Physical chemistry Revision

Mole Concept

At. Struc.

Chem. bonding

Thermodynamics

Solutions

Equilibrium

Kinetics

Electrochem.

Physical chemistry Revision

Moleconcept

$$n = \text{(moles)} \quad \frac{\text{Given mass}}{MM}$$

$$\text{One atom mass} = \frac{GIAM}{Av.No.}$$

6.023×10^{23}

Physical chemistry Revision

At. mass = Equivalent mass x Valency

$$= \frac{6.4}{\text{Specific heat}}$$

MM = 2 x Vapour density

MM of gas = mass of 22.4 L of vapour at STP

Physical chemistry Revision

$$\text{Eq. Weight} = \frac{\text{Atomic weight}}{\text{No. of } e^- \text{ lost (or) gained}}$$

(or)

Valency of ele.

or

Charge of eleme

or

Acidity / basicity

Physical chemistry Revision

Conc. terms :

$$\text{Molarity} = \frac{\text{no. of moles}}{\text{Vol. of Solution (L)}}$$

$$\text{Molality} = \frac{\text{no. of moles of Solute}}{\text{weight of Solvent (kg)}}$$

Physical chemistry Revision

$$\text{Normality} = \frac{\text{no. of gram equiv. of Solute}}{\text{Vol. of Solution (L)}}$$

$$\text{gram equi} = \frac{\text{weight of Solute}}{\text{eq. wt of Solute}}$$

Physical chemistry Revision

* $N_1 V_1 = N_2 \times V_2$

* $M_1 V_1 = M_2 \times V_2$ (same)

$n_1 A + n_2 B \longrightarrow$ Pdts

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

Physical chemistry Revision

M.F

$$x_A = \frac{n_A}{n_A + n_B} \qquad x_B = \frac{n_B}{n_A + n_B}$$

$$\boxed{x_A + x_B = 1}$$

$$\% \text{ by weight} = \frac{\text{wt. of Solute}}{\text{wt of Soln}} \times 100$$

Physical chemistry Revision

- % by Volume
- % by wt/vol
- $ppm = \frac{\text{mass of A}}{\text{mass of Solution}} \times 10^6$

Physical chemistry Revision

$$\text{Molality}_{(m)} = \frac{M}{\rho - \frac{M M_2}{1000}}$$

$$M = \frac{m\rho}{\left(1 + \frac{m M_2}{1000}\right)}$$

Physical chemistry Revision

At. Struc:

- Isotopes
- Isobars =
- Isotones / isoneutronic / Isotonic
- Isodiaphers = Same (no. of neu − no. of Pro)

Physical chemistry Revision

> Isosters = Same no. of atoms and e^-

(X) > Isoelectronic = Same no. of e^-

Physical chemistry Revision

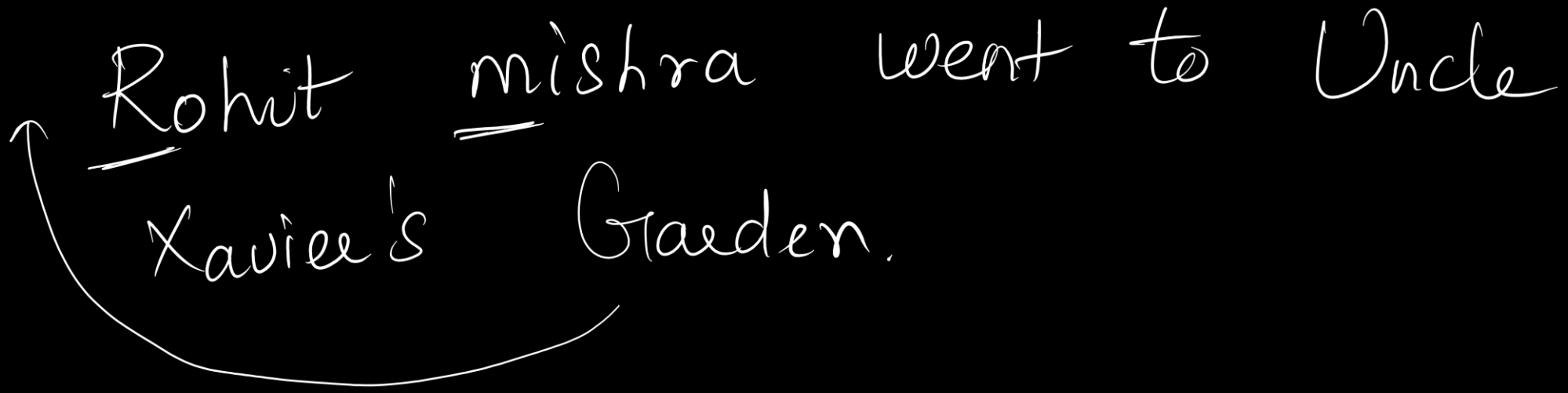
EMR

$$c = \nu\lambda$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

$$T = \frac{1}{\nu} = \frac{\lambda}{c}$$

Physical chemistry Revision



Physical chemistry Revision

$E = h\nu$

$E_T = N \times h\nu$

↳ Energy of one photon.

