

Mole concept & stoichiometry

- Relative atomic mass (of an element) : weighted average mass of one atom of the element compared to $\frac{1}{12}$ the mass of a ^{12}C atom
- Relative isotopic mass (of an isotope) : mass of an atom of the isotope compared to $\frac{1}{12}$ the mass of a ^{12}C atom
- Relative molecular mass (of an element/compd) : weighted average mass of a molecule of the element / compound compared to $\frac{1}{12}$ the mass of a ^{12}C atom
- Relative formula mass (of a compound) : weighted average mass of a formula unit of the compound compared to $\frac{1}{12}$ the mass of a ^{12}C atom.
- One mole contains exactly 6.02×10^{23} elementary entities
- Empirical formula : simplest formula that shows the relative number of atoms of each element present in a compound
- Molecular formula : formula that shows the actual number of atoms of each element present in one molecule of a compound

Gases

Assumptions of ideal gas :

- volume of ideal gas particles is negligible as compared to the volume of the container
 - There are no intermolecular forces of attraction between the particles of an ideal gas
 - collisions between the particles of an ideal gas are perfectly elastic
 - Gas particles are in rapid, continuous and random motion
 - Average kinetic energy of the particles is proportional to their absolute temperature
- } MOST ** IMPORTANT

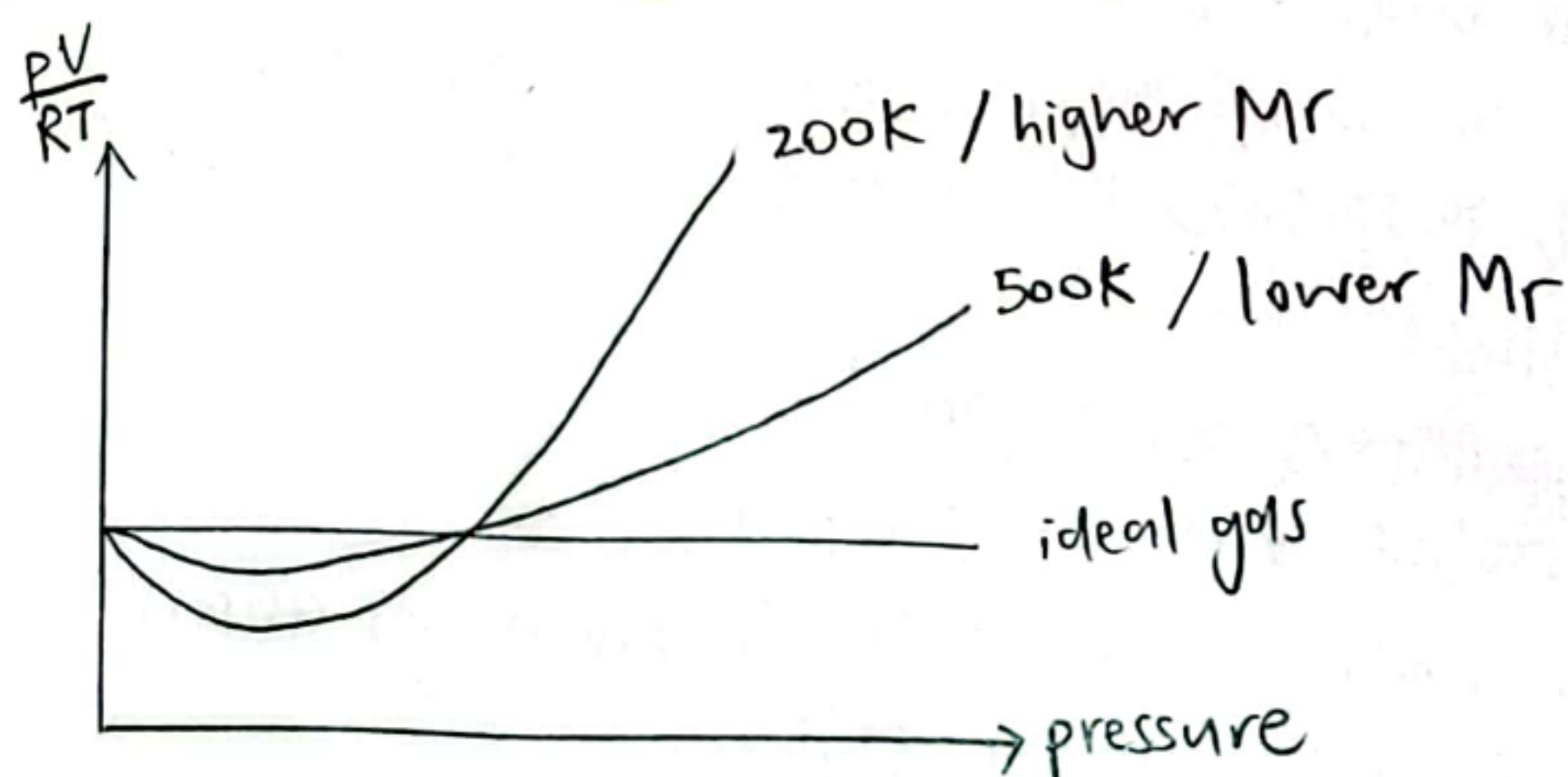
Conditions for more ideal gas :

① Higher temperatures

↳ particles have higher avg. KE → sufficient energy to overcome intermolecular FoA → intermolecular FoA less significant

② Lower pressure

↳ volume of container ↑ → particles are far apart → intermol. FoA less significant
→ vol. of particles become less significant compared to volume of container



Atomic structure

- Isotope: atoms of same element with same atomic number but different nucleon number
- Nucleon number: total number of protons and neutrons in the nucleus of an atom

Ionisation Energy across the period:

- no. of protons $\uparrow$, nuclear charge $\uparrow$
- successive e^- added to same outermost shell, shielding effect remains approx. the same
- effective nuclear charge $\uparrow$
- net attraction between nucleus and outermost electron $\uparrow$
- more energy req. to remove outermost $e^- \rightarrow \therefore 1^{st}$ IE generally $\uparrow$ across the period

Exceptions: 1^{st}

- Al smaller 1^{st} IE than Mg (ns^2 vs $ns^2 np^1$)
Mg: $1s^2 2s^2 2p^6 3s^2$ Al: $1s^2 2s^2 2p^6 3s^2 3p^1$
- * 1^{st} IE of Mg is lower than 1^{st} IE of Al, $\therefore$ less energy req. to remove $3p$ e^- as it is removed from a higher energy $3p$ subshell
[$\therefore 3s$ orbital lower energy, closer to nucleus $\rightarrow$ provide some shielding for $3p$ e^-] (additional)
- S smaller 1^{st} IE than P
S: $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$ P: $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
- 1^{st} IE of P lower than 1^{st} IE of S, $\therefore$ less energy req. to remove paired $3p_x$ e^- in P as it experiences interelectron repulsion

Ionisation Energy Down the Group / Between Periods

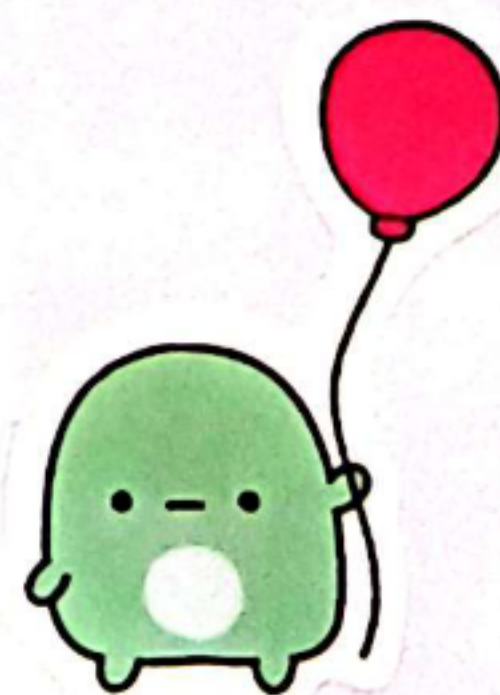
- no. of protons $\uparrow \rightarrow$ nuclear charge $\uparrow$
- no. of electron shell $\uparrow$ / — has 1 more electron shell than — $\rightarrow$ shielding effect increases significantly
- outermost e^- further ^{away} from nucleus
- net attraction between nucleus and outermost $e^- \downarrow$ *NOTE: NO ENC
- less energy req. to remove outermost $e^- \rightarrow \therefore 1^{st}$ IE generally $\downarrow$ DTG / $\downarrow$ significantly from — to —

Why Successive Ionisation Energy $\uparrow$

- no. of protons remain the same $\rightarrow$ constant positive nuclear charge
- more e^- are removed $\rightarrow$ no. of e^- in outermost shell $\downarrow \rightarrow$ shielding effect $\downarrow$
- effective nuclear charge $\uparrow$
- net attraction between nucleus and outermost $e^- \uparrow$
- more energy req. to remove outermost $e^- \rightarrow \therefore$ successive IE $\uparrow$

Atomic / Ionic radius

- Same as IE explanation across period
- Atomic / Ionic radius $\downarrow$ across the period
- Sharp $\uparrow$ in ionic radius from cation to anion, as anion contains 1 more e^- shell than cation



Chemical Bonding

- Ionic bond: electrostatic attraction between oppositely charged ions (state ions). Ions are formed by a complete transfer of electrons from a metal to a non-metal
- covalent bond: electrostatic attraction between a shared pair of e^- and positively charged nuclei
- metallic bond: electrostatic attraction between a lattice of positive ions and sea of delocalised valence electrons

VSEPR Theory: of the central atom

- Electron pairs in valence shell are located as far apart from one another as possible to minimise repulsion
- Repulsion between electron pairs increase in the order:
 $\hookrightarrow$ bond pair - bond pair < bond pair - lone pair < lone pair - lone pair

Strength of bonds

- covalent bond

- order of importance {
1. Bond order: triple bond > double bond > single bond
 $\hookrightarrow$:: of additional side on overlap of p orbitals to form π bond in multiple bonds $\rightarrow$ stronger bond
 2. Atomic radius: shorter atomic radius $\rightarrow$ shorter bond length $\rightarrow$ bond stronger
 $\hookrightarrow$:: shorter bond length $\rightarrow$ greater degree of orbital overlap $\rightarrow$ stronger bond
 3. Bond polarity: polar bond stronger than non-polar
 $\hookrightarrow$:: polar bonds have additional electrostatic forces of attraction from partial charge
 4. Type of hybrid orbital: graphite C-C > diamond C-C
 $\text{sp}^2\text{-sp}^2$ $\text{sp}^3\text{-sp}^3$
 $\hookrightarrow$ C-C in graphite involve head on overlap of $\text{sp}^2\text{-sp}^2$ orbital
 $\hookrightarrow$ more s character $\rightarrow$ greater degree of orbital overlap $\rightarrow$ stronger bond

- ionic bond

- Depends on lattice energy, $|LE| \rightarrow$ more exothermic LE, stronger ionic bond

$$\text{Factors: } |LE| \propto \frac{|z^+z^-|}{r_+ + r_-} \left\{ \begin{array}{l} \text{- product of ionic charges} \\ \text{- interionic radius} \end{array} \right.$$

- metallic bond

1. No. of delocalised valence e^- per cation $\rightarrow$ stronger electrostatic FoA $\rightarrow$ stronger bond
2. Size of cation $\rightarrow$ higher charge density $\rightarrow$ stronger electrostatic FoA $\rightarrow$ stronger bond

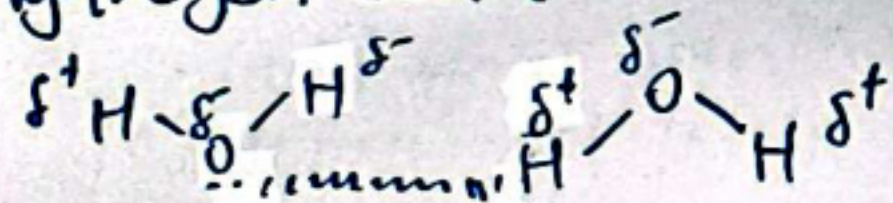
- id-id

1. size of electron cloud: greater size $\rightarrow e^-$ cloud more easily polarised $\rightarrow$ stronger id-id
2. shape of molecule:
 $\hookrightarrow$ more spherical/branching: less surface area of contact $\rightarrow$ weaker id-id
 $\hookrightarrow$ more elongated/less branching: more surface area of contact $\rightarrow$ stronger id-id
3. Packing (for solid state/mp only) $\rightarrow$ packed more closely $\rightarrow$ stronger id-id

- pd-pd

- Polarity of covalent bonds: $\uparrow$ polarity of covalent bonds $\rightarrow$ stronger electrostatic FoA between higher δ^+/δ^- dipole $\rightarrow$ stronger pd-pd

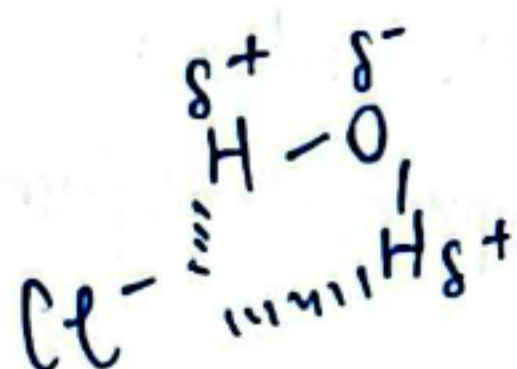
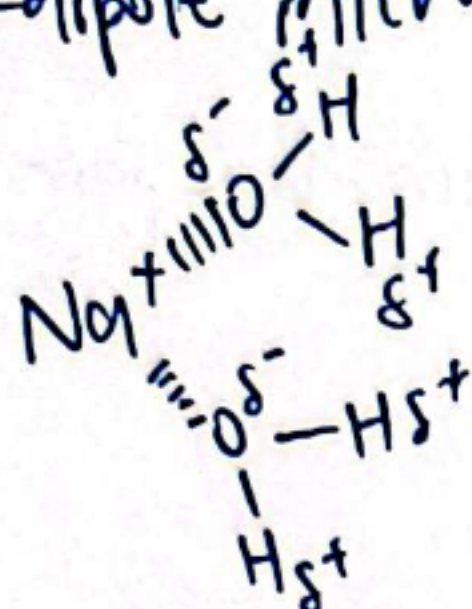
- hydrogen bond



1. Extensiveness of H bonding (avg no. of H bonds ^{per} molecule)
 - ↳ larger no. of H bond per molecule
 - ↳ intramolecular H bonding → ↓ extensiveness

2. Electronegativity ($F > O > N$)

- ion-dipole interaction



- ↑ charge density of ion → stronger
- ↳ ↓ ionic radius } stronger bond
- ↳ ↑ ionic charge

Physical Properties

- mp/bp

1. structure
2. bonding
3. particles

4. high/low amt of energy req to overcome ...

- giant ionic lattice (amino acids / NaCl)

→ strong ionic bonds between cations & anions

$$|U| \propto \frac{|z^+ z^-|}{r_1 + r_2}$$

- giant metallic lattice (mg / Na)

→ strong metallic bond between fully charged metal cation and sea of delocalised valence electrons

- giant molecular structure (diamond/graphite/siO₂)

→ strong covalent bonds between atoms throughout the structure

- simple molecular structure (CH₄, NH₃, AlCl₃)

→ - weak vdW / pol-pol forces of attraction between molecules
 - strong hydrogen bonds between molecules

- electrical conductivity

- presence of mobile charge carriers

↳ there are delocalised valence e⁻ / or mobile ions to act as charge carriers

- solubility

- energy released when (solute) forms — bond with (solvent)

- provides sufficient / insufficient energy

- to break — bonds between (solute) and — bonds between (solvent)

Ionic bond w/ covalent character $\boxed{+O-}$

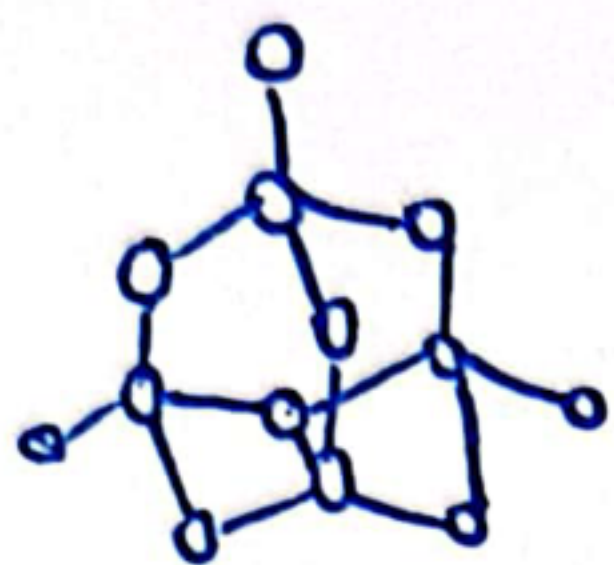
1. high ionic charge / small ionic radius of CATION
2. ↑ charge density and ∴ polarising power
3. distort/polarise e⁻ cloud of anion to greater extent
4. introducing a degree of covalent character

OR

1. large e⁻ cloud of ANION
2. more easily polarised by cation
3. introducing a degree of covalent character

