

CHEMISTRY

THEORY

Jing Ying



Contents

1 Atoms, Molecules, Stoichiometry

1.1 Relative Masses Of Atoms And Molecules

→ you should be able to define the following:

- ① relative atomic mass: the average mass of an atom of the element relative to $\frac{1}{12}$ th the mass of an atom of C-12.
- ② relative isotopic mass: the mass of an isotope relative to $\frac{1}{12}$ th the mass of an atom of C-12.
- ③ relative molecular mass: the average mass of one molecule (of an elem. or compound) relative to $\frac{1}{12}$ th the mass of an atom of C-12.
- ④ relative formula mass: the sum of the relative atomic masses of the atoms in a formula unit of the compound.

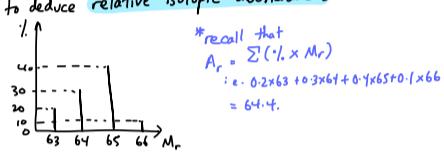
1.2 The Mole and Avogadro's constant

→ define Avogadro's constant, N_A , as the number of atoms in 12g of ^{12}C ($= 6.02 \times 10^{23}$)

→ define that the mole is equal to Avogadro's constant.

1.3 Determination Of Relative Atomic Masses

→ you should be able to analyse mass spectra diagrams, to deduce relative isotopic abundances.



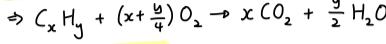
1.4 Calculation Of Empirical and Molecular Formulae

→ recall that the empirical formula is the simplest ratio of atoms of each element in the compound.

→ recall that the molecular formula shows the precise number of atoms of each element in 1 molecule (in the substance).

→ you should be able to calculate these two in problems involving:

- ① combustion data



- ② composition by mass

To calculate:

i) tabulate Mr of desired formula / elem.

ii) tabulate Mr of whole molecule

iii) calc. ratio, multiply by 100%.

1.5 Reacting Masses & Volumes (Of Solutions And Gases)

→ you should be able to write and construct balanced equations.

→ additionally, you must be able to perform calculations using the mole concept, involving:

- ① reacting masses (from formulae & eqns)

→ always convert to moles 1st!

- ② V of gases (e.g. combustion of hydrocarbons)

→ $V = 22.4n$ in RTP, $V = 22.4n$ in STP

- ③ V & conc. of solutions

→ $n = cV$ (*V is in dm³, c mol dm⁻³)

→ must reflect number of sf given in Q as well.

→ lastly, you must be able to deduce stoichiometric relationships from calculations.

2 Atomic Structure

2.1 Particles in the Atom

→ understand that the atom is composed of:

- ① protons / mass = 1, charge = +1

- ② neutrons / mass = 1, charge = 0

- ③ electrons / mass = $\frac{1}{1837}$, charge = -1

→ describe the behaviour of these particles in electric fields:

- ① protons are deflected towards the negative terminal

- ② electrons are deflected, more strongly, towards the positive terminal

- ③ neutrons are unaffected/undeflected

→ state that, in an atom:

- 1) the central nucleus contains almost all the mass of the atom

- 2) there is also a very concentrated positive charge at the nucleus

- 3) there is a negative charge around the nucleus, but negligible mass.

→ you should also be able to deduce $n(p)$, $n(n)$ & $n(e^-)$ given P and nucleon # & charge.

$$*\text{nucleon } \# = n(n) + n(p)$$

$$\text{charge} = n(p) - |n(e^-)|$$

2.2 The Nucleus Of The Atom

→ recognise isotopes are versions of an element — they have the same proton number, but different nucleon/neutron number.

→ use the symbolism ${}^A_Z X$ for isotopes; Z is atomic number, A is nucleon number.

2.3 Electrons: Energy Levels, Atomic Orbitals, Ionisation Energy

→ know your subshells

- ① the s subshell

→ one orbital (max $2e^-$)

→ spherical

- ② the p subshell

→ three orbitals (max $6e^-$)

→ dumbbell-shaped

- ③ the d subshell

→ five orbitals (max $10e^-$)

→ key exceptions:

- 1) Cu: $[Ar] 3d^5 4s^1$ not $3d^4 4s^2$

- 2) Cr: $[Ar] 3d^4 4s^1$ not $3d^5 4s^2$

→ half-filled 3d subshell more stable.

→ realise that ionisation energies, ΔH_i , are usually positive;

because stripping an e^- away is endothermic.

→ define first ionisation energy as the energy required to remove one mole of the most loosely held electrons from one mole of gaseous atoms to produce one mole of gaseous ions with a charge of +1. $X(g) \rightarrow X^+(g) + e^-$

→ from the above, define similarly the 2nd, 3rd and nth ionisation energies.

→ recall the determinants of magnitude of ΔH_i :

- ① nuclear charge:

→ as $\uparrow n(p)$, $\uparrow NC$

→ $\uparrow F$ bw p & e^- , $\therefore \uparrow \Delta H_i$

- ② distance of e^- from nucleus:

→ as \downarrow dist., $\downarrow F$ bw p & e^-

$\therefore \downarrow \Delta H_i$

- ③ shielding effect of inner e^- :

→ caused by full inner shells.

→ \uparrow shielding, $\downarrow F$ bw p & e^-

$\therefore \downarrow \Delta H_i$

→ successive ionisation energies \uparrow ,

because F bw remaining e^- and p

\uparrow

→ you should be able to infer the electronic configuration & position in the PT (grp. pdt), given a table of successive ionisation E

*HINT: Look for "big gaps" between ΔH_i .

That implies that the next e^- removed is a lower shell.

→ order in which orbitals are filled:

$n=1$: 1s → 2s → 2p → 3s → 3p → 3d → 4s → 4p

→ elect. config. notation:

i) $1s^2 2s^2 2p^6$ etc.

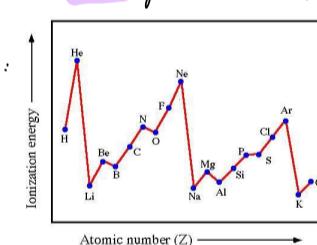
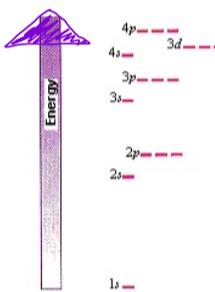
ii) dots-and-boxes notation (e.g. Na.)

iii) lone, before pair

iv) fill up successive subshells

v) each box max 2 e⁻ w/ opp. spins

→ appreciate use of chart-hand (e.g. [En])



- 1) down a group, $\downarrow \Delta H_i$
- 2) across a period, (generally) $\uparrow \Delta H_i$

→ \uparrow NC → both factors outweigh

→ \uparrow dist. from nucleus $\uparrow NC$

→ \downarrow dist. from nucleus bc \downarrow atomic size

Exceptions:

- 3) Be=B, Mg>Al ($\Delta H_i \downarrow$)

Be: $[He] 2s^2$ → new subshell

B: $[He] 2s^2 2p$ → \uparrow dist. from nucleus

Mg: $[Ne] 3s^2$ → both factors outweigh

Al: $[Ne] 3s^2 3p^1$ → NC

- 4) N>O, P>S ($\Delta H_i \downarrow$)

N: $[He] 1s^2 2s^2$ → pair of e^-

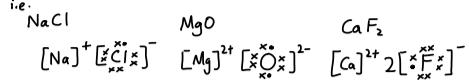
O: $[He] 1s^2 2s^2 2p^4$ → \uparrow repulsive F

S: $[Ne] 1s^2 2s^2 2p^6$

3 Chemical Bonding

3.1 Ionic Bonding

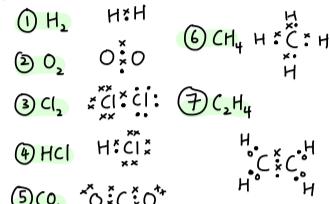
→ define **ionic bonding** as the electrostatic attraction between oppositely charged ions.



3.2 Covalent Bonding

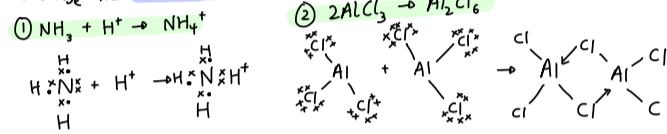
→ define **covalent bonding** as the electrostatic attraction between nuclei and localised shared pairs of electrons.

→ describe the **covalent bonds** in:

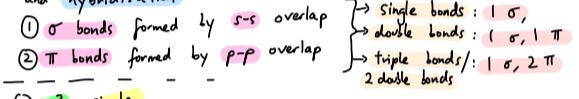


→ define **dative covalent / coordinate bonds** as a covalent bond, but both of the e⁻ in the pair derive from the same atom.

→ describe the **dative covalent bonds** in:

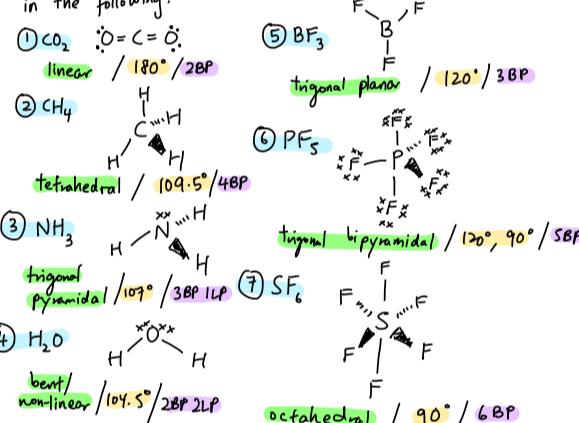


→ describe covalent bonding in terms of σ & π bonds, and hybridisation:



- (1) sp³: single
- (2) sp²: double
- (3) sp: triple or two doubles

→ you must also be able to explain the shapes, & bond angles, in the following:



→ you should be able to use the above to predict the **bond angles** in compounds.

3.5 Bonding & Physical Properties

→ recall the effect of different types of bonding on its physical properties:

(1) ionic, e.g. NaCl

- high MP & BP; a lot of strong bonds
- usually soluble; exceptions include AgCl
- high density; low volume, due to strong bonds, which ↓ size
- high polarity

(2) covalent

- low MP & BP; if polar will be higher
- solubility dependent on polarity of it & polarity of solvent (p-p, np-np)
- low density; if polar will be higher
- variable polarity

(3) metallic

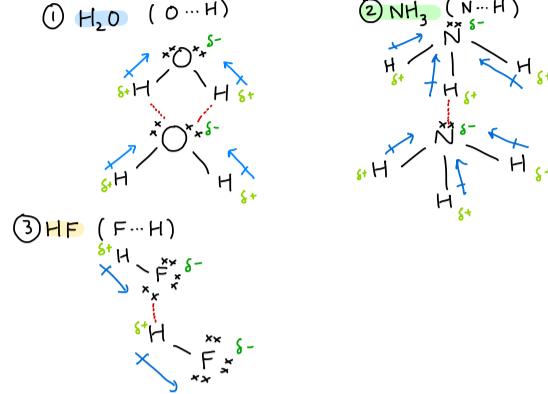
- high MP & BP; many strong metallic bonds
- insoluble; but some react
- usually high density; exceptions grp I metals

→ you must also understand the forming of bonds is exothermic, and the breaking of bonds is endothermic.

3.3 Intermolecular Forces, Electronegativity & Bond Properties

→ describe **hydrogen bonding** as an intermolecular bond, resulting from an electrostatic attraction between a proton, H⁺, and an electronegative atom.

Examples:



* hydrogen bonding only occurs between H and either N, O or F.

→ define **electronegativity** as the tendency of an atom to attract the localised shared pairs of electrons to itself.

→ appreciate that bond polarity, dipole moments and the behaviour of oxides w/ water is influenced by the difference of electronegativities of the atoms.

→ define **Van der Waals forces** as intermolecular F bw molecules.

(1) London dispersion F / temp. dipole-dipole bonds

→ London dispersion F are caused by the creation of temporary dipoles, due to the positions of shared e⁻ at a given point of time.

→ these are the weakest of all the IM forces.

(2) Permanent dipole-dipole bonds

→ Permanent dipole-dipole bonds are caused by the electrostatic attraction between opposite partial charges in molecules.

* hydrogen bonds are these, but between N-H, O-H or F-H.

→ also, you must be able to define the following:

① **bond energy**: a measure of the amount of energy needed to break one mole of bonds.

→ alternative names:
 1) bond strength
 2) bond enthalpy

② **bond length**: the average distance between the nuclei of two bonded atoms in a molecule.

③ **bond polarity**: describes how the e⁻ are shared between atoms.

→ a non-polar covalent bond occurs if the e⁻ are shared (roughly) equally bw the two atoms.

→ a polar covalent bond occurs if the e⁻ are generally closer to one atom than another.

→ from the terms above, you should be able to compare reactivities of compounds:

① ↓ bond length, ↓ reactivity

→ ↑ F.A bw nuclei & e⁻

② ↑ bond energy, ↓ reactivity

→ ↑ E needed to break bond(s)

③ ↑ polarity, ↑ reactivity

→ less even distribution of electrons

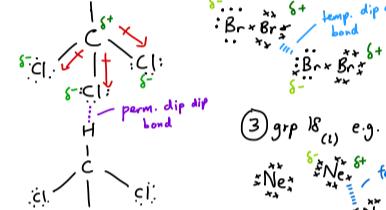
→ ↑ bond length

→ ↓ F.A bw nuclei & e⁻

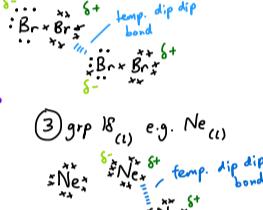
* at a particular pt in time

Examples

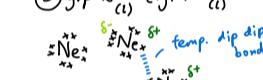
(1) CHCl_3 (l)



(2) Br_2 (l)

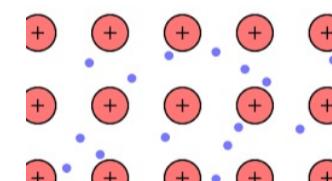


(3) grp 18 (l)



3.4 Metallic Bonding

→ define **metallic bonds** as the electrostatic attraction between the lattice of cations & the sea of delocalised electrons.



(4) hydrogen bonding

(i) boiling and melting points



observations:

① H_2O , HF & NH_3 have much higher boiling points than their "categories"

→ H_2O , HF & NH_3 have H bonding between molecules

→ the rest only have permanent dipole-dipole bonds

→ more thermal energy needed to break intermolecular forces in H_2O , HF & NH_3 , to vapourise

→ as H bonds are relatively stronger than permanent dipole-dipole bonds.

(2) as period increases (for p>3)

boiling point increases

→ size of respective atom increases

→ number of electrons increases

→ magnitude of temporary dipole-dipole bonds increases

→ more thermal energy needed to break intermolecular forces in successive molecules

2) surface tension & viscosity



observations:

① water has a high surface tension

→ there are hydrogen bonds between water molecules

→ this allows the molecules to stick together

→ importance: allows small insects to walk on water

② water also has high viscosity

→ viscosity is positively correlated with the strength of intermolecular forces

→ there are strong hydrogen bonds between molecules of water

4 States Of Matter

4.1 The Gaseous State, Ideal & Real Gases

- recall the basic assumptions of kinetic theory as applied to ideal gases:
 - ① particles are in constant random motion
 - ② the temperature of the system is directly proportional to the average kinetic energy of particles
 - ③ there are negligible interactions between particles, except for perfectly elastic collisions
 - ④ there are no/negligible intermolecular forces of attraction between particles
 - ⑤ particles behave as rigid spheres
 - ⑥ gas consists of particles or molecules with no/negligible volume.

- recall that for a gas to reach ideal behaviour:
 - 1) negligible intermolecular forces
 - 2) negligible molecular size

→ understand that an ideal gas obeys the ideal gas equation $pV = nRT$, where:

- ① p = pressure, in Pa or Nm^{-2}
- ② V = volume, in m^3
- ③ n = number of moles, in mol
- ④ R = the ideal gas constant, 8.31
- ⑤ T = temperature of system, in $^{\circ}\text{K}$ or $^{\circ}\text{C} + 273$

From this, you can infer that

$$M_r = \frac{pV}{nRT} \quad (\text{where } M = \text{mass, in g})$$

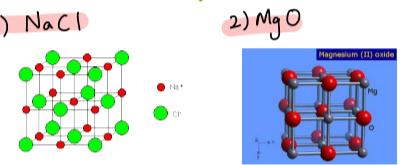
→ recall that at very high pressures and very low temperatures intermolecular forces become significant

- 1) intermolecular forces become significant
 - ⇒ ↓ dist.
 - ⇒ ↓ KE (for ↓ temp)
- 2) ratio of molecular size and gas volume becomes significantly high

4.3 The Solid State: Lattice Structures

- describe the structures of the compounds below:

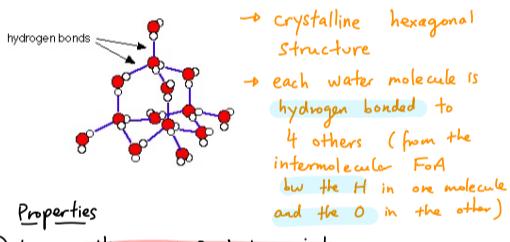
4.3.1 Ionic Compounds



- exist as giant ionic structures / ionic lattices
- cubic
- strong elec-static attraction between oppositely charged ions
- coordination number (max # of atoms bonded to central atom) is 6
- * MP of MgO more than MP of NaCl
 - ↑ charge density
 - ↑ bond strength

4.3.4 Hydrogen Bonded Compounds

- ice

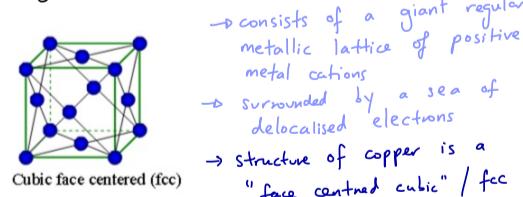


Properties

- ① Low melting point & boiling point
 - H bonds still weaker than intra-molecular forces
- ② Lower density than liquid H_2O
 - H bonds increase volume of solid
 - to form crystalline structure
 - mass remains constant
 - so (as $\rho = \frac{m}{V}$) density decreases
- ③ Poor conductor of electricity
 - absence of mobile charged particles in structure

4.3.5 Metallic Structures

- e.g. copper

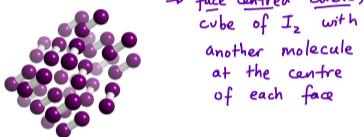


Properties

- ① Good electrical conductor
 - presence of delocalised e^-
- ② Strong
 - presence of many strong metallic bonds
- ③ High melting point & boiling point*
 - presence of many strong metallic bonds
 - that take a lot of energy to break
- ④ Insoluble
 - some react however

4.3.2 Simple Covalent Compounds

1) Iodine, I_2



→ face centred cubic; cube of I_2 with another molecule at the centre of each face

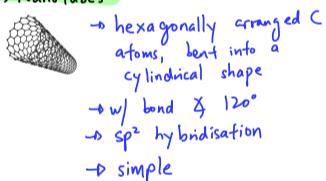
→ allotrope: forms of the same element, but different structures

→ fullerene: allotropes of carbon, but in the form of hollow spheres & tubes.

Properties

- ① Low melting & boiling point
 - weak intermolecular forces between molecules
- ② Solubility dependent on molecular polarity
- ③ Poor conductors of heat and electricity
 - exceptions: acids & bases

3) Nanotubes



→ hexagonally arranged C atoms, bent into a cylindrical shape

→ w/ bond \angle 120°

→ sp^2 hybridisation

→ simple

Properties

- ① High tensile strength
 - (resistance of a material to breaking under tension)
- ② High melting point
 - presence of many strong covalent bonds throughout structure
- ③ High electrical conductivity
 - presence of delocalised e^- throughout structure

4.3.6 Additional Stuff

→ you should be able to state resources are finite and outline the benefits of recycling:

- ① conserve energy
- ② land fills are filled up slower
- ③ conserves ore supplies
- ④ more cost-effective than extraction

Examples:

- ① Cu (↓ energy used for smelting)
- ② Al (↓ energy used for electrolysis)

→ you should be able to, given data about the physical properties of a substance, suggest the possible nature of that substance

1) bonding present

2) structure

4.2 The Liquid State

→ describe the following:

- ① liquid state: molecules can only slide past one another.
 - shape bounded by walls of container
 - intermolecular F are moderate

- ② melting: the process in which a substance Δ from a solid state into a liquid state, caused by heating.

→ energy transferred to solid.
→ vigorous vibration
→ lower forces of attraction
→ when temp. is high enough, solid changes into a liquid

- ③ vapourisation: the process in which a substance Δ from a liquid state into a solid state, caused by heating.

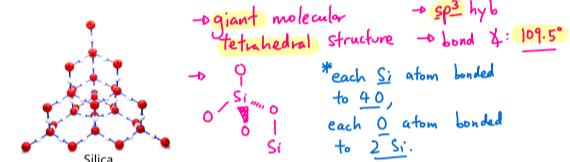
→ as temp. ↑, more particles have enough kinetic energy to escape surface of liquid
→ at a critical temperature, even the particles with the lowest kinetic energy can overcome the FoA
→ so liquid transitions into a gas.

- ④ vapour pressure: the pressure exerted by a gas in an (thermo-dynamic) equilibrium state, at a given temperature.

→ caused by particles hitting the walls of the container.

4.3.3 Giant Molecular Compounds

1) Silicon (IV) oxide, SiO_2



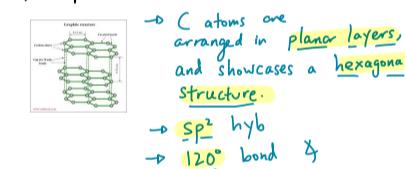
Properties

- ① High sublimation point
 - weak Ldn disp F
 - lack of giant structure
- ② Soft
 - weak Ldn disp F
- ③ Poor conductor of electricity
 - absence of delocalised e^-
- ④ Soluble in non-polar solvents
- ⑤ Reactive
 - high e^- density in parts of molecule

* → you must also realise the melting point of diamond is lower than the MP of graphite.

⇒ dia hyd: gra = sp^3
⇒ dia: 2517 s, 3517 p
gra: 3337 s, 6671 p
⇒ S's charact, ↓ bond length,
↑ s character, ↓ bond pair of e^-
⇒ FFA has nuclei & bonded pair of e^-
⇒ orbital is closer to nucleus

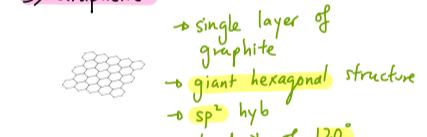
2) Graphite



Properties

- ① Lubricating
 - layers can slide past each other easily
- ② High melting point
 - presence of many strong C-C bonds
 - a lot of thermal energy needed to break bonds
- ③ Insoluble in all solvents
- ④ Good electrical conductor
 - due to "cloud" of delocalised electrons between layers.

