ATOMIC STRUCTURE

- 1. Some important features of the three fundamental particles
 - The charge on an electron is -1.602×10^{-19} C and its mass was found to be 9.11×10^{-28} g.
 - The specific charge (e/m ratio) of an electron is 1.76×10^8 C/g
 - Charge on one mole of electron is ≈ 96500 C or 1F.
 - Mass of a proton is found to be 1.673×10^{-24} g.
 - Charge on a proton is $+ 1.602 \times 10^{-19}$ C.
 - The specific charge (e/m ratio) of proton is 9.58×10^{-4} C/g.
 - Neutron is slightly heavier than proton. Its mass is found to be 1.675×10^{-24} g.
 - Specific charge of a neutron is zero.
- 2. Positrons are positive counter part of the electrons. Neutrinos and anti neutrons are the particles of small mass and zero charge. pi-mesons and µ mesons are the particles having a mass intermediate between that of the electron and proton. Mesons may be positively or negatively charged or neutral.
- Radius of nucleus is of the order of 10⁻¹⁵ and of atom is 10⁻¹⁰ m.
 Volume of the nucleus is about 10⁻⁴⁵m³. (volume of the nucleus is 10⁻¹⁵ times that of an atom).
 - Density of the nucleus is of the order of 10^{14} g cm⁻³.
- 4. Different types of atomic species
 - Isotopes have same atomic number (Z) but different mass number (A). ${}^{14}_{6}$ C, ${}^{12}_{6}$ C
 - Isobars have same mass number(A) but different atomic number (Z). ${}^{40}_{20}$ Ca, ${}^{40}_{19}$ K
 - Isotones have different mass number (A) as well as different atomic number (Z) but have same number of neutrons.
 - Isodiaphers have same isotopic number.
- **5.** Relationship between velocity (*c*), wavelength (λ) frequency (v) and wave number (\overline{v}).
 - (a) $c = v\lambda$ (b) $\overline{v} = \frac{1}{\lambda}$ (c) $\overline{v} = v/c$



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where, *c* is the velocity in ms⁻¹, v is the frequency in s⁻¹ and λ is wavelength in m. \overline{v} is wave number.

6. Relationship between energy (*E*), frequency (ν) and wavelength (λ).

$$E = hv$$
 or $E = \frac{hc}{\lambda}$ where, *h* is Planck constant, $h = 6.62 \times 10^{-34}$ Js.

Mass of electron at hight speed
$$m = \frac{m_0}{\sqrt{[1 - (u^2 / c^2)]}}$$

 $(m_0 \text{ is mass in rest}, u \text{ is velocity of } e^- \& c \text{ is velocity of light})$

Energy of photons $(E) = hv = \frac{hc}{\lambda}$

Also,
$$E = \frac{12375}{\lambda} eV$$
, if λ is in Å

7. Energy of electron in unielectron atomic system. Ex- H, He⁺, Li⁺⁺,

$$E_n = \frac{-1312 Z^2}{n^2} \text{kJ mol}^{-1}$$
$$E_n = \frac{2.17 \times 10^{-18} Z^2}{n^2} \text{J atm}^{-1}$$
$$E_n = \frac{-13.6}{n^2} Z^2 \text{ eV atom}^{-1}$$

or

UI

or

8. The number of spectral lines in the spectrum when the electron comes from n_2 level to $n_1 \text{ level} = \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

The intensities of spectral lines decreases with increase in the value for example, the intensity of first Lyman line $(2 \rightarrow 1)$ is greater than second line $(3 \rightarrow 1)$.

Energy difference is more at lower level as compare to higher level.

9. Energy of quantum emitted when electron drops from n_2 to n_1

$$\Delta E = 1312Z^{2} \left[\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}} \right] \text{kJ mol}^{-1} = 13.6 \text{ Z}^{2} \left[\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}} \right] ev \text{ atom}^{-1}$$

Frequency, $v = RZ^{2} \left[\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}} \right]$ where, $R = 3.289 \times 10^{15} \text{ s}^{-1}$
Wave number, $\overline{v} = R'Z^{2} \left[\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}} \right]$

178

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where, $R' = 109678 \text{ cm}^{-1}$

10. Radius of nth orbit,

$$r_n = \frac{n^2 \times 0.529 \times 10^{-10} \,\mathrm{m}}{Z} = r_0 \frac{n^2}{Z} \quad \text{Å}, r_0 = 0.53 \,\text{\AA}$$

Velocity of nth orbit,

$$V_n = \frac{2.188 \times 10^6 \times Z}{n} \text{ms}^{-1} = \frac{V_0}{n} \frac{Z}{n} \quad ms^{-1} V_0 = 2.2 \times 10^6 \text{mS}^{-1}$$

Number of revolutions in nth orbit = $\frac{V_n}{2\pi r_n}$

Mosley's law: $\sqrt{v} = a(Z-b)$ Where v is frequency of X-ray given out by metal of atomic number Z

Average atomic wt. =
$$\frac{\Sigma A_1 X_1}{\Sigma X_{Total}}$$

Angular momentum of electron in an orbit = $n \cdot \left(\frac{h}{2\pi}\right)$

11. According to de-Broglie, all the moving material objects possess wave like characteristics. It is applicable only in case of microscopic particles.

$$\lambda = \frac{h}{mv} = \frac{h}{P}$$
; where, $h = 6.626 \times 10^{-34}$ Js, $m =$ mass in kg

$$v =$$
 velocity (ms⁻¹) and $p =$ momentum (in kgms⁻¹).

de-Broglie equation: $\lambda = \frac{h}{mv} = \sqrt{\frac{h^2}{2 \times K. E. \times m}}$, $KE = \frac{1}{2}mv^2$

12. Heisenberg's uncertainty principle. It is impossible to determine both momentum and position of a sub atomic particle precisely and simultaneously.

$$\Delta x. \Delta p \ge \frac{h}{4\pi}$$
 where, $\Delta x =$ uncertainty in position and $\Delta p =$ uncertainty in momentum.

In terms of energy it is $\Delta t \cdot \Delta E \ge \frac{h}{4\pi}$

13. The wave function ψ represents an orbital where as ψ^2 signifies the probability for finding electron in that region for $\psi^2 = 0$ the probability for finding electron is zero. $\psi^2 dv$ represents the probability for finding electron in a small volume dV surrounding the nucleus.



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 $\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - \nu) \psi = 0$ is Schrödinger wave equation

- 14. The plane and point at which zero electron density exists ($\psi^2 = 0$) is known as nodal plane or nodal point e.g.. the probability of finding electron between is and 2s or between two lobes of p-orbitals is zero.
- 15. An orbital with quantum number

Angular or spherical nodes = l, nodal planes = l. Radial or spherical nodes = n - l - 1Thus, total nodes = n - 1

- 16. For one electron system, the energy of subshell depends only on the 'n'. It means in H-atom or one electron ion He⁺, Li⁺⁺, energy levels of orbitals in a shell are same.
- According to Aufbau: filling of subshells is as $E \propto (n+l)$.

If (n+l) is same then more 'n' more energy.

Example: 4s, 5d, 3p energy order (n + 1) is 4 + 0, 5 + 2, 3 + 1

 $\frac{5d > 4s > 3p}{2}$

In case one electron system it depends only on 'n'

Example: 4*s*, 4*p*, 3*d*

4s = 4p > 3d

According to pauli's principle. No two electrons can have all the four quantum numbers same .

Example: $4s^5$ or $3p^7$ not possible according to pauli's principles.

Note: Electron can't stay inside the Nucleous due to uncertainty principle.

For photo electric effect $\frac{hc}{\lambda} = W + KE$, W = Work function of metal or Ionisation energy of metal.

(i) lesser the value of W easy removal of electron, it is material property.

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(ii) $\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + KE$ or $hv = hv_0 + KE$ here λ_0 and v_0 are cut off wavelength and

cut off frequency.

In case of Rutherford's experiment- It was for the measurment of nucleous.

- (i) Gold foil was used
 (ii) Bombardment of α-partical was there.
- (iii) Number of ' α ' particals deflected at an angle

N
$$\approx \frac{1}{\left(\sin\frac{\theta}{2}\right)^4}$$
, $\theta = \text{angle of deflection.}$

• In Bohr's model one electron system is used example: H, He^+Li^{++} . etc.