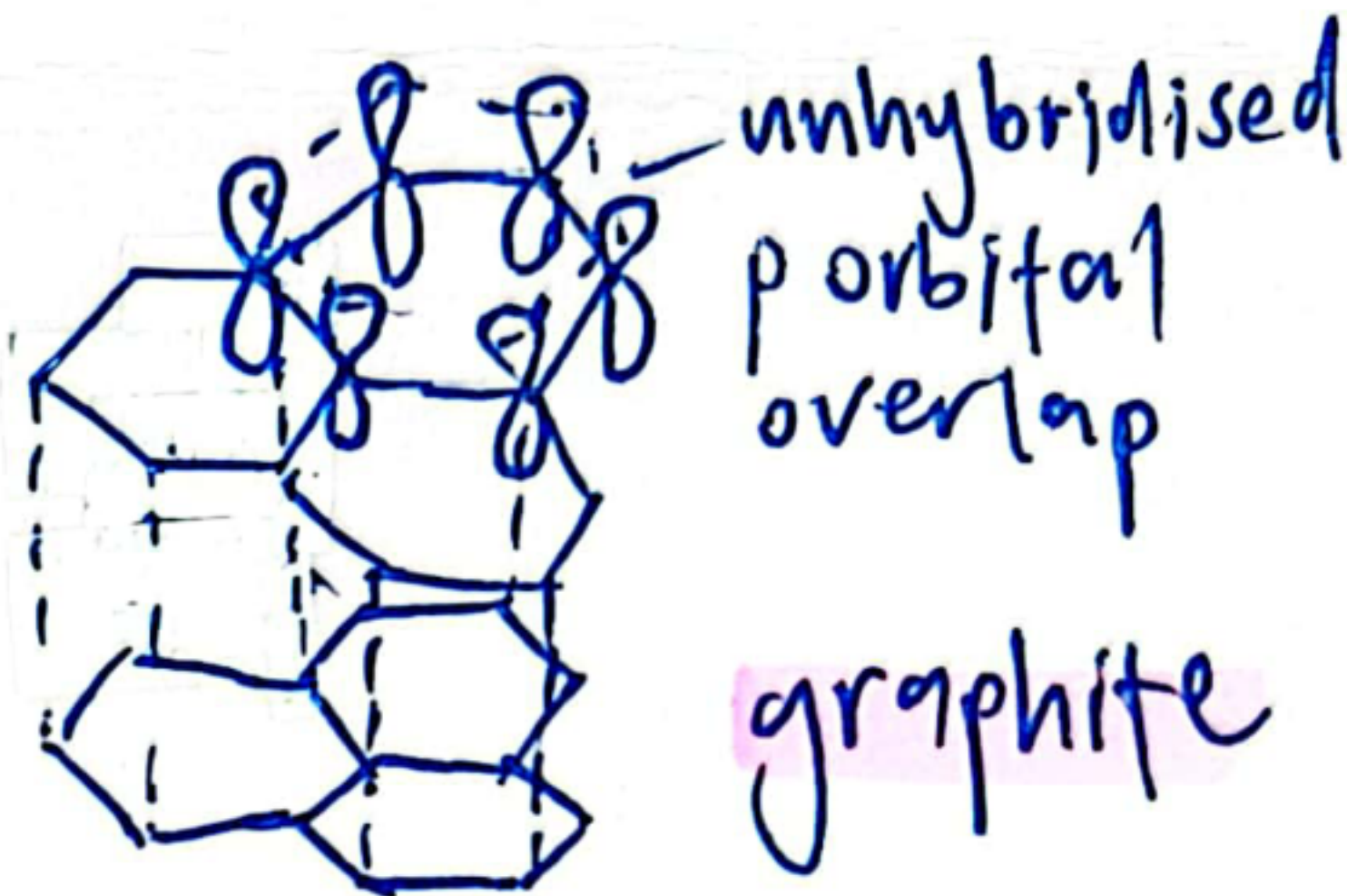


lattice structures



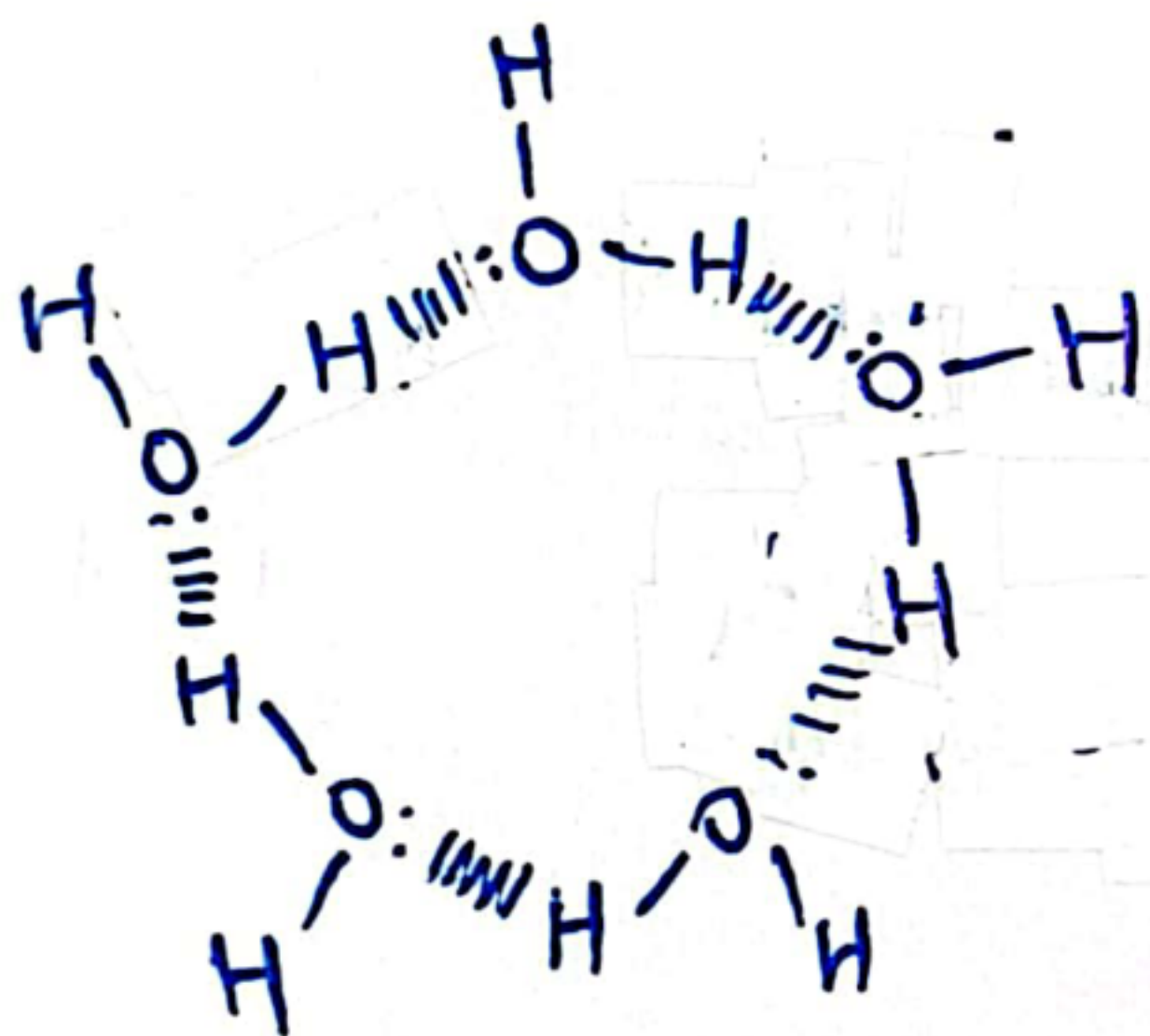
diamond

giant lattice w/ each C atom covalently bonded to 4 other C atoms in a tetrahedral arrangement w/ strong C-C bond



graphite

- giant covalent lattice w/ layers of atoms w/ each C atom covalently bonded to 3 other C atoms in a trigonal planar arrangement
- strong C-C bond, w/ weak id-id FoA btwn layers

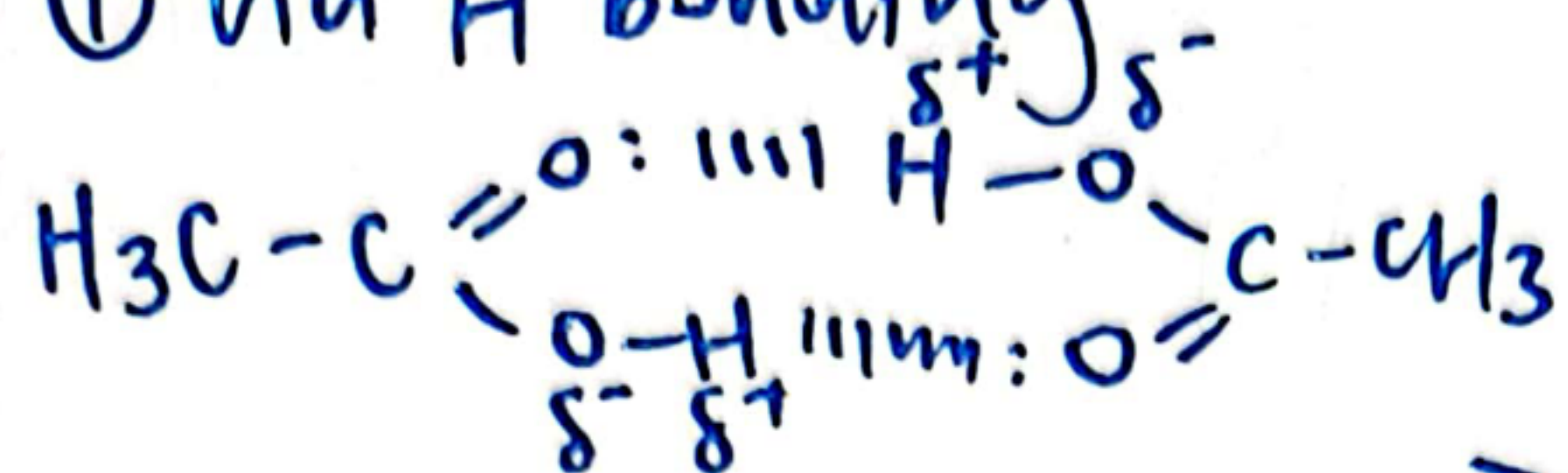


ice

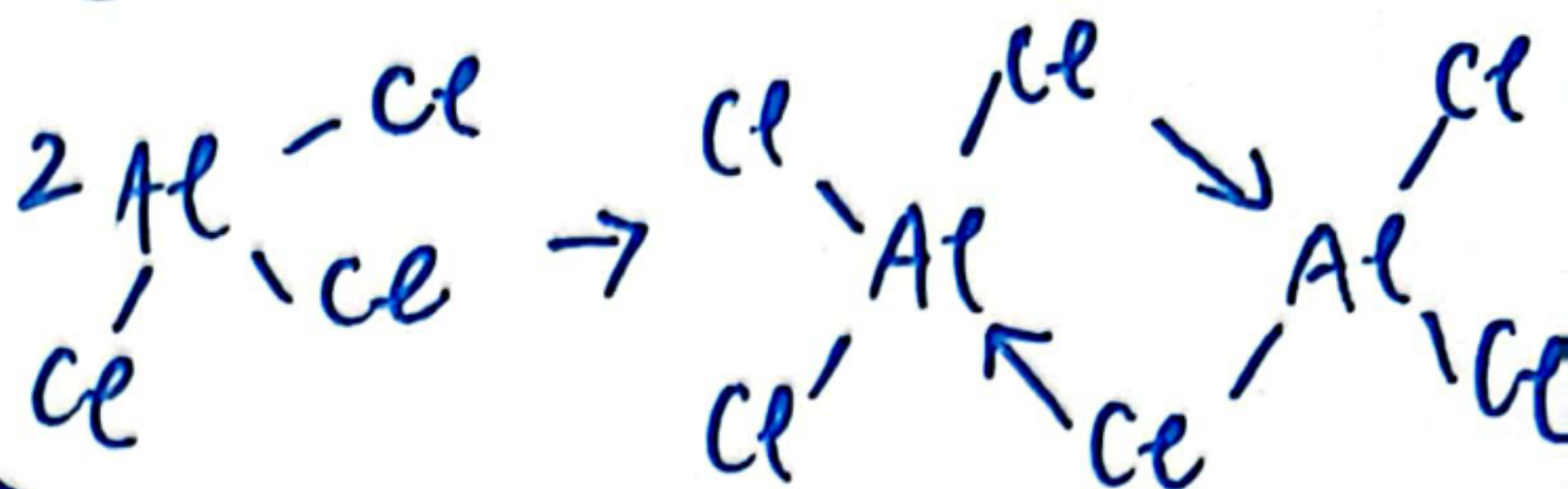
- giant lattice of H_2O molecules, w/ each O atom surrounded tetrahedrally by 4 H atoms (2 via covalent bond, 2 via H bond)
- open lattice str $\rightarrow$ empty spaces btwn H_2O mol.
 $\therefore \text{H}_2\text{O}(s)$ less dense than $\text{H}_2\text{O}(l)$
- strong O-H covalent bond, relatively strong H bond btwn H_2O molecules

Dimerisation

① via H bonding



② via dative bond

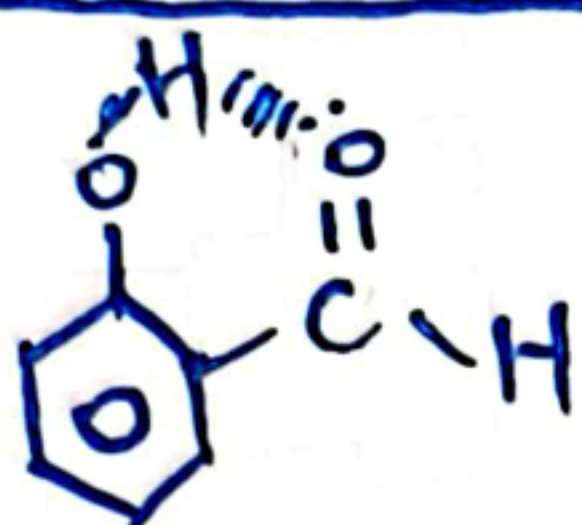


③ via cov bond w/ radicals

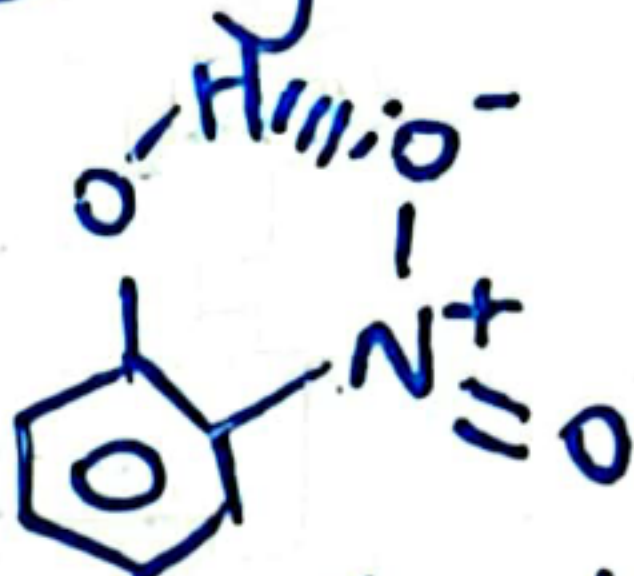


CH₃COOH forms H bond w/ another molecule of CH₃COOH, forming dimer w/ Mr 120.0 in non-polar organic solvents

Intramolecular H bonding



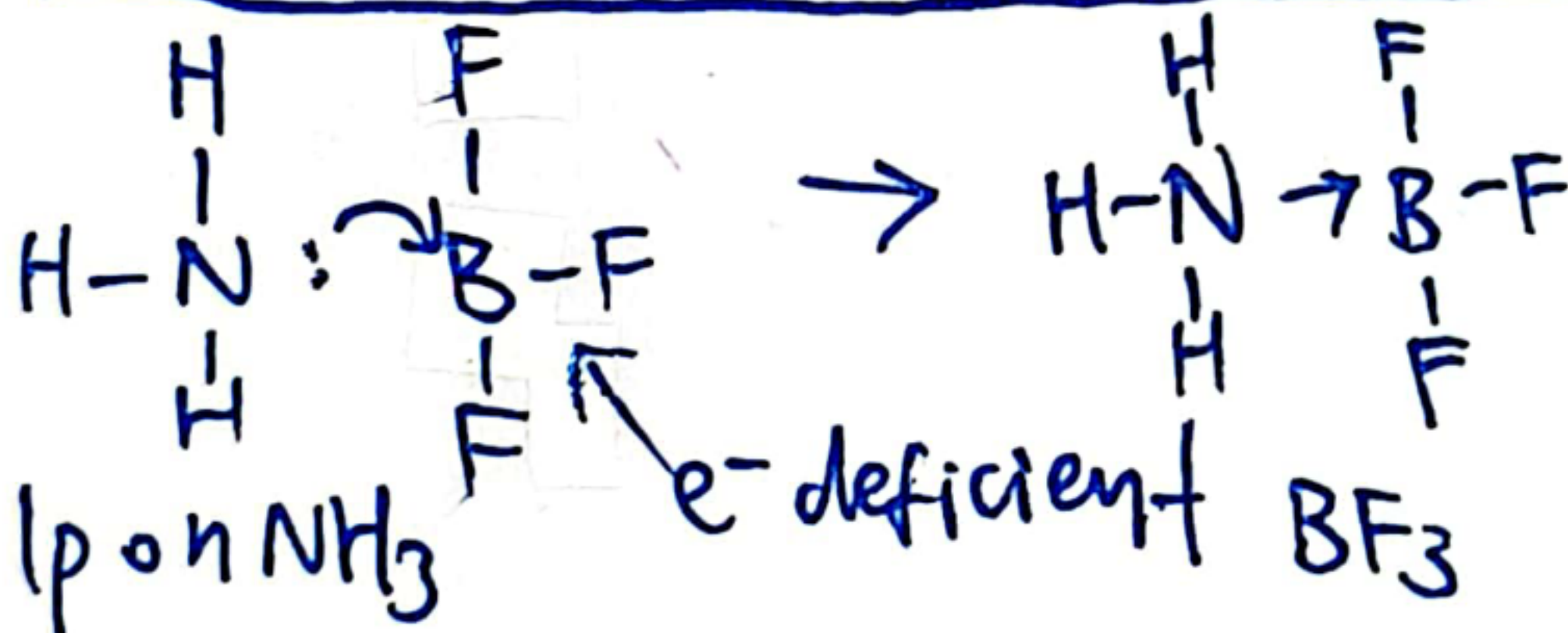
2-hydroxybenzaldehyde



2-nitrophenol

- due to close proximity of OH & — grps, intramol. H bond can be formed
- intermolecular H bonding less extensive
- ∴ less energy to overcome less extensive intermol. H bonding.