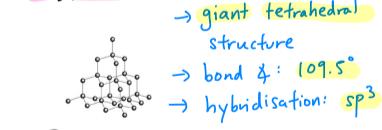
3) Graphene



Properties

- ① High melting point
 - presence of many strong covalent bonds
 - a lot of thermal energy needed to break bonds
- ② Insoluble in all solvents
 - attr. bw solvent molecules and C atoms will not be strong enough to overcome covalent bonds
- ③ Good conductor of electricity
 - presence of mobile delocalised e^- throughout structure
- ④ Reactive
 - extensive network of covalent bonds

4) Diamond



Properties

- ① Very hard
 - presence of numerous strong covalent bonds
 - stable tetrahedral structure
- ② High melting and boiling point
 - presence of many strong covalent bonds
 - that require a lot of thermal energy to break
- ③ Insoluble in all solvents
- ④ Poor conductor of electricity
 - absence of mobile charged particles

* exceptions:
graphite

Chapter 5: Chemical Energetics

What is ENTHALPY?

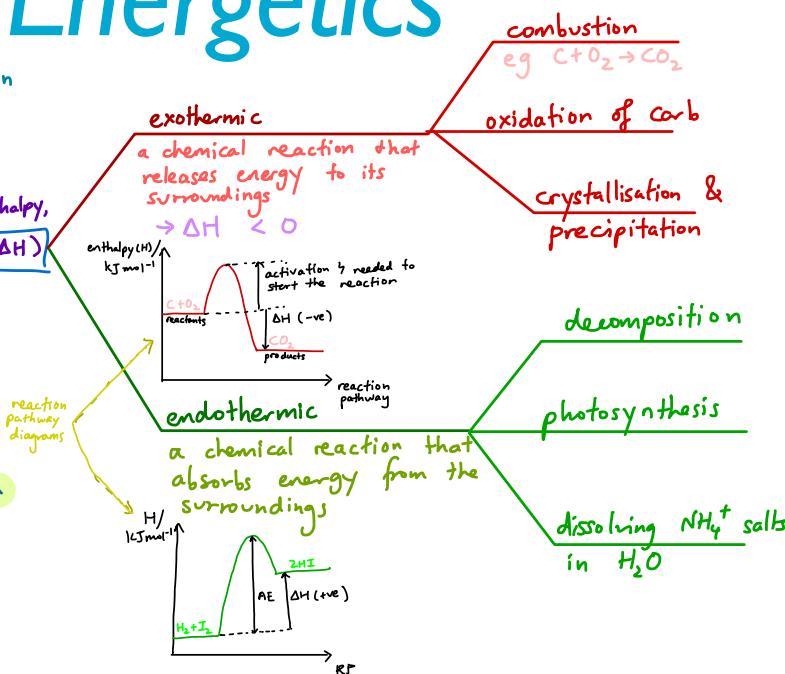
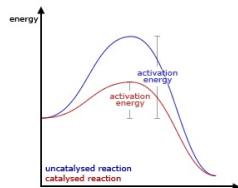
→ a measure of the energy stored in a system.

The relative enthalpies of a system differ between before and after a reaction. This results in the gain or loss of enthalpy, signified by the enthalpy change (ΔH)

→ in experimentation, ΔH is usually measured via the ΔT in temp.

ENTHALPY PROFILE DIAGRAMS w/ CATALYST

→ catalysts speed up reactions by lowering the activation energy needed to commence them.

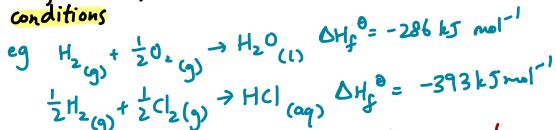


* exo reactions are energetically ↑ stable.
• products ↓ H
∴ ↑ stability
(this is why most chemical reactions are exo in nature)

TYPES OF ENTHALPY CHANGES

① STANDARD ENTHALPY CHANGE OF FORMATION / ΔH_f°

→ the enthalpy change when 1 mole of a compound is formed from its elements under standard conditions



• the ΔH_f° of an element in its normal physical state = 0

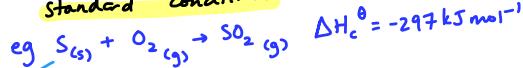
• if $\Delta H_f^\circ < 0$, compound is more stable than constituent elements.
if $\Delta H_f^\circ > 0$, compound is less stable than constituent elements.

* 0 indicates ΔH in standard conditions, i.e.
 $T = 298 \text{ K}$, $P = 1.01 \times 10^5 \text{ Pa} = 1 \text{ atm}$,
each subst involved in normal physical state

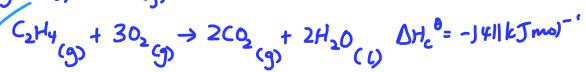
* There are three elements in which their ΔH_f° 's can be applied to both ΔH_f° & ΔH_c°
 ① $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$
 ② $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
 ③ $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

② STANDARD ENTHALPY CHANGE OF COMBUSTION / ΔH_c°

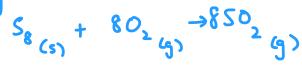
→ the enthalpy change when 1 mole of a substance is completely burnt in an excess of oxygen under standard conditions



* ΔH_c° is always negative



→ compound w/ C w/ ↓ oxidation # will release ↑ heat when combusted!



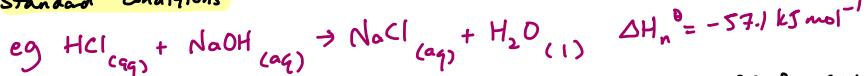
$\text{C:X} \quad \text{H:+1} \quad \text{O:-2}$

$$\therefore \text{C} = \frac{-6}{3} = -2$$

* C oxid. # not necessarily Z

(3) STANDARD ENTHALPY CHANGE OF NEUTRALISATION / ΔH_n^\ominus

→ the enthalpy change when 1 mole of water is formed by the reaction between acid and alkali under standard conditions



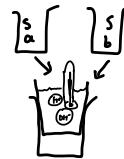
STRONG ACIDS & ALKALIS

$$\Rightarrow \Delta H_n^\ominus = -57.1 \text{ kJ mol}^{-1}$$

this is because the neutralisation only involves the formation of H_2O from hydroxide & hydrogen ions, i.e. $H^+ + OH^- \rightarrow H_2O$
since the process is the same for all, ΔH_n^\ominus is constant.

* mineral acids are always strong;
organic acids (acids w/ C) always weak.

* out of $\{HCl, HNO_3, H_2SO_4, H_3PO_4\}$ *



* ΔH_n^\ominus is always negative

WEAK ACIDS & ALKALIS

$$\Rightarrow \Delta H_n^\ominus > -57.1 \text{ kJ mol}^{-1}$$

eg $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ $\Delta H = -54.0 \text{ kJ mol}^{-1}$
this is bc, besides the reaction bw H^+ & OH^- , ΔH_n^\ominus will also involve other enthalpy terms involved in ionising the weak acid



(heat released is used to complete the ionisation of the weak acid/base)
(weak acid/base only ionise partially)
* less exothermic.

(4) STANDARD ENTHALPY CHANGE OF SOLUTION / ΔH_{sol}^\ominus

→ the enthalpy change when 1 mole of solute is dissolved in a solvent to form an infinitely dilute solution under standard conditions



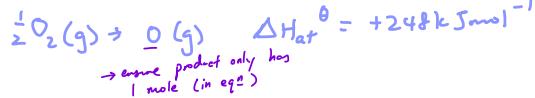
→ all solute can be dissolved;
don't measure under supersaturated solution.
(presence of ppt)

* ΔH_{sol}^\ominus can be +ve or -ve.

- if it has a ↑ +ve value, compound is insoluble in water
- if it has a ↓ +ve or -ve value, compound is soluble in water

(5) STANDARD ENTHALPY CHANGE OF ATOMISATION / ΔH_{at}^\ominus

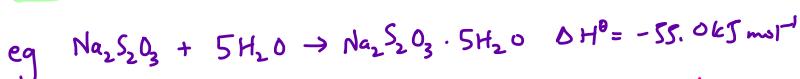
→ the enthalpy change when 1 mole of gaseous atoms is formed from its element under standard conditions



* ΔH_{at}^\ominus is always positive

(6) STANDARD ENTHALPY CHANGE OF HYDRATION OF AN ANHYDROUS SALT

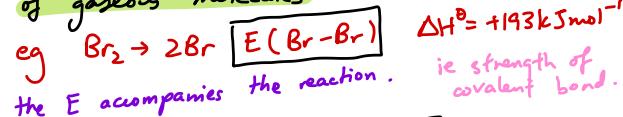
→ the enthalpy change when 1 mole of a hydrated salt is formed from one mole of the anhydrous salt under standard conditions



* ΔH^\ominus is always negative

BOND ENERGY (also known as bond enthalpy / bond dissociation energy)

→ amount of energy needed to break one mole of covalent bonds, in one mole of gaseous molecules



* bond energies are always positive
• bond energy is the energies required to break bonds
• bond breaking is always endothermic

FACTORS WHICH DETERMINE E_B ?

① Type of bond

$\times 3 > \times 2 > \times 1$
ie $N=N > O=O > H-H$

* ↑ E_B , ↓ reactivity
(e.g. N_2)

② Bond length

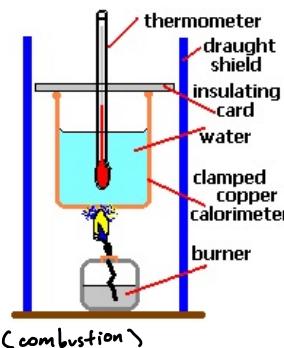
→ distance bw the nuclei of the two atoms joined by covalent bonds

* → dependent on size of atom:

↑ atomic size; :: ↓ BE.
↑ BL;
↓ orbital overlap;

EXPERIMENTAL DETERMINATION OF ENTHALPY CHANGES

Basic Calorimeter Set

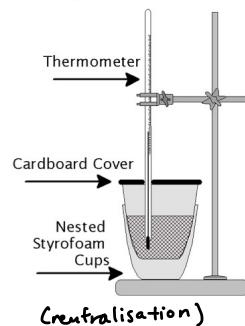


→ used to measure temperature change caused by a reaction

Errors

- incomplete combustion of fuel
- not all heat released transferred to water

Diagram of a Calorimeter



Mathematical Eq's for ΔH

$$\textcircled{1} \quad Q = -mc\Delta T \quad (\text{Q=heat absorbed})$$

$m = \text{mass of solution/g}$
→ only mass of solvent/solution
→ for ALL aq sol: $1\text{cm}^3 \equiv 1\text{g}$

$c = \text{spec. heat cap of H}_2\text{O}/4.18\text{J g}^{-1}\text{C}^{-1}$
 $\Delta T = \text{change of temp.}$ *not compulsory to
clg bw ${}^\circ\text{K}$ or ${}^\circ\text{C}$

$$\textcircled{2} \quad \Delta H = \frac{\text{heat evolved / absorbed}}{\text{no. of moles of limiting reagent}}$$

* answer must have:
 ① sign (ex/end) ③ unit (kJ mol^{-1})
 ② value

ΔH_c° by experiment

The unit for enthalpy change: kJ mol^{-1}

Enthalpy Change of Combustion by Experiment

Calculate the enthalpy change of combustion of methanol, CH_3OH by using the readings obtained from the experiment:

Mass of water in calorimeter	= 200g
Mass of methanol and burner at start	= 532.68g
Mass of methanol and burner at end	= 531.72g
Temperature of water at start	= 18.3°C
Temperature of water at end	= 28.6°C

$$Q = -mc\Delta T$$

$$= -(200 \times 4.18 \times 11.3)$$

$$\text{mass of H}_2\text{O}$$

$$= -9446.8\text{ J}$$

$$m_{\text{CH}_3\text{OH combusted}} = 0.96\text{ g} : M_r = 32.0\text{ g mol}^{-1}$$

$$\therefore n = \frac{0.96}{32} = 0.03\text{ mol.}$$

$$\Delta H = \frac{-9446.8}{0.03} = -315\text{ kJ mol}^{-1}$$

ΔH_n° by experiment

Enthalpy Change of Neutralization by Experiment

Calculate the enthalpy change of neutralization given that on mixing 100cm^3 of 0.500 mol dm^{-3} HCl(aq) with 100cm^3 of 0.500 mol dm^{-3} NaOH(aq) , then temperature of the mixture was found to have risen by 3.4°C

$$200\text{cm}^3 : M = 200\text{g}$$

$$Q = -mc\Delta T$$

$$= -(200 \times 4.18 \times 3.4)$$

$$= -(2842.4)\text{ J}$$

$$\Delta H = \frac{-2842.4 \times 10^{-3} \text{ kJ}}{0.5 \times 0.1 \text{ mol}}$$

$$\Delta H = -56.8 \text{ kJ mol}^{-1}$$

$\Delta H_{\text{sol}}^\circ$ by experiment

Enthalpy Change of Solution by Experiment

Scenario: The enthalpy change of solution of sodium hydroxide pellet can be obtained by using polystyrene cup as a calorimeter

Mass of water	= 100.45g
Mass of dissolved sodium hydroxide	= 1.50g
Temperature of water at start	= 18.0°C
Temperature of water at end	= 21.6°C

$$\Delta H = \frac{-1.51157 \text{ kJ}}{1.50 / (22.99 + 16.1)}$$

$$\Delta H = -40.3 \text{ kJ mol}^{-1}$$

$$Q = -mc\Delta T$$

$$= -(100.45 \times 4.18 \times 3.6)$$

$$= -1511.57 \text{ J}$$

* experimental value of ΔH_c is less accurate than ΔH_n

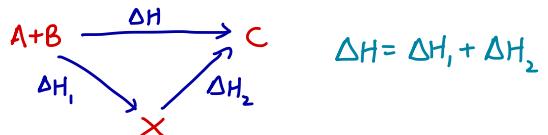
- ① Heat loss to surroundings
- ② Incomplete alcohol combustion
- ③ Evaporation of volatile alcohol
- ④ Combustion of impure alcohol

* only ΔH_c , ΔH_n & ΔH_{sol} can be determined experimentally.

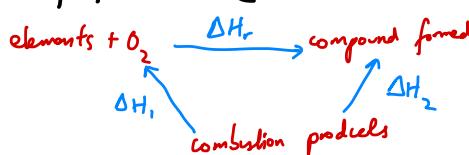
For the other ΔH mentioned, we can determine them theoretically through Hess's Law.

HESS'S LAW

→ total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place, as long as the initial and final conditions are the same.



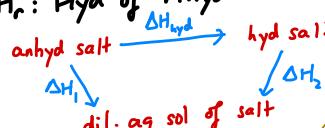
ΔH_f from ΔH_c



- ① Write balanced eqn for ΔH_f at the top.
- ② Write combustion products at bottom
- ③ Draw all arrows
- ④ Apply Hess's law, taking into account # of moles of each reactant & product formed.

- tips
- identify types of bonds in each reactant & product
 - reactants undergo bond breaking (+ve ΔH)
 - products undergo bond forming (-ve ΔH)
 - ΔH_r is net enthalpy Δ.

ΔH_r : Hyd of Ahyd salt



* ΔH_r cannot be determined directly:
 ΔH_r can only be determined by calculating ΔH_{sol} for both anhyd & hyd salts.

why?

- ① initial state is solid (impos. to measure temp.)
- ② humid environment
- ③ cannot verify when all salt has been hydrated.

Chapter 6:

Electrochemistry

* note:
 electrolysis of brine using a diaphragm cell,
 extraction of Al from bauxite, (inc. electrolysis)
 purification of Cu using electrolysis -
ALL REMOVED. (even from A2)

"redox reaction" — a reaction in which reduction & oxidation occur simultaneously.

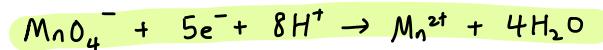
terms:

- ① **oxidation**: loss of e^- → ↑ ox.# / ↑ O } OIL RIG
oxidation is loss reduction is gain
- ② **reduction**: gain in e^- → ↓ ox.# / ↓ O }
- ③ **oxidising agent**: e^- acceptor, reduces species → eg $H_2 + I_2 \rightarrow 2HI$ ($H \rightarrow H^+ + e^-$)
→ acidified $KMnO_4$ & $K_2Cr_2O_7$, H_2O_2 , halogens (oxidants)
- ④ **reducing agent**: e^- donator, oxidises species → eg $H_2 + I_2 \rightarrow 2HI$ ($I + e^- \rightarrow I^-$)
→ $Na_2S_2O_3$ (sodium thiosulfate), halides, SO_2 (reductants)
- ⑤ **oxidation number**: a num. given to each atom/ion in a compound, that describes how oxid/red it is.
→ we use this to:
 - a) identify which reactions are redox
 - b) identify reducing & oxidising agents.
- ⑥ **disproportionation**: the simultaneous oxid. & redu. of the same species in a chemical reaction.
eg $Cu_2O + H_2SO_4 \rightarrow Cu + CuSO_4 + H_2O$
 (Cu^+) (Cu) (Cu^{2+})
↓ reduction ↑ oxidation

common examples of redox reactions

- ① between thiosulfate and iodine ions:
(starch catalyst)
- $$2S_2O_3^{2-} \text{ (aq)} + I_2 \rightarrow S_4O_6^{2-} \text{ (aq)} + 2I^-$$
- iodine acts as the weak oxidising agent
(by oxidising thiosulfate into tetra thionate ions)
 (S_2O_3) (S_4O_6)
- observations:
 - ① initial brown solution (due to I_2)
 - ② as thiosulfate is added, solution turns pale yellow (due to some I_2 being ionised into $2I^-$)
 - ③ final result of colourless solution (all I_2 ionised)
- Usually, starch indicator is added to achieve a sharper end pt.
★ blue-black → colourless.

- ② redox reaction of **manganate (IV) ions** in an **acidic solution**



→ potassium manganate (VII) acts as a strong oxidising agent

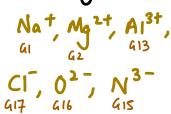
→ observations:

- ① initial deep purple solution (manganate (IV) ions)
- ② solution turns nearly colourless (manganate (IV) turns into manganate (II) ions)
- ③ final result: first extra drop of Manganate (VI) ions make (why?) solution permanent pale pink.

rules for working out oxidation numbers

① All neutral atoms have an ie Mg, Fe, H₂, O₂, S₈
oxidation num. (O_N) of 0.

② For simple ions, the O_N is the same as the ionic charge
ie Na⁺, Mg²⁺, Al³⁺,



However, there are EXCEPTIONS

- H has an oxidation state of -1 in group 1 metal hydrides. eg in KH and NaH
- O has an O_N of +1 in peroxides eg in H₂O₂
- O in compounds w/ more 4-ve atom (ie F₂O)
→ since F has an oxid. state of -1, and is more 4-ve, O has an O_N of +2.
- Halogenic compounds w/ more 4-ve atoms (ie FCl)
→ the more electronegative element gets the -1 oxidation state.

③ In a neutral molecule,
 $\sum O_N = \text{zero.}$

$$\text{ie Al}_2\text{O}_3 : 2\text{Al}^{3+} \& 3\text{O}^{2-} \\ \therefore 2(+3) + 3(-2) = 0.$$

④ In a polyatomic ion:

$$\text{eg NH}_4^+ \\ x + 4(1) = 1 \\ \therefore x = -3.$$

⑤ In complex ionic compounds:

$$\text{eg NH}_4\text{NO}_3$$

split into component ions: → NH₄⁺ NO₃⁻

$$\text{then compare: } x + 4(1) = 1 \quad y + 3(-2) = -1 \\ x = -3 \quad y = 5.$$

balancing chemical equations : methods

① balancing eqns for redox reactions in acidic solution.

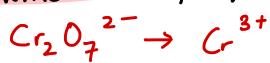
for instance, balance:



* some half equations are given in the DATA BOOKLET.

Steps:

i) Write the half equations.



ii) Balance each half reaction for elements other than H and O



iii) Balance each half-reaction for O by adding water molecules



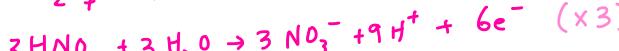
iv) Balance each half-reaction for H by adding hydrogen ions



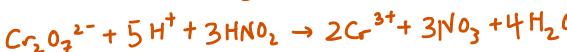
v) Balance each half-reaction for charge (by adding e⁻)



vi) Multiply by an appropriate factor



vii) Add balanced half reactions.



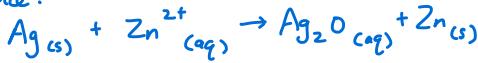
important!

→ never add O₂, O atom or O²⁻ to balance oxygen.

→ never add H₂, H atom to balance hydrogen.

(2) balancing eqⁿs for redox reactions in basic solution.

for instance:



Steps:

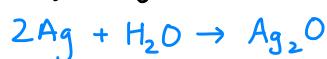
i) Write the half equations



ii) Balance each half-reaction for elements other than H & O



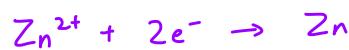
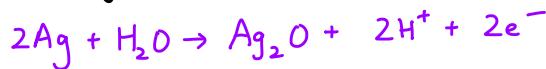
iii) Balance each half-reaction for oxygen by adding H₂O.



iv) Balance each half-reaction for hydrogen by adding H⁺



v) Balance each half-reaction for charge



(3) balancing chemical eqⁿs by using oxidation numbers.

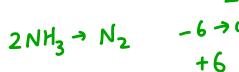
eg copper(II) oxide reacts with NH₃ to produce Cu, N₂ and H₂O.

steps:

i) write the unbalanced eqⁿ and identify the atoms which ΔO_N



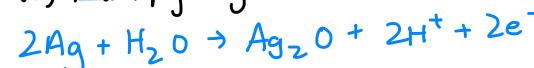
ii) deduce the ox.no change



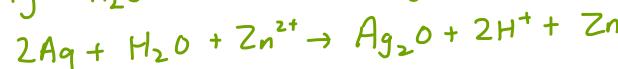
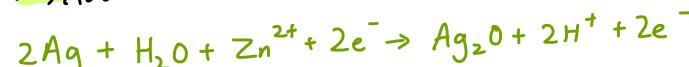
iii) balance the O_N charges



vi) Multiply by an appropriate factor.



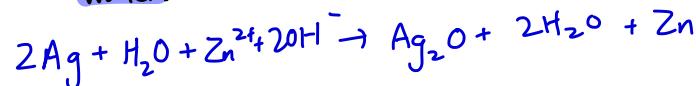
vii) Add balanced half-reactions



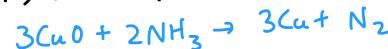
viii) Add OH⁻ to balance H⁺



ix) Combine H⁺ & OH⁻ to form water.



iv) add half eqⁿs



v) balance the remaining oxygen, hydrogen atoms



* always consider the mole!
ie 2N³⁻ = -6 (O_N)

Chapter 7: Equilibria

REVERSIBLE REACTIONS

→ a reaction in which the products can react to reform the original reactants.



→ we can use activation energy data to determine whether a reaction is reversible.

→ if $AE(M) \gg M$, backward reaction is unfavourable

→ thus irreversible reaction.

DYNAMIC EQUILIBRIUM

→ a reaction in which the molecules of reactants are being converted to products at the same rate as products are being converted to reactants.

characteristics:

① rate of forward reaction = rate of backward reaction

② conc. of reactants = *BUT [reactants] conc. of products = \ominus [products]

③ reactants continuously being converted to products, and vice versa

④ only occurs in closed system.