$h = 6.626 \times 10^{-34}$

Physical chemistry Revision

$$E_{photon} = \text{The. Eneegy} + \text{k.E}$$

$$= h\nu_0 + \text{k.E}$$

$$h\nu = h\nu_0 + kE$$

$$= h\nu_0 + \frac{1}{2} m v^2$$

$$KE = h(\nu - \nu_0)$$

Physical chemistry Revision

Bohr Model – Single e^-

$$mvr = \frac{nh}{2\pi}$$

Radius of bohr Orbit $r = \frac{0.529\, n^2}{Z}\,\text{Å}$

Physical chemistry Revision

Velocity of e^- $\quad V = \dfrac{2\pi k Ze^2}{nh}$

$$V = 2.18 \times 10^6 \frac{Z}{n} \text{ m/s}$$

$$PE = -\frac{kZe^2}{r}$$

Physical chemistry Revision

Total Energy = TE $\times Z^2$ (Same Orbit)

ΔE = ΔE (for H) $\times Z^2$ (Same trans)

Energy of n^{th} = $\frac{E_1}{n_1}$ [Same atom]

Physical chemistry Revision

Lyman — $n_{any} \rightarrow 1$ — UV

Balmar — $n_{any} \rightarrow 2$ — Vis

Pascher — $n_{any} \rightarrow 3$ — IR

Bracket — $n_{any} \rightarrow 4$ — IR

Pfund — $n_{any} \rightarrow 5$ — IR

Physical chemistry Revision

Rydberg Eqn:

$$\bar{\nu} = \frac{1}{\lambda} R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\nu = R_H C Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$R_H = 109678\ cm^{-1}$

Physical chemistry Revision

Max. no. of Spectral lines

$$N = \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

Total Emission lines $= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

$n \rightarrow 1$ $\quad \frac{n(n-1)}{2}$

Physical chemistry Revision

De-broglie

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

$$\lambda = \frac{h}{\sqrt{2mKE}}$$

$$\lambda = \sqrt{\frac{150}{V}}\ \text{Å}$$

Physical chemistry Revision

Uncertainty

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot m\Delta v \geq \frac{h}{4\pi}$$

Physical chemistry Revision

Quantum.

- Principal – Shell. (n)
- Azimuthal (l) – Subshell.
  - 3p
  - s – 0
  - p – 1
  - d – 2
  - f – 3
- Mag (m)
  - $-l$ to $+l$
  - -1 to $+1$
- Spin (s)
  - $-\frac{1}{2}$ and $+\frac{1}{2}$

