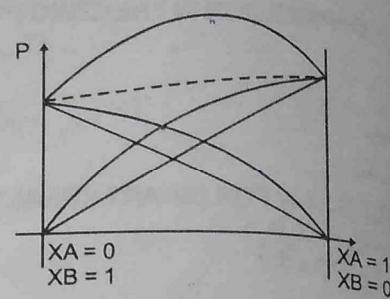
e.g. $\text{H}_2\text{O} + \text{CH}_3\text{OH}$.

$\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}$

$\text{C}_2\text{H}_5\text{OH} + \text{hexane}$

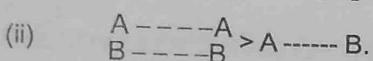
$\text{C}_2\text{H}_5\text{OH} + \text{cyclohexane}$.

$\text{CHCl}_3 + \text{CCl}_4 \rightarrow$ dipole-dipole interaction becomes weak.



(b) Negative deviation

(i) $P_T = \exp(-x_A p_A^0 + x_B p_B^0)$



strong force of attraction.

(iii) $\Delta H_{\text{mix}} = -\text{ve}$ (iv) $\Delta V_{\text{mix}} = -\text{ve}$ ($1\text{L} + 1\text{L} < 2\text{L}$) (v) $\Delta S_{\text{mix}} = +\text{ve}$ (vi) $\Delta G_{\text{mix}} = -\text{ve}$

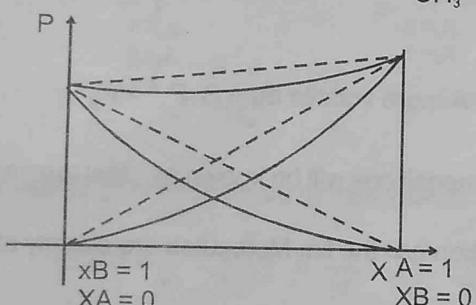
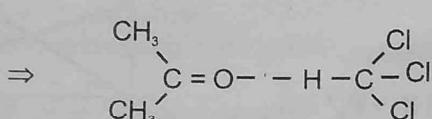
e.g.

$\text{H}_2\text{O} + \text{HCOOH}$

$\text{H}_2\text{O} + \text{CH}_3\text{COOH}$

$\text{H}_2\text{O} + \text{HNO}_3$

$\text{CHCl}_3 + \text{CH}_3\text{OCH}_3$



Immiscible Liquids :

(i) $P_{\text{total}} = P_A + P_B$

(iii) $P_B = P_B^0 X_B = P_B^0$

(ii) $P_A = P_A^0 X_A = P_A^0$

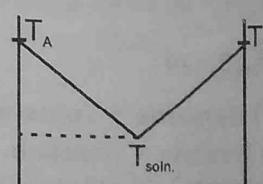
[Since, $X_A = 1$].

(iv) $P_{\text{total}} = P_A^0 + P_B^0$

(v) $\frac{P_A^0}{P_B^0} = \frac{n_A}{n_B}$

(vi) $\frac{P_A^0}{P_B^0} = \frac{W_A M_B}{M_A W_B}$

$$P_A^0 = \frac{n_A RT}{V} ; P_B^0 = \frac{n_B RT}{V}$$



B.P. of solution is less than the individual B.P.'s of both the liquids.

Henry Law :

This law deals with dissolution of gas in liquid i.e. mass of any gas dissolved in any solvent per unit volume is proportional to pressure of gas in equilibrium with liquid.

$$m \propto p$$

$$m = kp$$

$$m \rightarrow \frac{\text{weight of gas}}{\text{Volume of liquid}}$$

$k \rightarrow$ Henry constant (in atm^{-1}).

$P \rightarrow$ Pressure of gas.

SOLID STATE

○ Classification of Crystal into Seven System

Crystal System	Unit Cell Dimensions and Angles	Bravais Lattices	Example
Cubic	$a = b = c ; \alpha = \beta = \gamma = 90^\circ$	SC, BCC, FCC	NaCl
Orthorhombic	$a \neq b \neq c ; \alpha = \beta = \gamma = 90^\circ$	SC, BCC, end centred & FCC	S_8
Tetragonal	$a = b \neq c ; \alpha = \beta = \gamma = 90^\circ$	SC, BCC	Sn, ZnO_2
Monoclinic	$a \neq b \neq c ; \alpha = \gamma = 90^\circ \neq \beta$	SC, end centred	S_m
Rhombohedral	$a = b = c ; \alpha = \beta = \gamma \neq 90^\circ$	SC	Quartz
Triclinic	$a \neq b \neq c ; \alpha \neq \beta \neq \gamma \neq 90^\circ$	SC	H_2BO_3
Hexagonal	$a = b \neq c ; \alpha = \beta = 90^\circ ; \gamma = 120^\circ$	SC	Graphite

○ Arrangement of particle (Similar spherical balls) in a plane and generation of unit cells from that

(A) Square lattice.

Unit cells SC and BCC are based on this arrangement.

(B) Hexagonal arrangement

Unit cells

(i) HCP (Hexagonal close packed)

(ABABAB..... arrangement) and

(ii) FCC or CCP (cubical close packed) which represent ABCABCABC..... arrangement are based on this.

Characteristics of HCP.