HABER PROCESS



conditions: not necessary to memorize values.

① ↑ pressure of (60–250 atm) * ↑ P is costly to maintain.

→ to shift eq (\rightarrow)

③ Fe/Fe₂O₃ catalyst

* ↑ P is costly to maintain.

→ to ↑ rate

→ by providing an alternative path of lower E_a .

④ Removal of NH₃ thru condensation

→ to ↑ yield NH₃.

② ↑² temp. of 300–500 °C

→ if ↑² T, yield of NH₃ ↓ (altho ↑ rate)

→ if ↓ T, rate ↓ (altho yield ↑)

→ this temp is used mainly to speed up the reaction.

uses of NH₃ IRL:

① Nitrogenous fertilisers

② HNO₃

③ Explosives

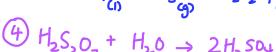
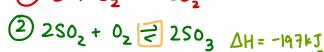
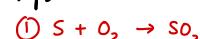
④ Refrigerant

⑤ Cleaning agents

⑥ Nylon

CONTACT PROCESS

→ the creation of H₂SO₄(aq). steps:



CHANGING REACTION CONDITIONS

→ Le Chatelier's Principle

→ if 1 or more factors that affect an equilibrium is changed, the pos of equilibrium shifts in the direction that reduces / opposes the change.

→ changing conditions of reaction methods:

① Concentration



a) if $c_{SCN^-} \uparrow$, eq shifts to (\rightarrow)

→ to remove extra SCN⁻

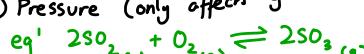
→ observation: redder solution

b) if $c_{SCN^-} \downarrow$, eq shifts to (\leftarrow)

→ to replace lost SCN⁻

→ observation: paler (red) solution

② Pressure (only affects g reactions)



a) when $\uparrow P$, eq shifts (\rightarrow)

Why? → to produce ↓ ↗ of g
the goes in the eq, and ignore everything else

hence: resultant mixture $\uparrow SO_3, \downarrow SO_2, O_2$

b) when $\downarrow P$, eq shifts (\leftarrow)

Why? → to produce ↑ ↗ of g

→ to ↑ P

hence: resultant mixture $\uparrow SO_2, O_2, \downarrow SO_3$

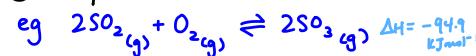


→ if no Δ in # of g in reaction;

changes in pressure will have no effect on the composition of eq mixture.

→ increasing the p will increase both the rate of the forward & backward reactions.

③ Temperature



a) when $T \uparrow$, pos of eq (\leftarrow)

Why? → endothermic reaction favoured

→ to remove extra heat ↴

→ result has $\uparrow SO_2, O_2, \downarrow SO_3$.

b) when $T \downarrow$, pos of eq (\rightarrow)

Why? → exothermic reaction favoured

→ to replace lost heat ↴

→ result has $\downarrow SO_2, O_2, \uparrow SO_3$.

→ catalysts do not affect the position of equilibrium.

→ it solely increases the rate of reaction, by providing alternative pathway of lower E_a .
* it does not directly ↓ E_a .

SIMILARITIES BW HABER & CONTACT EQ REACTIONS

① Both products are redox

② Both result in higher yield of products when pressure increased. (eq (\rightarrow))

③ Forward reactions are exothermic

conditions for ②:

i) 1-2 atm pressure

→ when $\uparrow P$, eq (\rightarrow)

∴ ↑ yield of SO₃

Then why p just above std atm?

→ ↑ K_p even at this p

→ eq ↑ (\rightarrow)

→ app. of ↑ p requires ↑ cost

ii) 400–450 °C temp

→ ↑ yield, while not significantly affecting rate

iii) V₂O₅ catalyst

→ to ↑ rate by providing an alternative path of ↓ E_a

iv) Air used to burn S, must be as pure as possible. Why? → will take up the "active site" of catalyst.

→ to prevent catalyst "poisoning"

EQUILIBRIUM CONSTANTS

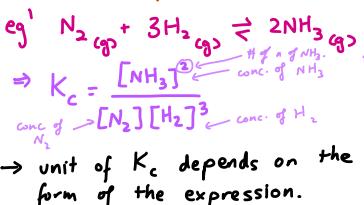
→ constants used to calculate eq. mixture composition.

① Homogenous eq

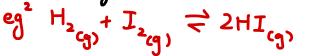
→ reactions in which all reacting species are in the same phase/state
eg $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

K_c

→ c refers to the concentration of reactants & products, in mol dm^{-3}
→ "equilibrium expression": a relationship which links K_c to the eq conc of reactants, products & the eqⁿ stoichiometry.
→ in the form $\frac{\text{products}}{\text{reactants}}$.



→ unit of K_c depends on the form of the expression.



$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

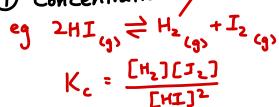
$$[K_c] = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]^2}$$

$[K_c] = [1]$ ∵ no unit

FACTORS THAT AFFECT EQUILIBRIUM CONSTANT

POSITION

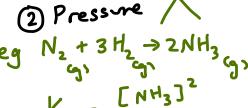
① Concentration



→ if more HI added, pos of eq (\rightarrow)

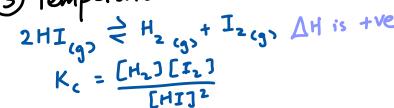
→ hence $[HI] \downarrow$, $[H_2, I_2] \uparrow$
→ at the end, eq restored
→ so conc does not change the EC.

② Pressure



→ if pressure increases, all conc. \uparrow as V \downarrow
→ but since K_c is a ratio, it remains unchanged.
→ so pressure also does not DEC.

③ Temperature



→ if T \uparrow , sys fav. endo.

∴ eq shifts right.

$$\therefore [H_2, I_2] \uparrow, [HI] \downarrow$$

∴ $K_c \uparrow$.
so temperature does affect the EC.

② Heterogeneous eq

→ reactions in which reactants & products are in different states
eg $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

* applied to all eq reactions

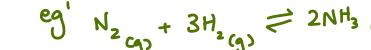
* except solids

Why? → solids cannot be quantified by conc.

K_p

→ p refers to the partial pressure of gas, in Pa

→ "partial pressure of gas": pressure exerted by any one gas in the mixture.



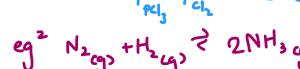
$$\Rightarrow K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

* reactants & products written as subscripts after p
* # n of each constituent written as superscripts after p.

→ similarly, K_p unit depends on the eq expression.



$$K_p = \frac{P_{PCl_3}}{P_{PCl_5} \cdot P_{Cl_2}} = \frac{[Pa]}{[Pa]^2} = Pa^{-1}$$



$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}} = \frac{[Pa]^2}{[Pa]^2} = [1]$$

MEANING OF "K"

- $K \gg 1 \Rightarrow$ eq (\rightarrow) ∵ favour products.
- $K \ll 1 \Rightarrow$ eq (\leftarrow) ∵ favour reactants.

* for $A + 2B \rightleftharpoons C + D$.

$$K_p = \frac{(\frac{n_c}{n_T} \times p)}{(\frac{n_d}{n_T} \times p)} \cdot \frac{(\frac{n_b}{n_T} \times p)^2}{(\frac{n_a}{n_T} \times p)}$$

* partial p of a (g) = mole fraction \times total pressure.

BRONSTED-LOWRY THEORY OF ACIDS & BASES

→ in water, (Arrhenius defⁿ)

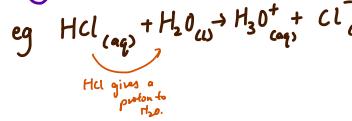
① An acid is a substance that donates H^+ when it dissociates in water

② A base is a species which accepts H^+ from acids.

→ BL defⁿ:

① An acid donates a proton;

② A base accepts a proton.



→ also:

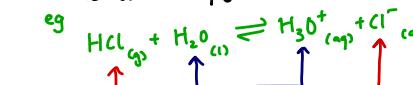
① "monoprotic acid": acids that only donate one proton, ie HCl , HNO_3

② "diprotic acid": acids that donate two protons, ie H_2SO_4

③ "triprotic acid": acids that donate three protons, ie H_3PO_4 .

CONJUGATE ACIDS & BASES

if a reactant is linked to a product by the transfer of a proton, this pair is a "conjugate pair".



① HCl donates a proton to H_2O .

→ hence Cl^- is the conjugate base of HCl ;

→ HCl is the conjugate acid of Cl^- .

② H_2O accepts a proton from HCl .
→ hence H_2O is the conjugate base of H_3O^+ ;
→ H_3O^+ is the conjugate acid of H_2O .

STRONG vs WEAK ACIDS & BASES

→ dependent on degree of dissociation.

→ strong acids/bases completely dissociate in solution.

→ eg mineral acids (HCl , HNO_3 , H_2SO_4 etc)

eg group 1 hydroxides (exc. Li) ($NaOH$, KOH etc)

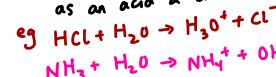
→ weak acids/bases only partially dissociate in solution.

→ eg organic acids, HCN , H_2S , H_2CO_3 (CH_3COOH etc)

→ eg NH_3 , some transition metal hydroxides.

AMPHOTERIC COMPOUNDS

→ a compound which simultaneously can act as an acid & a base.



Chapter 8:

Reaction Kinetics

WHAT IS RATE?

→ the changes in amt of reactants, or products, per unit time.

→ std unit: measured from the gradient of the conc-time graph.

e.g. $\text{mol dm}^{-3}\text{s}^{-1}$, $\text{mol g}^{-1}\text{s}^{-1}$

FACTORS AFFECTING RATE

COLLISION THEORY

→ in order to react with other op , the resultant op must collide:

- 1) w/ sufficient energy above the activation energy, and
- 2) in the correct orientation.

→ a collision that meets the above 2 criterion is deemed "successful".

→ hence, a reaction will speed up if:

- a) frequency of collisions ↑
- b) proportion of op w/ $E > E_a$ ↑.

Factors:

① Concentration

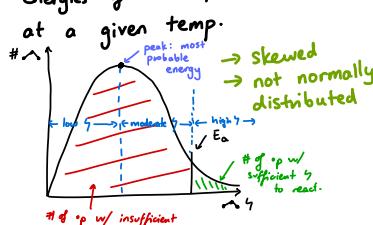
→ $\uparrow \text{conc.} \rightarrow \uparrow \text{rate}$

→ as $\uparrow \text{freq. of coll. bw } \text{op}$
*NOT $\uparrow \text{eff. collisions!}$

② Pressure

③ Temperature

Boltzmann Distⁿ graph:
a graph showing the distⁿ of energies of the op in a sample at a given temp.

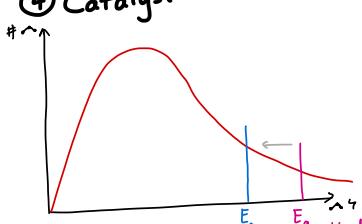


I: If $T \uparrow$:
→ curve shifts (\rightarrow)
→ peak ↓
→ but total area under curve $\propto E_a$ []
→ mean \uparrow ↓ ↑.
*→ proportion of molecules with energy $> E_a$ increases

II: If $T \downarrow$:
→ curve shifts (\leftarrow)
→ peak ↑
→ total area under curve $\propto E_a$ []
→ mean \uparrow ↓ ↓.

Why does $\uparrow T$ ↑ rate?
→ ave. KE of op ↑
→ more collisions
→ more successful collisions
→ more molecules possess molecular $\uparrow \geq E_a$.

④ Catalyst



→ catalysts (generally) increase the rate of reaction by providing an alternative mechanism of $\downarrow E_a$ \Rightarrow
→ $\therefore \uparrow \text{freq. of react.}$
→ $\therefore \uparrow \text{freq. of successful collisions.}$

⑤ Surface Area

→ the larger the size of reacting op , the \downarrow the total SA & contact bw reacting op .
→ $\therefore \downarrow \text{rate of reaction.}$

CATALYSTS

→ catalysts are substances that increases the rate of reaction, but remains chemically unchanged at the end of the reaction.

→ key insights:

① Minute amounts of catalyst are used, but the quantity of cat. will affect rate.

② Catalyst type also affects rate.

③ However, catalysts do not affect:

- ΔH_r :

- K_c & K_p ; and

- yield of products.

④ Catalysts also cannot initiate reactions, and

⑤ They are not used up during the reaction.

→ examples:

① Fe, in $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

② V_2O_5 , in $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$.

③ Transition elements in catalytic converters:

(rhodium, Rh) $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$

(palladium, Pd) $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$.
or platinum, Pt)

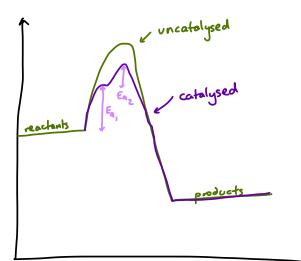
ACTIVATION ENERGY

→ the minimum energy that colliding op must possess for a successful collision to take place.

→ essential for:

1) breaking bonds in the reacting molecules

2) overcome repulsive forces.



→ why two humps?
→ two step reaction
ie $\text{A} + \text{B} \rightarrow \text{C}$
 $\text{C} + \text{D} \rightarrow \text{A}$

HOMOGENEOUS CATALYSTS

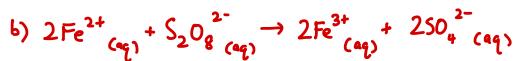
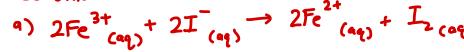
- a type of catalyst in which it occupies the same phase as the reaction mixture
- often occurs in (g) & (aq)
- usually transition elements, as they can Δ oxid. state.

→ examples:

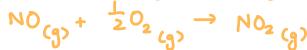
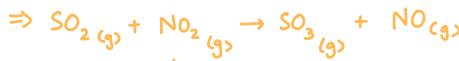
① The iodine-peroxodisulfate reaction



mechanism:



② Oxides of nitrogen & acid rain



③ Enzyme catalysis

→ "enzymes": biological catalysts

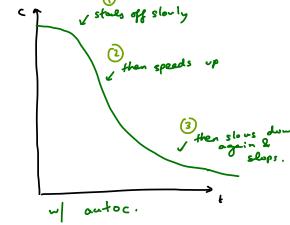
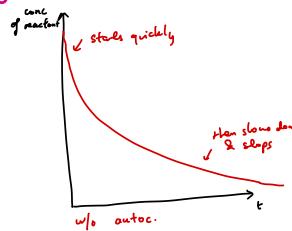
→ since most enzyme-catalysed reactions take place in (aq), they are examples of homogenous catalysis

similar to inorganic catalysts:

- i) it is not used up in the reaction, but speeds it up
- ii) it provides an alternative reaction pathway with a lower E_a .

AUTOCATALYST

- product of a chemical reaction acts as a catalyst in the reaction.



why?

- 1) ↓↓ amt of cat.
- 2) ↑↑ amt of cat.
- 3) ↓↓ conc. of reactant.

• specific characteristics

→ more efficient than inorg. cat.

→ no byproducts formed

→ optimum conditions:

37°C , pH 7, atm. p

Chapter 9: Chemical Periodicity (Period 3)

WHAT ARE P3 ELEMENTS?

Sodium (Na)	
Magnesium (Mg)	giant metallic
Aluminium (Al)	giant molecular
Silicon (Si)	giant molecular
Phosphorus (P)	simple molecular
Sulfur (S)	simple molecular
Chlorine (Cl)	exist as unitary "p"
Argon (Ar)	

PERIODIC PATTERN OF ATOMIC RADII

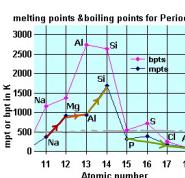
covalent radius → calc by identifying the dist bw 2 nuclei of the same type of bonded atom, then +2

VdW radius → calc by identifying the dist bw 2 nuclei of the atom that are not chem bonded, then +2
→ higher than ar
→ no overlap of e⁻ clouds.

atomic radius decreases as you go across the period.
Why?
1) #p ↑, NC ↑
2) Hence ↑Fa on outer shell e⁻
3) note: shielding

PERIODIC PATTERNS OF MELTING POINTS.

* MP < 500°C → low
MP > 500°C → high



① ↑ MP from Na to Mg

- Strength of metallic bonding ↑
- ↓ cation size
- ↑ # of delocalised e⁻
- ↑ Fa on outer shell e⁻ & sea of delocalised e⁻
- ↑ s needed to break metallic bonding in Mg, compared to Na

③ Sharp ↑ in MP of Si

- Because it exists as a giant molecular structure, held tog by strong covalent bonds

④ ↓ in MP across non-metal group

- S exists as S₈, P as P₄ & Cl as Cl₂
- solely weak VdW F exists bw
- hence S has the ↑ magnitude of VdW F due to greater number of e⁻, followed by P, then Cl.

② comparison among cations

From Na⁺ → Si⁴⁺, P³⁻ → Cl⁻, ionic radius decreases.
Why?
1) ions in these "groups" are ISOELECTRONIC (grps of atoms/ions w/ # of e⁻)
2) ↑#p ⇒ ↑NC
3) hence, outermost e⁻ in 2nd principal shell attracted closer to nucleus.

③ comparison between cations & anions

Anions have the bigger ionic radius.
Why?
they have one additional principal quantum shell.

PERIODIC PATTERNS OF ELECTRICAL CONDUCTIVITY

* Na, Mg, Al good conductors of electricity.

→ γ cond. ↑ across metal atoms.
Why? → # of valence e⁻ contributed to the delocalised e⁻ cloud ↑.

* Si is a semi-conductor

Why? → no delocalised e⁻ free to move within its structure.

* P, S, Cl are electrical insulators
Why? → no mobile e⁻ in Se, P₄ & Cl₂.

PERIOD 3 CHLORIDES

REACTION OF P3 ELEMENTS

WITH Cl₂

Na	• Na + $\frac{1}{2}$ Cl ₂ → NaCl
Mg	• bright white flame
Al	• 4Al + 3O ₂ → 2Al ₂ O ₃ (s) • bright white flame
Si	• Si + O ₂ → SiO ₂ (s) • white solid (SiO ₂)
P	• P + Cl ₂ → PCl ₃ (l) • P + Cl ₂ → PCl ₅ (s)
S	• S + Cl ₂ → SO ₂ (g) • SO ₂ (g) is toxic
Cl	• Cl + Cl ₂ → Cl ₂ (l) • Cl + Cl ₂ → Cl ₂ (g)

Si • Si + 2Cl₂ → SiCl₄

P • (excess Cl₂) P₄ + 10Cl₂ → 4PCl₅

Mg • Mg + Cl₂ → MgCl₂

Al • 2Al + 3Cl₂ → Al₂Cl₆

• colourless liquid forms

• colourless solid

• white solid

• white solid

• orange pungent liquid

CHLORIDES OF P3 ELEMENTS

	NaCl	MgCl ₂	AlCl ₃ (anhyd)	Al ₂ Cl ₆ (hydr)	SiCl ₄	PCl ₅	S ₂ Cl ₂
Structure	giant ionic	giant ionic	simple molecular	simple molecular			
When added to H ₂ O...	white solids dissolve to form colourless soln	white solids dissolve to form colourless soln	react to yield white fumes of HCl	react to yield white fumes of HCl			
pH	7	6.5	3	2	2	2	2
Oxidation #	+1	+2	+3	+4	+5	+1	

REACTION OF CHLORIDES WITH WATER

① NaCl + aq → Na⁺ + Cl⁻

② [Mg(H₂O)₆]²⁺ → [Mg(H₂O)₅OH]⁺ + H⁺ (pH = 6.5)

MgCl₂ + aq → Mg²⁺ + 2Cl⁻

③ Al₂Cl₆ + 12H₂O → 2[Al(H₂O)₆]³⁺ + 6Cl⁻

[Al(H₂O)₆]³⁺ → [Al(H₂O)₅OH]²⁺ + H⁺ → due to the +ve charge of water ~

AlCl₃ → [Al(H₂O)₆]³⁺ + 3Cl⁻

④ SiCl₄ + 2H₂O → SiO₂ + 4HCl(aq)

⑤ PCl₅ + 4H₂O → H₃PO₄ + 5HCl(aq)

complex ion will undergo polarisation, releasing an hydrogen ion

Chapter 10: Group 2

- alkaline earth metals
- outer shell config of ns^2
- reactive metals w/ low ionicity.

PROPERTIES

METALLIC RADIUS

- ↳ half of the dist. b/w nuclei in the giant metallic lattice
- ★ metallic radius ↑, ↓ the grp.
- why? → valence e^- occupy a new principal quantum shell further from the nucleus

DENSITY

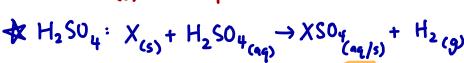
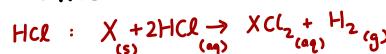
* group 2 metals are denser than group 1 metals (particularly Li, Na, K)

METALS + O₂

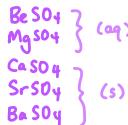
★ ALL G2 metals burn in O₂ to yield white solid metal monoxides.



METAL + ACIDS



* the solubility of G2 sulfates decreases down the group



METAL OXIDES

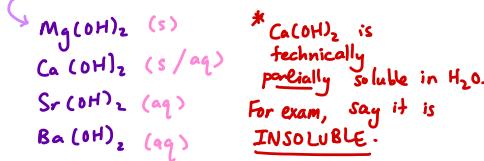
MgO - slightly soluble in H₂O (pH = 9)

CaO dissolve in H₂O to yield an alkaline solution

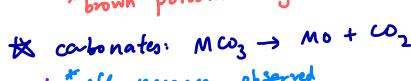
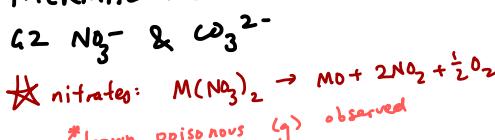
SrO (pH = 10-13)

BaO (pH = 10-13)

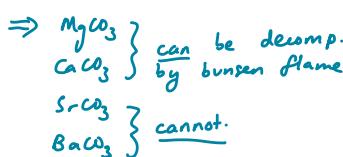
- ★ pH of group 2 oxides ↑, ↓ the grp.
- Why? • H₂O solubility of group 2 hydroxides ↑, ↓ the grp.
- hence more OH⁻ ionises



THERMAL DECOMPOSITION OF G2 NO₃⁻ & CO₃²⁻



↳ therm. stab. of CO₃²⁻ ↑ down the group



REACTIVITY (ABILITY TO REDUCE)

★ ↑, ↓ the grp.

- Why? • desp ↑ NC
- ↑ shielding from inner e⁻
- ↑ atomic radius
- ↓ FFA b/w nucle. & outer shell e⁻
- so ↑ easier to ionise.