Some Key Points

 α -Partical is He⁺⁺ P = 2 N = 2 e = 0Mass $(M_{\alpha}) = 4 \times m_p$ $m_p =$ mass of proton charge $(q_{\alpha}) = 2 \times q_p$ $q_p =$ charge of proton β - partical $\beta = -1^{e^0}$ γ - Partical is mass zero and charge zero. Mass $(M_{\beta}) =$ Me = 9.1×10^{-31} Kg

Charge $(q_{\beta}) = q_e = 1.6 \times 10^{-19}$ C.

Magnetic moment, (spin only) = $\sqrt{N(N+2)}$ B.M.

where, 'N' is the number of unpaired electrons. Units of magnetic moment is B.M.

Quantum Numbers

- They give complete information about the electron.
- First three quantum numbers n, l, m are the constants of Schrodinger wave equation. (intergal form).
- 'S' is for spin of electron and known as magnetic moment of electron
- 'n' gives the information about orbit, radius, speed, energy level and all the factors which are associated with 'n'
- For 'n', 1 is 0 to n-1, 1 = 0 for s, l=1 for p, l=2 for d, l=3 for f
- 'l' gives the information about subshell and style of wave.
- Orbital angular momentum $= \sqrt{l(l+1)} \frac{h}{2\pi}$ (momentum in orbital)
- Angular momentum $mvr = n_{\overline{c}}$





Orbit

Electron revolves in fixed energy path known as orbit.

- They are represented by K, L, M, N or $n = 1, 2, 3, 4, \dots$ Ο
- Motion of electron in the orbit is like a stationary wave. 0
- Number of waves developed by the electrons is equal to number of orbit. 0



Example: In this number of orbit is 4 because total number of waves develop are 4.

- There is no energy gain or loss when electron revolves around the nucleous. 0
- Energy gain or loss is only when electron is having jump from one orbit to another. 0

Orbital and Subshell

Orbital: It is the 3D part around the nucleus where the probability of finding the electrons is maximum.

It has maximum two electrons with opposite spin and it is represented by a

box as





p-Subshell

In case of p-subshell we are having dumbell shape and it is the combination of three orbitals. It starts from 2p. It is having three orbitals p_x , p_y and p_z .





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p- subshell can have maximum six electrons



It is 3p because it starts from 2p and second loop is in 3p, third loop is in 4p. Above we have 3p with 2 loops.

d-Subshell

It is combination of five orbitals having double dumbell shape. It is having maximum ten electrons.



Note: Any orbital is having maximum two electrons.

The State of Matter

- 1. Matter exists in three states of matter namely solid, liquid and gas. The fourth state of matter is plasma which exists only at very high temperature (10⁷ K). In plasma state, atoms of matter ionise into nuclei and electrons.
- 2. The two sets of conditions are widely used as standard values for reporting data.

Condition	Temperature	Pressure	V _m (Molar volume)
STP/NTP	273.15 K	1 atm	22.414 L
SATP	298.15 K	l bar	24.800 L

- (SATP—Standard Ambient Temperature and Pressure)
- **3.** The gases exhibit uniformity in their behaviour. These are governed by gas laws.

• Boyle's law
$$V \propto \frac{1}{p}$$
 or $pV = \text{constant}$ or $p_1V_1 = p_2V_2$

• Charle's law $V \propto T$ or $\frac{V}{T} = \text{constant or } \frac{V_1}{T_1} = \frac{V_2}{V_2}$

• Pressure-Temperature law
$$p \propto T$$
 or $\frac{p}{T}$ = constant

• For boyle's law T = Constant



• For Charl's law P = Constant



• Avogadro's law $V \propto n$ (n = number of moles of gas taken)



• Ideal gas equation pV = nRT; R is known as universal gas constant or molar gas constant.

•
$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ If P is in } \frac{N}{m^2} \text{ and V is in } m^3.$$

• $R = 0.082 L \text{ atm } \text{K}^{-1} \text{ mol}^{-1} \text{ If } P \text{ in atm and } V \text{ in litre.}$

General gas equation
$$\frac{P_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$
 or Pv =nRT

• Graham's law of diffusion Rate of diffusion of a gas, $r \propto \sqrt{\frac{1}{M}}$ (at constant p and T)

$$\frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$
 If n_1 and n_2 are moles of gas '1' and gas '2'
$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}} P_1$$
 and P_2 are Pressure of gas '1' and '2'.

Molecular mass of a gas = $2 \times$ vapour density

Dalton's law of partial pressures : $p = p_1 + p_2 + p_3 + ...$ where $p_1, p_2...$ are partial pressures of component gases.

• Partial pressure of 'A' $P_A = X_A$, P_T , X_A = mole fraction of 'A'.

(Dalton's law is valid for gases which do not react chemically).

• Partial pressure of water vapours in moist gas is referred as aqueous tension.

$$\frac{p_{dry gas}}{=} \frac{p_{moist gas}}{p_{moist gas}} - \frac{p_{water vapour}}{aqueous tension}$$

• For ideal gas
$$PV = nRT$$

(1) $P = \frac{n}{v}RT = CRT$ $C = Concentration$
(2) $P\frac{V}{n} = RT$ $P\overline{v} = RT$ $\overline{V} = Molar volume$
(3) $PV = \frac{wt}{mol.wt}RT$ $P = \frac{wt}{v}\frac{RT}{mol.wt} = d\frac{RT}{M}$ So, $d = \frac{PM}{RT}$

4. Kinetic theory of gases: It was developed by Maxwell in 1882 in collaboration with other scientists.



(1)	
(1)	Each gas consists of a large number of small particles either atoms, molecules,
	moving about at random,
(ii)	Volume of individual atom or molecule is negligible as compared to the total
	volume of gas.
(iii)	The gas particles act independently of one another, there is no attractive or
	repulsive forces between particles.
(iv)	Collisions of gas particles, either with other particles or with the walls of the
	container, are elastic because there is no change in energy during collisions.

- The pressure exerted by a gas is the result of collisions of the particles with the (v) walls of the container.
- At any particular time, different particles in a gas have different speeds hence (vi) different kinetic energy. However average kinetic energy of the gas particles is prportional to the absolute temperature of the gas. (Average KE \propto absolute temperature.)
- Kinetic gas equation $pV = \frac{1}{3}mNu^2$ (where m = mass of each molecule, N = total 5. number of molecules, u = rms velocity)

for one mole of gas, $pV = \frac{1}{3}Mu^2$; because $m \times N$ = molecular mass.

Root mean square velocity of the gas 6. $u_{rms} = \sqrt{\frac{3pV}{M}}$ or $\sqrt{\frac{3RT}{M}}$ or Most probable velocity $u_{mp} = \sqrt{\frac{2RT}{M}}$ Average velocity, $u_{av} = \sqrt{\frac{8RT}{\pi M}}$ $V_{rns} = 5\sqrt{\frac{T}{M}}, V_{mp} = 4.1\sqrt{\frac{T}{M}}, V_{av} = 4.5\sqrt{\frac{T}{M}}$ (M should be in Kg).

Relationship between velocities:

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$$u_{\rm rms}: u_{\rm av}: u_{\rm mp} = \sqrt{3}: \sqrt{\frac{8}{\pi}}: \sqrt{2}$$
 = 12248:11284:1



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 $u_{rms} = 1.2248 u_{mp}$ $u_{av} = 1.1248 u_{mp}$ $u_{rms} = 1.0854 u_{av}$

Note:

For one portical $V_{rms} = V_{av} = V_{mP}$

Average speed of a portical in one dimension is zero.