Dative bond in e⁻ deficient atoms



Chemical Energetics

- $\Delta H_{\text{rxn}}^\circ$ is the energy change when molar quantities of reactants as stated in the thermochemical equation react under std. conditions
- ΔH_f° is the energy change when one mole of a compound is formed from its constituent elements in their standard states under std. conditions $1 \text{ elements } () \rightarrow 1 \text{ cpd } ()$
- ΔH_c° is the energy change when one mole of a substance is completely burnt in excess O_2 under std. conditions $1 \text{ cpd} + n \text{ O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ ($\Delta H_c = -ve$, except N_2 $\because \text{N} \equiv \text{N}$ extremely strong)
- $\Delta H_{\text{hyd}}^\circ$ is the energy change when one mole of gaseous ions is surrounded by H_2O molecules, forming a solution at infinite dilution under std conditions ($\Delta H_{\text{hyd}} = -ve$, $\because$ of bonds formed btwn gaseous ions and dipoles at H_2O molecules)
 $|\Delta H_{\text{hyd}}| \propto \frac{|Z|}{r}$ ← factors that affect $1 \text{ ion}(g) + aq \rightarrow 1 \text{ ion}(aq)$
 str of ion-dipole interaction
- $\Delta H_{\text{sol}}^\circ$ is the energy change when one mole of cpd is dissolved by solvent such that further dilution produces no more heat change, under standard conditions
 $\Delta H_{\text{sol}} = \Delta H_{\text{hyd}} - LE$: $1 \text{ cpd} + aq \rightarrow \text{ion}(aq) + \text{ion}(aq)$
- ΔH_n° is the energy change when one mole of H_2O is formed during the neutralisation of an acid and an alkali, under std. conditions $\text{acid} + \text{base} \rightarrow \text{salt} + 1 \text{ H}_2\text{O}$
 $(\Delta H_n = -ve, \Delta H_n = -57 \text{ kJ mol}^{-1} \text{ for SA/SB rxn})$
- $\Delta H_{\text{atm}}^\circ$ is the energy change when one mole of gaseous atoms is formed from its elements, under standard conditions $\text{element} \rightarrow 1 \text{ atom}(g)$
 $(\Delta H_{\text{atm}} = +ve, \text{ bonds are broken } \therefore, \text{ no bonds formed})$
- **Bond Energy** is the energy absorbed to break one mole of covalent bond between two atoms in gaseous state ($BE = +ve$, covalent bonds broken, no bonds formed)
 $1 \text{ covalent cpd} \rightarrow 2 \text{ atoms}$
- **Ionisation Energy** is the energy change when one mole of electrons is removed from one mole of gaseous atoms to form one mole of singly charged ^{gaseous} cations
 $X^n(g) \rightarrow X^{(n+1)+}(g) + e^-$ ($\Delta H = +ve$, energy absorbed to overcome electrostatic attraction btwn e^- & nucleus to remove e^-)
- **Electron Affinity** is the energy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous anions
 $X^n(g) + e^- \rightarrow X^{(n-1)-}(g)$ ($1^{\text{st}} \text{ EA } \Delta H = -ve$, 2^{nd} and more EA $\Delta H = +ve$
 $\because$ of energy to overcome repulsion btwn e^- & anion)
- **Lattice Energy** is the energy change when one mole of ionic cpd is formed from its constituent gaseous ions at std conditions
 $\text{ion}(g) + \text{ion}(g) \rightarrow 1 \text{ ionic cpd}$ ($LE = -ve$, $\because$ energy evolved when ions come tog to form new bonds)
 $|LE| \propto \frac{Z^+ Z^-}{r_+ + r_-}$

Discrepancies for calculated ΔH

- ΔH determined experimentally
 - ↳ heat gain from surroundings (endo) / heat loss to surroundings (exo)
 - ↳ rxn does not occur rapidly enough for max T to be achieved before rxn mixture begins to return to room temp
- ΔH determined by BE
 - ↳ not in gaseous state + data booklet values is avg value
- LE
 - ↳ degree of covalent character
- $\Delta H_c \rightarrow$ insufficient $\text{O}_2 \rightarrow$ incomplete combustion

- Hess' Law: enthalpy change for a chemical rxn is the same regardless of the route the reaction takes, provided the initial states of the reactants and the final states of the products are the same.
- Entropy is the measure of disorder in a system

Factors affecting entropy

- Δ temperature
 - ↳ $\uparrow$ temp $\rightarrow$ system possesses more KE $\rightarrow$ more ways to distribute energy packets among particles $\rightarrow \uparrow$ disorder in system $\rightarrow \uparrow$ entropy
- mixing of particles
 - ↳ gas: more ways of arranging the gaseous particles $\rightarrow \uparrow$ disorder $\rightarrow \uparrow$ entropy $\rightarrow \Delta S = +ve$
 - ↳ dissolving: (solid) broken from orderly arrangement in solid lattice $\rightarrow$ can move around freely when dissolved $\rightarrow$ more ways of arranging particles $\rightarrow \uparrow$ disorder $\rightarrow \uparrow$ entropy $\rightarrow \Delta S = +ve$
- Δ phase (eg solid $\rightarrow$ liquid) $\rightarrow$ more ways to arrange particles $\rightarrow \uparrow$ disorder $\rightarrow \uparrow$ entropy $\rightarrow \Delta S = +ve$
- no. of particles (gases)
 - ↳ $\uparrow$ no. of particles $\rightarrow$ more ways to arrange molecules $\rightarrow \uparrow$ disorder $\rightarrow \uparrow$ entropy $\rightarrow \Delta S = +ve$
- Δ volume of gas
 - ↳ $\uparrow$ volume $\rightarrow$ more ways to arrange molecules $\rightarrow \uparrow$ disorder $\rightarrow \uparrow$ entropy $\rightarrow \Delta S = +ve$

Spontaneity ($\Delta G = \Delta H - T\Delta S$)

$\Delta G < 0$: spontaneous

$\Delta G > 0$: non-spontaneous

} Assumption:
 - ΔH & ΔS independent of temp.
 - valid so long no Δ phase

Effect of ΔT on ΔG

1. gives signs of ΔH , ΔS and $-T\Delta S$
2. $\Delta G = \Delta H - T\Delta S$
3. at high temp., $|T\Delta S| > |\Delta H|$ / $-T\Delta S$ becomes more +ve/-ve
4. $\therefore \Delta G$ becomes +ve/-ve at high temp.
5. rxn is more/ less spontaneous at high temp



$$\Delta G^\circ = -RT \ln K$$

Reaction Kinetics

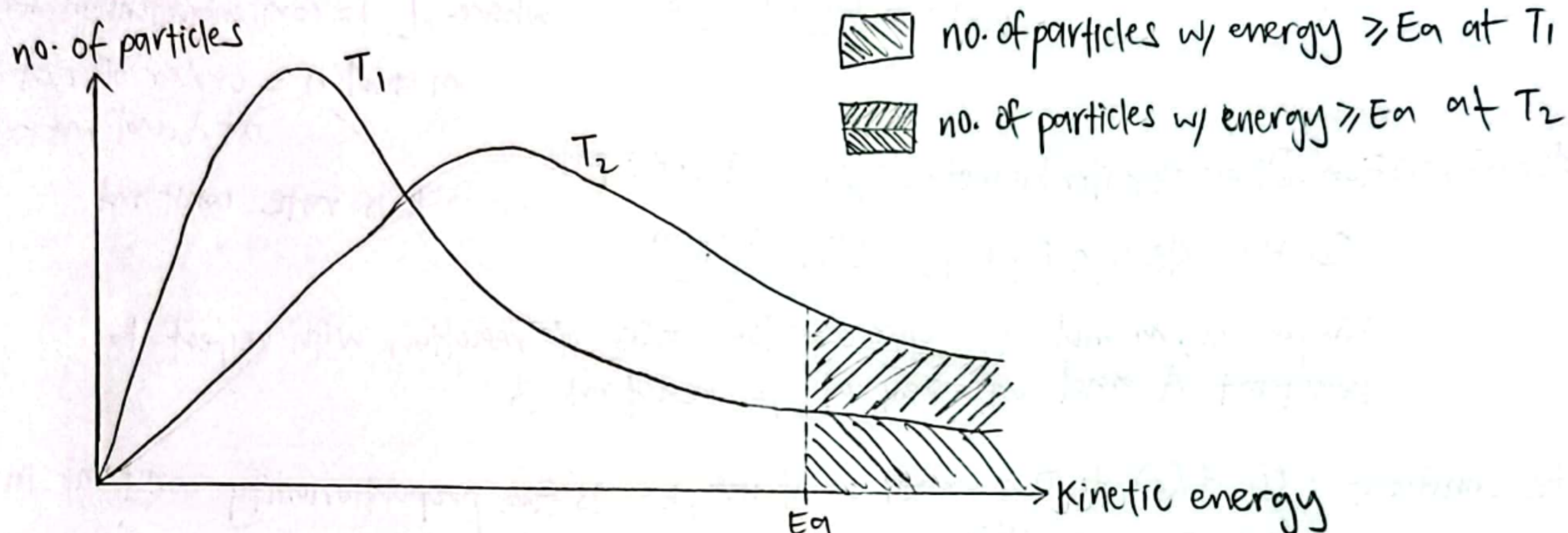
Factors affecting rate

- $\Delta [\text{reactant}]$

- $\uparrow [\text{]} \rightarrow$ reactant closer to one another $\rightarrow$ freq of effective collisions $\uparrow \rightarrow$ rate $\uparrow$
- Exceptions : - rxn is zero order wrt rxt
- catalyst already working at max capacity

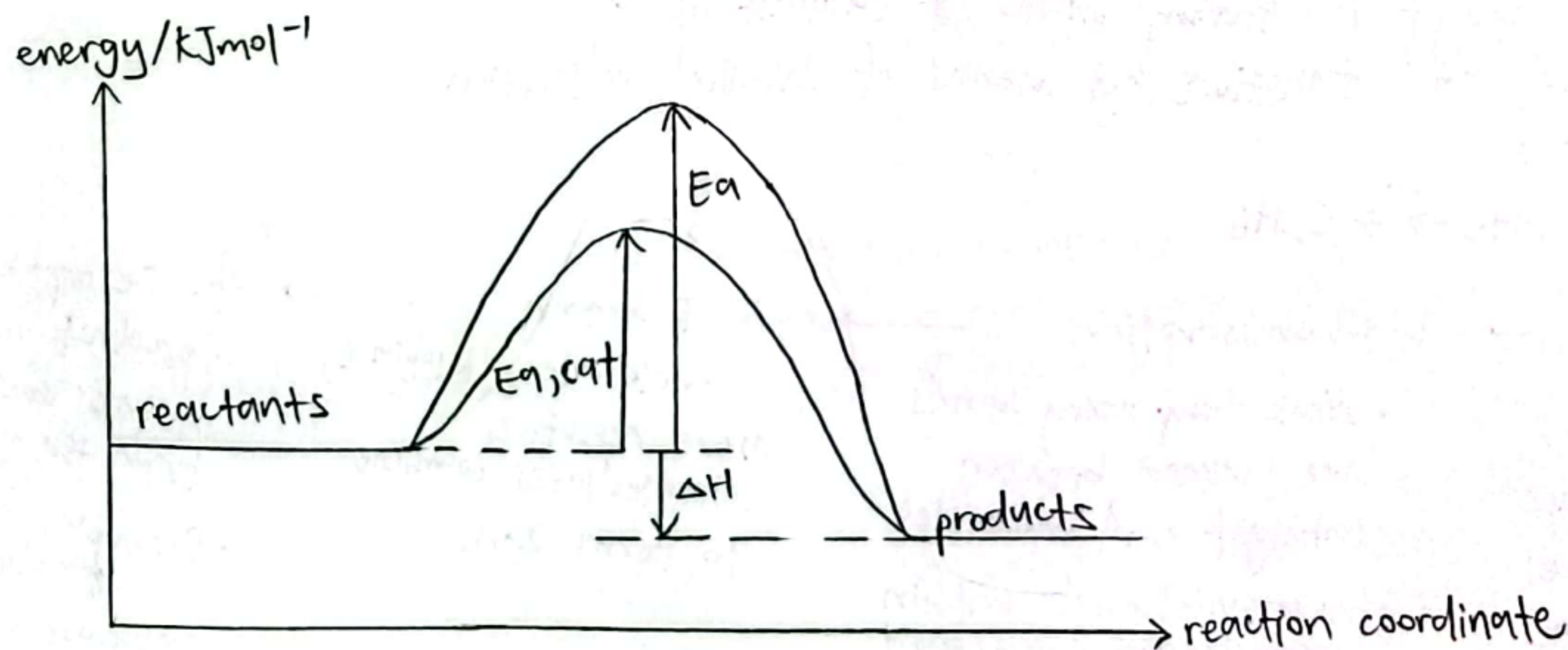
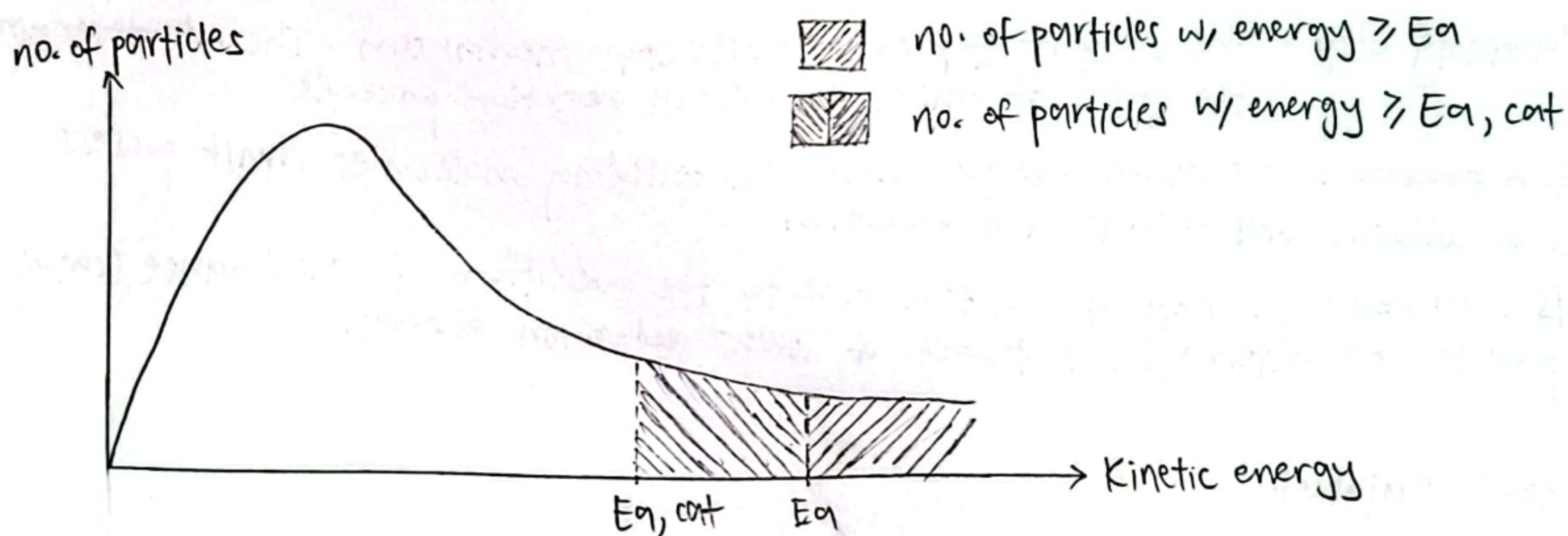
- ΔTemp

- temp $\uparrow \rightarrow$ avg KE $\uparrow \rightarrow$ more particles have energy $\geq E_a \rightarrow$ can be seen by the flattening of Maxwell-Boltzmann curve $\rightarrow$ freq of effective collisions $\uparrow \rightarrow$ rate const $\uparrow \rightarrow$ rate $\uparrow$



- Catalyst

- catalyst added $\rightarrow$ provides alternative pathway with lower $E_a \rightarrow \uparrow$ particles w/ energy $\geq E_a \rightarrow$ frequency of effective collisions $\uparrow \rightarrow$ rate const. $k \uparrow \rightarrow$ rate $\uparrow$



Factors affecting rate constant 'k'

Arrhenius equation: $k = Ae^{-\frac{E_a}{RT}}$

$E_a \rightarrow$ activation energy
 $T \rightarrow$ temperature

- Temperature $\uparrow \rightarrow e^{-\frac{E_a}{RT}} \uparrow \rightarrow k \uparrow$

- Catalyst $\rightarrow E_a \downarrow \rightarrow e^{-\frac{E_a}{RT}} \uparrow \rightarrow k \uparrow$

- Rate of reaction: change in concentrations of reactants or products per unit time
units: $\text{mol dm}^{-3} \text{ time}^{-1}$

- Rate equation: For a general rxn: $aA + bB \rightarrow \text{products}$

Rate equation is,

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

where $[] =$ concentrations in mol dm^{-3}

m and $n =$ order of rxn wrt
rxn A and wrt rxn B

k is rate constant

- Order of reaction: ① For the stoichiometric eqn: $aA + bB \rightarrow \text{pblts}$

② the rate eqn is, $\text{rate} = k[A]^m[B]^n$

The powers, m and n , represent the orders of reaction with respect to reactant A and with respect to reactant B

- rate constant: ① + ② + The rate constant, k , is the proportionality constant in the rate equation

- Half-life, $t_{1/2}$: time taken for the conc. of the reactant to fall to half of its original value
 $t_{1/2} = \frac{\ln 2}{k}$

- Rate determining step: The slowest step in a multi-step mechanism. The rds determines the speed at which the overall reaction proceeds

- Activation energy: minimum energy which the colliding molecules must possess before a collision will result in a reaction

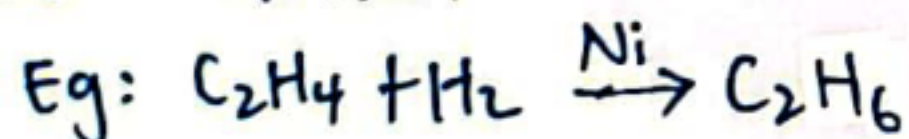
- Catalysis: increase in rate of reaction due to the addition of a substance (catalyst) which provides an alternative pathway of lower activation energy.