FLAME TESTS



Mg - bright white



Ca - brick red

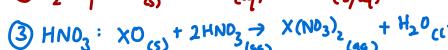
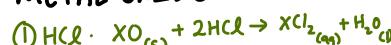


Sr - scarlet / red



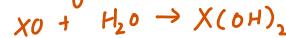
Ba - apple green

METAL OXIDE + ACIDS

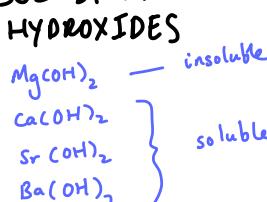


METAL OXIDE + H₂O

* most G2 oxides react w/ H₂O to form metal hydroxides:



SOLUBILITIES OF G2 HYDROXIDES



* Ca(OH)₂ appears as a white suspension.

* water solubility ↑, ↓ the grp

↳ Ca dissolves

↳ so pH ↑, ↓ the grp

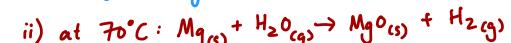
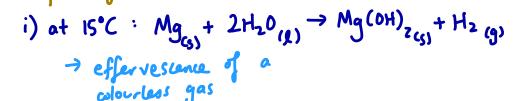
why? → ↑OH⁻ present.

↳ cloudy white suspension of Ca(OH)₂

↳ effervescence of a colourless gas

METAL + H₂O

★ Mg reacts differently with H₂O, depending on its temperature:



↳ exam expl: Mg(OH)₂ is decomposed into MgO at ↑T

★ Ca reacts more readily with cold water:



↳ Ca dissolves

↳ so pH ↑, ↓ the grp

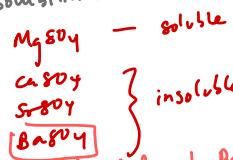
↳ cloudy white suspension of Ca(OH)₂

↳ effervescence of a colourless gas

SOLUBILITIES OF G2

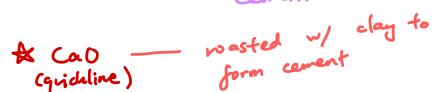
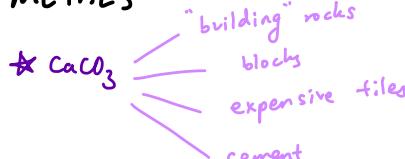
SO₄²⁻

★ solubilities decrease ↓ the group.



↳ note BaS₀ is insoluble.

APPLICATIONS OF G2 METALS



Why?

- 1) ↓ the grp, cation size ↑
- 2) ∵ ↓ charge ↑
- 3) so anion suffers ↓ polarisation / distortion

Chapter III: Group 17

PHYSICAL PROPERTIES

PHYSICAL STATES

F_2 rtp: colourless gas
BP: $-188^\circ C$
MP: $-220^\circ C$

Cl_2 rtp: green gas
BP: $-35^\circ C$
MP: $-101^\circ C$

Br_2 rtp: red-brown liquid
(brown as vapour)
BP: $59^\circ C$

I_2 rtp: purple-black solid
(violet as vapour)
BP: $184^\circ C$
MP: $114^\circ C$

* when dissolved in cyclohexane
(organic solvent):

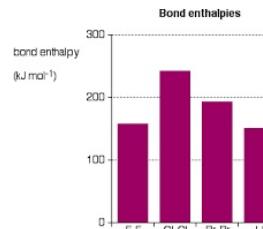
• Cl_2 is very pale green

• Br_2 is orange

• I_2 is purple



BOND ENTHALPIES IN HALOGEN; X-X



* decreases from Cl_2 to I_2

Why?

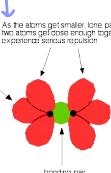
- atoms get larger down the group
- so bond length ↑
- so effective overlap of outermost orbitals ↓
- so FoA ↓

* why does F_2 not follow the trend?

→ atomic rad. of F is too small.

→ each atom has 3 lone pairs: as the bond is short, the LP get close enough to cause a significant amount of repulsion.

→ this repulsion is strong enough to counteract the attraction b/w the bond pair & the nuclei.



MP/BP / VOLATILITIES OF HALOGENS



* ↑ down the group

- Why? → $n(e^-)$ ↑ w/ ↑ atomic #
→ strength of VdW F ↑
→ ↑ req. to overcome FoA b/w molecules.

* "volatility": the ability of halogens to evaporate.

CHEMICAL PROPERTIES

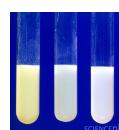
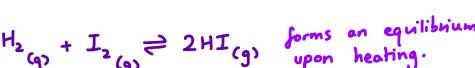
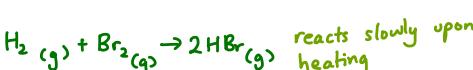
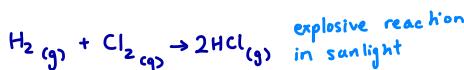
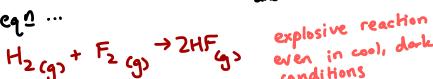
RELATIVE REACTIVITY AS OXIDISING AGENTS

* $F_2 > Cl_2 > Br_2 > I_2$
→ corresponds to trend in electronegativity.

Why?
→ atomic radius ↑ down the grp
→ ... ↓ foal bw p in nucleus & outer e^-
→ shielding effect ↑ down the grp
→ despite ↑ NC

REACTIONS WITH H₂

and its desc.



TEST FOR HALIDE IONS

* reaction between acidified silver nitrate and halide compounds yields a ppt
① AgCl - white ppt
- readily soluble in NH₃
($AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$)

② AgBr - cream ppt
- only soluble in concentrated NH₃
($AgBr + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Br^-$)

③ AgI - pale yellow ppt
- insoluble in NH₃ regardless of conc

THERMAL STABILITY OF HYDROGEN HALIDES

* thermal stability decreases down the group

Why?
→ ionic rad ↑
→ ↑ bond length
→ ↓ eff. overlap of outer shell w/ H₂
→ ↓ bond energy



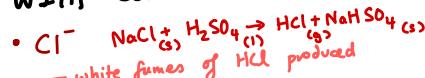
→ 20% of sample decomposes to release purple fumes, at $430^\circ C$
if a hot glass rod is placed in HI, decomposition immediately occurs



→ at $430^\circ C$, 10% of HBr decomposes to release red-brown fumes

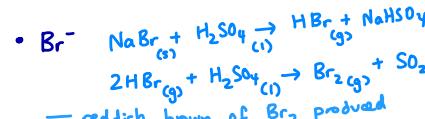


REACTION OF HALIDE IONS WITH CONC. H₂SO₄

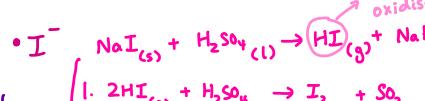
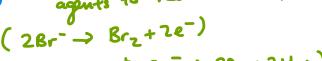


Why?
→ conc. H₂SO₄ is not a strong enough oxidising agent to oxidise Cl⁻ into Cl₂

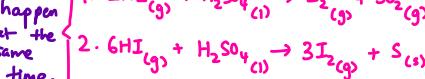
or Cl⁻ are not strong enough reducing agent to reduce H₂SO₄



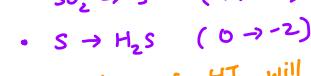
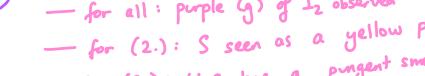
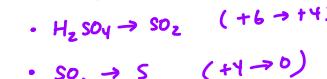
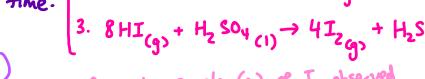
Why?
→ Br⁻ are strong enough reducing agents to reduce H₂SO₄



Why?
→ I⁻ are strong enough reducing agents to reduce H₂SO₄.



→ in fact, it can reduce it in three steps:



— for all: purple (g) of I₂ observed



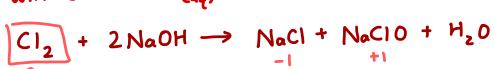
— for (2.): S seen as a yellow ppt resembling rotten eggs.

* any residue of HI will be contaminated by S_(s). Why? → weaker acid than H₂SO₄.

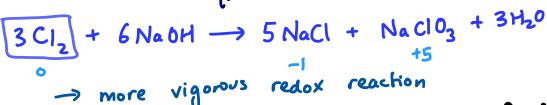
REACTION OF Cl_2 w/ $\text{NaOH}_{(\text{aq})}$

$\star \text{Cl}_2$ reacts differently w/ NaOH depending on the temp.

• with cold $\text{NaOH}_{(\text{aq})}$ — 15°C



• with hot $\text{NaOH}_{(\text{aq})}$ — 70°C

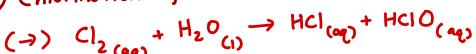


} when Cl_2 reacts with alkalis, they undergo disproportionation.

USES OF HALOGENS AND ITS COMPOUNDS

CHLORINE (AND ITS COMPOUNDS)

1) Chlorination of H_2O



→ chloric (I) acid, HClO , decomposes slowly in water to release reactive oxygen atoms that can kill bacteria in water.



2) Bleach

→ made up of equal mixture of NaCl & NaClO

→ oxygen atoms from chlorate (I) ions can oxidise dye and other coloured compounds.

3) Antiseptics & disinfectants

4) Chlorinated C compounds

e.g. solvents & plastics (PVC)

ITS COMPOUNDS

BROMINE

- agricultural chemicals
- flame-retardants & fire extinguishers
 - bromine gas is denser than air
 - so it can act as a cushion b/w fire & air

FLUORINE

- exists as the polymer of poly(tetrafluoroethene), ie teflon

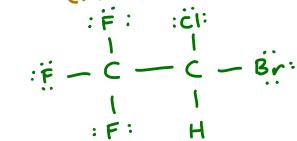
→ commonly used as a non-stick coating on pans.

Why? → C-F bond δ is \uparrow
→ so $\uparrow\uparrow$ thermal stability.

Br_2 , F_2 & Cl_2

→ anesthetics with the chemical

name of
2-bromo-2-chloro-1,1,1-trifluoromethane
(Chloroform)



Why? → due to high bond δ of 3 C-F bonds, it is inert
→ safe in (aq) environment in body.

Chapter 12:

Nitrogen & Sulfur

NITROGEN

* Why is N_2 unreactive?

→ exists as a diatomic molecule with a triple bond which has high bond energy.
→ hence $\uparrow\uparrow 4$ needed to break it.

→ N_2 does not react with O_2 under atmospheric conditions.

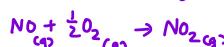
Why?
→ \uparrow bond δ in N_2
→ $\uparrow E_a$ in reaction
→ endot. reaction

* However, in car engines, N_2 & O_2 do react to form NO.

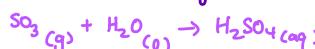
→ the $\uparrow\uparrow T$ & p in car engines provides enough δ to break the bonds, & provides E_a for the reaction.

FORMATION OF ACID RAIN

* NO_x is a pollutant as it catalyses the formation of SO_3 from SO_2 .



⇒ SO_3 formed will then react w/ H_2O to form H_2SO_4 , leading to acid rain



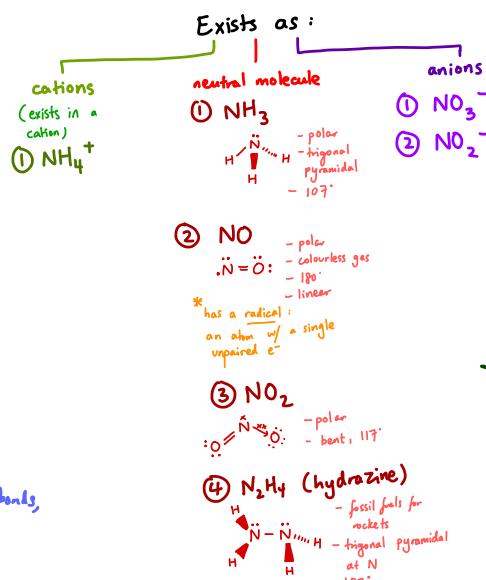
Why is acid rain bad?

- 1) - leaches nutrients from the soil
- so prevents healthy growth of plants
- 2) - increases conc. of heavy metal ions in water courses
- 3) - attacks leaf cuticles (waxy layer)
- leads to \uparrow water loss and \uparrow susceptibility to plant diseases
- 4) - \downarrow pH of water
- so aquatic organisms are killed
- 5) - corrosion of buildings and statues (esp. those made out of carbonate rocks)

ENVIRONMENTAL PROBLEMS CAUSED BY N COMPOUNDS

① - NO_3^- can be washed, or leached out of the soil, by rain into ground water.
- there, they can undergo eutrophication:
→ the enrichment of a body of water with an excess of nutrients.

- 1) algae blooms
- 2) blocks light, hence reduced photosynthesis
- 3) death of aquatic organisms, leads to bacterial decomposition
- 4) hence mass death of organisms due to low concentration of O_2



NITROGEN DIOXIDE

* NO_2 naturally occurs.

How?

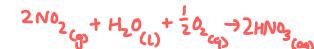
① Lightning provides the Ea for the reaction b/w N_2 & O_2



② NO will further oxidise into NO_2



③ NO_2 dissolves in water to form HNO_3 .



* NO_2 is also created via man-made sources.

① Nitrogen oxides are formed from fuel combustion in car engines under T & P .

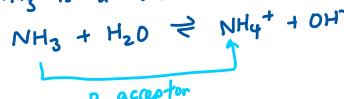
② Produced in power stations & furnaces.

NH_3 & NH_4^+ COMPOUNDS

* NH_3 is manufactured via the Haber process:



→ NH_3 is a weak alkali in (aq):



* NH_4^+ compounds can easily be identified by heating it with a stronger alkali (e.g. NaOH).

observation — effervescence of NH_3 , which turns damp red litmus paper blue.

* all NH_4^+ compounds are acidic.

* NH_4^+ compounds' uses:

- 1) N source in fertilisers
- 2) explosive

* Why don't we add $Ca(OH)_2$ to soil with NH_4^+ fertilisers?

→ loss of N_2 in the form of $NH_3(g)$



* NH_3 uses:

- 1) involved in the production of nitrogenous fertilisers through reactions with acids.
- 2) $2\text{NH}_3 + H_2SO_4 \rightarrow (\text{NH}_4)_2SO_4$
- 3) $3\text{NH}_3 + H_3PO_4 \rightarrow (\text{NH}_4)_2PO_4$

2) involved in the manufacture of $HNO_3(aq)$

→ HNO_3 is used for:

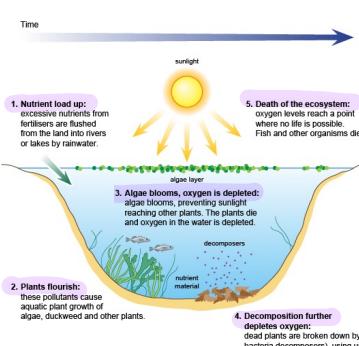
- 1) make NH_4NO_3 fertilisers
- 2) explosives
- 3) detergents, paints, pigments, dyes and nylon

3) cleaning agent

4) refrigerant

5) explosives

6) nylon



SULFUR

- non-metal
- exists as S_8 (yellow s)

SO_2

- polar.

* SOURCES:

- 1) combustion of fossil fuels
- 2) extraction of metals from sulfide ores
- 3) volcano eruptions.

\ddagger SO_2 is considered an environmental pollutant.
How can we reduce its polluting effects?

- 1) add $CaCO_3$ to burning coal to neutralise SO_2
- 2) use desulfurisation plants to reduce SO_2 emissions from furnace chimneys.
 \rightarrow gases washed w/ $Ca(OH)_2$

USES OF H_2SO_4

- fertilisers
- detergents
- paints
- pigments
- dyes
- synthetic fibres
- chemicals
- plastics
- batteries
- cleaning metals

THE HARMFUL EFFECTS OF VEHICLE EXHAUSTS

* CARBON MONOXIDE

- \rightarrow formed from incomplete combustion of fuels
- \rightarrow exposure to CO reduces the absorbing ability of red blood cells
- \rightarrow as haemoglobin has higher affinity to CO compared to O_2 .

* SULFUR DIOXIDE

- \rightarrow causes acid rain
- \rightarrow causes respiratory complications due to "burning sensations" in the nose & throat, and the obstruction of the airway.

* NITROGEN DIOXIDE

- \rightarrow formed from the reaction bw N_2 & O_2 in the engines.
- \rightarrow catalyses the formation of acid rain
- \rightarrow causes breathing problems.

* UNBURNT HYDROCARBONS

- \rightarrow global dimming
- \rightarrow gradual reduction in the amt of global direct irradiance at the Earth's surface
- \rightarrow due to ↑ presence of aerosol 'p' in atm, caused by pollution/dust/volcanic eruptions
- \rightarrow that reflect sunlight back into space.
- \rightarrow photochemical smog
- \rightarrow smog produced when UV reacts w/ nitrogen oxides in the atmosphere.

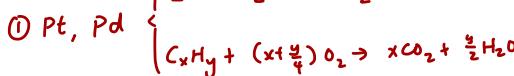
\rightarrow the 3 main pollutants that are present in car engine exhaust gases are SO_2 , CO , & NO_2 .
 \rightarrow exhaust fumes also contain $H_2O(g)$ & CO_2 .

Why? \rightarrow common products formed through fossil fuel combustion.

CATALYTIC CONVERTERS

\rightarrow used to remove the 3 main pollutants.

\rightarrow contains:



* catalytic converters are not perfect, however:

- \rightarrow toxic gases not removed until the catalytic converter is warmed up
- \rightarrow efficiency decreases over time.

* If question says:

- the oxides can be oxidised : CO , NO , SO_2
- the oxides can be oxidised in the atmosphere : NO , SO_2
- the oxides can be oxidised Spontaneously :

\rightarrow just rmb bc

NO

N

S

C

decreasing reactivity!

* N_2 occupies the (1) prop. in exhaust fumes.
 \rightarrow due to unreactivity.

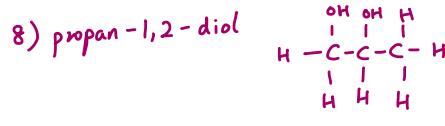
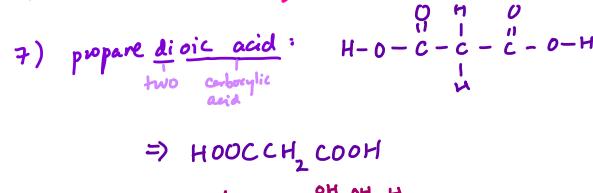
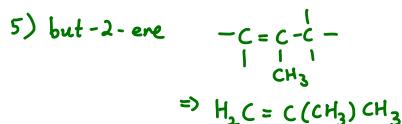
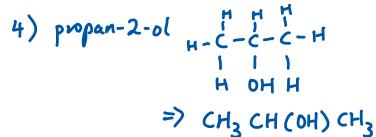
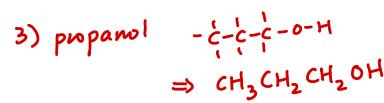
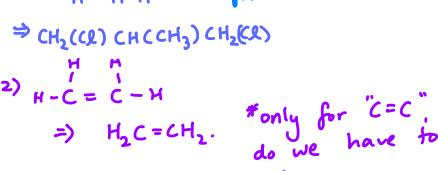
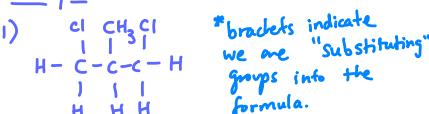
Chapter 13:

Intro to Organic Chemistry

UTILISING STRUCTURAL FORMULAS

↳ shows how the atoms are bonded to each carbon atom in the \wedge
 * L \rightarrow R
 * show C=C bonds in the formula.

examples



SKELETAL FORMULAE

→ a simplified representation of an organic structure

→ the displayed formula —

BUT! ALL C atoms & C-H bonds ONLY are omitted.



HOMOLOGOUS SERIES

→ elements of the same homologous series display:

1) same functional group;

2) same general formula;

3) each consecutive member differs by CH_2 / chain length increments each time;

4) gradual predictable Δ in their physical properties as the chain length \uparrow

5) similar / like chemical properties.

HS

alkane \longrightarrow "C-C"

alkene \longrightarrow "C=C"

halogenoalkane \longrightarrow primary / secondary / tertiary halogenoalkane

alcohol \longrightarrow primary / secondary / tertiary alcohol

carboxylic acid \longrightarrow carboxylic acid

aldehyde \longrightarrow aldehyde

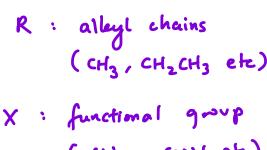
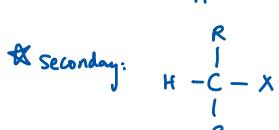
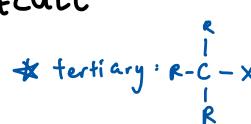
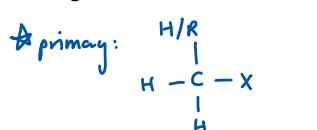
Ketone \longrightarrow Ketone

FUNCTIONAL GROUP

→ an atom / groups of atoms in an organic molecule that

* determine the characteristic reactions of a homologous series.

"ORDER" OF A MOLECULE



functional group	characteristic	shape / bond angle	additional info
1) alkanes	contains C-C	tetrahedral / 109.5°	
2) alkenes	contains C=C	trigonal planar / 120°	
3) cyclic hydrocarbons	carbon chain joins to itself to form a ring	tetrahedral / 109.5°	all cycloalkanes are non-planar (except cyclopropane)
4) halogenoalkanes	contains C-X (X = halogen)	tetrahedral / 109.5°	contains: F → fluoro- Cl → chloro- Br → bromo- I → iodo-
5) alcohols	contains -OH (suffix = -anol)	tetrahedral / 109.5°	↑ BP than other organic compounds. Why? → <u>H bond bw</u> ↗
6) carboxylic acids	contains -COOH (suffix = -oic acid)	trigonal planar / 120° (at $\text{C}^{\delta\text{+}}\text{-O-H}$)	
7) esters $(-\text{C}^{\delta\text{+}}\text{-O-})$	formed by reaction bw alcohol & carboxylic acid.	trigonal planar / 120° (at $-\text{C}^{\delta\text{+}}\text{-O-H}$)	
8) aldehydes	contains $(\text{H}_\text{R}-\text{C}^{\delta\text{+}}\text{-H})$ (suffix: -al)	trigonal planar / 120°	
9) ketones	contains $\text{R}-\overset{\delta}{\text{C}}\text{-R}$ (suffix: -one)	trigonal planar / 120°	<ul style="list-style-type: none"> not necessarily same R first member is propanone for pentanone and up, you have to indicate where the "one" is.

NAMING COMPOUNDS

3-chloro propanal
 prefix stem stem suffix

STEM

- # of atoms in carbon chain.
- LONGEST**
- | | |
|-----------|---------------------------|
| 1 → meth- | *not necessarily the most |
| 2 → eth- | the most |
| 3 → prop- | "visible" one. |
| 4 → but- | |
| 5 → pent- | |
| 6 → hex- | |
| : | |

STEM SUFFIX

→ type of C-C bonds that occur in the compound.

- | | |
|----------|----------------|
| -an → | C-C bonds only |
| -en → | 1 C=C |
| -dien → | 2 C=C |
| -trien → | 3 C≡C |

SUFFIX

→ oxygen-containing groups present in the compound.

- al → aldehyde
- one → ketone
- ol → alcohol
- oic acid → carboxylic acid

PREFIX

→ non-oxygen containing groups which substitute the H along C chain.