- 7. Kinetic energy of gas $KE = \frac{3}{2}nRT$, $\frac{KE}{n} = \overline{KE} = \frac{3}{2}RT$ known as average $\overline{K.E}$. (Depends only on Temperature)
- 8. Collision frequency and mean free path The number of collisions taking place in unit time per unit volume is called collision frequency (z).

$$z = \frac{\pi n^2 \sigma^2 u_{av}}{\sqrt{2}}$$

The average of distances travelled by a molecule between successive collisions is called mean free path (λ)

 $\lambda = \frac{1}{\sqrt{2\pi n\sigma^2}}$ (where, *n* is the number of molecules per unit molar volume)

- **9.** Vander Waal's equation Two faulty assumptions of kinetic theory due to which real gases deviate from ideal behaviour are as follows:
 - (i) The actual volume occupied by particles of gas is negligible as compared to the total volume of the gas.
 - (ii) The forces of attraction or repulsion between the particles of gas are negligible.
 The modified gas equation or vander waals' equation of state :

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$
 (for *n* moles of gas)

where, *a* and *b* are pressure correction and volume correction respectively Units of a are atm $L^2 \mod^{-2}$ or atm m⁶ mol⁻² or Nm⁴mol⁻² Units of *b* are L mol⁻¹ or m³ mol⁻¹

10. Deviations from ideal gas behaviour The deviations from ideal gas behaviour are expressed in terms of compressibility factor (Z)





- (i) Z = 1 for an ideal gas at all the conditions. The values of Z exhibit both positive (Z > 1) and negative deviations (Z < 1) from unity.
- (ii) For H_2 and He gases, pV > RT, *i.e*, Z > 1 or $V_m > 22.4$ L at NTP (V_m is actual molar volume of gas)
- (iii) All gases have $Z \approx 1$ at low pressure, at intermediate pressure and 273K some gases such as CH_4 , NH_3 , CO etc have Z < 1 and at high pressure all gases have Z > 1.
- (iv) An increase in temperature shows a decrease in deviation from ideal gas behaviour *i.e.*, pV approaches RT with rise in temperature of Z approaches unity.



Some Important Points for JEE/AIPMT

PV = nRT For boyle's law T = Constant dP.V + dv.P = $0\left(\frac{dP}{dV}\right)_T = -\frac{P}{V}$ For Charle's law P = Constant $\left(\frac{dV}{dT}\right)_P = \frac{nR}{P} = \text{Constant}$ Pay load is extra load. (Displaced air) Boyle's temperature is the characteristic temperature of the gas at which it obeys ideal gas nature. Below this temperature the value of Z at first decreases, approaches a minimum and then increases as the pressure is increased continuously $\left(T_b = \frac{a}{Rb}\right)$. (a' is known as liquefaction factor more the value of 'a' easy will be the liquefaction 'b' is known as Co-volume more the value of 'b' large will be the size of gas particals. (b = 4N_0 V_0) V_0 = \frac{4}{3}\pi r^3 Volume gas partical.



• $\frac{(an^2)}{V^2}$ is known as pressure correction. 'nb' is known as co-volume.

- 11. Critical constants Critical temperature (T_c) is the temperature below which a gas can be liquefied and above this it can not be liquefied. Critical pressure (p_c) is the minimum pressure which is required to liquefy a gas.
 - Critical volume (V_c) is the volume of one mole of gas which is occupied at critical temperature and critical pressure.
 - In terms of vander Waals' constants *a* and *b*

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

- $Z_C = \frac{3}{8}$ For critical state.
- Inversion temperature $T_i = \frac{2a}{Rb}$ Law of corresponding state $\left(P_r + \frac{3}{V_r^2}\right)$ $(3V_r - 1) = 8T_r$
- **12.** Liquid state Vapour pressure, surface tension and viscosity are some of the typical physical properties of liquids that arise due to two competing forces, the molecular interaction and thermal energy.

Variation of vapour pressure with temperature is given by Clausius Clapeyron equation.

$$P = P_0 e \left(-\frac{\Delta H_{vap}}{RT} \right) = P_0 e^{-\frac{\Delta H_{vap}}{RT}}$$

 ΔH_{vaP} = Heat of vapourisation of liquid.

Surface tension = Work to increase surface by unit area. Its SI unit is Nm⁻¹.
 Surface tension decreases when substances such as soaps, detergents are dissolved in a liquid. Rise in temperature also decreases surface tension.

Viscosity: It is defined as the resistance of a liquid to flow. Coefficient of viscosity (η is the tangential force per unit area required to maintain a unit velocity gradient. η is expressed in dyne/cm² or poise). Usually viscosity of a liquid decreases with the rise in temperature.



Chemical Equilibrium

- 1. A chemical equilibrium is a state at which the composition of a chemical system becomes constant under given set of conditions, It is dynamic in nature, both forward and backward reactions are in progress with the same speed. Presence of a catalyst does not affect the final state of the equilibrium catalyst decreases the time to archive equilibrium.
- 2. According to law of mass action the rate of forward reaction is directly proportional to the product of molar concentrations (active masses) of the reactants with each concentration term raised to the power equal to the number of times that reactant appear in the balanced equation.

$$aA + bB \rightleftharpoons cC + dD$$

According to law of mass action.

Rate of forward reaction, $r_f \propto [A]^a [B]^b$

Rate of backward reaction $r_b \propto [C]^c [D]^d$

At equilibrium $r_f = r_b$

- Active mass of a gas or liquid is equal to its molar concentration and the active mass of solids is constant.
- **3.** Law of chemical equilibrium.

$$aA + bB \Longrightarrow cC + dD$$

$$K_{c} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \quad \text{or} \quad K_{c} = \frac{[A]^{a}[B]^{b}}{[C]^{c}[D]^{d}} \quad K_{c} = \frac{1}{K_{C}}$$

where, [A], [B], [C] and [D] are molar concentrations of A, B, C and D at equilibrium and K_c is the equilibrium constant.

Equilibrium constant in terms of partial pressure

$$K_{p} = \frac{[p_{C}]^{c} [p_{D}]^{d}}{[p_{A}]^{a} [p_{B}]^{b}}$$



where, p_A , p_B , p_C and p_D are the partial pressures of A, B, C and D at equilibrium respectively. K_C and K_p have no units for a reaction when $\Delta n = 0$ Relationship between K_p and K_c

$$K_p = K_c (RT)^{\Delta ng}$$
 (where, $\Delta n_g = n_{\text{products}} - n_{\text{reactions}}$ gaseous

5. Equilibrium constant in term's of mole fractions

$$aA + bB \rightleftharpoons cC + dD$$
$$K_x = \frac{[X_C]^c [X_D]^d}{[X_A]^a [X_B]^b} \text{ it has no unit}$$

 K_x depends upon temperature,

 $K_p = K_x(p)^{\Delta n}$ (where, p is the external pressure)

- 6. Reaction quotient (Q) is the ratio of concentration terms having the same form as equilibrium constant expression at each point in a reaction.
 - (i) $Q = K_c$, reaction is in equilibrium
 - (ii) $Q < K_c$, reaction proceeds in forward direction
 - (iii) $Q > K_c$, reaction proceeds in backward direction
- 7. Relation between vapour density and degree of dissociation.

Degree of dissociation, $\alpha = \frac{D-d}{d(n-1)} = \frac{M_c - M_v}{M_v(n-1)}$

where, D and d are theoretical vapour density before and after dissociation and M_c and M_v are theoretical and observed molecular mass respectively and n are the number of moles of products formed by one mole of reactant.

- Presence of catalyst increases the rates of forward and backward reaction with the same rate and rate constant is changed but not the equilibrium constant.
- (i) Equilibrium is the main property of reversible reaction At equilibrium rate of forward reaction is equal to rate of backward reaction.
- (ii) Equilibrium constant is effected by temperature only.

$$K_{eq} = Ze^{-}\frac{\Delta H}{RT}$$

 $Z = \text{Constant } \Delta H = \text{Heat of reaction}$

4.



T =Temperature of process

R = gas constant



 $CaCO_3(s) \Longrightarrow CaO(s) + CO_2(g)$

- Active mass is the part of concentration which is involved in reaction and (iii) represented as $[] = \frac{n}{V}$
- Active mass is constant for solid and liquid. (iv)
- Catalyst does not affect the final state of the equilibrium. (v)

Example:

Example:

$$Kp = P_{CO_2}$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta n_g = 2 - (1+3) = -2$$

$$Kp = Kc(RT)^{-2}$$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad n = 2$$

$$\alpha = \frac{D-d}{d(2-1)} = \frac{D}{d} - 1$$

$$\Rightarrow \frac{D}{d} = \alpha + 1$$

- Equilibrium is of two type (vi)
 - (a) Homogenous (b) Heterogenous

In Homogenous all the reactants and products are in same phase and in hetrogeneous they are having different phase

Homogeneous $-PCl_5(g) \Longrightarrow PCl_3(g) + Cl_2(g)$

Hetrogeneous
$$-CaCO_3(s) \rightleftharpoons CaO(s) + Co_2(g)$$

Le chatelier's Principle: According to this, if we change the factor effecting equilibrium then equilibrium is readjusted and these factor are concentration, pressure, temperature and non reactive gas.