Heterogeneous Catalysis

- reactant and catalyst in different phase + catalysis defn

- usually a solid and functions by means of chemical adsorption

MODE OF ACTION



1. Diffusion



2. Chemisorption



3. Reaction



4. Desorption

- Reactant molecules, C_2H_4 & H_2 , diffuse towards the nickel catalyst surface
- Adsorb onto the surface of catalyst

- Weak temporary bonds are formed between catalyst and molecules
- covalent bonds within molecules weaken, lowering E_a

molecules dissociate; more reactive intermediates combine to form C_2H_6

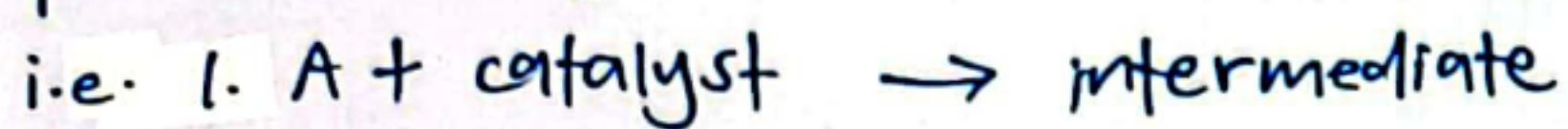
- product molecules break away from the surface
- Desorb away from catalyst surface

Homogenous Catalysis

- reactant and catalyst are in same phase + catalyst defn

MODE OF ACTION

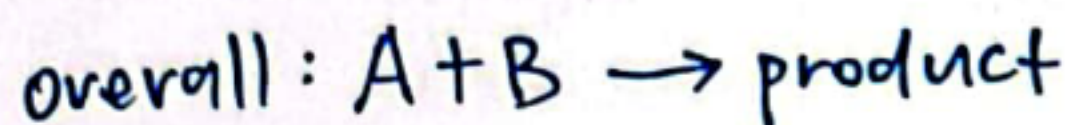
- A homogenous catalyst first forms an intermediate compound w/ one of the reactants which then reacts with the other reactant to form the final products & regenerate back the catalyst



Formation of intermediate



Regeneration of catalyst

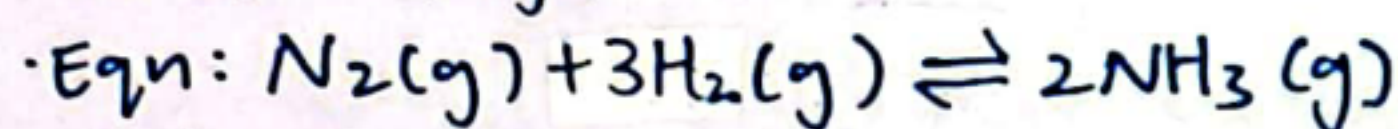


Examples for catalysis

Heterogenous

↳ Haber process

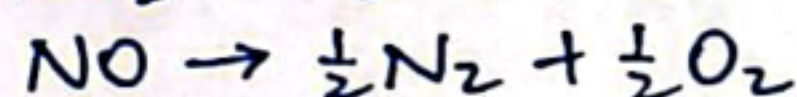
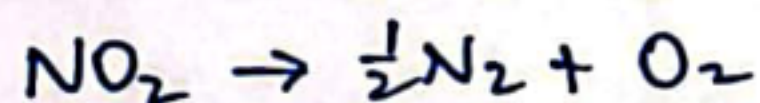
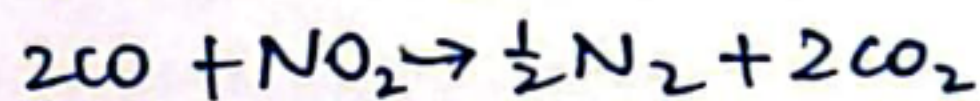
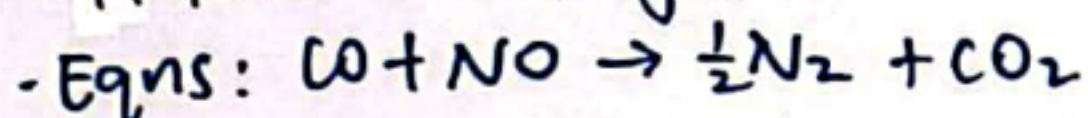
- Fe(s) catalyst



- mode of action

↳ Removal of oxides of nitrogen in exhaust gases from car engines

- platinum catalyst



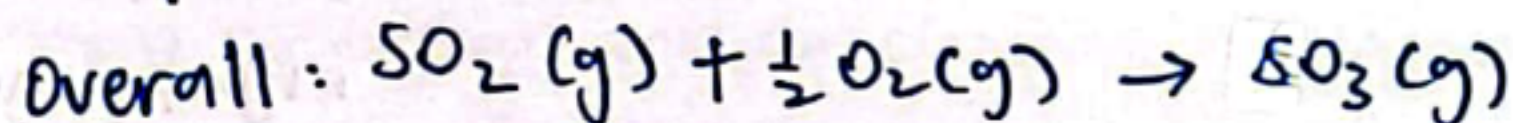
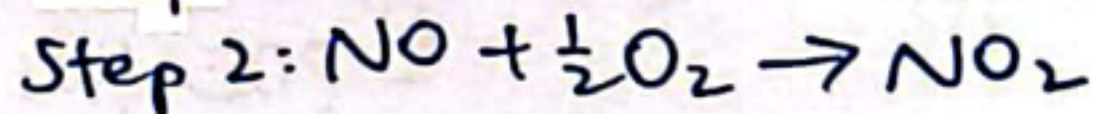
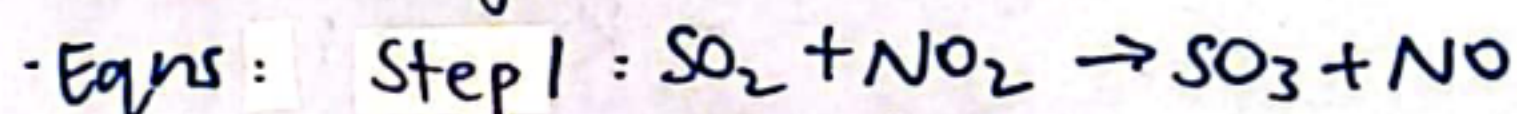
- mode of action

Homogenous

atmospheric

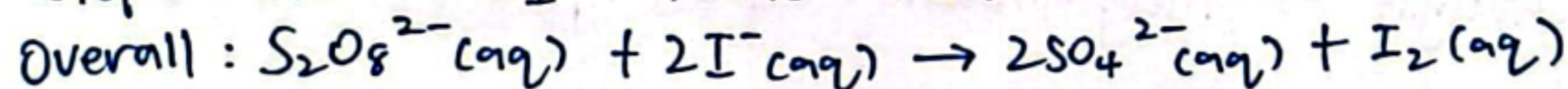
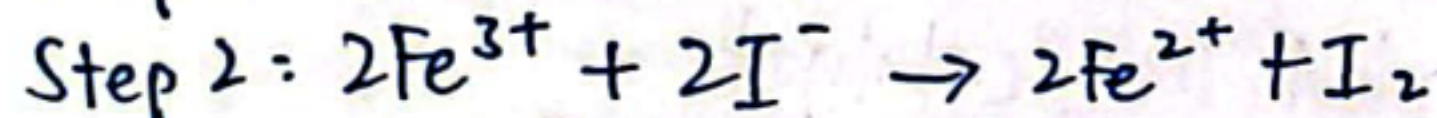
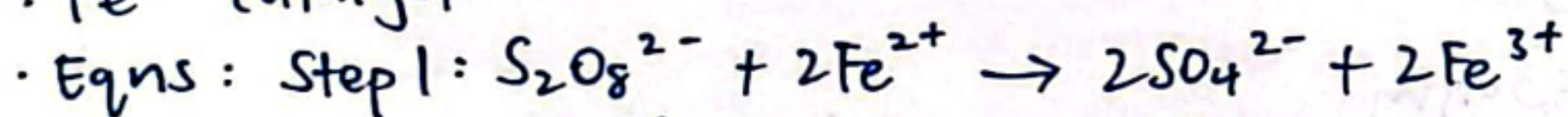
↳ Catalytic role of oxides of nitrogen in the oxidation of atmospheric SO_2

- NO_2 catalyst



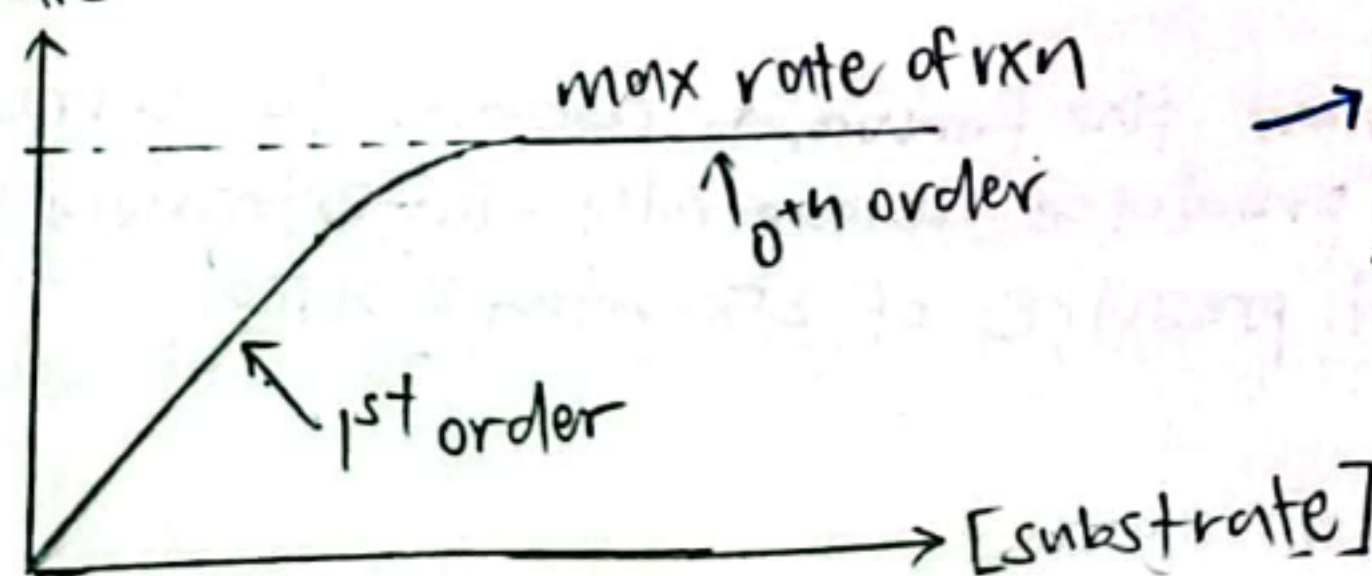
↳ Catalytic role of Fe^{2+} in $I^-/S_2O_8^{2-}$ reaction

- Fe^{2+} catalyst



Enzymes

- biological catalysts that catalyse biochemical reactions
- binds substrate at active site, in correct orientation → binding weakens bonds within substrate molecule, lowering E_a of reaction
- temp- and pH sensitive rate



→ at high substrate conc., the enzyme active sites are FULLY SATURATED ∴ max rate

Chem Equilibria

- **Reversible reaction**: a reaction that proceeds in both the forward and backward direction. The reaction contains quantities of all reaction species in the system
- **Dynamic equilibrium**: In a reversible system, dynamic equilibrium occurs when the rates of the forward and backwards reactions are the same. There is no net change in the concentration of the reactants and products
- **Le Chatelier's principle** states that when a stress is applied to a reversible system at equilibrium, the position of equilibrium will shift to minimise the stress

LCP Explanation

1. By Le Chatelier's Principle, (change in condition)
↳ $\uparrow/\downarrow$ temp / pressure / conc.
2. The forwards / backwards reaction is favoured to
3. Explain why $\rightarrow$ conc - to produce / use up —
temp - exo to produce heat
endo to absorb heat
pressure - to $\uparrow/\downarrow$ no. of gaseous particles
4. $\wedge$ causing POE to shift left / right
5. Describe any observations (if you ask for it)

ΔG° & POE

$$\Delta G^\circ > 0$$

- $[reactants] \gg [products]$
- $K \ll 1$
- POE lies very much to the left, most of reactants left unreacted

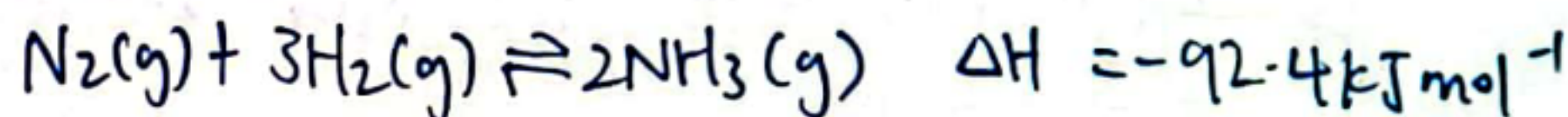
$$\Delta G^\ominus = 0$$

- $$-[\text{reactants}] = [\text{products}]$$
- $$-K = 1$$

$$\Delta G^\circ < 0$$

- $[reactants] \ll [products]$
- $K \gg 1$
- POE lies very much to the right, reaction is complete

Haber Process



Conditions: Temp $\rightarrow 500^\circ\text{C}$

Pressure $\rightarrow 250 \text{ atm}$

Catalyst $\rightarrow$ finely divided iron catalyst

Reason for conditions

- Temp

↳ By LCP, $\downarrow$ temp will favour forwards exothermic rxn to produce more heat, POE shift right to produce more NH_3 . But at low temp, rate of rxn is slow & system takes long time to reach equilibrium, $\therefore$ optimal temp of 500°C and catalyst used to ensure both yield and rate is high

- Pressure

↳ By LCP, $\uparrow$ pressure will favour the forward reaction to decrease the total amt of gases, POE shifts to the right to produce more NH_3 . But extremely high pressures will involve $\uparrow$ cost and equipment. $\therefore$ optimal pressure of 250 atm is used

Ionic Equilibrium

- Arrhenius acid/base forms H^+/OH^- ions in aqueous solution
- Lewis acid/base is an electron pair acceptor/donor
- Bronsted-Lowry acid/base is a proton donor/acceptor
- Weak acids/bases partially dissociates in water to produce a low concentration of H^+/OH^- ions
- Strong acids/bases completely dissociates in water to produce a high concentration of H^+/OH^- ions
- $pH = -\lg[H_3O^+]$ $pOH = -\lg[OH^-]$ $pH + pOH = 14.0$ $K_w = K_a \times K_b$ $pK_w = pK_a + pK_b$

Buffer

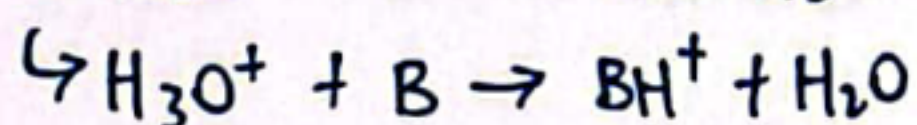
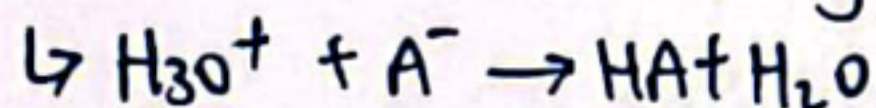
$$pH = pK_a + \lg \frac{[salt]}{[acid]}$$

$$pOH = pK_b + \lg \frac{[salt]}{[base]}$$

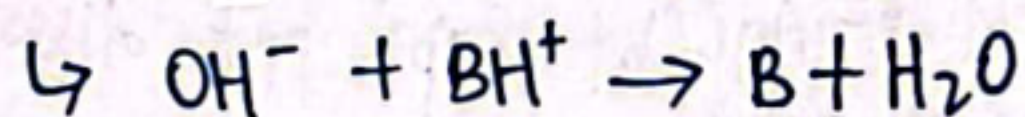
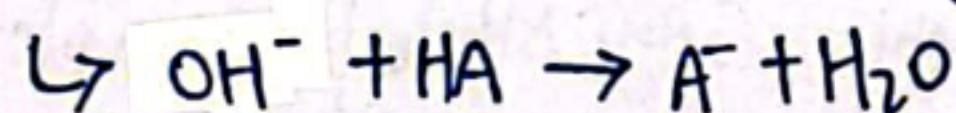
Buffer resists large changes in pH when small amounts of acid or base is added.