- | |
|---|
| CH_3 → methyl- |
| CH_2CH_3 → ethyl- |
| $\text{CH}_2\text{CH}_2\text{CH}_3$ → propyl- |
| Cl → chloro |
| Br → bromo |
| -OH → hydroxy |

RULES!

- ① **(1)** # given to prefixes.
- ② Pos. of prefix denoted as a #; a dash is used to separate # & word.
- ③ Like prefixes can be combined w/ one another, and are preceded by di-, tri- or tetra- to show multiple substitutions.
- ④ **★** Priorities in parent chain numbering:

Prefix → stem-suffix → suffix

(1)	(2)	(3)
Group	Suffix	Prefix
carboxylic acid	-oic acid	—
ester	-oate	—
aldehyde	-al	formyl-
ketone	-one	oxo-
alcohol	-ol	hydroxy-
alkene	-ene	—
alkane	-ane	alkyl

ISOMERISM → same molecular formula
→ diff. structural formula

```

graph TD
    Structural[structural] --> Position[position]
    Structural --> Chain[chain]
    Position --> Fa[Fa]
    Chain --> Optical[optical]
    Chain --> Stereo[stereo]
    Optical --> CisTrans[cis-trans.]
    Stereo --> Stereo
  
```

CHAIN

↳ isomers differ in their C skeleton.



POSITION

- ↳ different positions of FG
- ↳ same C skeleton, same homologous series, same Fls.



FUNCTIONAL GROUP

- ↳ isomers have different Fls
- ↳ different chemical & physical properties.



OPTICAL

→ exist as 2 non-superimposable images

→ occurs when there is a chiral centre in a molecule.

→ characteristics of chiral \wedge :

- 1) optically active
 - 2) displays a pair of non-superimposable optical isomers / enantiomers.

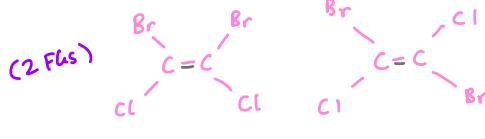
\rightarrow n chiral centres \Rightarrow 2^n optical isomers

→ optical isomers have like physical & chemical properties.

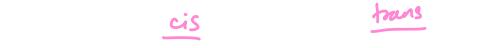


GEOMETRICAL (CIS-TRANS)

↳ arises due to restricted rotation from presence of 2x bonds



* Each C atom on either end of the 2π bond must be bonded to 2 non-identical F atoms.



* for 4 FUs:
 analyse p #.
 → identify 4 FUs on
 LHS, and RHS.



* for 4 FUs:
analyse p #.
→ identify 4 FUs on
LHS, and RHS.

- ★ Racemic mixture:
 - mixture that contains = amounts of each optical isomer
 - optically inactive.

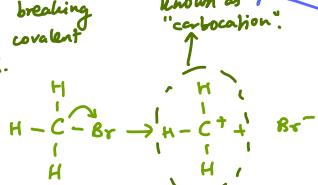
• 10

TYPES OF ORGANIC REACTANTS.

HOMO vs HETEROlytic FISSION

↓
both atoms at each end of the bond leave w/ 1e⁻ from a pair that formed the bond

uneven breaking of a covalent bond.



known as "carbocation".

primary H/R - C⁺ - H

secondary R - C⁺ - H

tertiary R₃C⁺



- Why?
 1) alkyl are e⁻ donating groups (+ve inductive effect)
 2) ∵ ↑ # of alkyl groups attached, ↓ Q/p
 3) ↑ stability.



NUCLEOPHILE v ELECTROPHILE

↓
donator of a pair of e⁻

↳ *not all nucleophiles are -vely charged!

eg OH⁻, CN⁻, NH₃

↓ receiver/acceptor of a pair of e⁻.

↳ strongly attracted to alkenes & benzenes.

eg NO₂⁺, Cl₂, Br₂

Chapter 14:

→ general formula: C_nH_{2n+2}

Alkanes

TRENDS IN PHYSICAL PROPERTIES

1) BP in aliphatic alkanes ↑.

↳ # of VdW F ↑

↳ as # of e⁻ ↑

2) Non-polar

↳ soluble in non-polar solvents (eg CCl_4)

↳ insoluble in polar solvents (eg H_2O)

CHEMICAL PROPERTIES

→ generally unreactive.

Why? 1) C-H bond $\leq M^2$

2) ΔE°_f energy diff. bw C & H

↳ non-polar bond

↳ too charge neutral to attract nucleophile or electrophile.

SOURCES OF ALKANES

↳ alkanes can be harvested from crude oil.

↳ a complex mixture of HC: alkanes, cycloalkanes & aromatic compounds.

two methods:

1) (physical) fractional distillation
→ the sep. of a mixture into its fractions by BP.

2) (chemical) cracking

APPLICATIONS:

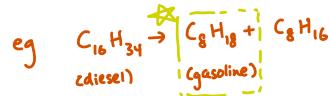
1) fulfill M demand for gasoline frac.

2) cracking yields ↓ BP alkanes, which are reactive.

↳ hence these can be converted into a variety of compounds, eg plastics.

CRACKING

↳ the process in which large, less useful HC \sim are broken down into smaller, more useful \sim .



• types:

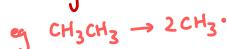
1) thermal — ↑↑ B, ↑↑ P

2) catalytic — ↑↑ B, suitable catalyst
(SiO_2 , Al_2O_3 , Pt,
zeolite, pumice,
ceramic)

• Mechanism:

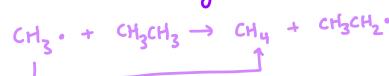
① Initiation

Two free rad. are formed through homolytic fission.



② Propagation

i) H abst.: a free radical removes the H from another larger \sim creating another radical



ii) Radical decom.: a free radical breaks apart into an alkene and another free radical.

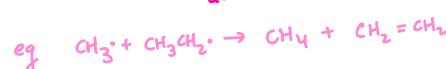


③ Termination

i) Recombination: two radicals combine to form 1 longer \sim



ii) Disproportionation: one radical transfers a H atom to the other, yielding one alkene & one alkyne.



ALKANE REACTIONS

COMBUSTION

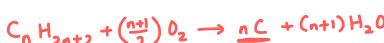
O₂ supply → reaction

excess $C_nH_{2n+2} + (\frac{2n+1}{2})O_2 \rightarrow nCO_2 + (n+1)H_2O$

1+o



v. 1+o



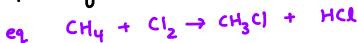
* recap: consequences of CO:

1) global dimming

2) photochemical smog

FREE-RADICAL SUBST^N

↳ Alkanes undergo subst^N reactions w/ halogens.



* it is a redox reactⁿ!

Mechanism

① Initiation:

Homolytic fission of Cl-Cl bond from UV light generates 2 free radicals:
 $Cl_2 \rightarrow 2Cl\cdot$

② Propagation:

Free radicals subsequently attack the HC molecules, leading to a chain reaction.



③ Termination

The chain reaction ends when two radicals combine to form a \sim .



:

REVIEW

Chapter 15: Alkenes

aliphatic alkenes

- Gen f: C_nH_{2n}
- contains $C=C$
- suffix: -ene

cycloalkenes

- a type of alkene HC which contains a closed ring of C
- does not display aromatic character.

Note:
Since aliphatic & cycloalkenes do not share a common GF.
they belong in different homologous series!

PHYSICAL PROPERTIES

BP

the BP of alkenes are very similar to the BP of their respective alkanes; however, the BP of alkenes are usually lower. Why? \rightarrow 2 fewer e^- (than alkanes) $\rightarrow \downarrow VdW F$

SOLUBILITY

\rightarrow non-polar.
soluble in non-polar solvents (eg CCl_4)
insoluble in polar solvents (eg H_2O)

ELECTROPHILIC ADDITION OF HX (aq)

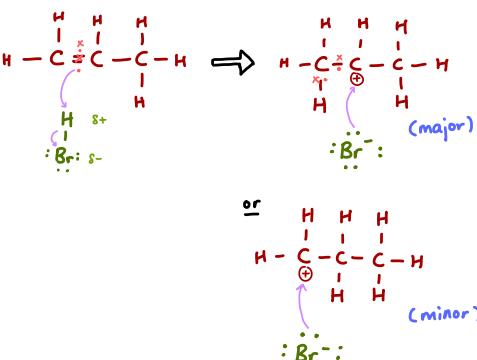
conditions room temp

reagent conc. sol. of HX

product halogenoalkanes



Reaction mechanism of electrophilic addition to alkenes (HBr + propene)



💡 Why is 2-bromopropane more prevalent than 1-bromopropane?

• Markovnikov's Rule — when HX is added to a $C=C$, H will attach to the C atom w/ the most H.

• Intermediate of 2-b has a secondary carbocation, but 1-b has a primary carbocation.

Secondary is more stable than primary because of the +ve inductive effect of alkyl groups.

CHEMICAL REACTIONS

💡 Alkenes undergo electrophilic addition with several reagents.

$\rightarrow C=C$ rich in e^- \rightarrow addition rctⁿ where a π bond is broken
 \Rightarrow attract electrophiles. and converted into 2 σ bonds.

ADDITION OF H_2 (g)

conditions high temp, Ni catalyst or rtp , Pt catalyst

reagent H_2

product alkane



💡 Ni is preferred over Pt, despite needing $\uparrow T$ to function.

Why? \rightarrow Ni $\downarrow \$$ & \uparrow abund. than Pt
 \rightarrow so \uparrow Ni can be used.
 \rightarrow even if some Ni poisoned, enough Ni remains for reaction catalysis.

ADDITION OF H_2O (g)

conditions $330^\circ C$, 6 MPa , H_3PO_4 catalyst

reagent H_2O (g)

product alcohols



ELECTROPHILIC ADDITION OF HALOGENS (Br_2)

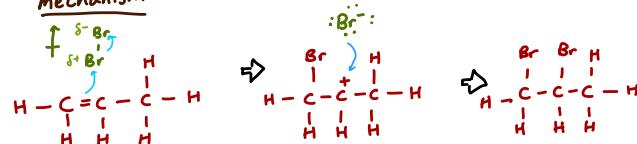
• Br_2 in organic solvent, eg CCl_4

conditions room temp

product halogenoalkane



mechanism



• Br_2 in H_2O , ie bromine water

conditions room temp
products halogenoalkane & alcohol

specialised test for alkenes.

OXIDATION WITH ACIDIFIED $KMnO_4$ (aq)

• Cold, dilute $KMnO_4$



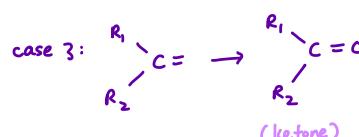
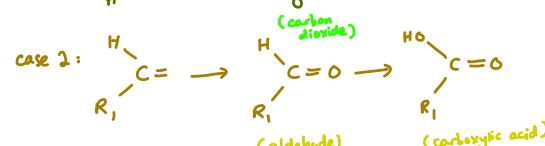
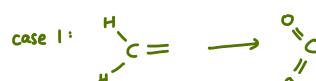
observation $KMnO_4$ decolourises

* note:

$K_2Cr_2O_7$ can't react, as it is not strong enough as an oxidising agent.

• Hot, concentrated $KMnO_4$

💡 Under harsh conditions, $C=C$ is broken completely



ADDITION POLYMERISATION

Unsaturated compounds can react with each other to form polymers.

- Addition polymerisation involves the breaking of π bonds, and subsequently the linking of monomers.

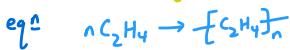
Def'n's

Polymer a long chain molecule made up of many repeat units

monomer a small reactive molecule that links together to form long chain molecules

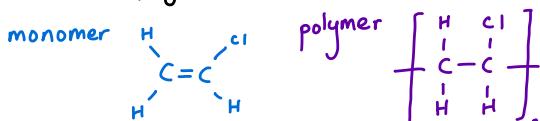
repeat unit a small unit from the polymer chain that can be built up by repetition.

conditions either M^2P or Ziegler-Natta catalyst



Examples of addition polymers

① PVC (poly (chloroethene))



② Poly (ethene) : high vs low density

high - very little branching along HC chains

- \uparrow MP & strength (\uparrow VdW, \uparrow SA)
- \uparrow density

low - high # of branch chains

- \downarrow MP & strength (\downarrow VdW, \downarrow SA)
- \downarrow density

Disadvantages of using poly(alkene) plastics

① Disposal

- ↳ poly(alkenes) exist as large \nwarrow
- ↳ so they are resistant to chemical attack
- ↳ & are non-biodegradeable.

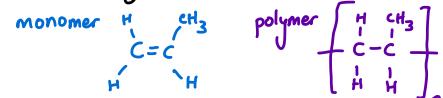
↳ they also take up landfill space

↳ and is dangerous if ingested by marine life.

② Burning of Plastic Waste

- ↳ releases toxic gases.
eg CO (incomplete combustion)
- ↳ for CN^- containing polymers,
HCN is released
- ↳ for Cl^- containing polymers.
HCl is released
↳ HCl is thermally stable.

③ Poly (propene)



characteristics

- 1) non-biodegradeable
- 2) unreactive (saturated)
- 3) does not absorb H_2O

uses

- 1) meshes for medical uses

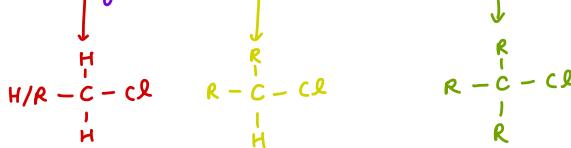
Chapter 16: Halogenoalkenes

Halogenoalkanes are halogen derivatives of alkanes.



Classification

we can classify halogen compounds as either primary (1°), secondary (2°) or tertiary (3°).



Physical properties

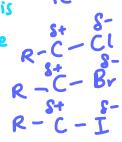
* Their BP \uparrow than alkenes & alkanes
 Why? → presence of polar dipole-dipole interaction / weak VdWF

CHEMICAL RCTNS OF HALOGENOALKANES

Most rctns of halogenoalkanes are nucleophilic substns.

→ this occurs when a nucleophile attacks the carbon-halogen bond.

why does this happen?
 → bc carbon-halogen bond is polar, as halogen is \uparrow -ve than C.



NUCLEOPHILIC SUBSTN w/ OH^-

reagent NaOH or KOH (aq)

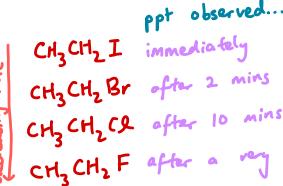
conditions heat under reflux

product alcohol

Rates of nucleophilic substn

We can identify the relative rate of reaction by adding AgNO_3 (aq) to the solution.

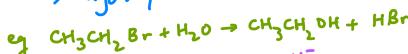
⇒ any halide ions formed will form ppt.
 ppt.



⇒ any halide ions formed will form ppt.

* a similar rctn to nuc substn can be done by adding hot water.

↳ hydrolysis.



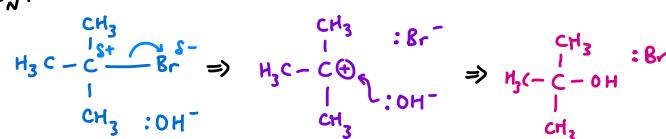
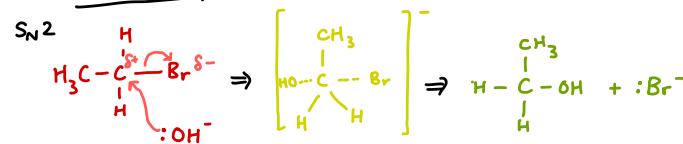
Note: - slower than w/ OH^-
 - OH^- more effective nucleophile than H_2O

* Heating under reflux.

Why?

- 1) allows B to be kept \exists at BP, to \uparrow rate
- 2) prevent evaporation of volatile organic compounds
- 3) ensure full rctn bw halogenoalkanes & reactants.

Mechanism of nuc substn w/ OH^-



* $\text{S}_{\text{N}}2$ vs $\text{S}_{\text{N}}1$
 $\text{S}_{\text{N}}2$: - 1° & 2°
 $\text{S}_{\text{N}}1$: - 2 step
 (transition)

NUCLEOPHILIC SUBSTN w/ CN^- IONS

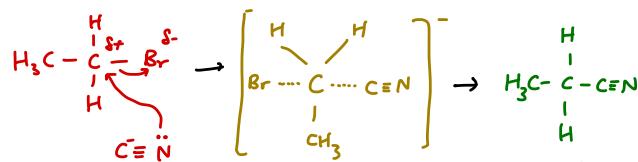
reagent ethanolic CN^- (KCN)

conditions heat under reflux

product nitriles ($\text{C}\equiv\text{N}$)



mechanism:



uses of nuc substn w/ CN^- ions:

↳ This process can be used to synthesise new compounds w/ one more C atom.

↳ the nitrile compounds can then be hydrolysed to form carboxylic acids.

(2) alkaline hydrolysis

reagent NaOH (aq)
 conditions heat under reflux



NUCLEOPHILIC SUBSTN w/ NH_3

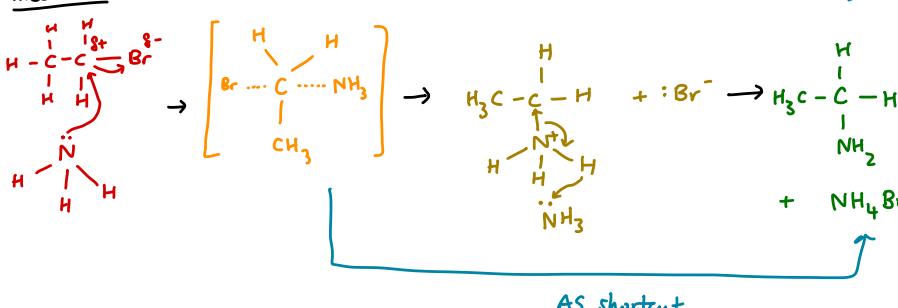
reagent ethanolic NH_3

condition heat in sealed tube

product amines ($-\text{NH}_2$)



mechanism:



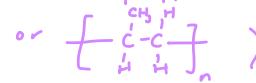
HALOGENOALKANES IN OUR WORLD

applications of halogenoalkanes:

1) halothane (CF_3CBrClH) as anaesthetics (replacement: N_2O)

2) teflon ($\left\{ \begin{array}{c} \text{F} \\ | \\ \text{C}-\text{C} \\ | \\ \text{F} \end{array} \right\}$) as non-stick lining of pans

3) PVC used in food packaging (replacement: polypropylene,



CFCs

properties:

• non-flammable

• non-toxic

• volatile

• chemically inert.

Why? C-H 2nd strongest bond

CFCs are harmful to the ozone layer.

↳ when they reach upper atm:

UV light breaks C-Cl, making Cl⁻.

↳ this attacks ozone molecules (O_3).

↑ Cl⁻ & Br⁻ can destroy O_3 .

replacements for CFC:

1) HFCs (hydrofluorocarbons)

→ easier to decompose

→ but flammable and can form toxic chemicals.

2) HFEs (hydrofluoroethers)

→ Cl replaced by F

→ more stable due to stronger C-F bond

Chapter 17:

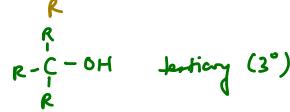
Alcohols, Carboxylic Acids and Esters

ALCOHOLS

Alcohols contain one or more -OH groups.

gen formula: $C_nH_{2n+1}OH$

Classification



PHYSICAL PROPERTIES

① Less volatile than alkenes or alkanes

Why? → presence of H bonds in \nwarrow

② H_2O solubility
→ solubility ↓ as C chain ↑
Why? → non-polarity ↑
→ H bond less significant.

⑥ Oxidation

Alcohols can be oxidised into aldehydes and carboxylic acids.

reagent: $K_2Cr_2O_7/H^+$ or $KMnO_4/H^+$

conditions: heat under reflux

product: aldehydes → carboxylic acids.

if solution formed is distilled off immediately, aldehyde is formed.

if solution formed is distilled after 15 mins, carboxylic acid is formed.

⑦ Triiodomethane reaction (Iodoform)

This test specifically tests for the presence of $\underline{CH_3CH_2(OH)}$ in the compound.

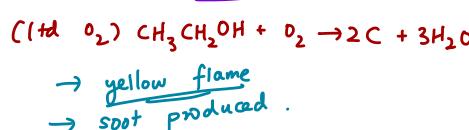
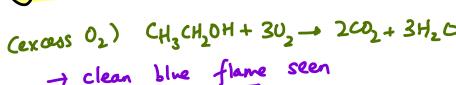
oxidation reaction

reagent: alkaline I_2
condition: warm

product: CHI_3 (yellow ppt)

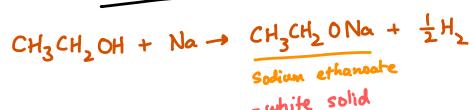
CHEMICAL REACTIONS

① Combustion



② Reaction with Na

Although alcohol is neutral, it can react with metals.



⇒ a redox rxn

⑤ Esterification

reagent: alcohol & carboxylic acid
condition: heat under reflux w/ conc H_2SO_4
product: ester + H_2O



iii) Phosphorous halides

③ Elimination

reagent: $H_2SO_4 / H_3PO_4 / Al_2O_3$ → acts as oxidising dehydrating agent
conditions: heat ($170^\circ C$)
product: alkene & water
to occur: neighbouring C must have H present.

* elimination of Cl
uses ethanolic NaOH. Remember the distinction

④ Substitution (form halogenoalkanes)

i) HCl & HBr

reagent: conc H_2SO_4 , $NaCl$ / $NaBr$
conditions: heat under reflux
product: halogenoalkane



ii) HI

reagent: conc H_3PO_4 , NaI
conditions: heat under reflux
product: halogenoalkane

Why H_3PO_4 ?
⇒ H_2SO_4 will oxidise HI into I_2

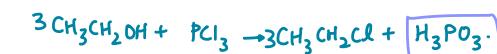
a) PCl_5

reagent: PCl_5 (solid)
condition: rtp



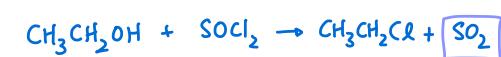
b) $PCl_3 / Br_3 / I_3$

condition: (Cl_3) heat
 (Br_3 / I_3) warm



iv) $SOCl_2$ (best one)

condition: warm at rtp

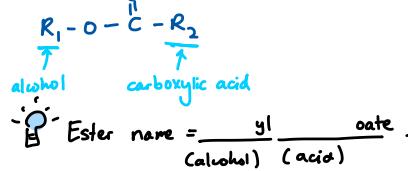


Why is this the best?

byproducts are gaseous
⇒ so distillation not req.
to obtain halogenoalkane.

ESTERS

NAMING



PHYSICAL PROPERTIES

- ① Partially soluble in water ★ applications IRL:
 - artificial flavourings
 - perfumes
 - nail varnish remover
 - solvent
- ② Liquid at rtp
- ③ Fruity aroma

CARBOXYLIC ACIDS

💡 Carboxylic contain —COOH in their — .