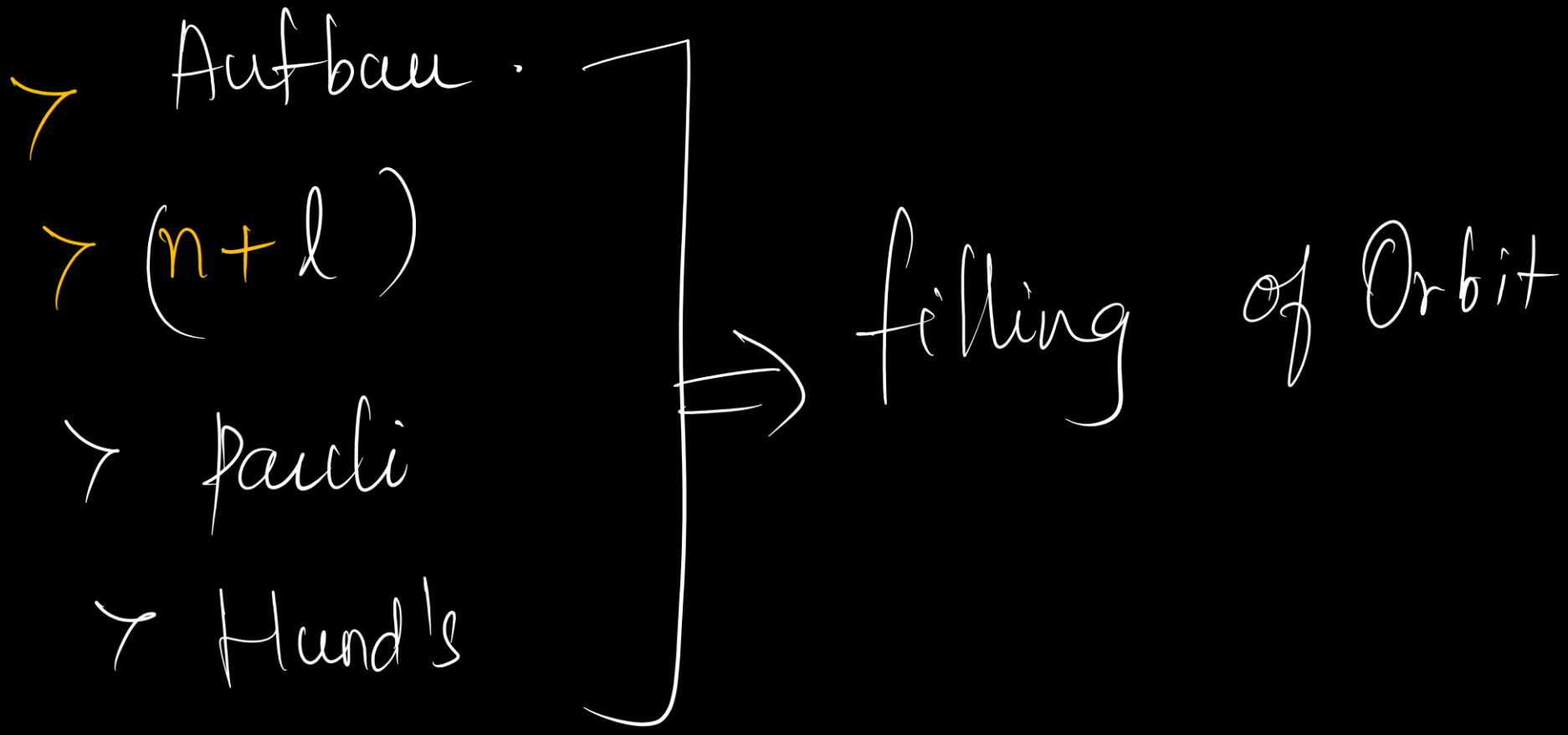
↑↓

Physical chemistry Revision

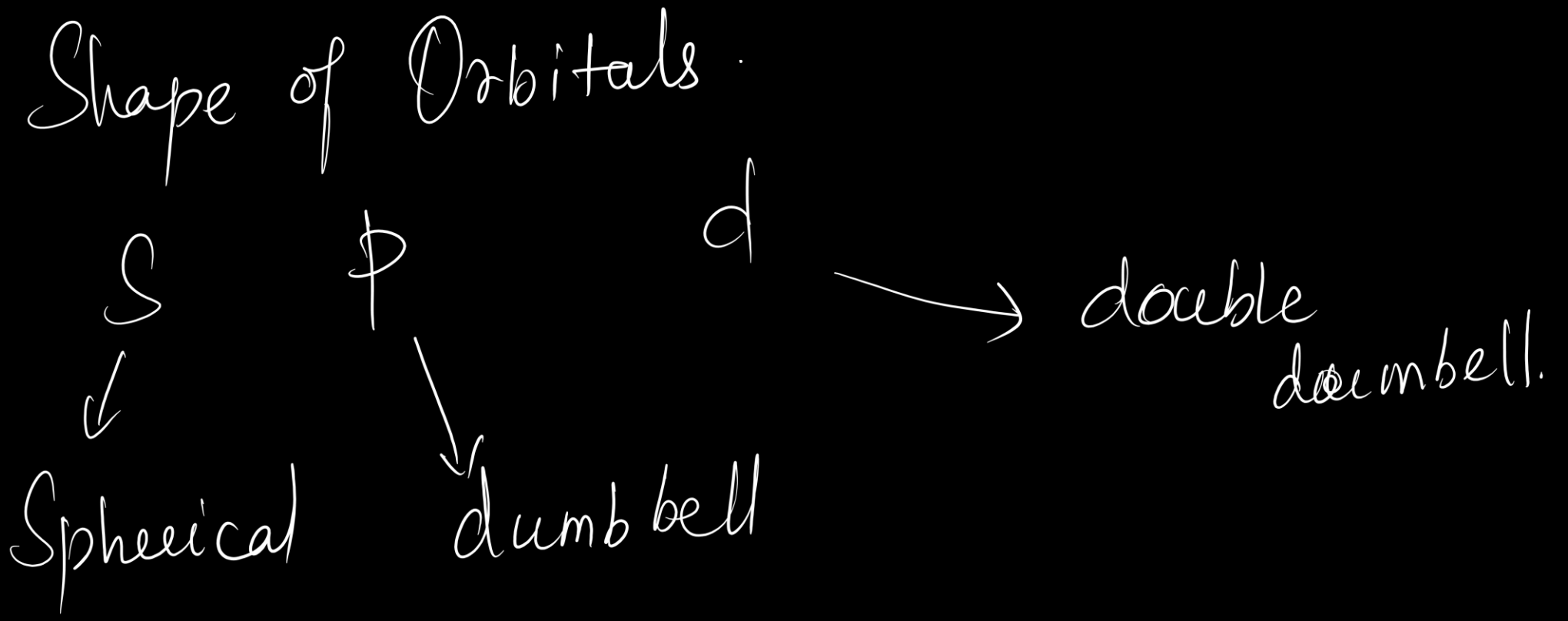
Orbital Ang. momentum

$$= \sqrt{l(l+1)}\ \frac{h}{2\pi}$$

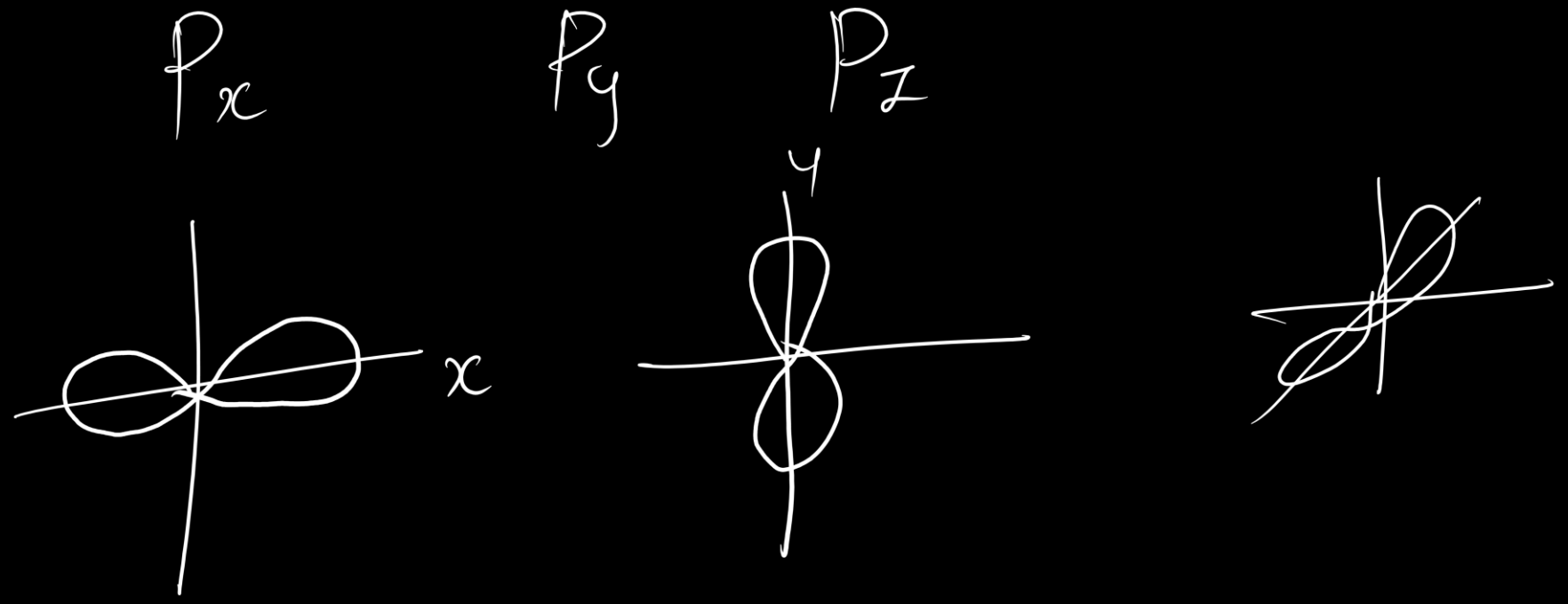
Physical chemistry Revision



Physical chemistry Revision

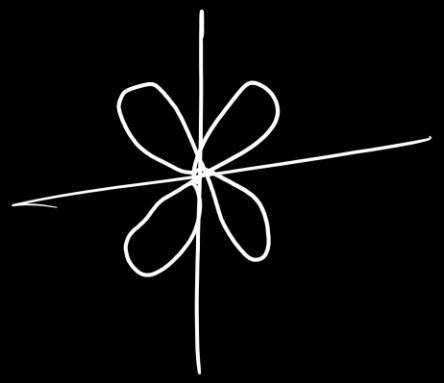