Effect of Concentration — If we increase the concetration of involved compound then equilibrium is shifted in opposite direction.



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Example: $PCl_5 \rightleftharpoons PCl_3 + Cl_2, Kc = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

If we increases concentration of PCl_5 it goes in forward direction and If we increase PCl_3 or Cl_2 or both then it proceeds in backward direction.

Example: NaNO₃(s)
$$\implies$$
 NaNO₂(s) + $\frac{1}{2}$ O₂(g), $Keq = [O_2]^{\frac{1}{2}}$

 $NaNO_3(s)$ and $NaNO_2(s)$ are not involved in the expression so, No effect of conc. of $NaNO_3$ and $NaNO_2$.

Effect of Pressure — If we increases the pressure then it goes in the direction where number of gas moles are less.

Example: $PCl_5(g) \Longrightarrow Pcl_3(g) + Cl_2(g)$

If we increase pressure it goes to back ward.

Example: $H_2(g) + Cl_2(g) \Longrightarrow 2HCl(g)$

On increasing pressure no effect because equal number of moles are there in both the sides.

Effect of temperature — If we increase the temperature equilibrium favours endothermic process (where heat is absorbed)

If '\alpha' is degree of dissociation then $\alpha = k \left(\frac{1}{p}\right)^{\frac{\Delta n_g}{2}}$

α < 10%

 Δn_g = gaseous products — gaseous reactions.

P = presuure of gaseous mixture

If nonreactive gas is added in the container

(a) At constant volume (b) At constant pressure

At constant volume there is no effect on equilibrium and degree of dissociation α .

At constant pressure, If non reactive gas is added then it behaves & just like pressure is decreasing and volume is increasing.

Some Important Points for JEE/AIPMT

- **1.** If temperature is increased for endothermic reaction then \mathcal{K}_{eq} is also increased.
- **2.** For equilibrium rate of forward reaction is equal to rate of backward reaction. But concentration of reactant and product may or may not be equal.





Ans. In case of $K_{eq} = 10^8$ Because $K_{eq} = 10^8 = \begin{bmatrix} B \\ [A] \end{bmatrix}$ so $[B] = 10^8$ [A] so B is more, so easily completed. Example: Which is more stable (a) A_2O_3 , $K = 10^{-6}$ (b) A_2O , $K = 10^8$ (c) AO, k = 10Ans. Since in (a) $K = 10^{-6}$ means less production so more stable.



Ionic Equilibrium

- **1.** Strong electrolyte is that which is 100% Ionised. HCl, NaCl, AgNO₃ etc.
- Weak electrolyte is that which is Ionised less then 100% HCN, H₂S, CH₃COOH etc.
 Strong base IA group and II A group base are strong base.
 Example: NaOH, KOH Ca(OH)₂ etc. Other are weak base.
 Weak acid HCN, H₂S, RCOOH, HF, N₃H, H₂CO₃ are weak acid other are strong acid.

Acid-base Concept

(A) Arrhenius Theory

According to arrhenius concept, acid is that which gives H^+ and base is that which gives OH^- .

At Infinite dilution all the acid and base are 100% ionised and this is known as leveling effect

 H_3PO_4 gives $3H^+$, H_3PO_2 gives H^+ , H_3PO_3 , gives $2H^+$

(B) Lewis Concept

According to this an acid is that which accept lone pair of electron and base is that which gives lone pair of electrons.

Lewis base-
$$NH_3$$
, H_2 O, $R = NH_2$, $R = NH = R$, $R = OH$

Lewis acid- BCl₃, BH₃, AlCl₃ (All 3 have incomplete octet)

(C) Bronstant and Lowery Concept

According to this, acid is that which gives H^+ and base is that which accept H^+ .

$$\frac{H_2O}{acid} + \frac{NH_3}{base} \longrightarrow \frac{NH_4^+}{conj \ acid} + \frac{OH^-}{conj \ base}$$



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Note: If in a mixture, one gives H^+ and other accept H^+ then it is known as autoprotonation

$$H_2O+H_2O\longrightarrow H_3O^++OH^-$$

• For H_2O , $H_2O \Longrightarrow H^+ + OH^-$

$$K = \frac{[H^{+}][OH^{-}]}{[H_{2}O]} = \frac{[H^{+}][OH^{-}]}{55.5} \quad [H_{2}O] = 55.5$$
$$K = \frac{K_{w}}{55.5}, K_{w} = [H^{+}][OH^{-}]$$

K is dissociation constant of water

 K_w is ionic product of water.

a(1- α) a α a α a α =10⁻⁷

 α is degree of ionisation of water $\alpha = \frac{10^{-7}}{55.5}$

•
$$K_w = 10^{-14} \text{ at } 25^{\circ}\text{C}$$

pH Scale



Note: As the temp is increased Kw is increased but PKw is decreased. $HA \rightleftharpoons H^+ + A^-$

For weak acid K_a × K_b = Kw K_a for acid HA, K_b for base A[−].



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- $pH = -\log_{10} [H^+]$ So $[H^+] = 10^{-PH}$
- pH + pOH = pkw pkw = 14 generally
- [H⁺] [OH⁻] = 10^{-kw}

For water $[H^+] = [OH^-]$, So $[H^+] = \sqrt{10^{-kw}}$

Note: If acid of concentration 10^{-7} M is there then PH \neq 7 it is PH < 7 because concentration of H⁺ from water is considered and common ion effect is there.

4. Ostwald dilution law: For a weak electrolyte of the type *AB*.

Dissociation constant $K = \frac{a\alpha^2}{1-\alpha} = a\alpha^2$

 $\alpha = \sqrt{\frac{K}{a}} = \sqrt{KV}$ where, a is the concentration in mol⁻¹ L and V is the volume of solution in L having 1 mol of electrolyte for weak monobasic acids,

$$\alpha = \sqrt{\frac{K_a}{a}}$$
 $a = \frac{n}{V}$ Concentration. $a\alpha = [H^+]$

For weak mono acidic base, $\alpha = \sqrt{\frac{K_b}{c}}$

 $a\alpha = [OH^-]$

- 5. Relative strengths of two weak monobasic acids strength of acid HA_1 strength of acid $HA_2 = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$
- 6. Conjugate acid-base pairs: Conjugate base of an acid is formed by the loss of a proton from acid. While conjugate acid is formed from a base by the gain of H^+ (proton). Such a pair of substances which can be formed from one another by the loss or gain of a proton are known as conjugate acid base pairs.

$$pX = -\log_{10} X, \qquad pk_a = -\log_{10} K_a$$
$$pk_a + Pk_b = Pkw \qquad pk_b = -\log_{10} k_b$$

Solubility and Solubility Product

7. Solubility product of a sparingly soluble salt *AxBy* is

$$AxBy \implies xA^{y+} + yB^{x-}, K_{sp} = [A^{y+}]^x, [B^{x-}]^y$$

In an ionic reaction precipitation takes place only if ionic product is greater than solubility product.



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9. Henderson equation

*p*H of an acidic buffer:
$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{Acid}]}$$

*p*H of a basic buffer: $pOH = pK_b + \log \frac{[\text{salt}]}{[\text{Base}]}$

pH = 14 - pOH

- (i) Buffer solution is that which is having constant pH value.
- (ii) Best buffer is that in which [acid] = [salt] or [base] = [salt]
- (iii) For buffer solution acid or base should be weak with strong base or acid salt.
- **Example:** (HCN+NaCN) (NH_4Cl+NH_4OH),

Salt Hydrolysis

A. In case of hydrolysis one part of the salt should be weak and the name of hydrolysis is on the basis of that part.

In this HCN is weak, due to this it is anionic hydrolysis and following points are there.

- 1. Anionic Hydrolysis and solution is basic.
- 2. pH > 7 or pH > $\frac{\text{pkw}}{2}$
- 3. Basic in nature so $[OH^-] = a\alpha$



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In this both are strong so it is netural in nature

- 1. No Hydrolysis
- 2. $pH = \frac{pkw}{2}$ or pH = 7 (at 25° C)
- 3. PH does't depends upon concentration.