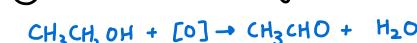
PHYSICAL PROPERTIES

- ① Simple aliphatic acids exist as LR_2 in rtp.
- ② High BP & solubility \Rightarrow due to H bonding bw — .
however, large carboxylic acids will have poor water solubility.
- ③ Weak acid.

FORMATION

💡 There are 2 main ways to obtain carboxylic acids.

① Oxidation of aldehydes / alcohols



② Hydrolysis of nitriles ($-\text{C}\equiv\text{N}$)

reagents: HCl (dil)
conditions: heat under reflux



CHEMICAL REACTIONS

① Hydrolysis ★ key: water.

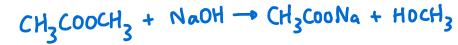
a) Acidic

reagent: HCl (dil) / H_2SO_4 (dil)
conditions: heat under reflux
product: carboxylic acid & alcohol



b) Alkaline

reagent: NaOH (dil)
conditions: heat under reflux
product: salt + alcohol
 \downarrow
acid



CHEMICAL REACTIONS

💡 As carboxylic acids are acidic, they undergo similar reactions as other acids:
 \rightarrow acid + metal
 \rightarrow acid + alkali
 \rightarrow acid + carbonate.

However, they also undergo a few more:

① Reduction

reagent: LiAlD_4 in dry ether
condition: rtp
products: alcohols



② Substitution with halides

(see alcohols) $\rightarrow \text{PCl}_5$
 $\rightarrow \text{PCl}_3/\text{Br}_3/\text{I}_3$
 $\rightarrow \text{SOCl}_2$

\Rightarrow product: acyl chloride



Chapter 18: Carbonyl Compounds

The 2 main functional groups that fall under this category are aldehydes & ketones.



PHYSICAL PROPERTIES

① Soluble in H_2O
Why? → can form H bonds w/ H_2O

② Higher BP than alkanes...
→ presence of permanent dipole moment
carbonyl compounds.
... but lower than alcohols.
→ no H bonds bw

PREPARATION

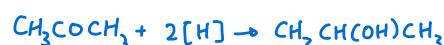
Aldehydes and ketones can be formed by the oxidation of 1° & 2° alcohols respectively.

* Remember, the products from the oxidation of primary alcohols must be distilled off immediately!

REDUCTION

Aldehydes and ketones can be reduced into alcohols w/ the use of a reducing agent.

- ⇒ LiAlH₄ in dry ether, or $\xrightarrow{\text{rtp}}$
- ⇒ NaBH₄ in alkaline $\text{Li}(\text{aq})$, or $\xrightarrow{\text{warm}}$
- ⇒ H_2 w/ Ni or Pt catalyst. → if excess: both C=C broken & carbonyl reduced.
if limited: only C=C broken.

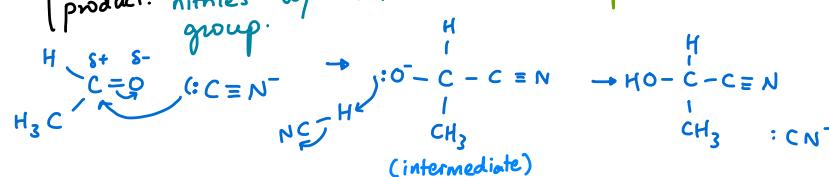


NUCLEOPHILIC ADDITION w/ HCN

Aldehydes & ketones can be converted into nitriles via nucleophilic addition w/ HCN.

reagent: a) HCN + trace NaOH
b) NaCN + H_2SO_4
c) HCN w/ NaCN catalyst

condition: 10°C - 20°C
product: nitriles w/ -OH group.



* asymmetrical carbonyl compounds will lead to the formation of 2 optical isomers in = amt.

Why? → planar structures
→ equal chance of nucleophilic attack from both sides.

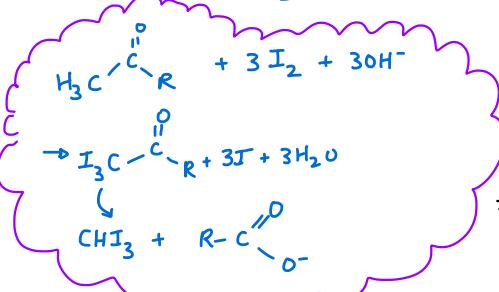
TESTS FOR CARBONYL COMPOUNDS

① w/ 2-4-DNPH
note:
⇒ condition: rtp
⇒ result: orange ppt
1) condensation process
2) applicable for both aldehydes & ketones

② Tri-iodomethane (iodoform) reaction

The iodoform reaction tests specifically for the group $\text{CH}_3\text{CO}-$.

reagent: alkaline solution of I_2
condition: warm
product: CHI_3 (yellow ppt)



TESTS TO DISTINGUISH ALDEHYDES FROM KETONES

We can use the fact that aldehydes can be further oxidised to distinguish them from ketones.

① Fehling's solution
⇒ alkaline Cu^{2+} (clear blue solution)
condition: warm
observation: opaque red ppt
idea: $\text{Cu}^{2+} \rightarrow \text{Cu}^+$

② Tollen's reagent
⇒ $\text{AgNO}_3 + \text{NaOH} + \text{NH}_3$
(ie alkaline AgNO_3)
 $\text{Ag}^+ \rightarrow \text{Ag}$
condition: warm
observation: Silver ppt

③ via conventional oxidising agents
(ie $\text{K}_2\text{Cr}_2\text{O}_7$ & KMnO_4)
⇒ condition: heat

* replace the $\text{C}-\text{O}^-$ with $\text{C}(=\text{O})-\text{O}^-$

IR SPECTROSCOPY

IR Spectroscopy is a method used to determine the functional groups present in a compound.

IR spectroscopy is also a method to determine the pollution in the air.

How? → each FG has a characteristic absorption freq in the IR range of wavelengths.

⇒ given a diagram, just refer to table in booklet to identify.

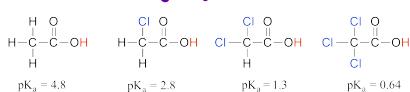
Chapter 26: Carboxylic Acids and Their Derivatives

ACIDITY OF CARBOXYLIC ACIDS

The acidity of a carboxylic acid is determined primarily by two factors:

① The number of e^- withdrawing groups

$\Rightarrow \uparrow \# \text{ of grps.} \uparrow \text{ acidity.}$



($\uparrow pK_a$,
 $\downarrow \text{acidity}$)

Why?

$\rightarrow e^-$ withdrawing grp weakens O-H bond

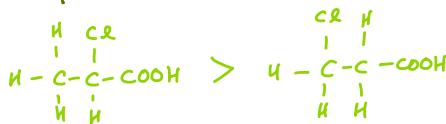
\rightarrow it also stabilises the carboxylate ion

($R-C-O^-$) by allowing delocalisation of e^- around $-COO^-$ group.

* basically, it depolarises the C-O⁻ bond, making it less susceptible to attacks by H⁺.

② Distance between the e^- withdrawing group and -COOH group

$\Rightarrow \uparrow \text{dist}, \downarrow \text{acidity}$

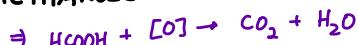


Why?
- the C-O bond is less polarised
- because influence of e^- -withdrawing group is less.

OXIDATION OF SELECTED CARBOXYLIC ACIDS

Usually, carboxylic acids cannot be oxidised; however, there are 2 exceptions:

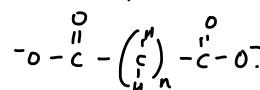
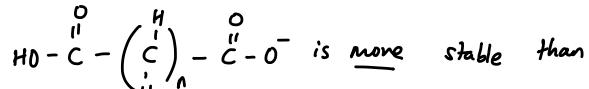
METHANOIC ACID — HCOOH



ETHANEDIOIC ACID — HOOCCOOH



Also,



Why? \rightarrow δ -static attr. bw H+ & -1 is less than δ -static attr. bw Hf & -2.

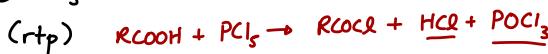
ACYL CHLORIDES

\therefore Acyl chlorides have the FG
 $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{Cl} \end{array}$

FORMATION OF ACYL CHLORIDES

\therefore Acyl chlorides can be prepared by nucleophilic substn of carboxylic acids w/ Cl^- ions.

① PCl_5 (can be prepared w/ red P & Cl_2)



② PCl_3 $3\text{RCOOH} + \text{PCl}_3 \rightarrow 3\text{RCOCl} + \underline{\text{H}_3\text{PO}_3}$

(heat)

③ SOCl_2 $\text{RCOOH} + \text{SOCl}_2 \rightarrow \text{RCOCl} + \text{SO}_2 + \text{HCl}$

NAMING ACYL CHLORIDES

\therefore Replace the suffix of the acid's name, "-oic acid", with "-oyl chloride".

e.g. ethanoic acid \rightarrow ethanoyl chloride
 propanoic acid \rightarrow propanoyl chloride etc.

PHYSICAL PROPERTIES

(a) Colourless (l.)

(b) id-idF & perm.d-dF exist bw \sim

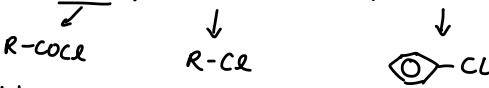
(c) \uparrow BP than halogenoalkanes.

Why? $\rightarrow \uparrow$ perm. d-dF.

\because C connected to 2
 \hookrightarrow -ve groups.

RELATIVE EASE OF HYDROLYSIS

OF ACYL, ALKYL & ARYL CHLORIDES



\therefore Acyl chlorides $>$ alkyl chlorides $>$ aryl chlorides.

Why?

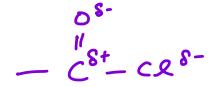
- C attached to 2 \hookrightarrow -ve atoms
- so \uparrow δ^+ on C
- so \uparrow susceptible to attack

Why?

- p orbitals from Cl overlap w/
 ring of delocalised p e⁻ in benzene ring
- so C-Cl develops partial double bond
 character
- so \uparrow difficulty to hydrolyse.

CHEMICAL REACTIONS

\therefore Due to the presence of 2 \hookrightarrow -ve atoms connected to the C, (O & Cl), the C has a relatively large partial +ve charge.



\Rightarrow hence, it is susceptible to nucleophilic attack, in which it undergoes the following general reaction.

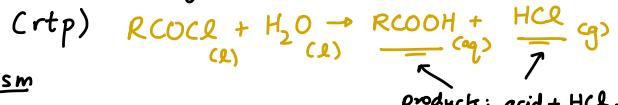


where Z is a nucleophile.

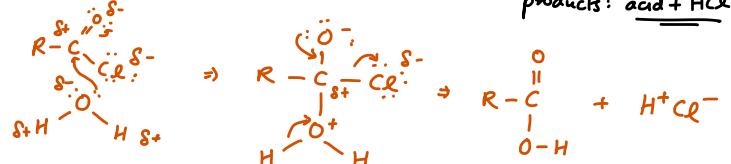
\Rightarrow consequently, we classify this reaction as a "nucleophilic substn" reaction.

① Hydrolysis of Acyl Chlorides

\therefore Recall that hydrolysis describes the "breaking down" of a \sim by H_2O .



Mechanism



Chapter 27: Organic Nitrogen Compounds

AMINES

Functional group: $\begin{array}{c} R \\ | \\ N \\ | \\ R \end{array}$

$\Rightarrow 1^\circ$ (primary): $R-NH_2$

2° (secondary): $R-N(R)-H$

3° (tertiary): $R-N(R)_2$

NOMENCLATURE

The name of the amine is derived from the identities of the alkyl groups connected to it.

Steps:
 ① Delete -e from alkane group
 ② Replace w/ -amine.
 e.g. methanamine

CH_3-NH_2 methanamine
 $CH_2CH_3-NH_2$ ethanamine

$(CH_3)_2 NH$ N -methyl methanamine
 $CH_3CH_2NHCH_3$ N -methyl ethanamine
Attached to N longest carbon chain attached

PHYSICAL PROPERTIES

BASICITY

The basicity of amines ($\& NH_3$) is the "availability" of the LP of e^- on the N atom to bond with H^+ ions. (recall base = H^+ acceptor)

Hence:

basicity of alkylamine > basicity of ammonia > basicity of phenylamine

Why? -alkyl group is $s+g-$ $R-NH_2$
 - so LP is "pushed away" and hence is more "available" to H^+

Why? - the LP is delocalised into the benzene ring.
 - hence the LP is less "available" to H^+ ions



WATER SOLUBILITY & BP

The H_2O -solubility and boiling points are dependent on the length of the alkyl chain(s):

when chain length \uparrow \rightarrow BP \uparrow (because id-id F \uparrow)
 solubility \downarrow (due to H bonding bw $H_2O \nwarrow$ & amine \nearrow)
 * amines have \downarrow BP than alcohols.
 Why? \rightarrow O more electronegative than N
 \rightarrow so strength of H bonds $\uparrow\uparrow$ in alcohols.

1° BP $>$ 2° BP $>$ 3° BP.
 less polar only perm. than 1o. dipole F. no H bonds.

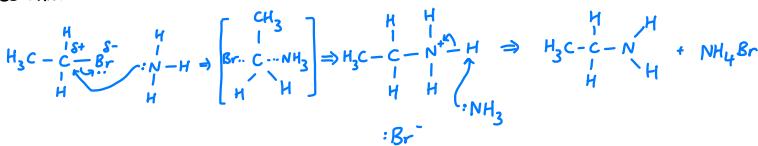
NUCLEOPHILIC SUBSTN OF HALOGENOALKANES W/ NH_3 (AS)

Reagent: ethanolic NH_3
 Condition: heat in sealed tube

Note: we add excess NH_3 to prevent the formation of $2^\circ/3^\circ$ amines.
 (Chlorogenoalkanes can react w/ amines)

example: $CH_3Cl + NH_3 \rightarrow CH_3NH_2 + HCl$
 $(NH_3 + HCl \rightarrow NH_4Cl)$

mechanism:



NUCLEOPHILIC SUBSTN OF HALOGENOALKANES W/ CN^- , FOLLOWED BY REDUCTION

(1st step) reagent: ethanolic KCN
 condition: heat under reflux

(2nd step) reagent: LiAlH₄ in dry ether or H_2 over Ni catalyst (at 140°C)

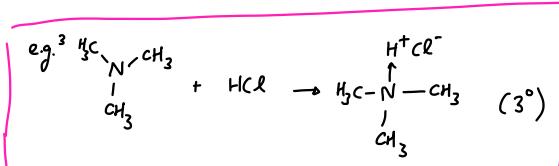
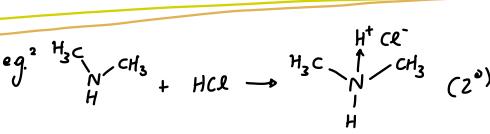
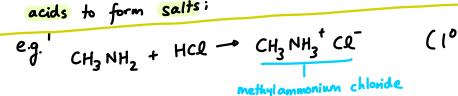
example:

(1st step) $CH_3Br + KCN \rightarrow CH_3CN + KBr$

(2nd step) $CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2$

CHEMICAL REACTIONS

As amines are bases, they can neutralise acids to form salts:



REACTION W/ H_2O

Amines undergo an equilibrium reaction with water to form their respective ammonium ion and hydroxide ions.

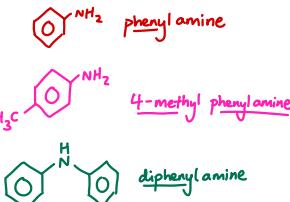
e.g.



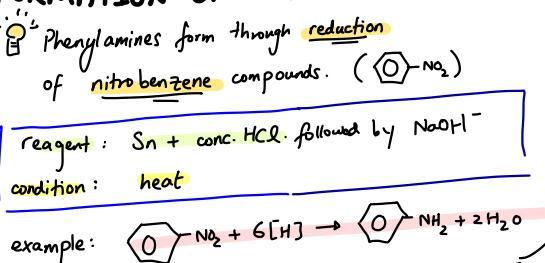
(this shows it is a weak base)

PHENYLAMINES

NOMENCLATURE



FORMATION OF PHENYLAMINES

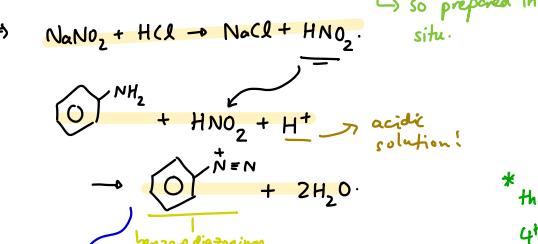


DIAZOTISATION

Diazotisation is the process in which a diazonium ($\text{N}^+ \equiv \text{N}^-$) salt is prepared via reacting a phenylamine with nitrous acid (HNO_2).

Step 1: Creation of the benzenediazonium ion

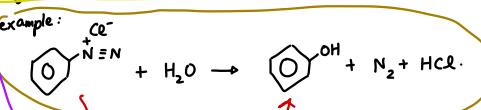
reagents: NaNO_2 , HCl
condition: temp. $< 10^\circ\text{C}$.



Reaction of diazonium salts

Diazonium salts can be decomposed by hot water to form phenols.

reagent: H_2O at temp. $> 60^\circ\text{C}$. ("boil in hot water")

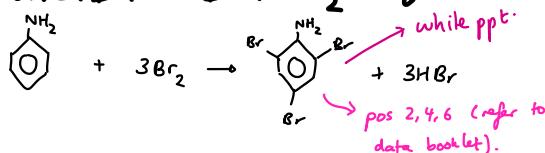


CHEMICAL REACTIONS

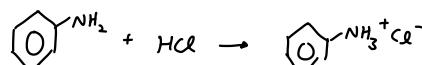
Since -NH_2 is an electron-donating group, the e^- density of the benzene ring increases, making it more susceptible to electrophilic attack.

hence, it can undergo electrophilic substitution.

REACTION WITH Br_2 (aq)



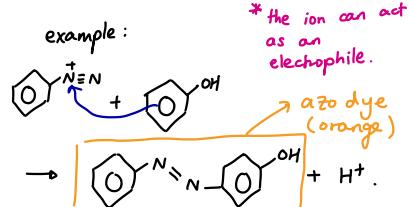
REACTION WITH HCl



it is often used in the creation of "azo dyes":
food colouring
dye
indicator.

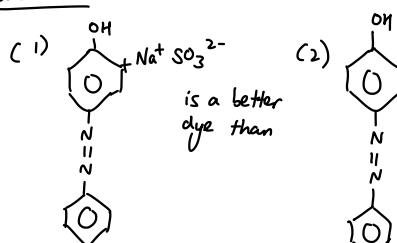
Step 2: Coupling reaction

reagent: phenol in alkaline condition.
condition: NaOH (aq)



* the ion will be substituted onto the 4th position of the phenol.
If it is occupied, it will occupy the 2nd or 6th pos instead.

Take note:



Why?
→ (1) is more soluble in water
→ it can form ion-dipole bonds w/ H_2O molecules
→ ion-dipole are stronger than H bonds.

TEST TO DISTINGUISH ALIPHATIC VS. PHENYL AMINES

This is also a test to differentiate 1°, 2° & 3° amines:

1°: N_2 produced

2°: coloured salt

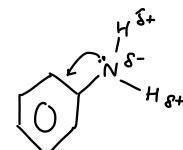
3°: solution (salt is soluble)

The diazotisation reaction can be used to differentiate phenyl and aliphatic amines;

whilst phenylamines will yield a coloured product: (azo dye)



aliphatic amines will only yield an alcohol, N_2 and H_2O ; which are all colourless.

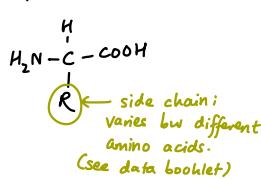


* the LP of e^- in N delocalises into the benzene ring.

AMINO ACIDS

Amino acids contain both an amino ($-NH_2$) group and an acid ($-COOH$) group, hence their name.

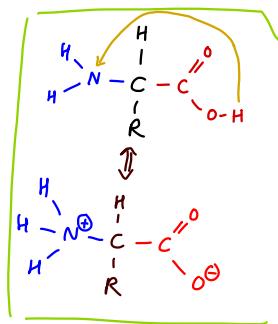
Structure:



ZWITTERION CHARACTERISTIC OF AMINO ACIDS

Due to the presence of both a basic ($-NH_2$) and acidic ($-COOH$) FG, each molecule can react with itself.

↳ This results in a "zwitterion": a species with both a +ve and -ve ionic charge (so net charge = 0).

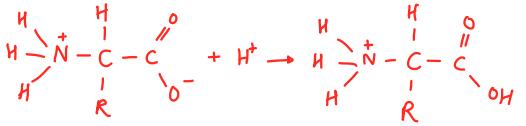


BUFFER SOLUTION PROPERTY OF AMINO ACIDS

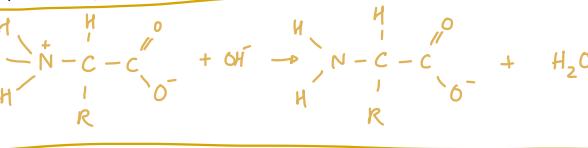
The zwitterion characteristic of amino acids makes them able to act as a "buffer solution";

↳ a solution that resists changes in pH when a small amount of an acid/base is added.
(CA2 phys chem)

(in acids)

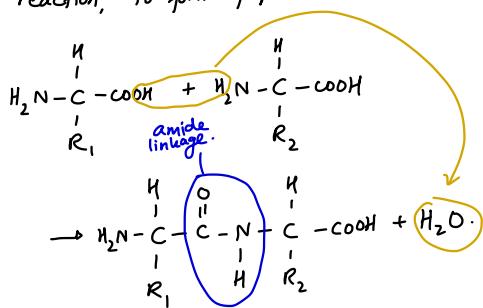


(in bases)



FORMATION OF PEPTIDES

Amino acid molecules can react together, through a condensation (removal of H_2O) reaction, to form peptides.

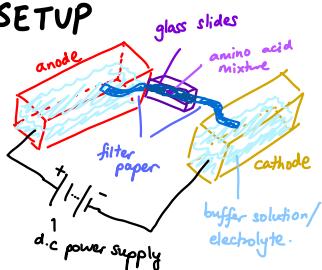


* two amino acids → dipeptide.
3 amino acids → tripeptide.
many amino acids → polypeptide
polypeptides react together to form proteins.

PAPER ELECTROPHORESIS

Paper electrophoresis is an analytical technique used to separate, identify and purify proteins.
(it is similar to "paper chromatography")

SETUP



WORKING PRINCIPLE

When a current is passed through the mixture:

↳ the +vely charged amino acids will move towards the cathode (-);
↳ the -vely charged amino acids will move towards the anode (+).

* The factors that affect the speed of the amino acids are:

- 1) Temperature;
- 2) Magnitude of pd applied;
- 3) RMM / size of α ; and
- 4) Charge (magnitude).