Physical chemistry Revision



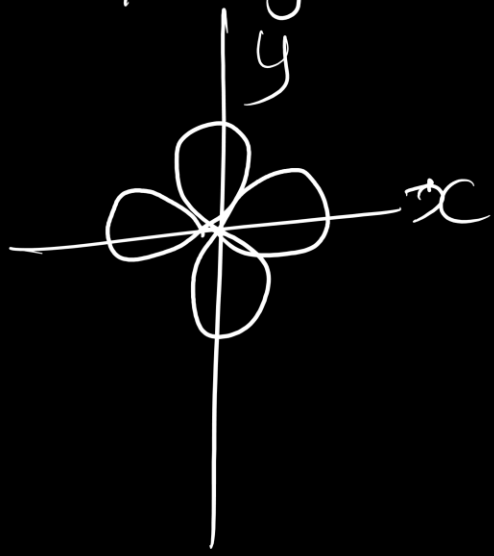
Physical chemistry Revision

d_{xy} d_{yz} d_{zx} $d_{x^2-y^2}$ d_{z^2}

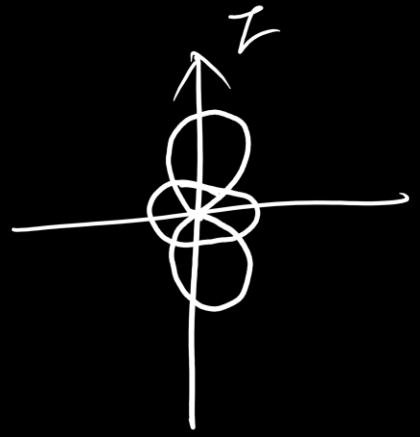


between

between.



between.



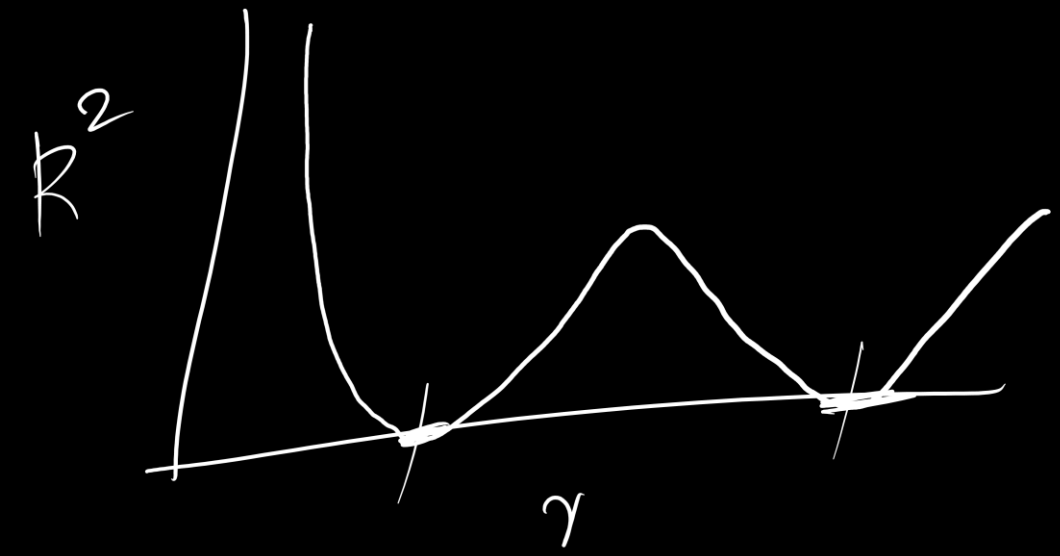
Physical chemistry Revision

Nodes — Radial = $n-l-l$.