Note: Nature of the solution depends upon the hydrolysis

Example: $CuCl_2$ is having acidic solution $CuCl_2 + H_2O \rightarrow Cu(OH)_2 + HCl$ this is due to cationic hydrolysis because $Cu(OH)_2$ is weak base.

If solution are mixed then

For acid if N_1, V_1 are given for base If N_2, V_2 are given then $[H^+] = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$ for acidic; $[OH^-] = \frac{N_2V_2 - N_1V_2}{V_1V_2}$ for base.

Some Important Points for JEE/AIPMT

1. As the temperature is increased Kw is increased and PKw is decreased so neutral point decreases.

Example: At 25°C PH of NaCl (aq) (Neutral) is '7'. But as the temp increases neutral point become pH < 7 and as the temp decreases neutral point pH > 7

2. $0.1 \text{ NH}_2\text{SO}_4$ pH = $-\log_{10} \text{ N} = -\log_{10} 0.1 = 1$ $0.1 \text{ MH}_2\text{SO}_4$ pH = $-\log_{10} 0.2 = \log_{10} 0.2$ F = Number of H⁺ $\frac{\text{N}}{\text{M}}$ = F

Note: If Normality is given then no need to calculate number of H^+ .

3.
$$HA \longrightarrow H^+ + A^- \alpha = \sqrt{\frac{ka}{a}} = \sqrt{\frac{ka}{\frac{n}{V}}} = \sqrt{\frac{ka.V}{n}}$$
 if dilution is there then α increases.

4. Acidic order is $BI_3 > BBr_3 > BF_3$



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Oxidation Number (O.N.)

- It is the charge appearance on the given
 Example: Na⁺ means O.N. is +1, SO₄⁻⁻ means O.N. is -2
- Oxidation number may be positive, negative.
- For the group element in the periodic table oxidation number can not be more than group number.

Example:

Element Group		Oxidation Number	
Na, K, CS, Rb	Ist A	+1	
Be, Ca, Mg, Ba, Sr	IInd A	+2	
B, Al	IIIrd A	+3	
Carbon Family	IV A	-4 to $+4$	
Nitrogen Family	VA	-3 to $+5$	
Oxygen Family	VI A	-2 to + 6	
Halogen Family	VII A	-1 to $+7$	

For Some Famous Metals

Mn	+ 2 to + 7
Cr	+ 2 to + 6
Fe	+ 2 or + 3
Cu	+ 1 or + 2
РЬ	+ 2 or + 4

For 'F' oxidation number is always '-1' because it is most electronegative, element so always have – ve value.

• For Hydrogen 'H', it is +1 if bonded with non metal and -1 if bonded with metal.



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Oxidation Number or Oxidation State

Oxidation Number	Valency
O.N. is the charge (real or imaginary) present on the atom of the elements when it is in combination. It may have plus or minus sign.	It is the combining capacity of the element. No plus or minus sign is attached to it.
O.N. of an element may have different values. It depends on the nature of compound in which it is present	Valency of an element is usually fixed.
O.N. of the element may be a whole number or fractional.	Valency is always a whole number.
O.N. of the element may be zero.	Valency of the element is never zero except of noble gases.

Calculation and use of Oxidation Number

1. For the calculation sum of all the oxidation numbers is equal to charge appear on the given.

Example: H_2SO_4 for 'S' O.N. is calculated as, For H= +1 for 0=-2 Let for 's' It is x. So put all the values in the given.

 $1 \times 2 + x + -2 \times 4 = 0; 2 + x - 8 = 0 x = +6$

Note: O.N. Can not be more than group number (remember it) means O.N. of 'S' is having maximum value +6 not more than, this is because its group is 16^{th} or VI A.

Note: Oxidation number of molecule is zero. Example: F_2 , Cl_2 , O_2 , H_2O , NH_3 , S_2 , S_4 etc.



 $\begin{array}{c} \textcircled{R} \\ \textcircled{R} \\ \textcircled{R} \\ H_2 \\ \texttt{S}_4 \\ \texttt{O}_6 \end{array} \qquad \begin{array}{c} O \\ \textcircled{R} \\ \texttt{H}_2 \\ \texttt{S}_4 \\ \texttt{O}_6 \end{array} \qquad \begin{array}{c} O \\ \textcircled{R} \\ \texttt{H}_2 \\ \texttt{S}_4 \\ \texttt{O}_6 \end{array} \qquad \begin{array}{c} O \\ \textcircled{R} \\ \texttt{S}_5 \\ \texttt{S}_5 \\ \texttt{S}_5 \\ \texttt{O}_6 \end{array} \qquad \begin{array}{c} O \\ \textcircled{R} \\ \texttt{S}_5 \\ \texttt{S}_5 \\ \texttt{S}_5 \\ \texttt{O}_6 \end{array} \qquad \begin{array}{c} \texttt{S} \\ \texttt{S}_5 \\$

Use of Oxidation Number

• Oxidiser and Reducers

(i) Oxidiser is that which oxidises the other and it's oxidation number decreases in the process.

Reducer is that which reduce the other and it's oxidation number increases in the process.

$$Fe^{+2} + Sn^{+4} \longrightarrow Sn^{+2} + Fe^{+3}$$

It is a redox reaction Fe^{+2} is reducing agent and Sn^{+4} is oxidising agent.

- F_2 is the best oxidising agent while Cs is the best reducing agent.
- In aqueous medium best reducer is Li.
- If any molecule is having an atom in it's highest oxidation state then it is good oxidiser.
- H_2SO_4 , $K_2Cr_2O_7$, KMnO₄ etc are good oxidiser.

Some Important Points for JEE/ AIPMT

Redox Reaction

We are having three types of redox reaction.

- (a) Intermolecular(b) Intramolecular (c) Disproportionation
- (a) Intermolecular is that in which one is oxidised and another is reduced.

$$Fe^{+2} + Sn^{+4} \longrightarrow Sn^{+2} + Fe^{+3}$$

Equivalent weight in this case $E = \frac{\text{molecular weight}}{\text{change in O.N. X Number of atoms}}$

Example: $K_2 Cr_2^{+6} O_7 \longrightarrow Cr^{+3}$ $E = \frac{M}{(6-3) \times 2} = \frac{M}{6}$

(b) Intramolecular- In this, one atom is oxidised and another atom is reduced.

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 $As_{2}S_{3} \xrightarrow{+3} Carbon As^{+2} + SO_{2}^{+4}$ In As₂S₃ As = +3 S = -2 As converts from +3 to +2 S converts from -2 to +4

Equivalent weight

Molecular weight

 $E = \frac{1}{(\text{change in O.N. of Ist atom X Number of atoms}) + (\text{change in O.N. of IInd atom X Number of atoms.})}$

$$E = \frac{M}{1 \times 2 + 6 \times 3} = \frac{M}{2 + 18} = \frac{M}{20}$$

(c) Disproportionation reaction- In this one atom of molecule is oxidised as well as reduced

$$H_3PO_3 \xrightarrow{\Delta} H_3PO_4 + PH_3$$

In H_3PO_3 O.N. of P is +3 and in H_3PO_4 and PH_3 it is +5 and -3 means oxidation as well as reduction equivalent weight is :

$$E = E_{oxd} + E_{red}$$

= $\frac{M}{(5-3)} + \frac{M}{(3-(-3))}$ or $E = \frac{M}{2} + \frac{M}{6}$
= $\frac{3M+M}{6} = \frac{4M}{6} = \frac{2M}{3}$ or $E = \frac{2M}{3}$

Use in Acidic Strength of Oxides of Non Metals

Nonmetallic oxide in higher oxidation state is more acidic.