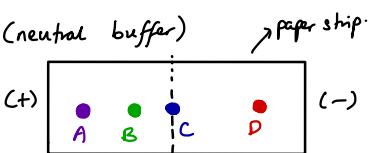
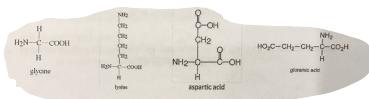
* The factors that affect the direction of movement of the amino acid are:

- 1) charge on amino acid;
- 2) pH of buffers
- 3) size of amino acid.

neutral: all ionise except neutral
acidic: only alkaline FG ionise
alkaline: only acidic FG ionise.

EXAMPLE

A, B, C and D are a mixture of the following proteins:



② Spot D is lysine.
Why? \rightarrow α has a charge of +1 in neutral condition.
(extra $-NH_2$ group).

★ Note:

① in an acidic buffer, none of the $-COOH$ groups would ionise;

\hookrightarrow hence all the amino acids will have a +ve charge, and move towards the anode (-).

② in an alkaline buffer, none of the $-NH_2$ groups would ionise;

\hookrightarrow hence all the amino acids will have a -ve charge, and move towards the cathode (+).

Observations:

① Spot C is glycine.
Why? \rightarrow no net ionic charge.

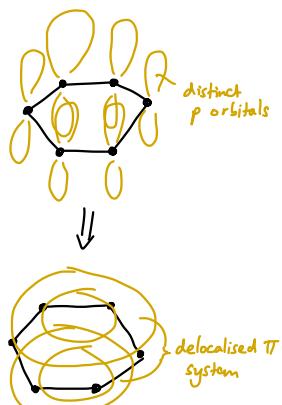
③ Spot A is aspartic acid. B is glutamic acid.

Why? \rightarrow 1) Both have a charge of -1.

2) But A is farther away than B $\therefore RMM_A < RMM_B$.

Chapter 25: Benzene And Its Compounds

- + The benzene ring consists of 6 C atoms in a regular hexagon.
- + Each C atom is connected to a H atom and to its 2 neighbouring C atoms by σ bonds.
- + The unhybridised p orbital (lone e^-) on each C overlap with each other, forming a delocalised six-centre molecular π orbital (i.e. delocalised π system).

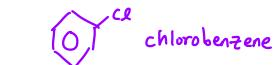


STRUCTURE

- All C display sp^2 hybridisation
- Bond angle = 120°
- All of the C=C bonds have equal length

NOMENCLATURE

"Arenes / aryl compounds / aromatic compounds" refer to organic HCs containing one or more benzene rings.



precedence decreases
(upper will become suffix etc)

PRECEDENCE OF NOMENCLATURE

FG	prefix	suffix
-COOH (acid)	-	-oic acid
-COO- (ester)	-	(-ylo)-oate
-COCl (acyl halide)	-	-oyl halide
-CONH- (amide)	-	-amide
<hr/>		
-C≡N (nitrile)	cyno-	-nitrile
-COH (aldehyde)	formyl-	-al
-CO- (ketone)	OXO-	-one
-OH (alcohol)	hydroxy-	-ol
-N- (amine)	amino-	-amine
-C=C- (alkene)	en-	-ene
-C-C- (alkane)	an-	-ane
<hr/>		
-X (halide)	fluoro/chloro/ bromo/iodo-	
<hr/>		
-NO ₂ (nitroso)	nitro-	-

CHEMICAL REACTIONS OF BENZENE

Alkenes and benzenes undergo wildly different chemical reactions.

ELECTROPHILIC SUBSTITUTION

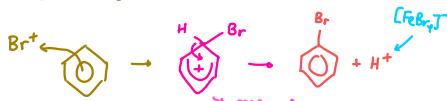
OF HALOGENS

Case 1 "just" benzene

reactant: molten bromine / chlorine gas

condition: warm in presence of $FeBr_3 / AlBr_3$ catalyst

mechanism:



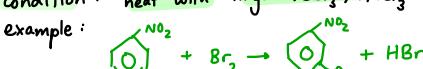
electrophilic attack of bromine cation on benzene ring

case 2 benzene w/ e^- withdrawing group (e.g. $-NO_2$, $-NH_3^+$, $-CN$) \rightarrow more stable than benzenes:

The halogen is substituted onto the 3rd / 5th position.

reactant: molten bromine / chlorine

condition: heat with rhod. $FeBr_3 / AlBr_3$



* in data booklet:
(LH) e^- donating
(RH) e^- withdrawing

case 3 benzene with e^- donating group (e.g. $-OH$, alkyl, $-NH_2$, $-Cl$) \rightarrow less stable than benzenes:

The halogen is substituted onto the 2nd / 4th / 6th position.

reactant: aqueous bromine / chlorine

condition: heat with $FeBr_3 / AlBr_3$

example:



* hence aqueous bromine is enough to start the reaction.

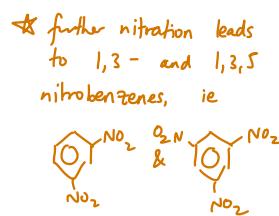
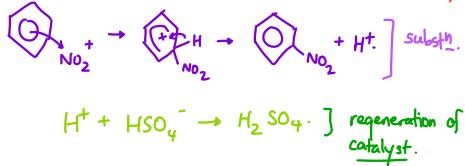
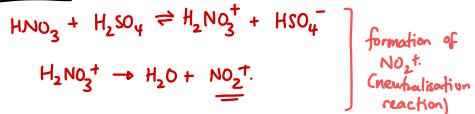
- lone pairs on atoms connected to ring delocalise into π structure
- electron density increases
- increased reactivity
- more susceptible to electrophilic attack

ELECTROPHILIC SUBSTN OF NO₂

For -NO₂ to be substituted, we need to create NO₂⁺ cations.

reactant: conc. HNO₃ & H₂SO₄
condition: heat under reflux at 55°C

mechanism:



FRIEDEL-CRAFTS REACTION

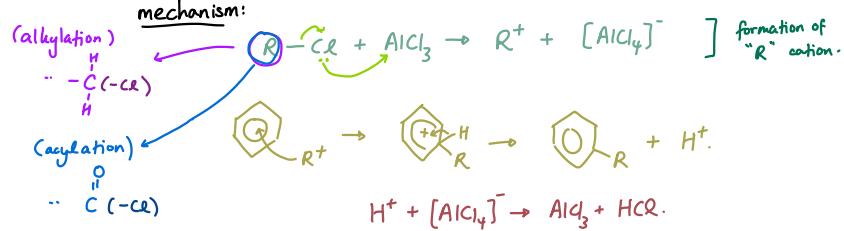
Friedel-Crafts reactions involve the introduction of a side chain into a benzene ring.

Two types:

- ① alkylation (alkyl)
- ② acylation (contains C=O , ie -COOH, -COR)

*type of reaction: electrophilic substitution.

reactant: halogenoalkane (alkylation), acyl chloride (acylation)
condition: heat w/ AlCl₃ catalyst.

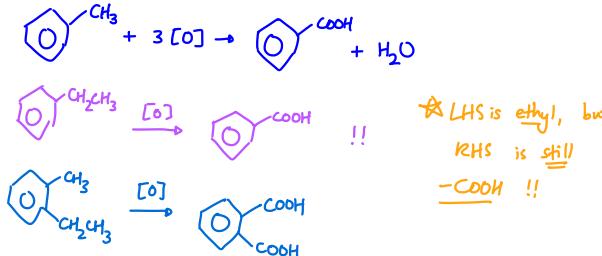


OXIDATION IN THE SIDE CHAIN

Any alkyl group on a benzene ring can be oxidised to form just a -COOH group.

reactant: KMnO₄/H⁺ or KMnO₄/OH⁻ + H₂SO₄
condition: heat under reflux

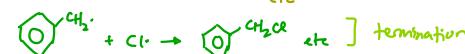
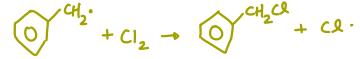
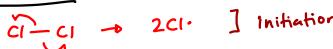
example:



FREE-RADICAL SUBSTITUTION OF METHYL SIDE CHAIN

reactant: Cl₂
condition: UV light

mechanism:



HYDROGENATION OF THE BENZENE RING

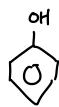
The benzene ring, under certain conditions, can undergo an addition reaction with H₂.

reactant: H₂ (g)
condition: heat at 200°C & 30 atm in the presence of Ni

reaction:

$$\text{C}_6\text{H}_6 + 3\text{H}_2 \rightarrow \text{Cyclohexane}$$

PHENOLS



(phenol)

💡 Phenols are compounds that contain an -OH group on a benzene ring.

PHYSICAL PROPERTIES

MP/BP

💡 Phenols have a higher MP than other similar aryl compounds.

Why? → H bonding bw molecules.

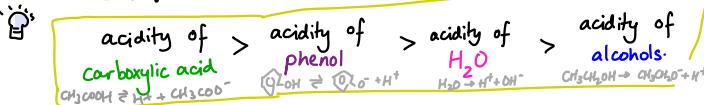
H₂O SOLUBILITY

💡 Benzenes are only slightly soluble in water.

Why? → large non-polar benzene ring
→ deep H bonding w/
H₂O molecules.

ACIDITY

💡



① Why acid > phenol?

- C=O bond has a negative inductive effect on the O-H effect on the O-H bond
- which weakens it
- this also delocalises the charge on the anion, stabilising it
- so concentration of [H⁺] is greater.

② Why phenol > H₂O?

- the lone pair of electrons overlaps w/ the delocalised π system
- so negative charge of phenoxide ion is spread out across the whole molecule
- so charge density decreases
- so stability increases
- so pos of eq shifts to the right, favouring greater formation of H⁺.
- hence, the negative charge on the oxygen atom is intensified.
- so charge density increases.
- so stability decreases.
- so pos of eq shifts to the left, leading to lesser formation of H⁺.

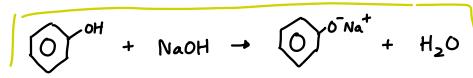
*key idea: talk about the weakening of O-H bond or stabilisation of anion.

③ Why alcohols < H₂O?

- alkyl groups have a +ve inductive effect (e⁻ donating group).
- hence, the negative charge on the oxygen atom is intensified.
- so charge density increases.
- so stability increases.
- so stability decreases.
- so pos of eq shifts to the left, leading to lesser formation of H⁺.

CHEMICAL REACTIONS

NEUTRALISATION



REACTION W/ METAL



★ phenols are not strong enough to react with carbonates.

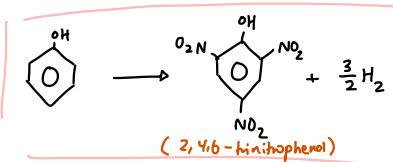
ELECTROPHILIC SUBSTITUTION

💡 As the oxygen atom's lone pair of electrons can delocalise into the π system of the benzene ring, the charge density of the system increases; hence, it is more susceptible to electrophilic attack.

W/ NO₂

reactant: dilute/conc. HNO₃
condition: room temperature

reaction:

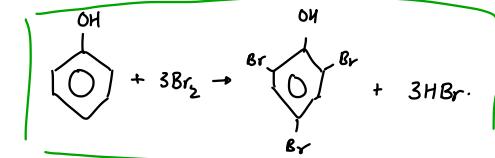


W/ Br₂

reactant: Br₂ (aq)

(-OH is e⁻ donating)

reaction:



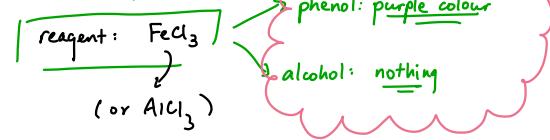
★ observations:

- white ppt
- steamy fumes

- bromine decolourises.

TEST TO IDENTIFY PHENOLS

💡 There is a specific method used to distinguish aliphatic alcohols and phenols.



Chapter 23: Entropy and Gibbs Free Energy

ENTROPY, S

Entropy is a measure of the disorder/randomness of a system (reactants + products).

- ↳ "disorder" refers to
1) the arrangement of particles, and
2) the kinetic energies of the particles.
(stability ↑ as entropy ↑)

Symbol: S unit: $\text{J K}^{-1} \text{mol}^{-1}$
(ΔS : entropy change)

FACTORS THAT AFFECT A SYSTEM'S ENTROPY

CHANGE IN PHASE

Why? It has to do with the arrangement of the op in the phases:

(Solid)
- regularly arranged
- particles close together
- particles can only vibrate

(Liquid)
- irregular arrangement
- op slide past each other

(Gas)
- irregular arrangement
- move freely in space
- far from each other

CHANGE IN NUMBER OF PARTICLES

The more "complex" a substance is, the lower its entropy is.

Examples:
 $S_{\text{CaCO}_3} < S_{\text{CaO}}$ (CaCO_3 has more "shit" than CaO)
 $S_{\text{C}_2\text{H}_6} < S_{\text{C}_2\text{H}_4}$ (C_2H_6 is a bigger molecule than C_2H_4)
 $S_{\text{Na}_2\text{O}} > S_{\text{MgO}}$ (Na_2O has weaker ionic bonds than MgO , so less "ordered")

CHANGE IN TEMPERATURE

The higher a substance's temperature is, the higher its kinetic energy.

Why? → op have more vibrational energy

CHANGE IN HARDNESS

Harder substances have lower entropy.
(eg $S_{\text{diamond}} < S_{\text{graphite}}$)

STANDARD MOLAR ENTROPY

"Standard molar entropy" is the entropy of one mole of substance in its standard state under standard conditions (298 K, $1.01 \times 10^5 \text{ Pa}$)

↳ symbol: S° (ΔS° if changing)

as all substances have entropy,
 S° is always positive!

RELATIONSHIP BETWEEN SPONTANEITY AND ENTROPY

A reaction is spontaneous if

$$\Delta S^\circ > 0.$$

MIXING OF PARTICLES

When two different substances mix together, their entropy increases. (more disorder!)

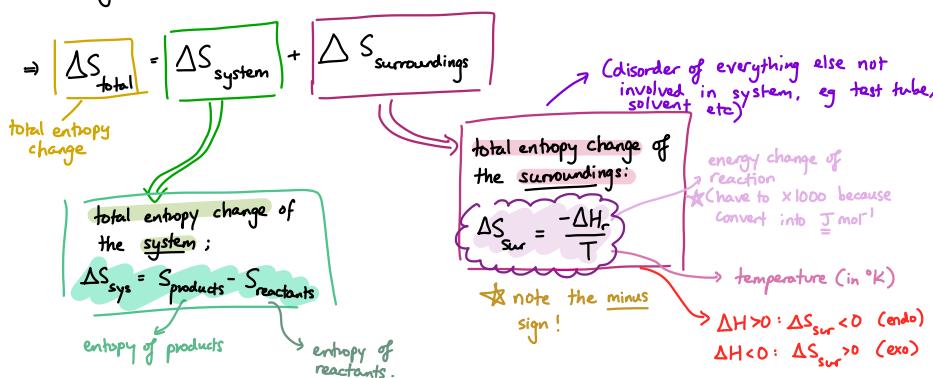
Examples: 1) diffusion (g & g)
2) dissolving (g/l/s & l)

ENTROPY CHANGES OF VARIOUS TYPES OF CHEMICAL REACTIONS

Chemical reaction/physical change	Example	Entropy change
Melting	$\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$	increase
Boiling	$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$	↑
Condensation	$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	↓
Sublimation	$\text{I}(\text{s}) \rightarrow \text{I}(\text{g})$	↑
Vapour deposition	$\text{I}(\text{g}) \rightarrow \text{I}(\text{s})$	↓
Precipitation	$\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$	↓
Dissolving a solute to form a solution	$\text{NaCl}(\text{s}) + \text{aq} \rightarrow \text{NaCl}(\text{aq})$	↑
Crystallization	$\text{NaCl}(\text{aq}) \rightarrow \text{NaCl}(\text{s})$	↓
Chemical reaction: solid/liquid forming a gas	$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	↑
Chemical reaction: gases forming a solid/liquid	$2\text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) \rightarrow 3\text{S}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	↓
Increase in number of moles of gas	$2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	↑

CALCULATING TOTAL ENTROPY CHANGE

For any chemical reaction, there is always a change in entropy.



ENTROPY AND TEMPERATURE

We can use entropy calculations to show how the feasibility of a reaction changes as temperature increases.

(for endothermic reaction) as $T \uparrow, \Delta S_{\text{sys}} \uparrow$.

Hence, since $\Delta S_{\text{sys}} \square, \Delta S_{\text{total}} \uparrow$.

\Rightarrow more feasible.

(for exothermic reaction) as $T \uparrow, \Delta S_{\text{sys}} \downarrow$.

Hence, since $\Delta S_{\text{sys}} \square, \Delta S_{\text{total}} \downarrow$.

\Rightarrow less feasible.

* Hence, the feasibility of endo rxns increases, and the feasibility of exo rxns decreases, as temperature \uparrow .

GIBBS FREE ENERGY, G

"Gibbs free energy" refers to the maximum amount of "non-expansion work" that can be done by the system.
 ↳ i.e. "useful" energy (not lost as heat).

MATHEMATICAL DEFINITION

$$\Delta G = \Delta H_{\text{reaction}} - T\Delta S_{\text{system}}$$

keep in $^{\circ}\text{K}!!$ \Rightarrow must $\div 1000$ bc unit of ΔG is kJ mol^{-1} .

symbol: G (ΔG : change; ΔG^\ominus : std. change)
 unit: kJ mol^{-1}

EFFECT OF TEMPERATURE CHANGE ON FEASIBILITY.

$\Delta G = \Delta H_{\text{reaction}} - T\Delta S_{\text{system}}$.
 Hence, as T increases, ΔG decreases.
 So, at a critical temperature T_0 , $\Delta G = 0$.
 At this temperature, the reaction becomes feasible.

This can be used to calculate T_0 , if we know ΔS_{system} and ΔH_r .

SPONTANEITY & GIBBS FREE ENERGY

We can use Gibbs free energy to determine whether a reaction will be spontaneous or not.

* if $\Delta G < 0$, the reaction is spontaneous / feasible.

Chapter 22:

Reaction Kinetics

RATE EQUATION

The rate equation is a method to illustrate the relationship bw how the concentrations of a reaction's reactants affects its rate.

for the rxn $aA + bB \rightarrow cC + dD$, the rate eqⁿ is given by

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

rate of reaction
rate constant
(unit dep on rxn)
conc. of A
"order" of [A]
conc. of B
"order" of [B]

only includes reactants that affect the rate.

ORDER OF REACTION (m, n)

defⁿ: the power to which the conc. of the reagent is raised to in the rate eqⁿ.

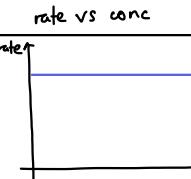
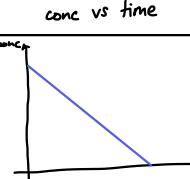
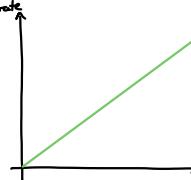
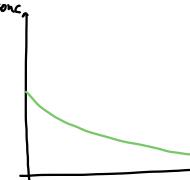
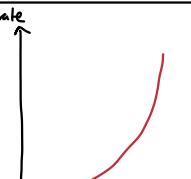
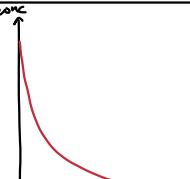
Example: rate eqⁿ is rate = $k[H_2]^2[NO]$.

rate $\propto [H_2]^2 \rightarrow$ order of $[H_2]$ is 2
rate $\propto [NO] \rightarrow$ order of $[NO]$ is 1

$$\text{overall order} = \text{sum of orders of reactants in eqⁿ}$$

$$\text{so overall order of rxn above} = 2+1 = 3.$$

HOW ORDER AFFECTS RATE

Order	What this means	rate vs conc	conc vs time	trend of $T_{1/2}$ over time
Zero	reactant does not affect rate at all $\text{rate} = k$			half-life <u>decreases</u> over time
One	rate or conc of reactant $\text{rate} = k[A]$			half-life <u>stays the same</u> over time. $T_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$
Two	rate or conc of reactant squared $\text{rate} = k[A]^2$			half-life <u>increases</u> over time.

Take note that, for gaseous reactions, the conc in the eqⁿ may be replaced with partial pressures.

e.g. for $N_2 + 3H_2 \rightleftharpoons 2NH_3$, rate eqⁿ is

$$\text{rate} = kP_{H_2}^2P_{N_2}$$

★ rate eqⁿs can only be determined theoretically!

★ for AL,
 $0 \leq m, n \leq 2$,
 $m, n \in \mathbb{Z}$.

HALF LIFE

defⁿ: the time taken for the concentration of a reactant to fall to $\frac{1}{2}$ of its original value.

$$\text{For 1st order rxn, } T_{1/2} = \frac{\ln 2}{k} \text{ (see below)}$$

MOLECULARITY

defⁿ: the number of molecules that come together to react in an elementary reaction.

deduced from mechanism of reaction.

★ experimentally determined.

EXPERIMENTAL DETERMINATION OF RATE EQNS AND CALCULATION OF RATE CONSTANT

Example 1

e.g.

Difficulty level 1:

Determine the rate law and calculate the rate constant for the following reaction from the experimental data:



Experiment	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

$$E1, E2 \rightarrow [S_2O_8^{2-}] \text{ (}) ; [I^-]^{(2)}, \text{ rate } \pm 2$$

so order of $[I^-] = 1$

$$E2, E3 \rightarrow [S_2O_8^{2-}]^{(2)}, \text{ rate } \times 2 \quad ([I^-] \text{ (})$$

so order of $[S_2O_8^{2-}]$ is 1

$$\Rightarrow \text{rate eqn}^2 \text{ is rate} = k [I^-][S_2O_8^{2-}]$$

Example 2

Difficulty level 3

The depletion of ozone, O_3 , in the upper atmosphere can be caused by the reaction of automobile exhaust gases, such as NO, with the ozone. The reaction between $O_3(g)$ and $NO(g)$ has been studied and the following data were obtained at $25^\circ C$.

Experiment	$[NO(g)] / mol dm^{-3}$	$[O_3(g)] / mol dm^{-3}$	Rate / $mol dm^{-3} s^{-1}$
1	1.00×10^{-4}	3.00×10^{-6}	0.660×10^{-4}
2	1.00×10^{-4}	6.00×10^{-6}	1.32×10^{-4}
3	3.00×10^{-4}	9.00×10^{-6}	5.94×10^{-4}
4	4.50×10^{-4}	7.20×10^{-6}	

O_3 easy to determine. Case method from E1)

$$\left(\frac{e^3}{e^2}\right) \Rightarrow \frac{\text{rate}_f}{\text{rate}_i} = \left(\frac{[O_3]_f}{[O_3]_i}\right)^m \left(\frac{(3.00 \times 10^{-6})}{(1.00 \times 10^{-6})}\right)^1$$

$$\frac{5.94}{1.32} = \left(\frac{9.00}{6.00}\right)^m (3)^1$$

$$1.5 = 1.5^m \Rightarrow m = 1.$$

KINETICS & REACTION MECHANISMS

Many reactions happen in many steps. We call this the "reaction mechanism".

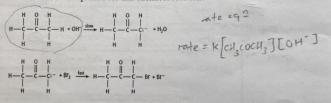
the step that is the slowest determines the rate of the mechanism.

hence, the "rate-determining" step is the slowest step in the mechanism.

the reactants in the slowest step will appear in the rate eqn.