Nodes — Angular = l

Total no. of Nodes = $n-1$

Physical chemistry Revision

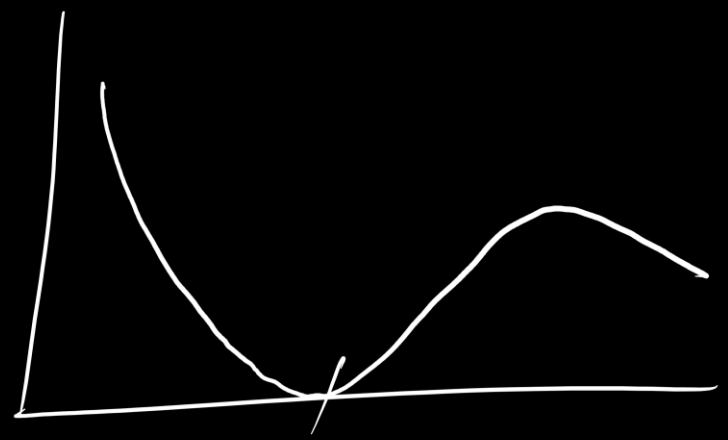


3S

$(3-1) = 2$

Physical chemistry Revision

2s



(2-1) = 1

Physical chemistry Revision

F.F > H.F > R

Stable.

Physical chemistry Revision

Chemical Bonding.

Lewis Octet Rule.

Physical chemistry Revision

(1) Electron deficient

BeF_2, $BeCl_2$, BH_3, BF_3,

$AlCl_3$. $\Rightarrow$ Less than 8e$^-$

Physical chemistry Revision

② Electron rich.

IF_7, SF_6, PCl_5, XeF_6

Physical chemistry Revision

(3) odd electron.

NO, ClO_2, NO_2.

Physical chemistry Revision

Types of Bonds:

Strong bond : Ionic > Covalent ≃ Coordinate > Metallic

Physical chemistry Revision

Weak bonds Hbonding > Vander waal

Physical chemistry Revision

Prop of Ionic cpd:

$\Delta EN > 1.7$

$\Delta H = (S.E + IE + D/2) - EA + U$

= total energy absorbed − T.E released

Physical chemistry Revision

- Electrostatic attrac.
- Solid – bad Cond.
  aq. / molten – good Cond.
- Isomorphism. – NaF & MgO
  Same (no. of e^-) 11+9 12+8

Physical chemistry Revision

M.pt & b.pt : Hight.

LiH > NaH > KH > CsH.

Physical chemistry Revision

Solubility: Soluble in polar.

↳ dielectric Constant ∝ Sol.

↳ Lattic. Energy $\propto \frac{1}{Sol}$

↳ H.E ∝ Solutiong

Physical chemistry Revision

Hydration Energ > lattice energy

Physical chemistry Revision

~~1007.~~

Covalent character ∝ polarisation

∝ Z_{eff}.

Physical chemistry Revision

i) Charge of Cation $\propto$ Pol.

ii) Size of Cation $\propto \frac{1}{\text{Pol.}} \propto \frac{1}{\text{Co.ch.}}$

iii) Size of Anion $\propto$ Pol. $\propto$ Co.Cha.

Physical chemistry Revision

VBT

Hybridisation,

Shape.

MOT

Mag. nature.

Physical chemistry Revision

MOT : $B.O = \frac{1}{2}(\text{Bond } e^- - \text{Anti-bond } e^-)$

$B.O \propto \text{Strength} \propto \frac{1}{B.L.}$

- $e's \leq 14$
- $e's \geq 14$

Physical chemistry Revision

$\underline{\alpha} \; 14$

$(\pi_{2p_x} = \pi_{2p_y})$, σ_{2p_z}, $(\pi^*_{2p_x} = \pi^*_{2p_y})$

$\sigma^*_{2p_z}$.

Physical chemistry Revision

≥ 14

σ_{2p_z} $(\pi_{2p_x} = \pi_{2p_y})$ $(\pi^*_{2p_x} = \pi^*_{2p_y})$

$\sigma^*_{2p_z}$

Physical chemistry Revision

VSEPR ⇒ Lone pair + b.p geo.

sp^2 NO_2^- ⇒ $\frac{5+6\times2+1}{8} = \frac{18}{8}$

V-Shape = 2+1

b.p l.p.

more than (8) ÷ 8

= 8 ÷ 2.

Physical chemistry Revision

Thermodynamics:

Enthalpy (H)

$$H = E + PV$$

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = \Delta E + P\Delta V + V\Delta P$$

$$\Delta H = \Delta E + \Delta n_g RT$$

Physical chemistry Revision

1st Law of Th.

$$q = \Delta E - w$$

$$\Delta E = q + w$$

+ve absorbed −ve evolved

Physical chemistry Revision

> Isothermal. $dT = 0$

$\Delta E = 0$, $\boxed{q = -w}$ ideal gas only

> Adiabatic. $q = 0$

$\Delta E = w$

Physical chemistry Revision

> Isobaric Process

$dP = 0$ $\quad q_p = \Delta H$.

(1) irreversible $\quad w = -P_{ext} \times \Delta V$

(2) Reversible $\quad w = -\int_{V_1}^{V_2} P\,dV$

Physical chemistry Revision

(3) Reversible Isothermal.

$$w = -2.303\, nRT \log \frac{V_2}{V_1}$$

(4) Adiabatic $W = \Delta E$

ideal gas $w = nC_v(T_2 - T_1)$

$$w = \frac{nR}{\gamma - 1}(T_2 - T_1)$$

Physical chemistry Revision

(5) $P_{ext} = 0$. ideal gas expand.

(6) Rev. > irrev.