Example: CO_2^{+4} is more acidic then CO^{+2}

 $SO_3 > SO_2$ $Cl_2O_7 > Cl_2O$

• If oxides are of same group with same oxidation number then more nonmetallic oxide more acidic

 $Cl_2O_7 > Br_2O_7 > l_2O_7$

• Nonmetalllic nature is Cl > Br > I



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- So acidic order is $Cl_2O_7 > Br_2O_7 > l_2O_7$
- Same case is with hydroxy acids. H₂SO₄ > H₂SO₃, HNO₃ > HNO₂ (More the oxidation number more acidic)

 $HCIO_4 > HCIO_3 > HCIO_2 > HCIO$ $HCIO_4 > HBrO_4 > HIO_4$

Note: For H_3PO_4 , H_3PO_3 , H_3PO_2 acidic order is as.

$$H_3PO_4 < H_3PO_3 < H_3PO_2$$
 (According to K_a of acid)

• From left to right in periodic table acidic nature increases

Electrochemical Series

ले	Li	अल	Al	Ni	नही	Pt
के	K	मिया	Mn	Sn	सुना	Au
वा	Ba	জী	Zn	Pb	ਧਟ	
सुरी	Sr	फे	Fe	Н	हम गाये	
को	Ca	को	Cr	Cu	CHAPA	(Cu Hg Ag
ना	Na	सीडी	Cd	Hg	CHAPA	Pt Au)
मुझे	mg	को	Co	Ag		

Properties of Electrochemical Series

- 1. Li is the best reducer having maximum negative reduction potential.
- 2. CHAPA (Cu Hg Ag Pt Au) are known as noble metals. Upper one can remove lower one from it's solution
- 3. One from it's solution

 $Zn+CuSO_4 \longrightarrow ZnSO_4 + Cu$



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 $Cu + ZnSO_4 \longrightarrow No reaction$

because Zn is above Cu

 $KMnO_4$ is having different reactions in acidic medium, basic medium and neutral medium as oxidiser.

$$KMnO_{4} \xrightarrow[]{H^{+}} Mn^{+2} \text{ acidic medium}$$

$$KMnO_{4} \xrightarrow[]{OH^{-}} MnO_{2} \text{ Neutral medium}$$

$$KMnO_{4} \xrightarrow[]{H_{2}O} MnO_{4}^{--} \longrightarrow MnO_{2} \text{ Basic medium}$$

Note: It is best oxidiser in case of acidic medium.

• $K_2Cr_2O_7$ is having reaction as in acidic medium

$$K_2Cr_2O_7 \xrightarrow[+2.5]{H^+} Cr^{+3}$$

• $\operatorname{Na}_2 \operatorname{S}_2 \operatorname{O}_3 + \operatorname{I}_2 \longrightarrow \operatorname{Nal} + \operatorname{Na}_2 \operatorname{S}_4 \operatorname{O}_6^{+2.5}$

It is known as iodiometric test

- Lower oxidation number is having name 'ous' and higher is having name 'ice'.
 Example: FeCl₂- Ferrous chloride FeCl₂- Ferric chloride.
- $\odot~$ In complex formation oxidation state remains constant except ${\rm Cu}^{+2}$. It converts into ${\rm Cu}^{+}$,

Example:

$$\begin{array}{c}
Cu^{+2} \longrightarrow Cu^{+} \\
FeCl_{2} + KCN \longrightarrow Fe(CN)_{2} \xrightarrow{KCN} K_{4} [Fe(CN)_{6}] \\
FeCl_{3} + KCN \longrightarrow Fe(CN)_{3} \xrightarrow{KCN} K_{3} [Fe(CN)_{6}] \\
CuCl_{2} + KCN \longrightarrow Cu(CN)_{2} \longrightarrow Cu_{2} (CN)_{2} + |CN| \\
Cu_{2} (CN)_{2} \xrightarrow{KCN} K_{3} [Cu(CN)_{4}] \\
\end{array}$$
Note: Here KCN is like complexing and reducing agent.

In case of transition metal oxide more the oxidation number more will be acidic nature. $CrO_5 > Cr_2O_3$ acidic order.



RHELIOS -

The Solid State

- 1. The solids are of two types—amorphous solids and crystalline solids. In amorphous solids, constituents do not possess orderly arrangement over the long range and do not have sharp melting points while in crystalline solids constituents are arranged in an orderly manner over long distances and have sharp melting points. Crystalline solids are anisotropic while amorphous solids are isotropic.
- 2. Depending upon the nature of interparticle forces, the solids are classified into four groups—ionic solids (ionic forces) e.g. NaCl, KCl, KNO₃ etc, metallic solids (metallic bonds) e.g., Na, Cu, Fe etc; covalent solids (covalent bonds) e.g. diamond, quartz etc., and molecular solids (hydrogen bonds or van der Waals' forces) e.g. solid CO_2 I₂ etc.
- 3. A crystal possesses three types of symmetry—Plane of symmetry, axis of symmetry and centre of symmetry. In a cubical crystal, there are 9 plane of symmetry, 13 axis of symmetry and 1 centre of symmetry.
- 4. A regular array of points (showing atoms or ions) in three dimensions is commonly called as space lattice or crystal lattice and three dimensional group of lattice points which when repeated in space generates the crystal called unit cell.
- 5. Each unit cell is characterised by distance, c,b and a along three edges and angles α , β and y between these edges.

System	Primitives or axial distance	Interfacial or axial angles	Maximum elements of symmetry	Examples
 Cubic Tetragonal Orthorhombic Monoclinic Triclinic Hexagonal Rhombohedral or Trigonal 	$a = b = c$ $a = b \neq c$ $a \neq b \neq c$ $a = b \neq c$ $a = b \neq c$ $a = b = c$	$\alpha = \beta = \gamma = 90^{\circ}$ $\alpha = \beta = \gamma = 90^{\circ}$ $\alpha = \beta = \gamma = 90^{\circ}$ $\alpha = \gamma = 90^{\circ}, \beta \neq 90^{\circ}$ $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$ $\alpha = \beta = 90^{\circ}, \gamma = 120$ $\alpha = \gamma = 90^{\circ}, \beta \neq 90^{\circ}$	9 planes, 13 axis, 1 centre 5 planes, 5 axis 3 planes, 3 axis 1 plane, 1 axis No plane, no axis 7 planes, 7 axis 7 planes, 7 axis	NaCI, KCl, ZnS, Ag SnO ₂ , NiSO ₄ , ZnO ₂ , Sn Rhombic S. BaSO ₄ , KMO ₃ , PbCO ₃ Monoclinic S, CaSO ₄ , $2H_2O$ CuSO ₄ $5H_2O$, H_3BO_3 ZnO, SiO ₂ (silica), HgS Calcite, NaNO ₃

Seven Primitive Unit Cells



-Trick & Tech-

There are seven crystal systems and fourteen Bravais lattice (unit cells) corresponding to these seven crystal systems.

- 6. For a cubic system, there are only three types of unit cells. Simple cubic unit cell, body centred cubic unit cell and face centred cubic unit cell.
- 7. The two common types of close packing in two dimensions are square close packing and hexagonal close packing. In square close packing about 52.4% of available space is occupied by spheres whereas hexagonal close packing occupies only 60.4% of the space by spheres.
- 8. In case of three dimensional close packing, the two common types of close packing are obtained from hexagonal close packed layers are

Hexagonal Closed Packing (HCP)

- (a) AB AB AB type(c) Packing fraction 74%
 - (e) Volume V = $24\sqrt{2r^3}$

Cubic Closed Packing (CCP)

- (a) ABC ABC type
- (c) Packing fraction 74%
- (e) Volume V = $16\sqrt{2r^3}$

- (b) Coordination number 12
 (d) Total atoms in unit cell 6
 (b) Coordination number 12
 (d) Total atoms 4
- **10.** The number of nearest neighbours with which a given sphere is in contact is called coordination number.
 - (a) In simple cubic structure coordination number is 6 : 6
 - (b) If F.C.C. Structure : Coordination number 6 : 6 For salt like structure.
 - (c) For B.C.C. Structure Coordination number is 8 : 8.
 - (d) For H.C.P and C.C.P. Coordination number is 12 : 12
- For ionic solids, the ratio of the radius of cation to that of anion is called radius ratio.
 Crystals of AB type with different structural arrangement

Radius ratio	Coordination number	Structural arrangement	Example
Above 0.732	8	Cubic	CsCl, CsBr, NH ₄ Br
0.732-0.414	6	Octahedral	NaCl, NaBr, CaS
0.414-0.225	<mark>4</mark>	Tetrahedral	HgS, ZnS, BaS
0.225-0.155	<mark>3</mark>	Triangular	Boron oxide



12. Bragg's equations: (X-ray diffraction) $n\lambda = 2d \sin \theta$, where, *n* is the order of reflection, λ is the wavelength of X-ray light used, *d* is the distance between two planes.