Acidic/Basic buffer: mixture of weak acid/base and conjugate base/acid

- When small amount of acid is added: Most of the added H_3O^+ reacts with the large reservoir of A^-/B , keeping pH fairly constant



- When small amount of base is added: Most of the added OH^- reacts with the large reservoir of HA/BH^+ , keeping pH fairly constant

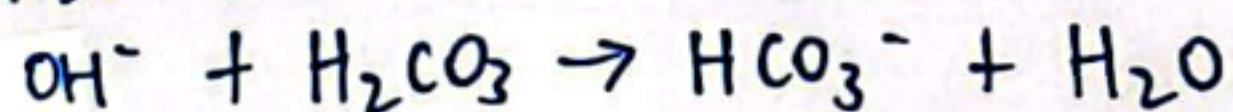


maximum buffering capacity (MBC)

- occurs when $[salt] = [acid]/[base]$

- $pH = pK_a$ / $pOH = pK_b$

H_2CO_3/HCO_3^- buffer system in blood



Choosing indicators $\rightarrow$ sharp colour change at equivalence point on adding single drop of titrant

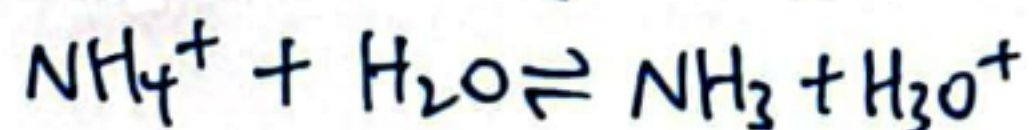
Explanation: the working range of indicator lies within the sharp pH change at equivalence point

Methyl orange 3-4 basic $\rightarrow$ endpoint $\rightarrow$ acidic
yellow $\rightarrow$ orange $\rightarrow$ red

Phenolphthalein 8-10 acidic $\rightarrow$ endpoint $\rightarrow$ basic
colourless $\rightarrow$ pink $\rightarrow$ red

Salt hydrolysis (to answer whether (salt) forms acidic/basic/neutral solution)

Acids (eg NH_4^+ , CH_3CO_2H)



NH_4^+ hydrolyses in water to produce H_3O^+ ions, forming an acidic solution

Bases (eg $CH_3CO_2^-$, NH_3)



$CH_3CO_2^-$ hydrolyses in water to produce OH^- ions, forming a basic solution

• Solubility is the maximum amount of substance that can dissolve in a solvent at a given temperature to form a saturated solution

$$\text{solubility} = \frac{\text{max amt that can dissolve}}{\text{volume of solvent}}$$

• Solubility product, K_{sp} , of a sparingly soluble salt is the product of the equilibrium concentrations of the ions in a saturated solution, each raised to the power of its coefficient in the equilibrium equation

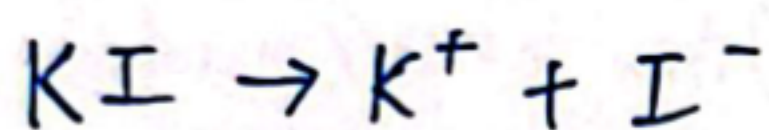
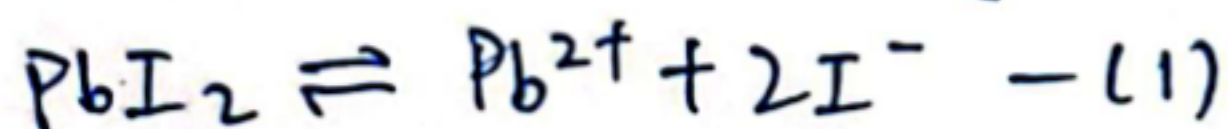
$$\text{For a sparingly soluble salt } A_xB_y, \quad \left\{ \begin{array}{l} \text{- varies w/ temp} \\ \text{- } \downarrow K_{sp}, \downarrow \text{ solubility} \end{array} \right.$$

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Factors Affecting Solubility

• Common Ion Effect

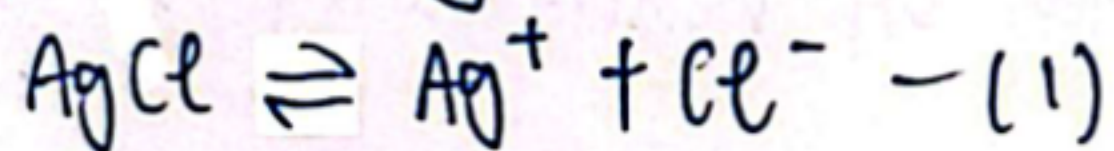
eg. decreased solubility of PbI_2 in KI



Presence of common ion I^- increases $[I^-]$ due to KI . By LCP, POE in (1) shifts left, reducing $[I^-]$ $\therefore$ solubility of PbI_2 reduced

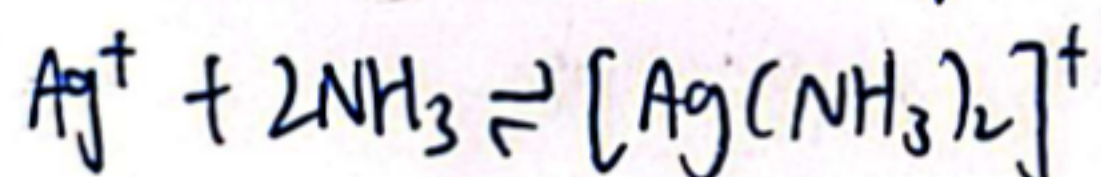
• Formation of Complex Ion

eg solubility of Ag in NH_3



When NH_3 added, Ag^+ is removed to form soluble $[Ag(NH_3)_2]^+$ complex ion, causing $[Ag^+]$ in (1) to decrease, POE of (1) shifts right and ppt dissolves.

When IP of $AgCl < K_{sp}$ of $AgCl$, $AgCl$ dissolves completely



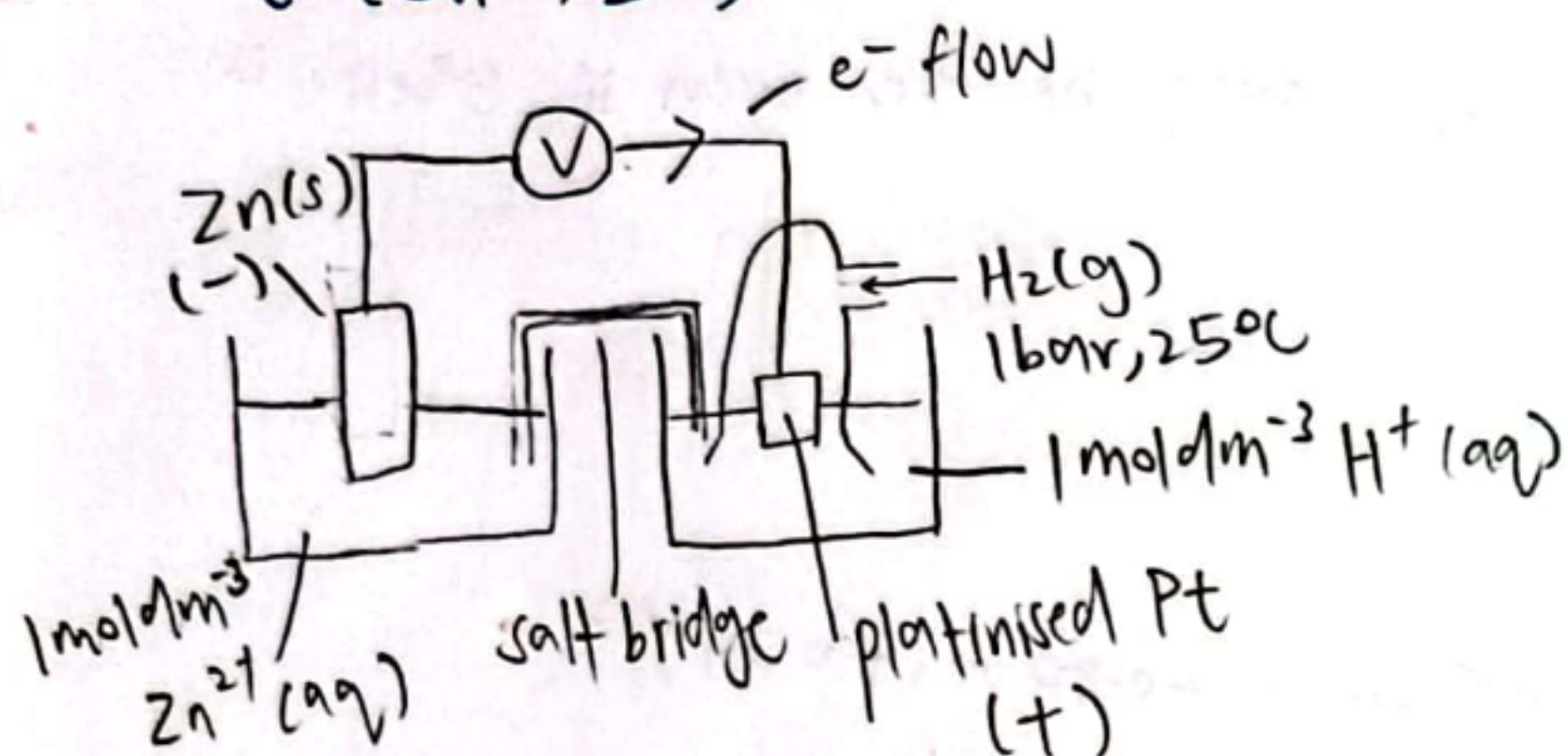
Electrochemistry

- Standard Electrode Potential, E° of half cell is the maximum potential difference (pd) between electrode potentials of the half cell and standard hydrogen electrode (SHE) measured under standard conditions
 $\rightarrow 25^\circ\text{C}, 1\text{ bar}, [\text{ions}] = 1\text{ mol dm}^{-3}$
- Standard Cell Potential, E°_{cell} is the maximum potential difference between two electrodes of a galvanic cell measured under standard conditions

Half cells

Metal / Ion

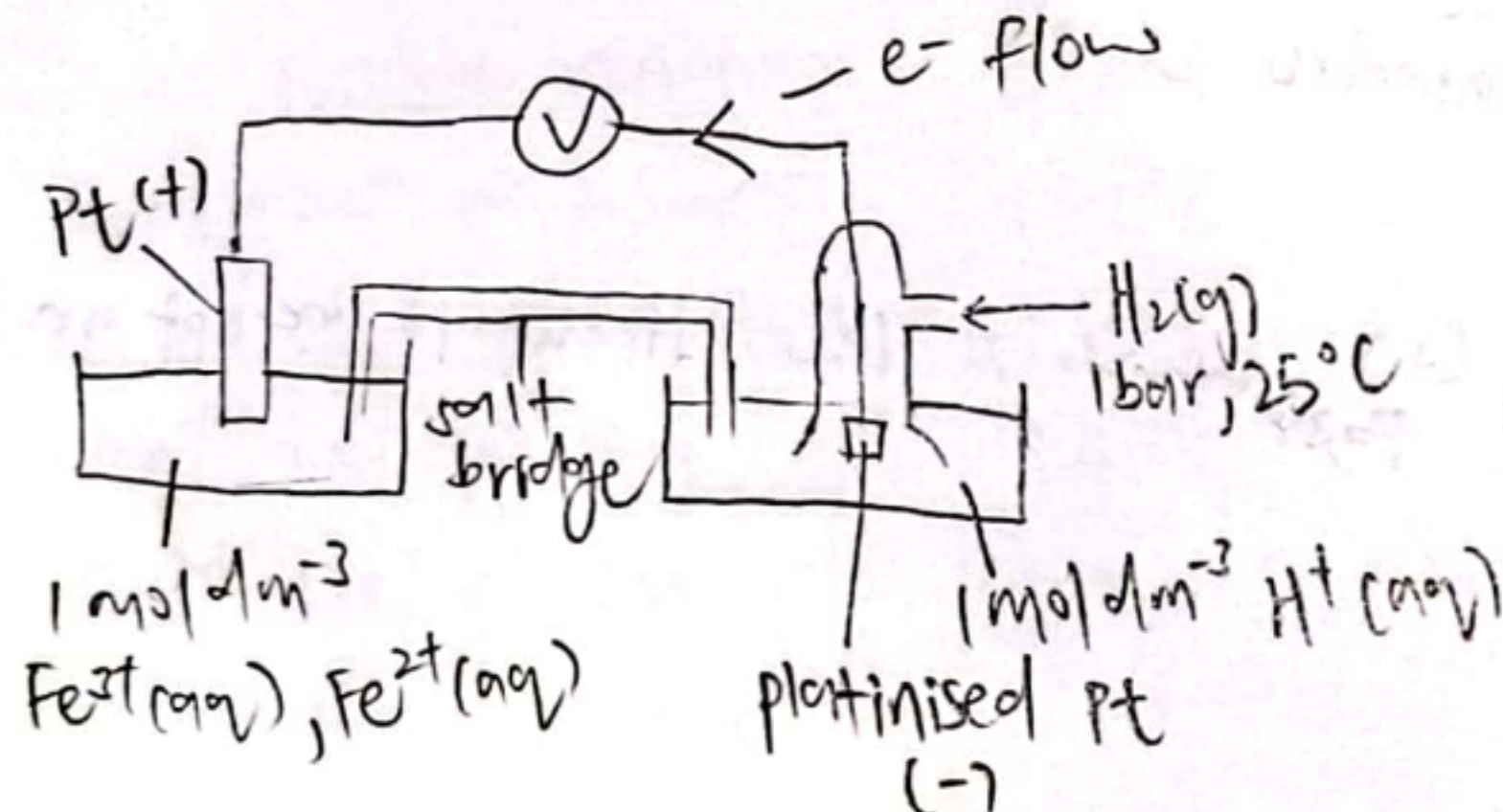
$$E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76\text{ V}$$



$\therefore \text{Zn}^{2+}/\text{Zn}$ undergo oxidation

2 Ions

$$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77\text{ V}$$



$\therefore \text{Fe}^{3+}/\text{Fe}^{2+}$ undergo reduction

Strength of OA / RA

- the more positive / negative the value of $E^\circ(\text{X}/\text{Y})$
- the more reduction / oxidation of is favoured
- the stronger the oxidising / reducing agent

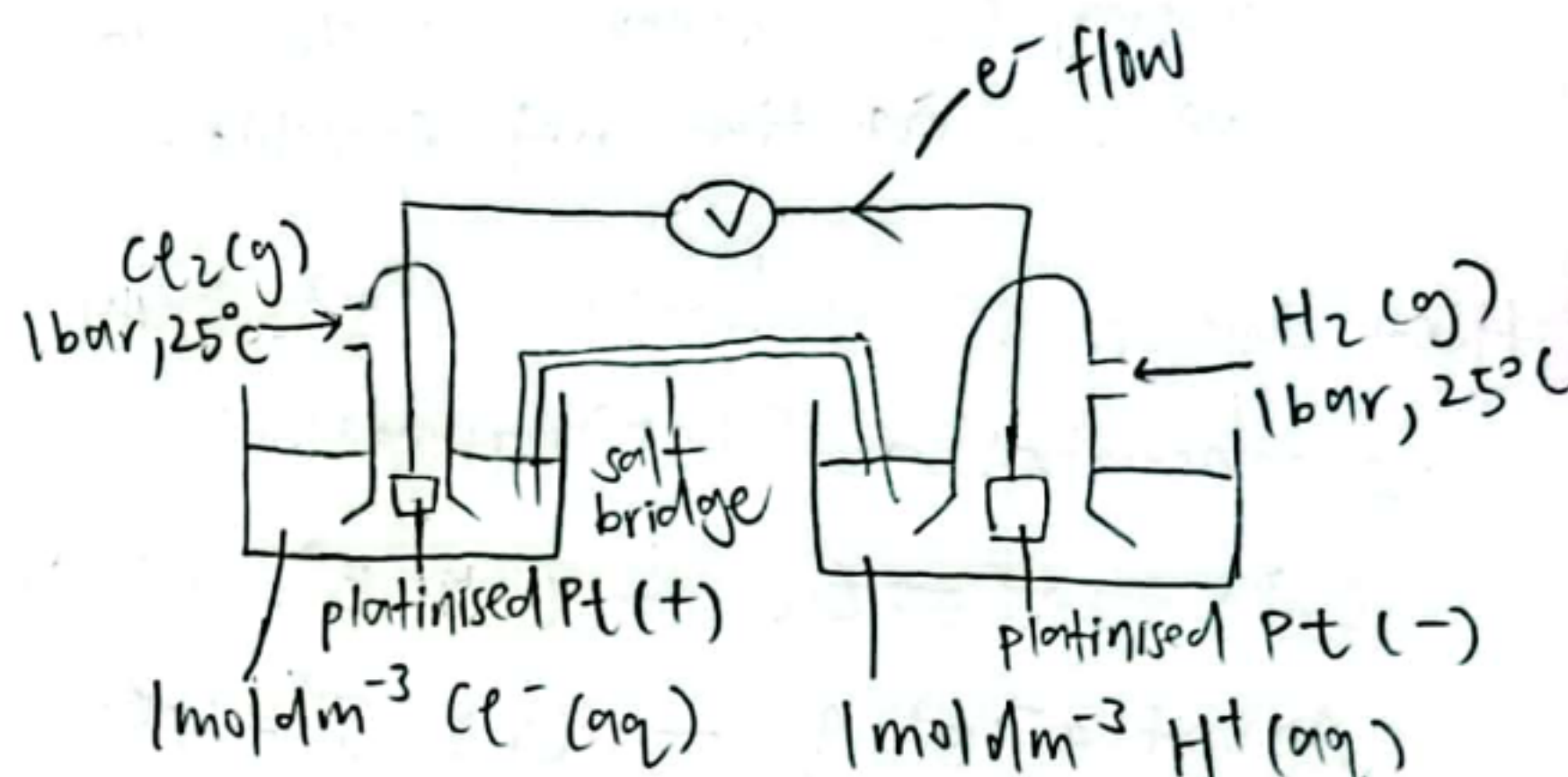
~~the stronger oxidising strength~~
~~the stronger reducing strength~~

Preferential reaction for electrolysis

- Since $E^\circ(\text{O}_2/\text{H}_2\text{O}) = +1.23\text{ V}$ is less than $E^\circ(\text{Cl}_2/\text{Cl}^-) = +1.36\text{ V}$,
 H_2O is preferentially oxidised at anode / Cl_2 preferentially reduced at cathode to form O_2 gas / Cl^- ions