Physical chemistry Revision

Entropy : (S) $\Delta S = \frac{q_{rev}}{T}$

① $\Delta S = 2.303\, n R \log \frac{V_2}{V_1}$

② $\Delta S = S_{Pdts} - S_{reactant}$

Physical chemistry Revision

(3) $\Delta S_{total} = \Delta S_{syst} + \Delta S_{surr.}$

(4) $\Delta S_{total} = \frac{q}{T_{system}} + \frac{-q}{T_{surr.}}$

(5) rev. adia $\Delta S = 0$.

Physical chemistry Revision

Change of fusion $\Delta S = \frac{\Delta H}{T}$

Vapourisation $\Delta S = \frac{\Delta H_v}{T}$

Physical chemistry Revision

Free Energy : (G)

$$G = H - TS$$

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

$$\Delta G = G_{pdts} - G_{reactants}$$

Physical chemistry Revision

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

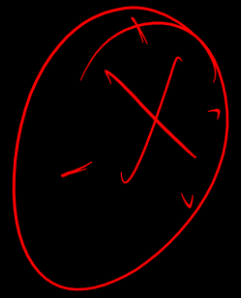
Physical chemistry Revision

ΔH	ΔS	$\Delta G_1 = \Delta H - T\Delta S$	Beh.
-ve	+ve	ΔG_1 = -ve	Spon.
+ve	-ve	+ve	non-spo
+ve	+ve	ΔG_1 = -ve ($\Delta H > T\Delta S$) ΔG_1 = +ve ($\Delta H < T\Delta S$)	spo non-spo
-ve	-ve	ΔG_1 = -ve ($\Delta H > T\Delta S$) ΔG_1 = +ve ($\Delta H < T\Delta S$)	Spon non-spon

Physical chemistry Revision

Equilibrium.

$$aA + bB \rightleftharpoons xX + yY$$



$$K_c = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

Physical chemistry Revision

$$K_p = \frac{(P_X)^x (P_Y)^y}{(P_A)^a (P_B)^b}$$

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

$$\Delta ng = n_p - n_r$$

Physical chemistry Revision

Factors

> Catalyst – ~~X~~

> $k' = 1/k$ reaction is reversed

> $k' = n\sqrt{k}$ " is divided by factor n

> $k' = k^n$ " is multiplied.

Physical chemistry Revision

> $K = k_1 \times k_2 \times k_3 \ldots k_n$.

(multiple Step)

Physical chemistry Revision

Eff. of temp

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

Physical chemistry Revision

Reaction Quotient

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

$Q = K_c$ (at eqm)

$Q < K_c$ (forward)

$Q > K_c$ (backward)

Physical chemistry Revision

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = -2.303\, RT \log K_c$$

$K_c = 1 \quad \Delta G^\circ = 0$ (eqm)

$K_c > 1 \quad \Delta G^\circ = -ve$ (forward)

$K_c < 1 \quad \Delta G^\circ = +ve$ (backward)

Physical chemistry Revision

Lechatlier Principle — balancing

- ↑ Conc
  - Rxt ⇒ forward
  - Pxt ⇒ backward.
- ↑ temp — Endo (Abs) ↓, temp-exo (evol)
- ↑ Pressure — ↓ n — ↓ P ⇒ ↑ n

PV=nRT

Physical chemistry Revision

No Effect – Catalyst, inert gas, Const Vol;

At Const P – ↑ n.

Physical chemistry Revision

Ionic Eqm:

Electrolytes
- Strong — $\alpha = 1$
- weak — $\alpha < 1$

α ↑ dissn Const

Physical chemistry Revision

- Arrhenius
  - Acid – H^+ Producer
    - HCl, H_2SO_4
  - Base – produces OH^-
- Bronsted-Lowry
  - Acid – H^+ donor
  - Base – H^+ Acceptors
    - $:NH_3 \rightarrow NH_4^+$

Physical chemistry Revision

Lewis
- Acid - e⁻ pair acceptors
  - BF_3, $AlCl_3$
- Base - e⁻ pair donors
  - NH_3, H_2O, F^-

Physical chemistry Revision

- Common ion Effect

Suppression of diss^{n}.