(i) C.No = 12 (ii) No. of atoms per unit cell = 6 (iii) Packing efficiency = 74%

○ ANALYSIS OF CUBICAL SYSTEM

	Property	SC	BCC	FCC	
(i)	atomic radius (r)	$\frac{a}{2}$	$\frac{\sqrt{3}a}{4}$	$\frac{a}{2\sqrt{2}}$	$a = \text{edge length}$
(ii)	No. of atoms per unit cell (Z)	1	2	4	
(iii)	C.No.	6	8	12	
(iv)	Packing efficiency	52%	68%	74%	
(v)	No. voids				
	(a) octahedral (Z)	—	—	4	
	(b) Tetrahedral ($2Z$)	—	—	8	

○ NEIGHBOUR HOOD OF A PARTICLE :

(I) Simple Cubic (SC) Structure :

Type of neighbour	Distance	no.of neighbours
nearest	a	6 (shared by 4 cubes)
(next) ¹	$a\sqrt{2}$	12 (shared by 2 cubes)
(next) ²	$a\sqrt{3}$	8 (unshared)

(II) Body Centered Cubic (BCC) Structure :
Type of neighbour Distance no. of neighbours

nearest	$2r = a \frac{\sqrt{3}}{2}$	8
(next) ¹	$= a$	6
(next) ²	$= a\sqrt{2}$	12
(next) ³	$= a \frac{\sqrt{11}}{2}$	24
(next) ⁴	$= a\sqrt{3}$	8

(III) Face Centered Cubic (FCC) Structure :
Type of neighbour Distance no. of neighbours

nearest	$\frac{a}{\sqrt{2}}$	$12 = \left(\frac{3 \times 8}{2} \right)$
(next) ¹	a	$6 = \left(\frac{3 \times 8}{4} \right)$
(next) ²	$a\sqrt{\frac{3}{2}}$	24
(next) ³	$a\sqrt{2}$	12
(next) ⁴	$a\sqrt{\frac{5}{2}}$	24

○ DENSITY OF LATTICE MATTER (d) = $\frac{Z}{N_A} \left(\frac{M}{a^3} \right)$

where N_A = Avogadro's No. M = atomic mass or molecular mass.

○ PACKING EFFICIENCY

$$PE = \frac{Z \times \frac{4}{3} \pi r^3}{a^3} \times 100$$

Z = number of atom per unit cell.

○ IONIC CRYSTALS

C.No.	Limiting radius ratio $\left(\frac{r_+}{r_-} \right)$
3	0.155 – 0.225 (Triangular)
4	0.225 – 0.414 (Tetrahedral)
6	0.414 – 0.732 (Octahedral)
8	0.732 – 0.999 (Cubic).

○ EXAMPLES OF A IONIC CRYSTAL

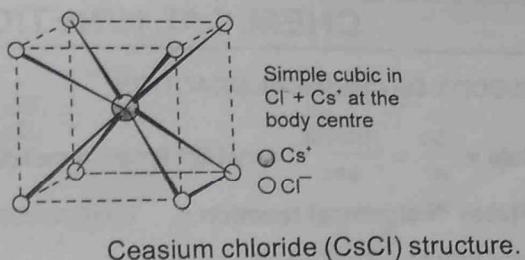
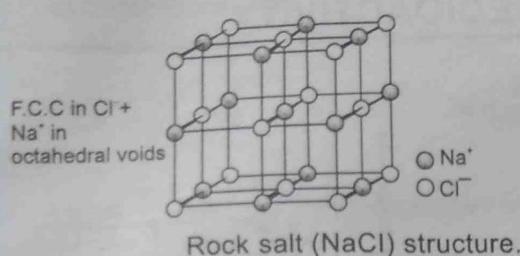
(a) Rock Salt (NaCl) Coordination number (6 : 6)

(b) CsCl C.No. (8 : 8)

Edge length of unit cell :-

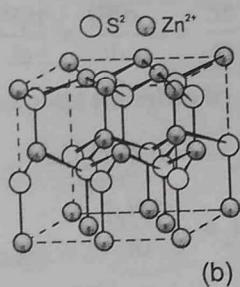
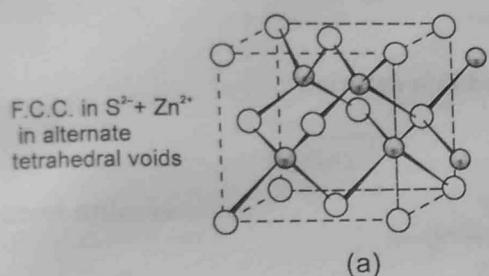
$$a(fcc) = 2(r_{Na^+} + r_{Cl^-})$$

$$a_{sc} = \frac{2}{\sqrt{3}}(r_+ + r_-)$$

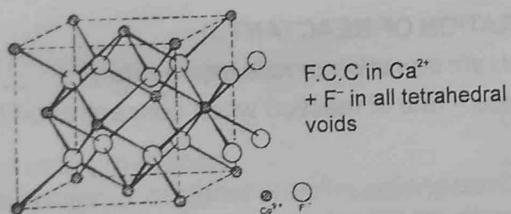


(c) Zinc Blende (ZnS) C.No. (4 : 4)

$$a_{\text{fcc}} = \frac{4}{\sqrt{3}} (r_{\text{Zn}^{2+}} + r_{\text{s}^{2-}})$$

(d) Fluorite structure (CaF_2) C.No. (8 : 4)

$$a_{\text{fcc}} = \frac{4}{\sqrt{3}} (r_{\text{Ca}^{2+}} + r_{\text{F}^-})$$



(e) Diamond

FCC lattice of carbon and carbon is occupy four out of eight tetrahedral voids

$$Z = \frac{\text{number of carbon atom}}{\text{unit cell}} = 8$$

$$4 r_c = \frac{\sqrt{3}}{2} a_{\text{fcc}} ; \quad P_f = \frac{8 \times \frac{4}{3} \pi r^3}{(\frac{8}{\sqrt{3}} r)^3} \times 100 = 0.34$$

○ Crystal Defects (Imperfections)