Gas / Ion

$$E^\circ(\text{Cl}_2/\text{Cl}^-) = +1.36\text{ V}$$



$\therefore \text{Cl}_2/\text{Cl}^-$ undergo reduction

Advantages of batteries in electric cars

- electric motor 90% efficient, petrol only 25% efficient
- delivers a large current for a short time
- provides a high voltage
- rechargeable

Advantages of a H_2/O_2 fuel cell

- high power efficiency (up to 70% efficiency)
- no pollution $\therefore$ no need burn fuel

Intro to Organic Chem

Cis-trans Isomerism

- occurs when there is restricted rotation about
 - C=C bond in an aliphatic alkene or
 - C-C bond in a small rigid ring
- and when there are two different groups on each carbon of the double bond

Enantiomers - pair of chiral compounds that are isomers

- rotate plane polarised light

stereoisomers ✓

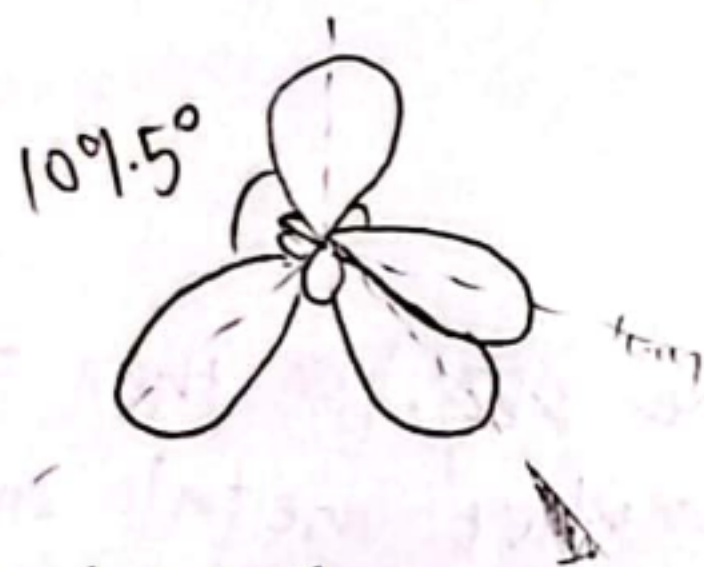
Optically active molecules have:

1. a chiral carbon (4 diff atoms bonded to it)
2. non-superimposable mirror images
3. no plane, axis or centre of symmetry

Constitutional isomerism
- compounds having same molecular formula but have different structural formula

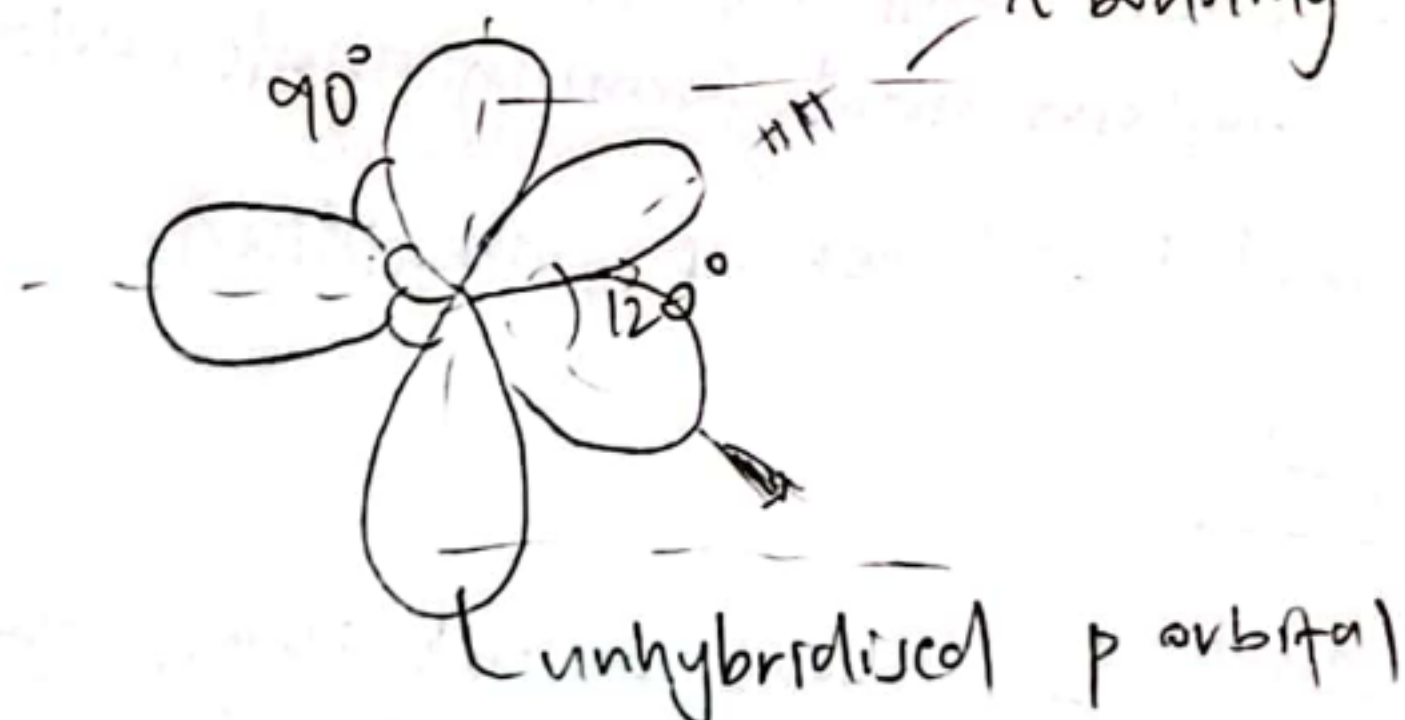
sp³ hybridisation (ethane)

- formed through combination of one s and three p orbitals
- tetrahedral shape



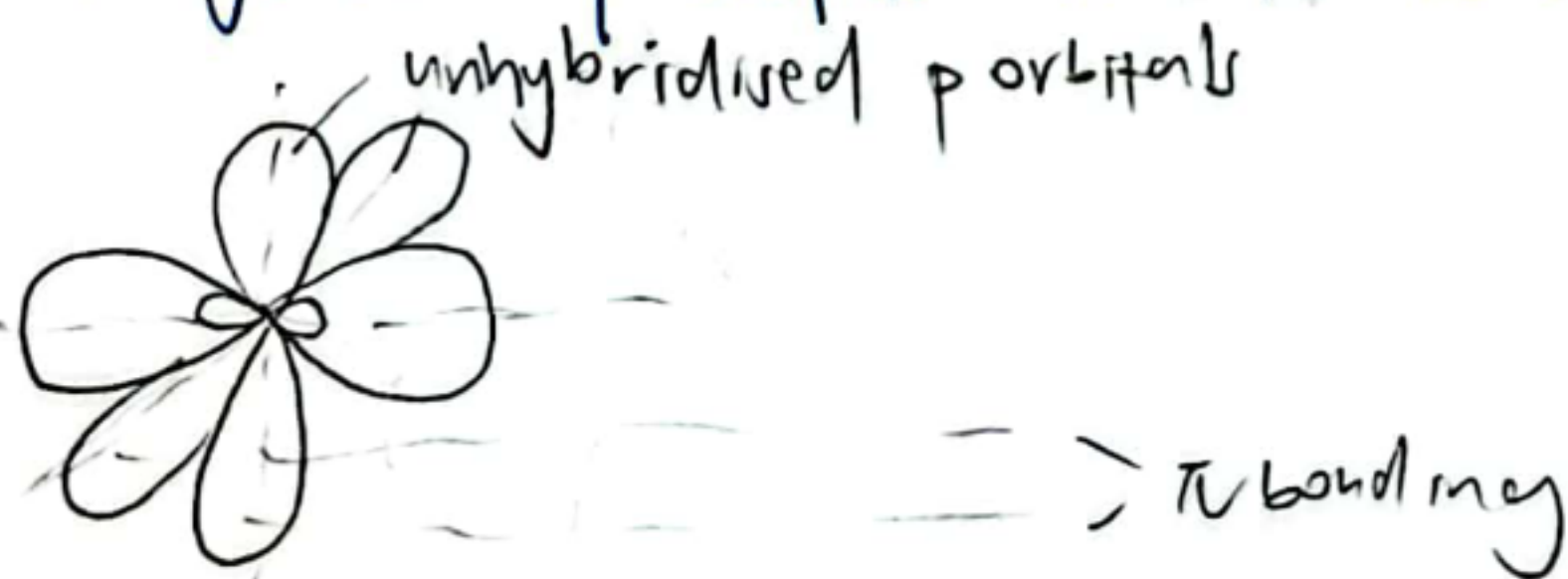
sp² hybridisation (ethene)

- formed through combination of ones and two p orbitals
- unhybridised p orbital used for π bonding



sp hybridisation (ethyne)

- formed through combination of one s and one p orbital
- two unhybridised p orbitals used for π bonding



Stereoisomerism

- compounds with same molecular formula but with different spatial formula

Alkanes

Homolytic Fission - process where a covalent bond is broken, forming two radicals

Why Alkanes are unreactive:

1. Non polar bond

↳ C-H bond is non-polar → alkane molecules do not attract reactive species

2. Bond strength

↳ C-C and C-H bond relatively strong

Heterolytic fission - breaking of covalent bond, and more electronegative atom takes both bonding electrons to form an anion, leaving a cation

Undergo FRs because:

alkanes saturated ^{does not} → undergoes addition rxn ~~to form a single product~~

Brief exposure to UV light / Why $X\cdot$ is a homogenous catalyst

• UV light produces $X\cdot$ radicals that initiate chain reactions of the propagation step to produce more radicals for reaction to sustain

Alkenes

Undergo EA because:

1. e^- rich C=C bond attracts e^- deficient electrophiles

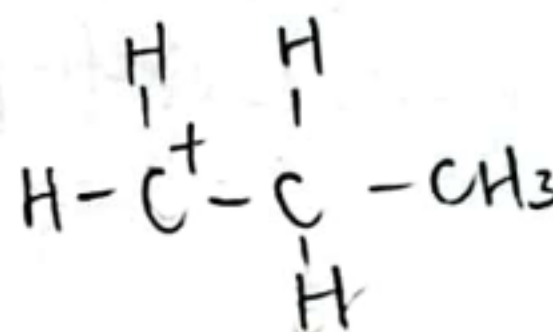
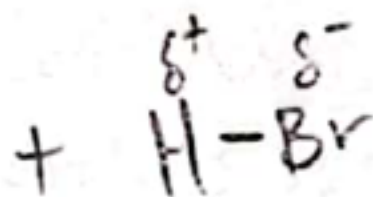
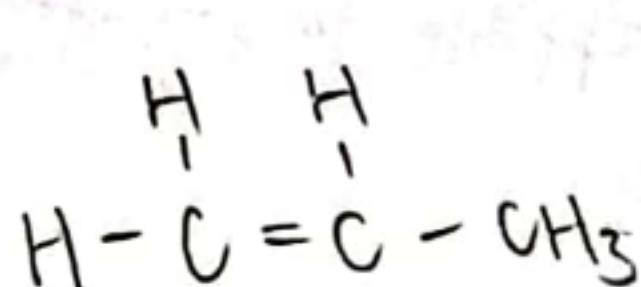
2. C=C bond in alkene is unsaturated ∴ a small molecule can be added across to form a single ppt

presence of more e^- donating alkyl grp → ↑ e^- density carbocation centre
→ disperse +ve charge, stabilising carbocation

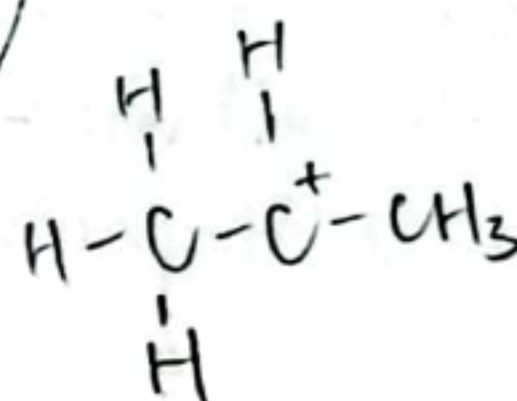
Markonikov's Rule

• major product of addition reaction is formed from the most stable carbocation i.e. most substituted C atom in C=C

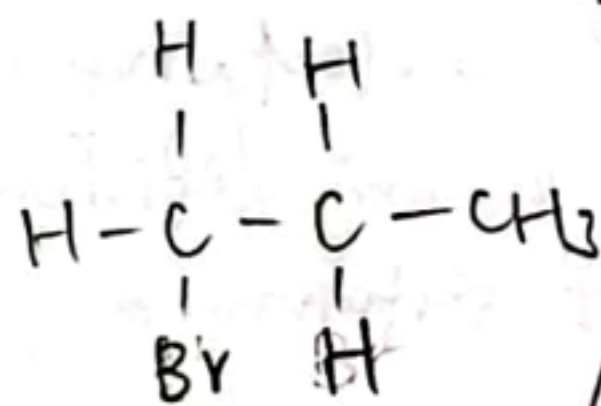
eg



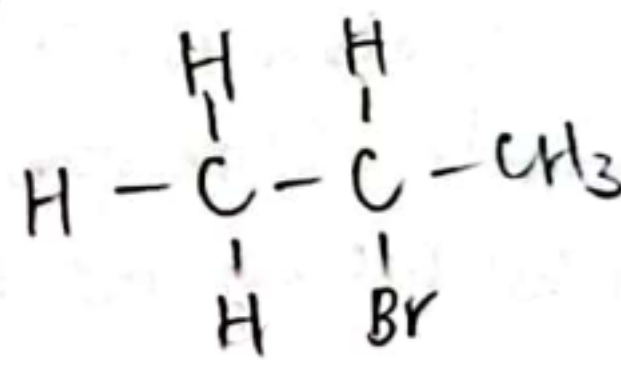
minor



major



minor



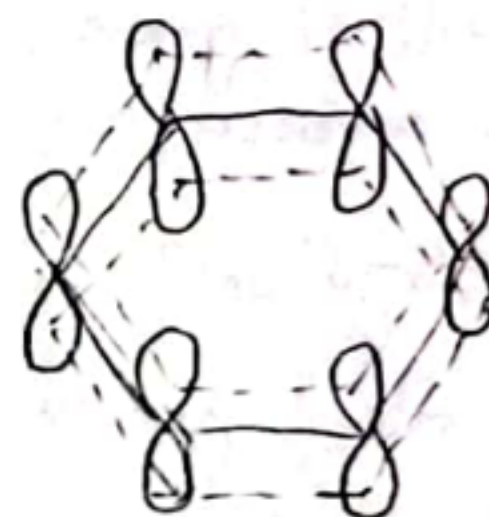
major

Benzene

Structure of benzene + aromatic stability

• each C atom in benzene is sp^2 hybridised. It has 3 sp^2 hybrid orbitals and one unhybridised p orbital - The sp^2 hybrid orbitals form three σ bonds with two other C atoms and one H atom via head on overlap on the same plane.

• The 6 p orbitals on the C atoms are close enough to one another for side on overlap to form a ring of delocalised π electrons above & below the plane, giving rise to extra stability in benzene



Benzene undergo ES because:

- delocalised π electron cloud in benzene has a large e^- density to attract e^- deficient electrophiles, making it susceptible to electrophilic attack
- undergo substitution to maintain the ring of delocalised πe^- cloud that provides aromatic stability

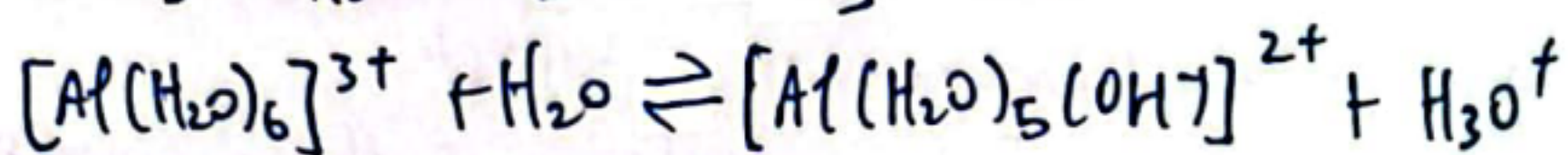
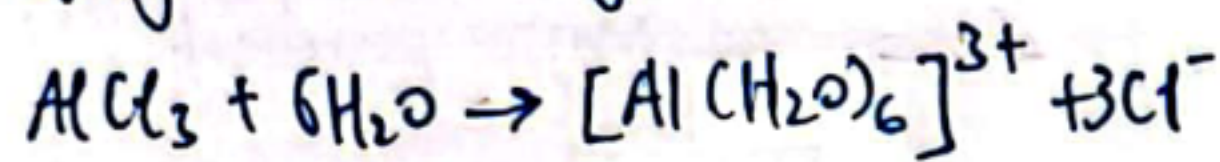
Role of $AlCl_3$ in ES:

- acts as a Lewis acid catalyst by accepting an electron pair from Cl to produce strong electrophile Cl^+

Role of H_2SO_4 in ES:

- acts as a Brønsted-Lowry acid catalyst, donating a proton to HNO_3 to produce the stronger electrophile NO_2^+

Why $AlCl_3$ anhydrous:



- $AlCl_3$ undergoes hydration in presence of water, followed by hydrolysis to form an acidic solution. $\therefore AlCl_3$ cannot act as a Lewis acid as there is no more energetically accessible and vacant orbitals in Al to accept a lone pair of e^- from Cl

Benzene vs Alkene reactivity

- Benzene reacts less readily w/ electrophiles than alkenes
 - $\therefore$ benzene is less e^- rich due to the delocalisation of πe^- cloud
- } think stronger e^+ electrophile needed vs X_2 in alkene