Physical chemistry Revision

1. $kIA + SB \quad - K_h = \frac{K_\omega}{K_a} \qquad h = \sqrt{\frac{K_h}{C}}$

$$P_H = \frac{1}{2}\left[Pk_\omega + Pk_a + \log C\right]$$

Physical chemistry Revision

(2) SA + WB — Cationic ✓

- pH < 7 ✓ $K_h = \frac{K_w}{K_b}$

- $h = \sqrt{\frac{K_h}{C}}$

$$pH = \frac{1}{2}\left[pK_w - pK_b - \log C\right]$$

Physical chemistry Revision

(3) WA + WB $\Rightarrow$ both $pH = 7$ $(K_a = K_b)$

$$K_h = \frac{K_w}{K_a K_b}$$

$$h = \sqrt{K_h}$$

$$pH = \frac{1}{2}\left[pK_w + pK_a - pK_b\right]$$

Physical chemistry Revision

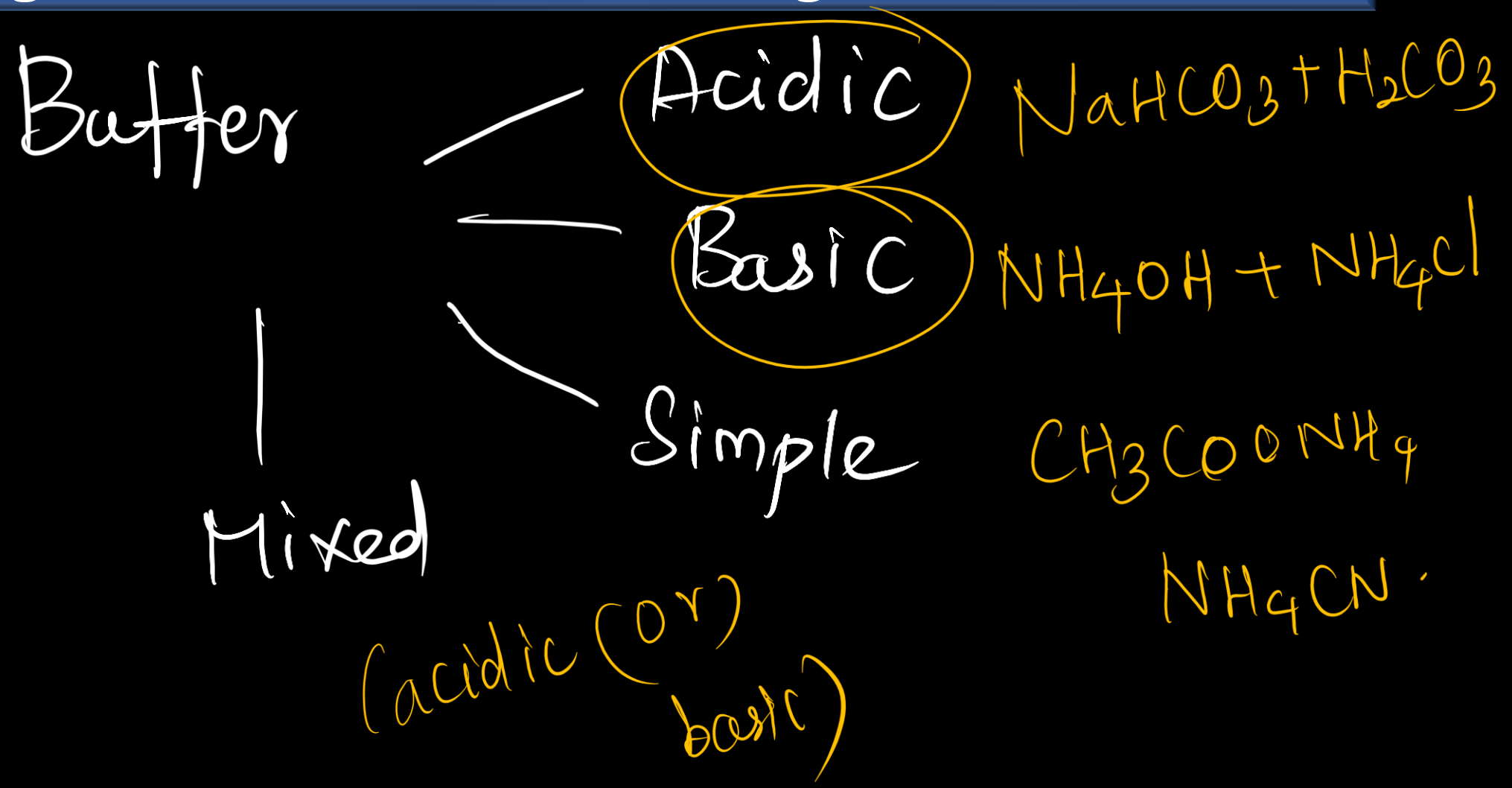
1) AB $\quad S = \sqrt{K_{sp}} \quad K_{sp} = S^2$

2) AB_2 $\quad S = \sqrt[3]{K_{sp}/4} \quad K_{sp} = 4S^3$ ✓

3) A_2B $\quad K_{sp} = 4S^3$ ✓

4) A_3B_2 $\quad K_{sp} = 108S^5$ ✓

Physical chemistry Revision



Physical chemistry Revision

Ostwald's dilution Law (weak electrolyte)

$$K = \frac{C\alpha^2}{1-\alpha}$$

$\alpha < 1$

Physical chemistry Revision

Acidic buffer $= pH = pKa + \log \frac{[salt]}{[Acid]}$

Basic buffer $= pOH = pK_b + \log \frac{[salt]}{Base.}$

B. Capacity $= \frac{n}{\Delta pH}$

$pH + pOH = 14$

Physical chemistry Revision

Kinetics

Rate of disappearance $= -\frac{d[A]}{dt}$

Rate of appearance $= +\frac{d[A]}{dt}$

Physical chemistry Revision

Order

$mA + nD \longrightarrow C$

$$\frac{dx}{dt} = k[A]^x[D]^y$$

$x+y$

> T, Catalyst, Nat. of Reactant

Physical chemistry Revision

Zero Order

$H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$.

$$[A]_t = [A]_0 - kt$$

mol $L^{-1} S^{-1}$

Half-life $t_{1/2} = \dfrac{[A]_0}{2t}$

Physical chemistry Revision

1st Order

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

S.I

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

Physical chemistry Revision

Ac. Energy . (Excess Energy)

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

→ Ac.t energy

→ temp.

→ Preexp. factor

Physical chemistry Revision

Temp Co-efficient

$$\mu = \frac{K_{T+10}}{K_T}$$

273

283.