• If 'A' at corner 'B' at face C at edge and D at centre in cubic then formula is.

$$\frac{A}{8} \times 8 \qquad \frac{B}{2} \times 6 \qquad \frac{C}{4} \times 12 \qquad \frac{D}{1} \times 1 \qquad AB_3C_3D$$

- For F.C.C. A at corner B at face then formula $\frac{A}{B} \times 8$, $\frac{B}{2} \times 6$ AB_3
- For F.C.C. (salt like) NaCl, etc. Then Cl at corner and face Na at edge and center then formula $\frac{Na}{4} \times 12 + Na + \frac{Cl}{8} \times 8 + \frac{Cl}{2} \times 6$ 4Na + 4Cl = 4NaCl. From center
- 14. Void- It is 3D space in the solid.

234

Tetrahedral void-Coordination number = 41. $\frac{r_{\text{void}}}{0.225}$ or -=0.2252. ratom Number of voids = 2x Number of atoms 3. Coordination number = 6Octahedral void-1. $r_{void} = 0.414$ 2. ratom **3**. Number of voids = Number of atoms

- **15.** Relation between number of voids and spheres in close packing. In close packing of *n* spheres.
 - No of octahedral voids = n

• No of tetrahedral voids = 2n

If an oxide is formed in which 'A' in tertahedral void and 'B' in octahedral then formula is 2A O B i.e. A_2BO .

because for one oxide 2 tetrahedral void and one octahedral.

Diamond coordinate number is four, and unit cell has eight carbon atoms, 4 atoms form FCC lattice and 4 atoms occupy half of the tetrahedral voids alternately.

In Diamond

- **1.** Coordination number = 4
- 2. In a unit cells eight carbon atoms

3. 4 atoms form FCC lattice and 4 atoms occupy half of the tetrahedral voids alternately.

16. Relation between nearest neighbours distance (d), atomic radius (r) and edge length (a) of cubic unit cell.

Simple cubic	Body centred cubic	Face centred cubic
$d = a$ $r = \frac{a}{2}$	$d = \frac{\sqrt{3a}}{2} = 0.866 a$ $r = \sqrt{3} \frac{a}{4} = 0.433 a$	$d = \frac{a}{\sqrt{2}} = 0.707 a$ $r = \frac{a}{2\sqrt{2}} = 0.3535 a$

Cubic System	Relation between radius and edge length	Density	Number of atom per unit cell.	Packing fraction
Simple Cubic	$r = \frac{a}{2}$	$d = \frac{\frac{At. wt.}{No}}{a 3}$	1	0.52
Body Simple Cubic	$r = \frac{a\sqrt{3}}{4}$	$d = \frac{2 \times \frac{At. wt.}{No}}{a 3}$	2	0.68
FaCl centre Cubic	$r = \frac{a\sqrt{2}}{4}$	$d = \frac{4 \times \frac{At. wt.}{No}}{a 3}$	4	0.74



17. Defects in crystalline solids :

- Electronic imperfections result from the loss of electrons from their atoms and ions in covalent compounds and ionic crystals respectively. This results in formation of hole.
- Atomic imperfections result from displacement or loss of atoms or ions in their periodic arrangements in crystals. These are known as point defects.
- The most common lattice imperfections are line defects or dislocation. These defects arise due to displacement of row of lattice sites.
- Schoattky defect is caused when equal number of cations and anions are missing from their lattice sites. Due to this defect density of the crystal decreases.
- Frenkel defect is caused when cations are missing from their lattice sites and occupy interstitial sites. Density of the crystal remains same but dielectric constant increases.
- **F-centres** are the sites from where anions are missing and the vacant sites are occupied by electrons. F-centres contribute to colour of the crystal.
- In doping, small amount of foreign impurity is added in the host crystal to increase its electrical conductivity.
- Doping of group 14 elements with group 15 elements produces excess of electrons (n type semiconductors) and doping of group 14 elements with group 13 elements produces holes (p-type semiconductors) in the crystal.
- 18. Paramagnetic substances are attracted by the magnetic field and have unpaired electrons while diamagnetic substances are weakly repelled by magnetic field and do not have any unpaired electron.
 - In metals, valence band is partially filled or it overlaps with conduction band. This results in movement of electrons under an applied electric field and metals show conductivity.
 - In semiconductors, there is a small energy gap between valence band and conduction band. Due to this some electrons may jump to conduction band and show some conductivity. Their conductivity increases with rise in temperature.
 - In insulators such as diamond there is large energy gap and electrons can not jump to conduction band.

236

Electrochemistry

Electrolytes and Electrolysis

- 1. **Definition:** "The substance whose aqueous solution undergo decomposition into ions when electric current is passed through are known as electrolytes and the whole process is known as electrolysis or electrolytic decomposition"
- Electrodes which do not take part in chemical change involved in cell are known as inert electrode. e.g., Graphite, Platinum.
 Electrodes which take part in chemical change involved in a cell known as active
- electrode e.g., Hg, Au, Cu, Zn and Ni electrode etc.3. The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below.

For cations:

For anions: SO₄²⁻,NO₃,OH⁻,CH₃COO⁻,Cl⁻,Br⁻,l⁻

4. Faraday's laws

Ist Law According to this the amount of discharged is directly proportional to charged applied.

 $W \times Q$ or Q W = ZQ W = Z i t

IInd Law According to this equivalents of depositted is equal to $\frac{Q}{r}$

Equivalence = $\frac{Q}{F}$ Q = Charge applied F = farady constant = 96500 C.

5. Discharging

Example:	NaCl (aq) is discharged]
Cathode	$H^{+} \longrightarrow H_{2}$ because discharging potential of $H^{+} < Na^{+}$
Anode	$CI^- \longrightarrow CI_2$ because discharging potential of $CI^- < OH^-$
	So final is NaOH + H ₂ +Cl ₂



Trick & Tech-

6. Primary Cells: In these cells the electrode reaction cannot be reversed by an external electric energy source,. In these cells reactions occure only once and after use they become dead.

Therefore, they are not chargeable. Some common examples are, dry cell, mercury cell, daniel cell and alkaline dry cell.

Secondary cells: In the secondary cells, the reactions can be reversed by an external electrical energy source. therefore, these cells can be recharged by passing electric current and used again and again. Examples of secondary cells are, lead storage battery and nickel-cadmium storage cell.



Electrochemical or Galvanic cell "Electrochemical cell or galvanic cell is a device in which a spontaneous redox reaction is used to convert chemical energy into electrical energy i.e., electricity can be obtained with the help of oxidation and reduction reaction".

246

RHELIOS .

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- Electrochemical cell consists of two vessels, two electrodes, two electrolytic solutions and a salt bridge.
- The two electrodes taken are made of different materials and usually set up in two separated vessels.
- The electrolytes are taken in the two different vessels called as half-cells.
- The two vessels are connected by a salt bridgeporoues pot.
- Like electrolytic cell, in electrochemical cell, from outside the electrolytes electrons flow from anode to cathode and current flow cathode to anode.
- In a electrochemical cell, reaction.

$$Fe^{+2} + 2e^{-} \longrightarrow FeQ_{red} = \frac{1}{[Fe^{+2}]}E_{red} = E_{red} - \frac{0.0591}{2}\log_{10}\frac{1}{[Fe^{+2}]}$$

 $E_{cell} = E_{oxd} + E_{red}$

Salt bridge and its significance:- Salt bridge is U- shaped glass tube filled with a gelly like substance, agar (plantgel) mixed with an electrolyts like KCl, KNO₃, NH₄NO₃ etc.

7. Emf of the cell is the difference of reduction potential of cathode and anode.

$$\mathsf{E}_{\mathsf{cell}}^{\circ} = \mathsf{E}_{\mathsf{cathode}}^{\circ} - \mathsf{E}_{\mathsf{anode}}^{\circ} = \mathsf{E}_{\mathsf{oxd}} + \mathsf{E}_{\mathsf{red}}.$$

Lower is the value of reduction potential, greater is its reducing power.

Metals having lesser value of standard potential can displace the other from its aqueous salt solution.