Effect of substituents on reactivity & directing effect

- Activating groups $\rightarrow$ make aromatic ring more reactive than benzene
- e^- donating groups $\uparrow e^-$ density in benzene ring at the 2- and 4-positions
- makes 2- and 4-position more electron rich and more susceptible to electrophilic attack $\therefore$ 2, 4-directing
- Deactivating groups $\rightarrow$ make aromatic ring less reactive than benzene
- e^- withdrawing group $\downarrow e^-$ density in benzene ring from the 2- and 4-positions
- makes 3-position relatively richer in e^- and more susceptible to electrophilic attack $\therefore$ 3-directing

Alkyl Halides

Undergo NS because:

- RX C atom is bonded to electronegative X atom, $\therefore C-X$ bond is polar, causing alkyl halide C centre to be e^- deficient and susceptible to attack by electron rich nucleophiles
- substitution as it is saturated, $\therefore X$ atom is replaced by nucleophile during rxn

Why $3^\circ RX$ undergo S_N1 NS:

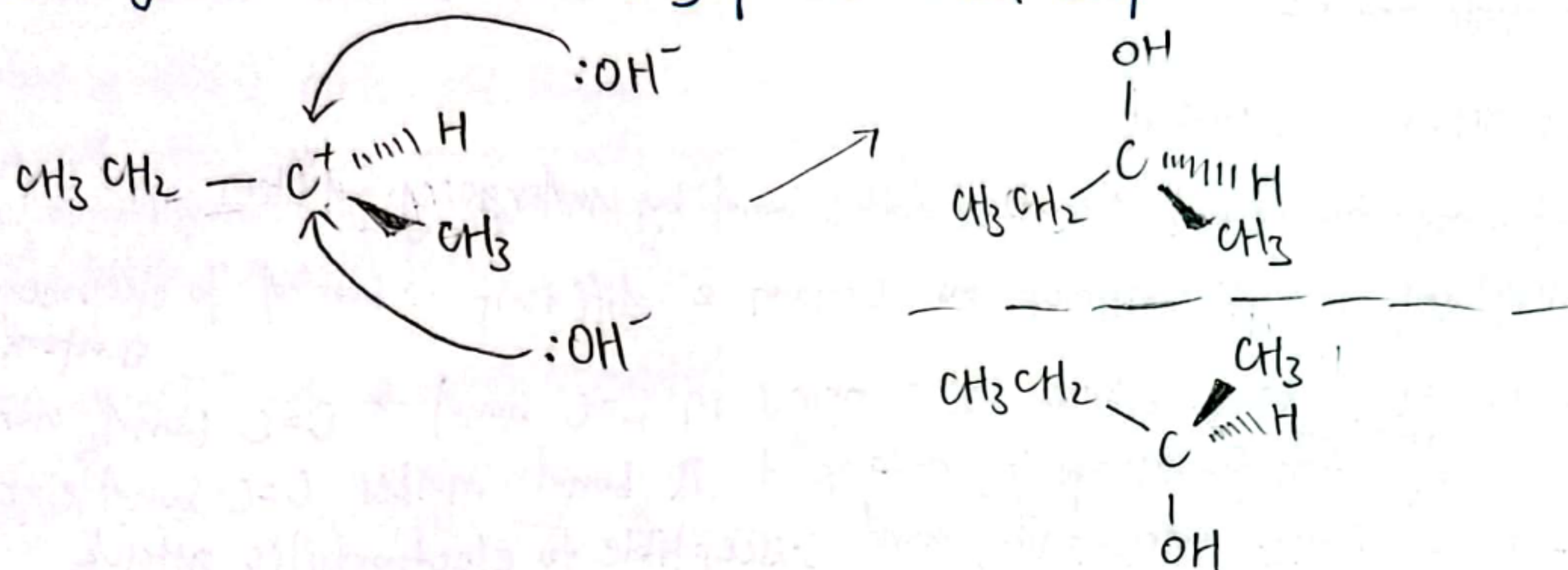
- e^- donating alkyl groups $\uparrow e^-$ density of carbocation centre $\rightarrow$ disperse the positive charge on the carbocation $\rightarrow \therefore$ stabilising the carbocation

Why $1^\circ RX$ undergo S_N2 NS:

- lesser bulky alkyl groups that crowd the backside of the e^- deficient alkyl halide carbon atom $\rightarrow$ lesser steric hindrance for the incoming nucleophile

Racemic mixture from S_N1 NS (+ why optically inactive)

- nucleophile can attack the trigonal planar carbocation carbon centre from either side of the plane with equal probability $\rightarrow$ both enantiomers are formed in equal amounts, forming racemic mixture (why racemic)
- optically inactive as each enantiomer rotates plane polarised light in opposite directions but same magnitude, $\therefore$ their rotating powers cancel out



Inversion of configuration in S_N2 NS:

- nucleophile attacks from the backside of the alkyl halide C atom in S_N2 mechanism, which results in an inversion of configuration during the reaction

Relative reactivity of RCl , RBr , RI :

- Down the group, atomic radius ^{of X} increases $\rightarrow$ bond length of $C-X$ increases
- $\therefore$ bond strength decreases $\rightarrow$ $\therefore$ lesser energy needed to break the weaker $C-X$ bond
- rate of hydrolysis / reactivity increases (slowest) $R-Cl < R-Br < R-I$ (fastest)

Unreactivity of aryl halides

- the p orbital of Cl atom overlaps with the π orbital of benzene ring, causing the lone pair of e^- on Cl atom to delocalise into benzene ring $\rightarrow \therefore C-Cl$ bond has some double bond character
- rear side of $C-X$ bond is blocked by bulky benzene ring which provides steric hindrance
- π electron cloud of benzene ring will repel lone pair of e^- of incoming nucleophile

main reason — 1

other reasons (if more mark) — 2, 3

Hydroxy Compounds

Undergo NS because:

- $C-OH$ bond is polar because the C atom is bonded to a more electronegative O atom.
- $\therefore$ the C atom with the $-OH$ group is electron deficient & carries a partial +ve charge and is susceptible to nucleophilic attack
- Substitution as $R-OH$ is saturated

Why phenol undergoes ES very readily

- $-OH$ group in phenol is a strong EDG $\rightarrow$ activates the ring strongly by increasing the e^- density of the benzene ring $\rightarrow$ susceptible to electrophilic substitution.

Carbonyl compounds

Undergo nucleophilic addition because:

- O atom is more electronegative than C atom, making $C=O$ bond polar and carbonyl C atom e^- deficient $\rightarrow$ C atom susceptible to nucleophilic attack
- addition as a small molecule can be added across the unsaturated $C=O$ to form a single product

Carbonyl vs Alkenes reactivity

- both react similarly to saturate the double bond by undergoing addition
- carbonyl susceptible to nucleophilic attack as C atom e^- deficient $\therefore$ bonded to electronegative O atom
- no electronegativity difference between 2 C atoms in $C=C$ bond $\rightarrow$ $C=C$ bond non-polar and no electron^{deficient} C atom for nucleophilic attack + π bond makes $C=C$ bond e^- rich $\rightarrow$ repels approach of nucleophile and susceptible to electrophilic attack

Ketone vs Aldehyde reactivity

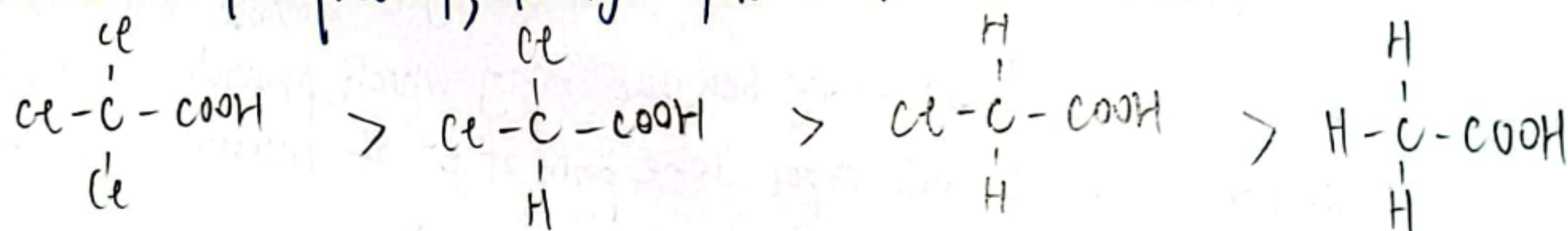
- $\rightarrow$ Ketone generally less reactive to nucleophilic attack than aldehydes
- presence of more e^- donating alkyl groups $\rightarrow$ carbonyl C atom in ketone less e^- deficient than that in aldehyde $\rightarrow$ less susceptible to nucleophilic attack
- presence of more bulky alkyl group $\rightarrow$ carbonyl C atom experiences more steric hindrance than aldehyde $\rightarrow$ prevent nucleophiles from attacking carbonyl C atom

Carboxylic acids

Chlorine-substituted ethanoic acids

1. No. of substituent groups

- more Cl atoms present, stronger the acid



- Cl is e^- withdrawing group $\rightarrow$ more Cl atoms, the $-ve$ charge on carboxylate ion is dispersed to greater extent $\rightarrow$ stabilise the conjugate base
- POE for acid dissociation shifts right $\rightarrow$ carboxylic acid more acidic $\rightarrow$ stronger acid

2. Position of substituent group

- closer the Cl atom to the carboxylate group, greater the e^- withdrawing effect $\rightarrow$ $-ve$ charge on the carboxylate ion is more dispersed $\rightarrow$ stabilise conjugate base to a greater extent
- POE for acid dissociation shifts right $\rightarrow$ carboxylic acid more acidic $\rightarrow$ stronger acid

Why diprotic acids $K_{a2} < K_{a1}$

- Harder to remove a positively charged proton from a negatively charged ion due to electrostatic attraction

Nitrogen compounds

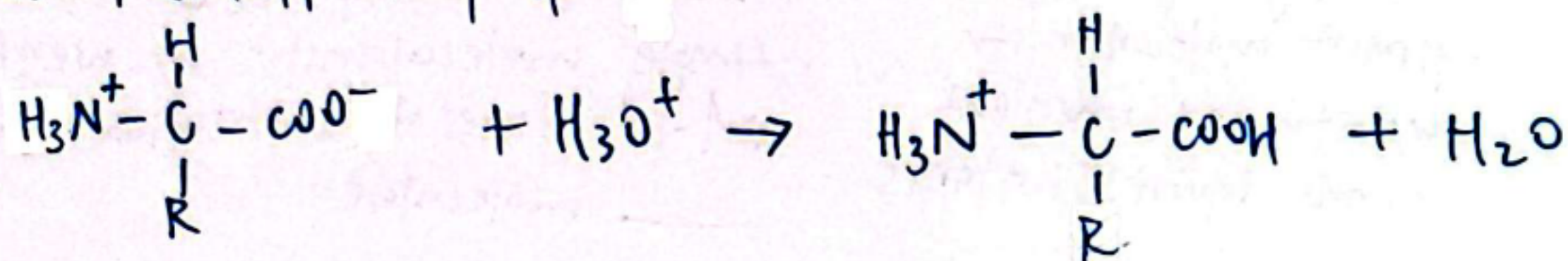
Basicity of 1°/2°/3° amines

- $R_3N > R_2NH > RNH_2 > NH_3$ for base strength
- e⁻ donating alkyl group increases e⁻ density on N atom → ↑ availability of lone pair of e⁻ on N atom to form dative bonds with proton → base str. increases

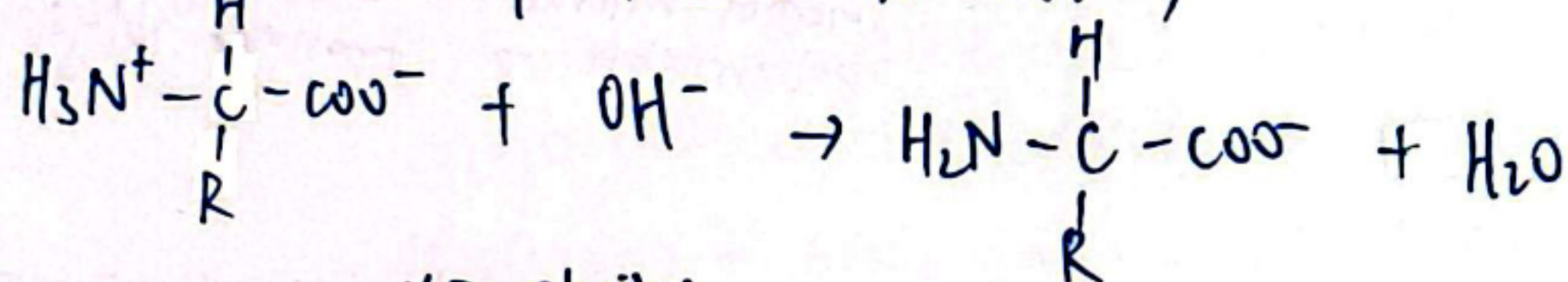
How amino acids act as buffer

- aqueous solution of amino acids contains both -COO⁻ and -NH₃⁺ groups, ∴ α-amino acids are amphoteric. Since buffer is able to resist large changes in pH when small amt of acid/base is added to it,

- when small amt of acid is added,



- when small amt of base is added,



Acidity / Basicity / Reactivity Comparison

Case 1: orbital overlap

- p orbital of X/O/N atom overlaps with π orbital of benzene ring / C=O / C=C
- lone pair of e⁻ in X/O/N delocalises into benzene ring / C=O / C=C

Case 2: substituent

1. e⁻ donating / withdrawing group increases / decreases the electron density on the C/N atom
2. acyl chloride bonded to 2 highly electronegative Cl and O atoms while alkyl halide bonded to only one electronegative Cl atom → acyl chloride C atom more e⁻ deficient → more susceptible to Nu attack

Acidity: -ve charge on O atom more effectively dispersed over — / dispersed into benzene ring → stabilises the conjugate base to greater extent → pK_a of dissociation of acid lies more to the right → donates H⁺ more readily → stronger acid

Basicity: ↑ availability of lone pair of e⁻ on N atom to form dative bond / → base w/ a proton
strength increases

Period 3

- Ionic radius $\therefore \downarrow$ from Na^+ to Si^{4+} and $\downarrow$ from P^{3-} to Cl^-
 - nuclear charge increase and shielding effect remain approx. the same
 - effective nuclear charge $\uparrow$, net attraction between nucleus and outermost e^-
 - $r(\text{cations}) < r(\text{atomic})$ as cations have less electron shell
 - $r(\text{anions}) > r(\text{atomic})$ as anions have more e^- than protons, $\therefore$ net attractive force on valence e^- lesser
 - $r(\text{anions}) > r(\text{cations})$ as anions has 1 additional electron shell

- Melting point

- high mp, $\uparrow$ from Na to Al
- giant metallic str, strong metallic bonds b/w cations and sea of delocalised valence e^-
- mp $\uparrow$ from Na to Al due to $\uparrow$ metallic bond str as $\uparrow$ no. of valence e^-
- Si highest mp
- giant molecular str w/ strong covalent bonds b/w Si atoms
- Low mp, $\text{S}_8 > \text{P}_4 > \text{Cl}_2 > \text{Ar}$
- simple molecular str w/ weak id-id forces of attraction b/w molecules
- mp in order $\text{S}_8, \text{P}_4, \text{Cl}_2, \text{Ar}$ as larger e^- cloud $\rightarrow e^-$ cloud more polarisable $\rightarrow$ stronger id-id

- Electrical conductivity

- high conductivity, $\uparrow$ from Na to Al as $\uparrow$ no. of delocalised valence e^- to act as charge carriers.
- low conductivity as Si is a metalloid/semiconductor
- non-conductor as e^- are localised in covalent bonds $\therefore$ no delocalised valence e^- to act as charge carrier

Chloride Reactions:

- with water

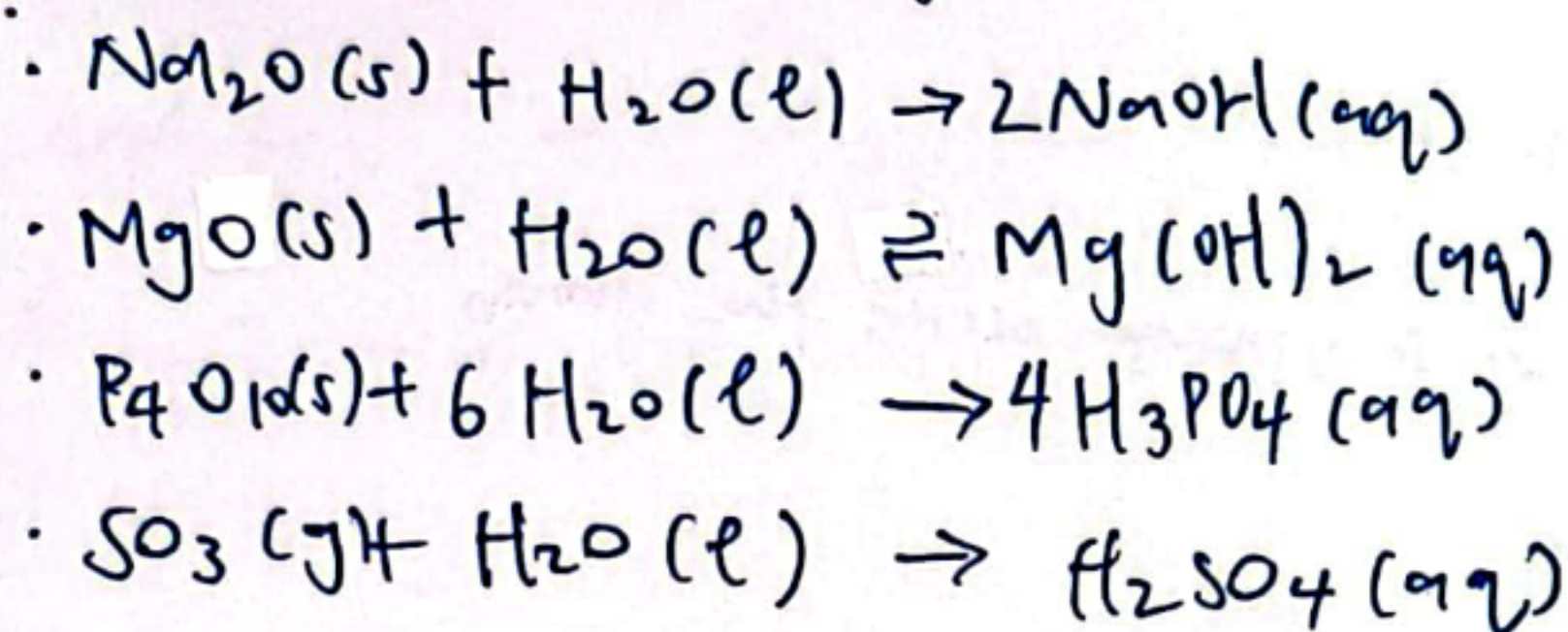
	NaCl (s)	MgCl_2 (s)	AlCl_3 (s)	
Structure	giant ionic	giant ionic	simple molecular	* little amt of H_2O :
Reaction	hydration to form ions	hydration + slight hydrolysis (due to high charge density)	hydration + hydrolysis	$\text{AlCl}_3(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{Al}(\text{OH})_3(\text{s}) + 3\text{HCl}(\text{g})$
	$\text{NaCl}(\text{s}) + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	$\text{MgCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Mg}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$	$\text{AlCl}_3(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{Cl}^-(\text{aq})$	
		$[\text{Mg}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons [\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^+(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$	
pH	7	6.5	2-3	
	$\text{SiCl}_4(\text{l})$	$\text{PCl}_5(\text{s})$		
Structure	simple molecular	simple molecular		
Reaction	hydrolysis	hydrolysis		
	$\text{SiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_2(\text{s}) + 4\text{HCl}$	$\text{PCl}_5(\text{s}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + 5\text{HCl}(\text{aq})$		
		* cold water: $\text{PCl}_5(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{POCl}_3(\text{aq}) + 2\text{HCl}(\text{g})$		
pH	1-2	1-2		