> Catalyst & Nature of reactant

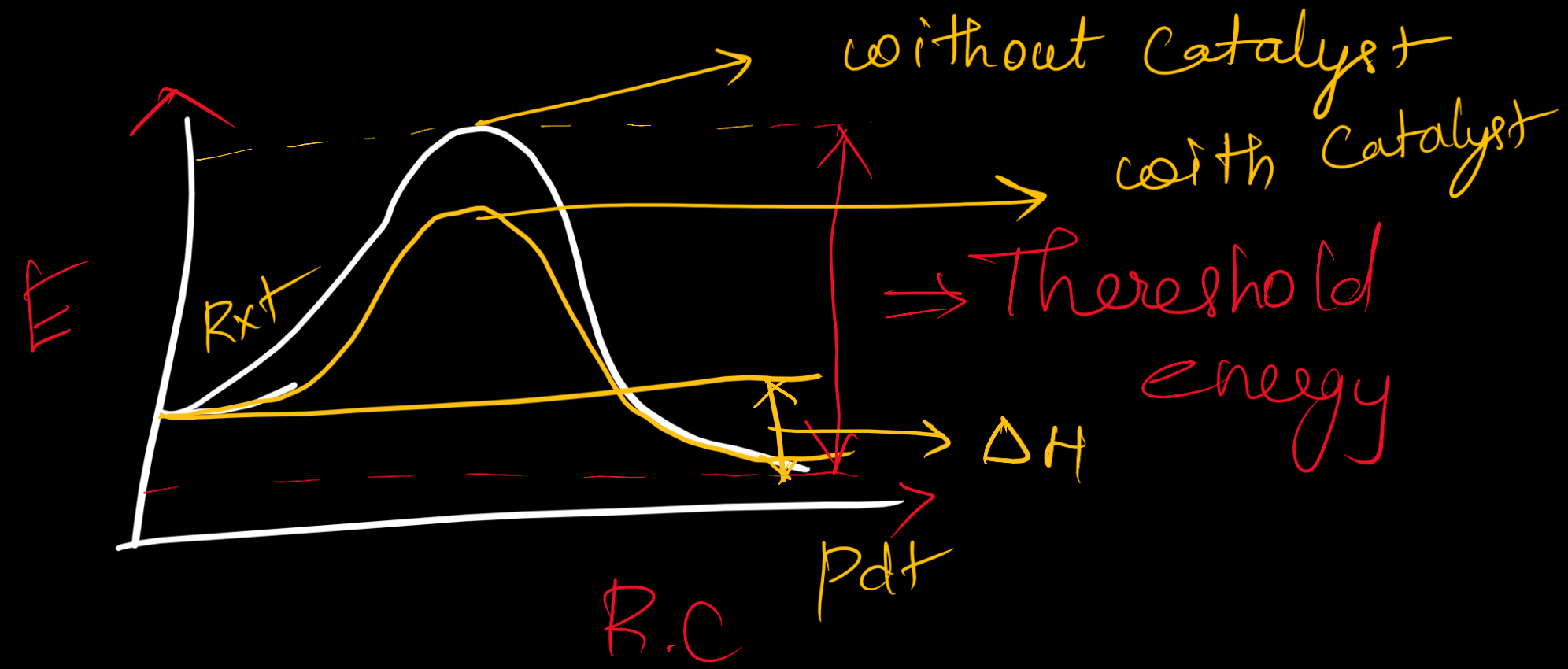
Physical chemistry Revision

Collision theory

> threshold energy

> Proper Orientation

Physical chemistry Revision



Physical chemistry Revision

Threshold energy = P.E + A.E

$$\Delta H = H_p - H_R$$

$$= (Ea)_f - (Ea)_b$$

Physical chemistry Revision

Solutions

Raoult's Law.

$$P_A = x_A P_A^\circ$$

$$P_B = x_B P_B^\circ$$

Physical chemistry Revision

Volatile

$$P_T = P_A + P_B$$

Non-Volatile.

$$\frac{P^\circ - P_S}{P_0} = \frac{n_2}{n_1 + n_2}$$

Physical chemistry Revision

Osmotic Pressure

$\pi = CRT$

$R \rightarrow 0.0821\ L\,atm\,K^{-1}$

$C \rightarrow$ Molar Conc.

Physical chemistry Revision

$\pi_1 = \pi_2$ Isotonic $\Rightarrow$ Same Os. pressure

Hypotonic $\Rightarrow$ $\downarrow$ Os. pressure.

Hypertonic $\Rightarrow$ $\uparrow$ Os. pressure.

Physical chemistry Revision

1. Elevation in b.pt

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

$m \longrightarrow$ molality.

Physical chemistry Revision

2. Dep. in F. pt

$\Delta T_f = K_f \times m$ → Molality

↳ molal depression Const

Physical chemistry Revision

3. $K_b = \frac{RT_b^2}{1000 \times l_v}$ → latent heat

$K_f = \frac{RT_f^2}{1000 \times l_f}$

Physical chemistry Revision

③ Lowering of V.P.

④ OSmotic Pressue.

Physical chemistry Revision

Van't Hoff (i)

$$i = \frac{\text{Observed Value}}{\text{Calcul. Value}} = \frac{M_{cal}}{M_{obs.}}$$

$$MM \propto \frac{1}{\text{coll. prop.}}$$

Physical chemistry Revision

$$\Delta T_b = i\, k_b\, m$$

$$\Delta T_f = i\, k_f\, m$$

$$\pi = i \frac{n}{V} RT \qquad \left(C = \frac{n}{V} \right)$$

Physical chemistry Revision

Assn $i^{\circ} = 1 - \alpha + \frac{\alpha}{n}$

$$\alpha = \frac{1 - i^{\circ}}{1 - \frac{1}{n}} = \frac{1 - i}{\frac{n-1}{n}}$$

Physical chemistry Revision

$i > 1$ dissn

$i < 1$ Assn.

NaCl, $CaCl_2$ ⇒ Remove Snow

Ethylene glycol ⇒ Radiator.

Physical chemistry Revision

Henry's Law:

$$m \propto P$$

$$x_A = k_H P_A$$