Emf of a cell involving following reaction $aA + bB \longrightarrow xX + yY$

Nernst equation,
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[X]^{x} [Y]^{y}}{[A]^{a} [B]^{b}} V$$
 (at 298 K)

where, [X][Y][A] and [B] are molar concentration of X, Y, A and B respectively and n is the number of electrons involved in the cell reaction.

9. For a cell reaction in equilibrium at 298 K

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c \text{ V}$$



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10. Gibbs energy change, $\Delta G^{\circ} = -nFE^{\circ}$, where F = 1 faraday = 96500 C mol⁻¹ (charge on one mole electron).

 $\Delta G^{\circ} = -2.303 RT \log K_{c}, \text{ where } K_{c} \text{ is equilibrium constant.}$ $E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_{c} \text{ V}$

Some Important Points for JEE/ AIPMT

Concentrated cell is having different concentration but same electrodes.
 Ag|Ag⁺ ||Ag⁺ |Ag

 $\mathsf{E}_{\mathsf{oxd}} = \mathsf{E}_{\mathsf{oxd}}^{\circ} - \frac{0.0591}{\mathsf{n}} \log_{10} \mathsf{Q}_{\mathsf{oxd}}$ $Ag \longrightarrow Ag^+ Q_{oxd} = [Ag^+]_L$ $E_{\text{red}} = E_{\text{red}}^{\circ} - \frac{0.0591}{n} \log_{10} \frac{1}{Q_{\text{red}}} \qquad \qquad Ag^{+} \longrightarrow Ag \ Q_{\text{red}} = \frac{1}{[Ag^{+}]_{P}}$ $E_{cell} = E_{oxd} + E_{red} = -\frac{0.0591}{n} \log_{10} \frac{Q_{oxd}}{Q_{oxd}}$ $E_{cell} = \frac{-0.0591}{n} \log_{10} \frac{[Ag^+]_L}{[Ag^+]_r}$ **12A.** Pt $H_2 | H^+ || H^+ |H_2$ Pt P_1 C_1 C_2 P_2 $Q_{oxd} = \frac{[H^+]^2}{P_4} = \frac{C_1^2}{P_1}$ $H_2 \longrightarrow 2H^+ + 2e^ Q_{red} = \frac{P_2}{[H^+]^2} = \frac{P_2}{C_2^2}$ $2e^{-}2H^{+} \longrightarrow H_{2}$ $\mathsf{E}_{\mathsf{cell}} = -\frac{0.0591}{2} \log_{10} \frac{\mathsf{Q}_{\mathsf{oxd}}}{\mathsf{Q}_{\mathsf{oxd}}}$ $E_{cell} = -\frac{0.0591}{2} \log_{10} \left(\frac{C_1}{C_2} \right)^2 \left(\frac{P_2}{P_1} \right)$ Case I $C_1 < C_2$ $P_1 = P_2$ $E_{cell} = +ve$ Case II $C_1 = C_2$ $P_2 < P_1$ $E_{cell} = +ve$ 12.B Pt Cl₂|Cl⁻||Cl⁻|Cl₂ Pt $P_1 \quad C_1 \quad C_2 \quad P_2$

HELIOS

248

HELIOS



13. A battery consists of two or more voltaic cells connected in series. Mainly two types of cells are used in battery.

Primary cells such as dry cell (Lechianche cell), mercury cell cannot be used again (not rechargeable).Dry cell has a potential of 1.5 V.

Secondary cells such as lead storage battery, Ni—Cd Storage cell can be used again (rechargeable). During charging, the electrode materials are converted back to their original forms and the cell once again starts generating electricity.

- 14. Fuel cells are voltaic cells in which reactants are continuously supplied to the electrodes. The common example of fuel cell is hydrogen-oxygen fuel cell. These cells convert energy from combustion of fuel directly into electrical energy.
- 15. Corrosion is basically an electrochemical phenomenon, It is the process of slow oxidation of metals into undesirable compounds by action of moisture and other gases present in atmosphere. The miniature cell reaction is

$$2Fe(s)+O_{2}(g)+4H^{+}(aq)\longrightarrow 2Fe^{2+}+2H_{2}O(I)$$
$$4Fe^{2+}(aq)+O_{2}(g)+4H_{2}O(I)\longrightarrow 2Fe_{2}O_{3}(s)+8H^{+}$$

Hydrated ferric oxide (Fe_2O_3 . xH_2O) is rust.

Corrosion of metals can be prevented by barrier protection, electroplating, galvanization and by connecting object metal to a more electropositive metal (cathodic protection) etc.

- **16.** Electrochemistry is the branch of physical chemistry which deals with the relationship between electrical energy and chemical changes taking place through redox reactions.
- 17. $R = \rho \cdot \frac{l}{a}$; where, R = resistance in ohms, a = area of cross-section of electrodes in cm² l = distance between electrodes in cm. and ρ resistivity in ohm cm. units of cell constant = cm⁻¹



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18. Specific conductance κ (kappa) = $\frac{1}{2}$ Conductance $C = \frac{1}{R}$ $\kappa = C \frac{l}{R}$ = Cell constant. When l = 1 cm and a = 1 cm²; $\kappa = C$ Units of conductance are Ω^{-1} or siemens, *S*. Units of specific conductance (κ) are Ω^{-1} cm⁻¹ or S cm⁻¹. 19. Equivalent conductance $\uparrow eq = \frac{\kappa}{C_{eq}} = \frac{\kappa \times 1000}{\text{Normality}}$; where C_{eq} is the concentration of the solution in g_{eq} cm⁻¹. Units of equivalent conductance is Ω^{-1} cm² (g_{eq})⁻¹ or S cm² (g_{eq})⁻¹. 20. Molar conductance, $m = \frac{\kappa}{C_{m}} = \frac{\kappa \times 1000}{\text{molarity}}$; where, C_m is the molar concentration of solution in mol cm⁻³. Units of molar conductivity are Ω^{-1} cm²mol⁻¹ or S Cm² mol⁻¹. 21. According to Kohlcausch's law, molar conductance at infinite dilution;

$$^{\infty}_{\text{eletrolyte}} = ^{\infty}_{\text{cation}} + ^{\infty}_{\text{anion}}$$

 $\gamma_{\text{cation}}^{\infty}$ and $\gamma_{\text{anion}}^{\infty}$ are limiting ionic conductivities expressed in S cm² mol⁻¹.

22. Degree of dissociation

 $\alpha = \frac{\text{molar conductance at given concentration}({}^{c}_{m})}{\text{molar conductance at inifite dilution}({}^{\infty}_{m})}$

Equivalent and molar conductance of a solution increases with dilution whereas the specific conductance of the solution decreases.





250

- 11. The rate of reaction depends upon the physical state of reactants and activation energy of reactants. Usually rate of reaction increases with increase in surface area of reactant particles, and the reactions having low activation energy are fast where as reactions having high activation energy are slow.
- **12.** Rate of reaction increases by the presence of a catalyst. It increases the rate of reaction by providing alternative path of lower activation energy to the reactants.

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•
$$K = A e \frac{-Ea}{RT} T \longrightarrow \infty then K = A$$

• Unit of A = unit of K



It is endothermic reaction

• Catalyst decreases activation energy and a new path is devloped.



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$$2O_3 \longrightarrow 3O_2$$

 $-\frac{d}{dt}[O_3] = k \frac{[O_3]^2}{[O_2]} = k[O_3]^2 [O_2]^{-1}$

Therefore, order with respect to oxygen is -1.

8. Rate of reaction depends upon temperature.

Temperature coefficient = $\frac{\text{rate constant at 308 K}}{\text{rate constant at 298 K}} = \frac{K_{308}}{K_{298}}$

The value of temperature coefficient for most reactions lies between 2 to 3.

- **9.** According to collision theory, rate of reaction depends upon collision frequency and effective collisions. For effective collisions molecules should have proper orientation and sufficient energy (energy equal greater than the threshold energy).
- **10.** Arrhenius equation is a mathematical expression to give a quantitative relationship between rate constant and temperature.

$$k = A \cdot e^{-E_a/RT}$$

where, A is frequency factor, E_a is activation energy, R is gas constant and T is temperature.

- $\log k = \log A \frac{E_a}{2.303RT}$
- A plot of log k with $\frac{1}{T}$ gives a straight line with slope = $-\frac{Ea}{2.303R}$



• If k_2 and k_1 are rate constants at temperature T_2 and T_1 then

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