Oxide reactions :

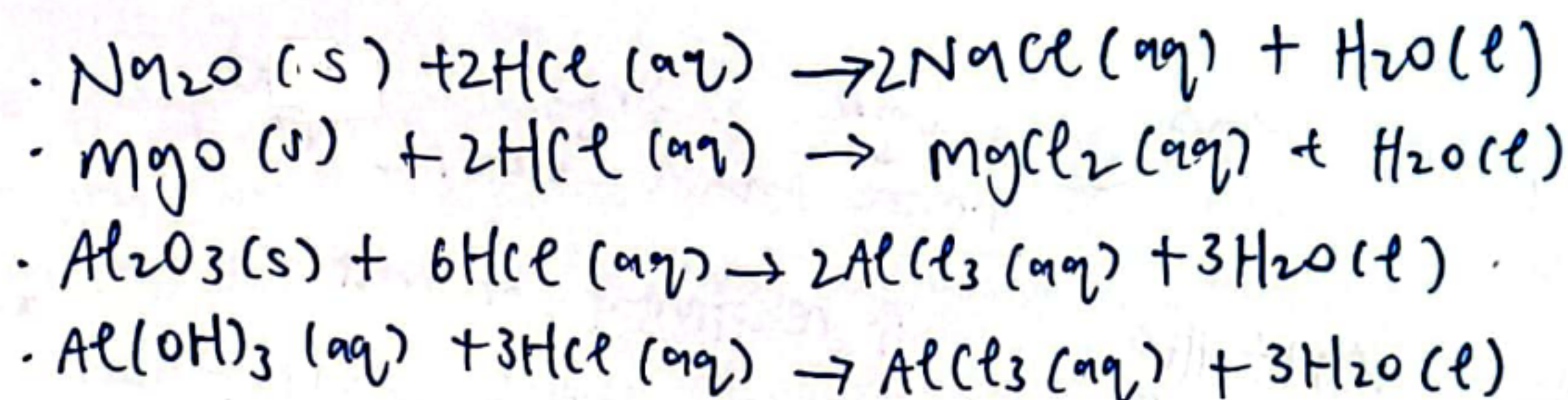
	$\text{Na}_2\text{O(s)}$	MgO(s)	$\text{Al}_2\text{O}_3(\text{s})$	$\text{SiO}_2(\text{s})$	$\text{P}_4\text{O}_{10}(\text{s})$	$\text{SO}_3(\text{g})$
Structure	Giant ionic	Giant ionic	Giant ionic	Giant molecular	Simple molecular	Simple molecular
Acid/Base nature	Basic	Basic	Amphoteric	Acidic	Acidic	Acidic
pH of solution	13	9	7	7	1-2	1-2
		(sparingly soluble)	(insoluble)	(insoluble)		
		∴ strong ionic bonds		strong covalent bonds		

Reactions

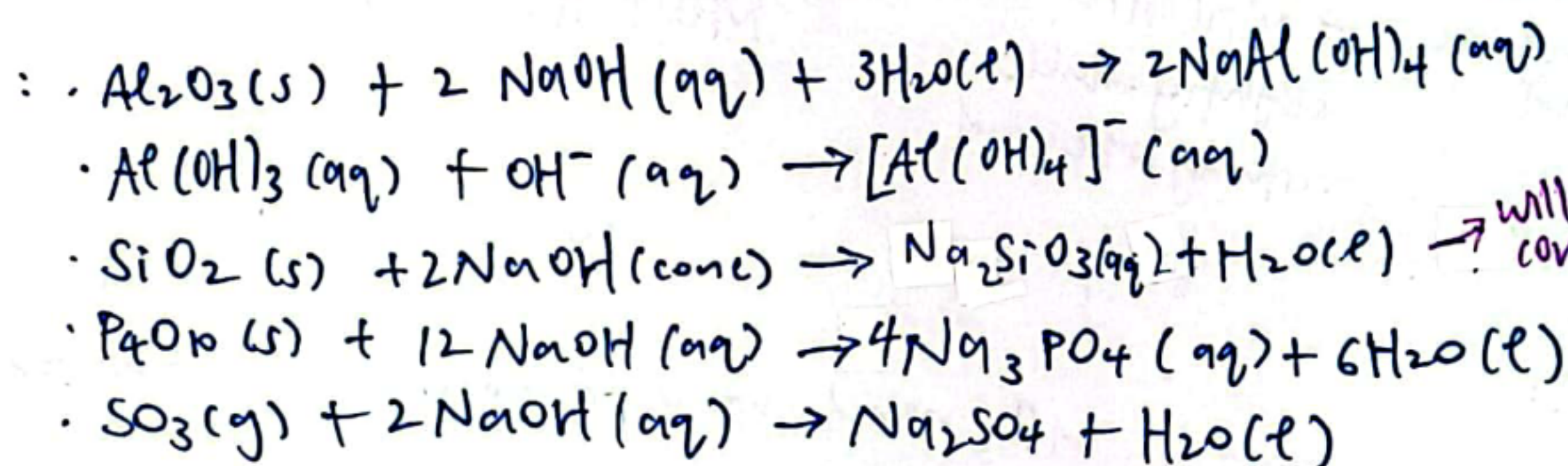
w/ water :



Reactions w/ acid :



Reactions w/ base :



will only react w/ conc. NaOH at HIGH TEMP.

Why oxidation number of oxides ↑ across period :

- no of valence e^- available for bond formation ↑

Why p and s show several oxidation no. :

- they can expand their octet as they contain vacant and energetically available 3d orbitals

Group 2

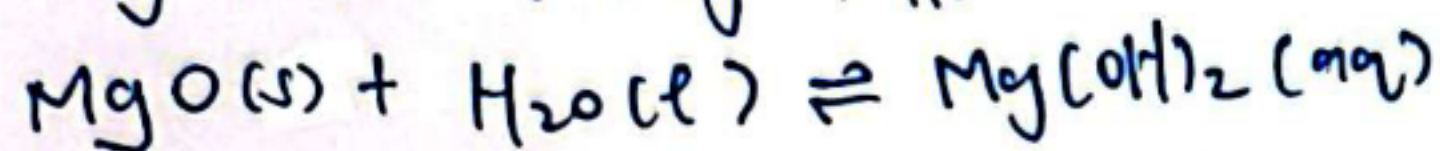
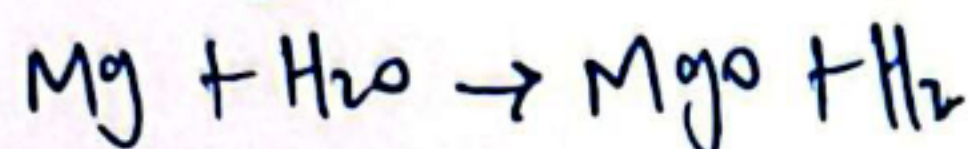
• Reactivity / Reducing strength:

- ↑ from Mg to Ba → seen by the more negative $E^\circ(M^{2+}/M)$ values → M more readily oxidised
- explanation: ionisation energy explanation

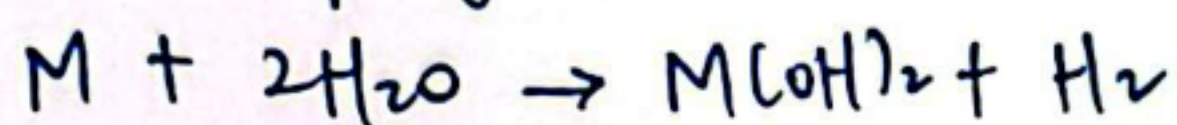
• Reaction with water

- Be: No reaction w/ cold water or steam ∴ of protective layer of BeO (Be diagonal r/s w/ Al, properties similar to Al_2O_3)

- Mg: slowly w/ cold water, vigorously w/ steam



- Ca to Ba: rapidly w/ cold water, w/ ↑ vigour down the group



Oxides:

Nature	BeO ionic and amphoteric	MgO	CaO ↓ ionic and	SrO ↓ basic	BaO
Reaction w/ water	insoluble ∴ strong ionic bond	$MgO + H_2O \rightleftharpoons Mg(OH)_2$ slightly soluble ∴ strong ionic bond	↑ reactivity w/ water $MO + H_2O \rightarrow M(OH)_2$		
pH	7	8-9	10-13		
Reaction w/ acid / base	acid: $BeO + 2HCl \rightarrow BeCl_2 + H_2O$ base: $BeO + 2NaOH + 2H_2O \rightarrow Na_2Be(OH)_4$	all react w/ acid to give salt + water $MO + 2HCl \rightarrow MCl_2 + H_2O$			

Thermal decomposition of nitrate / carbonate / hydroxide

- $M(NO_3)_2 \rightarrow MO + 2NO_2 + \frac{1}{2}O_2$
- $MCO_3 \rightarrow MO + CO_2$
- $M(OH)_2 \rightarrow MO + H_2O$

Thermal stability

- down the group, ionic radius ↑, charge density ↓
- cations lower polarising power → e^- cloud of NO_3^- / CO_3^{2-} less polarised
- ∴ N-O / C-O bond less weakened, more energy needed to break bond
→ thermal stability ↑ dty.

Group 17

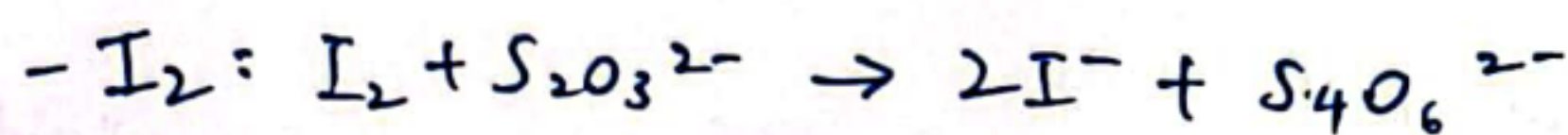
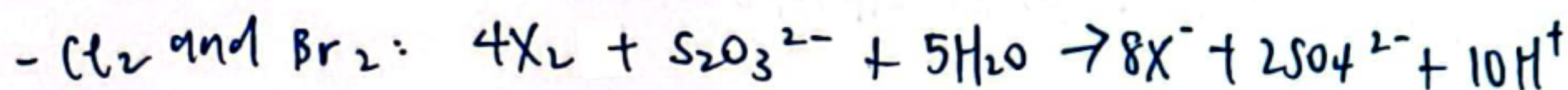
- Volatility

- all volatile, volatility ↓ from Cl_2 to I_2 .
- ∴ strength of id-id btwn molecules ↑ → size of e^- cloud ↑ → e^- cloud more polarisable

- Reactivity / Oxidising strength

- ↓ from Cl_2 to I_2 as seen by the less positive $E^\circ(\text{X}_2/\text{X}^-)$ values, X_2 less readily reduced
- explanation: ↓ electronegativity (std explⁿ) + ↓ how strongly nucleus attract incoming e^-

- Reaction w/ thiosulfate, $\text{S}_2\text{O}_3^{2-}$



- Thermal Stability

- $2\text{HX}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{X}_2(\text{g})$
- Down the group, atomic radius ↓ → lower degree of orbital overlap between H and X atoms
- Bond strength and therefore bond energy decreases
- Less energy req. to break H-X bond → thermal stability decreases.

HCl low tendency to decompose

HBr decomposes slightly

HI decomposes readily

Transition Elements

- A **transition element** is a d-block element which forms one or more stable ions with a partially filled d subshell
- A **ligand** is a molecule or anion that has one or more lone pair of electrons for dative bond formation w/ a transition metal atom or ion
- A **complex ion** is a central metal atom/ion surrounded by molecules or anions which forms dative bonds to the metal centre
- **Coordination number** indicates the number of dative bonds around the central atom or ion in the complex

Atomic radius / 1st IE from s block to d block

- ↑ nuclear charge from Ca to Sc → e^- added to inner 3d subshell, ∴ shielding of 4s e^-
- shielding from the 3d e^- is ineffective → ENC ↑ → net attraction btwn nucleus and outermost e^- ↑ → ...

Atomic radius / 1st IE across period

- ↑ nuclear charge as no. of protons ↑ → additional e^- added to inner 3d orbitals → shielding effect ↑ → ENC remain approx. constant → net attraction btwn nucleus and outermost e^- approx constant → ...

• 3rd IE and higher

- $\uparrow$ across period $\rightarrow$ 3d e^- are now outermost $e^- \rightarrow$ nuclear charge $\uparrow$ as proton no. $\uparrow$
 $\rightarrow$ shielding effect remain approx. the same $\rightarrow$ ENC $\uparrow \rightarrow$ net attraction b/w nucleus and outermost $e^- \uparrow \rightarrow$ 3rd IE $\uparrow$ across period.

• Melting point

- higher than s-block elements, mp $> 1000^\circ\text{C}$
- both 3d and 4s e^- can be delocalised as close in energies $\rightarrow$ form stronger metallic bonds than s-block elements like Ca which has only 2 valence e^- for metallic bond formation

• Density

- denser than s-block, gradually $\uparrow$ across period
- $\rho = \frac{\text{mass}}{\text{volume}} \rightarrow$ smaller atomic radius + larger atomic mass

• Electrical conductivity

- Higher than s-block, gradually $\uparrow$ across period
- Both 3d and 4s e^- are delocalised as they are close in energies $\rightarrow$ more available charge carriers

• Variable oxidation states

- Transition elements can lose different numbers of 4s and 3d e^- as they are close in energies $\Rightarrow$ max os = no. of 4s + no. of unpaired 3d e^- . After Mn, pairing of e^- occurs

- s-block metal readily lose all 4s e^- to gain noble gas configuration
 $\rightarrow$ subsequent removal of e^- is from inner quantum shell $\rightarrow$ req. large amt of energy
 $\therefore$ fixed o.s.

* CrO_4^{2-} ions formed instead of Cr^{6+}

- Formation of Cr^{6+} will require very high IE
- $\text{Cr}^{6+}(\text{aq})$ will also have very high charge density and high polarising power
 $\rightarrow$ will polarise water ligands to form CrO_4^{2-}

• Formation of complex ions

- Transition elements have vacant 3d orbitals of low energy levels that can accommodate lone pair of e^- donated by ligands (also $\because$ metal ion have high charge density)
- s-block metal do not have vacant 3d orbitals of compatible energy to accommodate the lone pairs (also $\because$ it has low charge density)

• Colour of complex ions

- In an octahedral complex ion, presence of ligands causes the energy level of the five 3d orbitals to split into two different energy levels
- Energy difference, ΔE corresponds to wavelengths of light in visible spectrum
- when light energy corresponding to ΔE is absorbed, an electron is promoted from d orbital of lower energy to one of higher energy
- unabsorbed wavelengths are transmitted, colour observed is complementary to colour absorbed

Explanation for 1m qn

- has partially filled d-orbital so that d-d transitions are possible

- s-block metal is white/colourless as electronic transition of 4s e^- to 4p orbital involve absorption of energy outside the visible region



Crystal Field Theory / why there is splitting of energy levels

- $d_{x^2-y^2}$ and d_{z^2} orbitals have lobes directed along the x, y, z axes pointing towards approaching ligands while d_{xy} , d_{yz} , d_{xz} orbitals have lobes that are directed between the axes along which the ligands approach
- $\therefore e^-$ in the $d_{x^2-y^2}$ and d_{z^2} orbitals experience stronger repulsion from the lone pair of e^- in ligands than those in d_{xy} , d_{yz} and d_{xz} orbitals
- $d_{x^2-y^2}$ and d_{z^2} are higher energy d-orbitals, while d_{xy} , d_{yz} and d_{xz} are lower energy d-orbitals

END of notes (for now? hopefully?)

Soluble complexes

- $[Ag(NH_3)_2]^+$
- $[Zn(OH)_4]^{2-}$
- $[Al(OH)_4]^-$
- $[Zn(NH_3)_4(H_2O)_2]^{2+}$
- $[Cu(NH_3)_4(H_2O)_2]^{2+}$
- $[CuCl_4]^{2-}$
- $[Cr(OH)_6]^{3-}$