PREDICTION OF ORDER FROM MECHANISM

For example:
The reaction illustrated below is second order overall and the reaction mechanism is shown. What is rate equation for this chemical reaction?

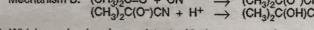
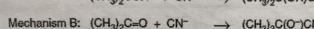
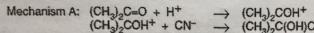


order for both = 1. (only solution)

VERIFICATION OF POSSIBLE MECHANISMS FROM KINETIC DATA

Given that the rate equation = $k[(CH_3)_2C=O][CN^-]$

Two different mechanisms have been suggested for this reaction

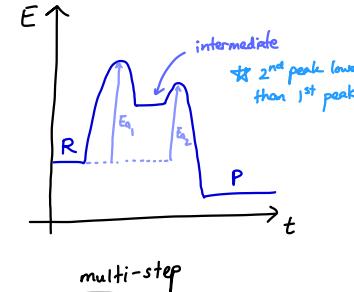
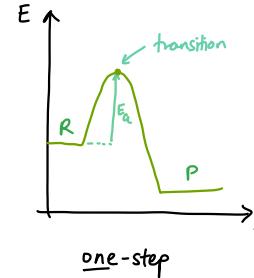


(i) Which mechanism is consistent with the rate equation you deduced, and which step in this mechanism is the slower (rate determining) step? Explain your answer.

mechanism B. Why?

→ 1st ratⁿ has both reactants in rate eqn.
→ so, 1st ratⁿ is slowest ratⁿ.

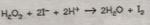
REACTION PROFILE



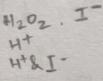
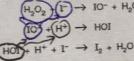
TEST YOURSELF

What if 2nd step onwards is slowest?

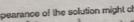
1. In the late 19th century two pioneers of the study of reaction kinetics, Vernon Harcourt and William Essen, studied the rate of the reaction between hydrogen peroxide and iodide ions in acidic solutions.



This reaction is considered to go by the following steps.



The general form of the rate equation is as follows.



(a) Suggest how the appearance of the solution might change as the reaction takes place.

solution becomes brown

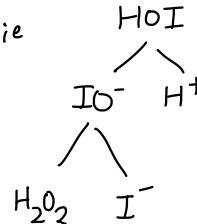
(b) Suggest values for the orders a, b and c in the rate equation for each of the following cases.

case	numerical value		
	a	b	c
step 1 is the slowest overall	1	1	0
step 2 is the slowest overall	0	0	1
step 3 is the slowest overall	0	2	2

2.

equation
The foll

ie



Alternatively, if step 2 is the slowest,

then HOI ($= H_2O_2 + I^- + H^+$), H^+ & I^- should appear. So $[H^+]$ and $[I^-]$ affects rate twice, which means their respective orders is 2;

$$\text{ie rate} = [H^+]^2 [I^-]^2 [H_2O_2].$$

If step 2 is the slowest, then IO^- and H^+ should appear in the rate eqn.

But since the constituents of IO^- are H_2O_2 & I^- ,

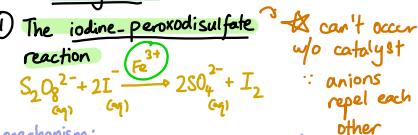
then the rate eqn is

$$\text{rate} = k[H_2O_2][I^-][H^+].$$

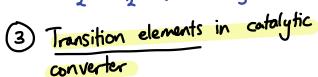
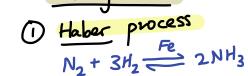
CATALYSIS

Recap: catalysis can be divided into two categories:

homogenous



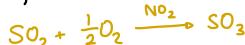
heterogenous



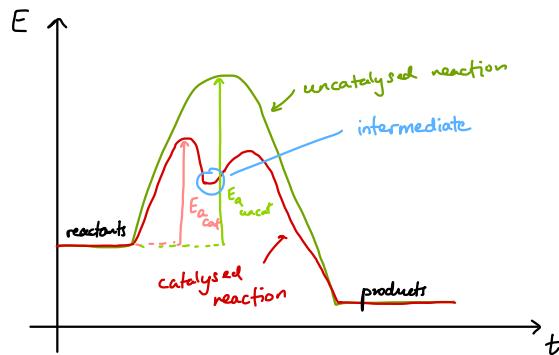
② The decomposition of hydrogen peroxide



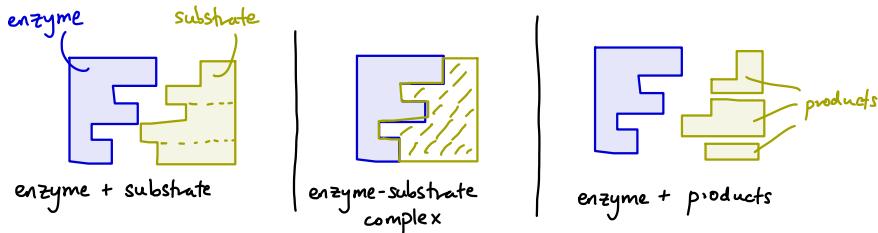
② The formation of acid rain



REACTION PROFILE OF A CATALYSED REACTION



CATALYTIC ROLE OF ENZYMES



- * The substrate has a shape complementary to the active site.
- The substrate then binds to the active site.
- The interaction causes a specific bond to be weakened, lowering E_a.
- An enzyme-substrate complex is subsequently formed,
- and then the products are released from the enzyme.

RELATIONSHIP BETWEEN TEMPERATURE AND RATE

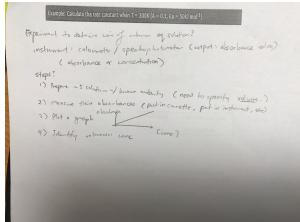
The positive relationship between rate and temperature can be shown mathematically using Arrhenius' equation:

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

Diagram illustrating the Arrhenius equation:

- rate constant
- freq factor (constant)
- activation energy (in J mol^{-1})
- kelvin temperature
- gas constant (8.31)
- e (2.718...)

EXPERIMENT TO DETERMINE CONC OF UNKNOWN SOLUTION



Chapter 21: Further Aspects of Equilibria

IONIC PRODUCT OF WATER (K_w)

$\therefore K_w$ = equilibrium constant for the ionisation of water



$\Rightarrow K_w$ is given by the formula

$$K_w = [H^+][OH^-] \quad (= 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at std conditions})$$

④ Relation between K_w & T

\hookrightarrow if $T \uparrow$, eq shifts to right, so $K_w \uparrow$

BUT

* as $T \uparrow$, $K_w \uparrow$.
Then $[H^+] \uparrow$. ($\therefore -\log_{10}[H^+] \downarrow$).

Hence,

the pH decreases when T increases.

pH OF PURE WATER

In pure water, $[H^+] = [OH^-]$.

Hence $[H^+] = [OH^-] = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$. (at rtp)

Then, the pH of pure water, at rtp.

is equal to $-\log_{10}(10^{-7}) = 7$.

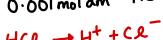
pH OF STRONG ACIDS

* Assumptions $\rightarrow [H^+]$ from H_2O is negligible

$\therefore [H^+] = [H^+]$ from acids.

Examples

① 0.001 mol dm⁻³ HCl



$\therefore n_{H^+} = n_{HCl}$

$\therefore [H^+] = [HCl]$

$\therefore pH = -\log_{10}[H^+]$

$= -\log_{10}(0.001)$

$= 3$.

② 0.10 mol dm⁻³ H_2SO_4



$\therefore n_{H^+} = 2n_{H_2SO_4}$

$\therefore [H^+] = 2[H_2SO_4]$

$\therefore pH = -\log_{10}[H^+]$

$= -\log_{10}(2 \cdot 0.10)$

$= 0.70$.

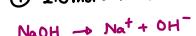
pH OF STRONG BASES

* Assumptions $\rightarrow [OH^-] = [OH^-]$ from base

$[OH^-]_{H_2O}$ negligible

Examples

① 2.0 mol dm⁻³ NaOH



$\therefore [OH^-] = [NaOH]$.

$$[H^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

$$\therefore [H^+] = \frac{1.00 \times 10^{-14}}{[OH^-]}$$

$$= \frac{1.00 \times 10^{-14}}{2}$$

$$= 5.00 \times 10^{-15}$$

$$\therefore pH = -\log_{10}[H^+]$$

$$= -\log_{10}(5.00 \times 10^{-15})$$

$$= 14.3.$$

Alternative method:

$$pH + pOH = 14$$

$$\therefore pH = 14 - pOH$$

$$= 14 + \log_{10}(2)$$

$$= 14.3.$$

ACID DISSOCIATION CONSTANT, K_a

④ Example of use

Calculate pH of 0.1 mol dm⁻³ solution of ethanoic acid, given $K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$

$$*\quad [H^+] = [X^-] \quad \therefore K_a = \frac{[H^+]^2}{[HX]} \quad \therefore pH = -\log_{10}\sqrt{0.18 \times 10^{-5}}$$

$$\therefore 1.8 \times 10^{-5} = \frac{[H^+]^2}{0.1} \quad \therefore 2.8723$$

$$\therefore [H^+] = \sqrt{0.18 \times 10^{-5}} \quad \therefore 2.9.$$

RELATION BETWEEN K_a & pH

$$*\quad K_a = \frac{[H^+]^2}{[HX]} \quad \therefore K_a \propto [H^+]^2.$$

$\therefore K_a \uparrow$ (or $pK_a \downarrow$) $\Rightarrow [H^+] \uparrow$ and hence $pH \downarrow$ (stronger acid).

Note that

$$pK_a = -\log_{10} K_a$$

INDICATORS AND ACID-BASE TITRATIONS

An "indicator" is a dye that changes colour over a specific pH range.
 ↳ usually weak acids, where acid & anion colour are different.

TITRATION CURVES

Titration curves show how the pH of an acid/base changes during a titration (where it is neutralised.)

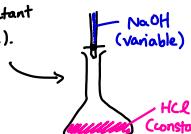
DRAWING TITRATION CURVES

#1 STRONG ACID + STRONG BASE

Ex 25cm³ of 0.1M HCl w/ 50cm³ of 0.1M NaOH

Method:

Step 1 Draw a diagram to identify what reactant is being neutralised (in the conical flask).



Step 2 Identify initial pH.

$$\text{pH} = -\log_{10} [\text{H}^+]. \quad \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$$

$$\therefore \text{pH} = -\log_{10} [\text{HCl}]$$

$$= -\log_{10} (0.1) = 1.0.$$

Step 3 Identify V of reactant (NaOH) at endpoint.

$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

$$n_{\text{HCl}} = 25 \times 10^{-3} \times 0.1 = 2.5 \times 10^{-3}$$

$$\therefore n_{\text{NaOH}} = 2.5 \times 10^{-3} \quad \therefore V_{\text{NaOH}} = \frac{n}{c} = \frac{2.5 \times 10^{-3}}{0.1} = 25 \times 10^{-3} \text{ dm}^3 = 25 \text{ cm}^3.$$

Step 4 Identify final pH.

$$n_{\text{HCl}} = 2.5 \times 10^{-3} \text{ mol.} \Rightarrow n_{\text{H}^+} = 2.5 \times 10^{-3}$$

$$\Rightarrow n_{\text{NaOH}} = 50 \times 10^{-3} \times 0.1 = 5.0 \times 10^{-3} \text{ mol.}$$

$$\therefore n_{\text{OH}^-} \text{ left} = 5.0 \times 10^{-3} - 2.5 \times 10^{-3} = 2.5 \times 10^{-3} \text{ mol.}$$

$$\therefore [\text{OH}^-] = \frac{2.5 \times 10^{-3}}{(50+25) \times 10^{-3}} = \text{V of both acid + alkali}$$

$$= 0.0333.$$

$$\rightarrow K_w = [\text{H}^+] [\text{OH}^-] = 1.00 \times 10^{-14}$$

$$\therefore [\text{H}^+] = \frac{1.00 \times 10^{-14}}{[\text{OH}^-]}$$

$$= \frac{1.00 \times 10^{-14}}{0.0333}$$

$$= 3.0030 \times 10^{-13}.$$

$$\rightarrow \text{final pH} = -\log_{10} (3.0030 \times 10^{-13}) = 12.5224 = 12.5.$$

* note for step 4:
 If no final V is given, we assume an infinite amount of the reactant was added.

This infers the final pH = reactant pH.

In this example,

$$\text{final pH} = -\log_{10} [\text{H}^+] = -\log_{10} \frac{k_w}{[\text{OH}^-]} = -\log_{10} \frac{10^{-14}}{0.1} = 13.0 \text{ (instead of 12.5.)}$$

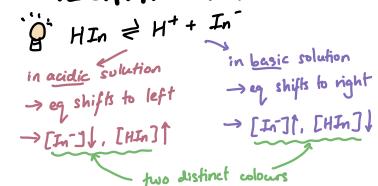
SELECTING A SUITABLE INDICATOR

Each indicator's "pH range" is unique. For an indicator to be viable for use in a neutralisation reaction, the range must fall within the steep region of the titration curve.

examples)	indicator	pH range
	methyl orange	3.2 - 4.4
	bromophenol blue	2.8 - 4.6
	phenolphthalein	8.2 - 10.0

acid → alkali
 colour change
 red → yellow
 yellow → blue
 colourless → pink

MECHANISM



#2 STRONG ACID + WEAK BASE

Ex

20.0 cm³ of 0.100 mol dm⁻³ HCl was slowly added to a 10.0 cm³ sample of 0.150 mol dm⁻³ pipendine. The pH was measured throughout the addition.

On the following axes, sketch how the pH will change during the addition of a total of 20.0 cm³ of 0.100 mol dm⁻³ HCl. Mark clearly where the end point occurs.

$$\text{pH of pipendine} = 11.9$$

Method is the same as case #1
 However, note the steep region is

$$3.5 - 7.5.$$

(step 1) HCl (variable)
 pipendine (constant)

(step 2) pH_i = 11.9 (given)

$$(step 3) n_{\text{base}} = 0.150 \times (10 \times 10^{-3}) = 1.50 \times 10^{-3}$$

$$\therefore n_{\text{H}^+} = 1.50 \times 10^{-3} \quad \because 1:1 \text{ mole ratio}$$

$$\therefore V_{\text{HCl}} = \frac{n}{c} = \frac{1.50 \times 10^{-3}}{0.10} = 1.5 \times 10^{-3} \text{ dm}^3 = 1.5 \text{ cm}^3.$$

$$(step 4) \text{After all H}^+ \text{ added,}$$

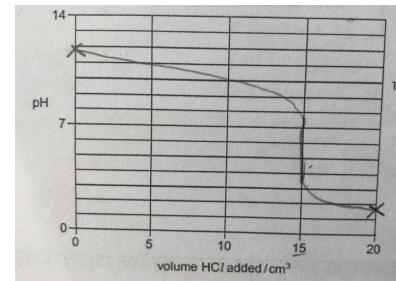
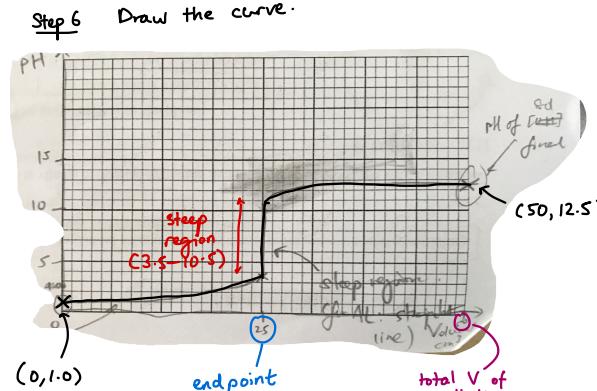
$$n_{\text{H}^+} = 0.100 \times (20 \times 10^{-3}) = 2.0 \times 10^{-3}$$

$$\Rightarrow n_{\text{H}^+ \text{ remaining}} = 2.0 \times 10^{-3} - 1.50 \times 10^{-3} = 5.00 \times 10^{-4}$$

$$\therefore [\text{H}^+] = \frac{5.00 \times 10^{-4}}{(20+10) \times 10^{-3}} = 0.01666.$$

$$\therefore \text{pH} = -\log_{10} (0.01666) = 1.77815 \dots = 1.78.$$

(step 6)



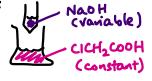
#3 WEAK ACID + STRONG BASE

Ex

Use the following axes to sketch the titration curve you would obtain when 20 cm^3 of 0.10 mol dm^{-3} NaOH is added gradually to 10 cm^3 of 0.10 mol dm^{-3} $\text{C}_1\text{CH}_2\text{CO}_2\text{H}$, with the K_a of 1.3×10^{-3} mol dm^{-3} .

Steep region: $7.5 - 11$

Method:



(Step 1) We can calculate $[\text{H}^+]$ from K_a :

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+]^2}{[\text{HA}]}$$

$$\therefore [\text{H}^+] = \sqrt{K_a[\text{HA}]} = \sqrt{(1.3 \times 10^{-3})(0.10)} = 0.0114017.$$

$$\therefore \text{pH}_i = -\log_{10}(0.0114017) = 2.94.$$

(Step 2: pH_f) $n_{\text{CH}_3\text{COOH}} = (10 \times 10^{-3}) \times 0.10$



$$\therefore n_{\text{NaOH}} = 1.0 \times 10^{-3}$$

$$\therefore V_{\text{NaOH}} = \frac{n}{c} = \frac{1.0 \times 10^{-3}}{0.10} = 10 \times 10^{-3} \text{ dm}^3 = 10 \text{ cm}^3.$$

(Step 3-5) Calculation of V used at half end point ($V = \frac{1}{2}V_{\text{endp}}$)

\therefore At the half end point, $[\text{salt}] = [\text{acid}]$. Hence, as K_a of a buffer sol. = $\frac{[\text{H}^+][\text{salt}]}{[\text{acid}]}$, we see that $K_a = [\text{H}^+]$, or $\text{pH} = \text{p}K_a$

$$\Rightarrow \text{pH}_{\frac{1}{2}} = -\log_{10}(1.3 \times 10^{-3}) = 2.88605 \quad V_{\frac{1}{2}} = \frac{10 \text{ cm}^3}{2} = 5 \text{ cm}^3.$$

(Step 4: pH_f) After all OH^- added,

$$n_{\text{OH}^- \text{ total}} = (20 \times 10^{-3}) \times 0.10 = 2.0 \times 10^{-3}.$$

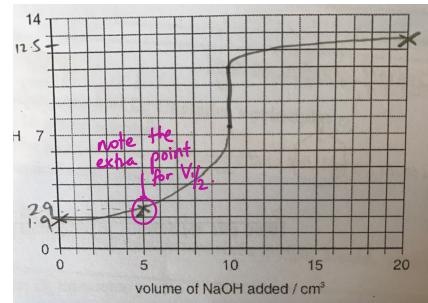
$$\Rightarrow n_{\text{OH}^- \text{ excess}} = 2.0 \times 10^{-3} - 1.0 \times 10^{-3} = 1.0 \times 10^{-3}.$$

$$\therefore [\text{OH}^-] = \frac{1.0 \times 10^{-3}}{(20 + 10) \times 10^{-3}} = 0.03333.$$

$$\Rightarrow [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.03333} = 3.003 \times 10^{-13}.$$

$$\therefore \text{pH} = -\log_{10}(3.003 \times 10^{-13}) = 12.5.$$

(Step 6)



#4 WEAK ACID + WEAK BASE

For this case, the steep region is too faint to be detected by any indicator.
(extra info)

#5 POLYBASIC ACIDS

For polybasic acids, there are 2 or more endpoints.

Ex 20cm³ of 0.1M H_2SO_4 titrated w/ 0.1M NaOH

(Step 1)

(Step 2: pH_i) $[\text{H}_2\text{SO}_4] = 0.1$ diprotic! $\therefore [\text{H}^+] = 0.1 \times 2 = 0.2$

$$\therefore \text{pH}_i = -\log_{10}(0.2) = 0.7.$$

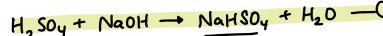
(Step 4: no V of NaOH given so assume inf V .)

$$[\text{OH}^-] = 0.1 \quad \therefore \text{pH} = -\log_{10}(10^{-13}) = 13.$$

$$\therefore [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.1} = 10^{-13}.$$

(Step 3) Identify the two endpoint volumes

$\therefore \text{H}_2\text{SO}_4$ undergoes a two step neutralisation process w/ NaOH:



\hookrightarrow each stage has its own endpoint.

For (1) \rightarrow

$$n_{\text{H}_2\text{SO}_4} = (20 \times 10^{-3}) \times 0.1 = 2.0 \times 10^{-3}$$

$$1:1 \quad \therefore n_{\text{NaOH}} = 2.0 \times 10^{-3}$$

$$\Rightarrow V_1 = \frac{n}{c} = \frac{2.0 \times 10^{-3}}{0.1} = 20 \times 10^{-3} \text{ dm}^3$$

$$V_1 = 20 \text{ cm}^3.$$

For (2) \rightarrow

$$n_{\text{H}_2\text{SO}_4} = 2.0 \times 10^{-3}$$

$$n_{\text{NaOH}} = 2.0 \times 10^{-3}$$

$$\therefore V = 20 \text{ cm}^3 + 20 \text{ cm}^3 \quad \text{from (1)}$$

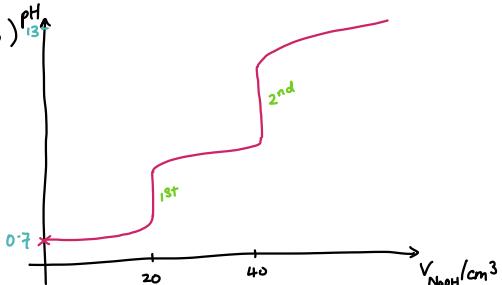
$$\therefore V_2 = 40 \text{ cm}^3$$

(Step 5) Just remember the 1st steep region is shorter than the 2nd steep region.

(1) $\sim 3\text{ pH}$

(2) $\sim 5\text{ pH}$)

(Step 6)



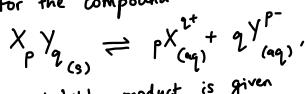
SOLUBILITY PRODUCT, K_{sp}

The solubility product, K_{sp} , is the product of the concentrations of each ion in a saturated solution of a sparingly soluble salt at 298 K, raised to the power of their relative concentrations.

↳ it is a measure of an ionic compound's solubility in water.

Mathematical visualisation

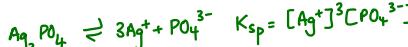
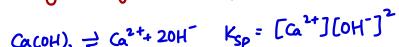
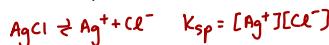
④ For the compound



the solubility product is given by

$$K_{sp} = [X^{q+}]^p [Y^{p-}]^q$$

Examples



USING K_{sp} IN PROBLEMS

Ex 1

Silver phosphate, Ag_3PO_4 , is sparingly soluble in water.

(i) Write an expression for the solubility product, K_{sp} , of Ag_3PO_4 , and state its units.

$$Ag_3PO_4 \rightleftharpoons 3Ag^{+} + PO_4^{3-}$$

$$K_{sp} = [Ag^{+}]^3 [PO_4^{3-}]$$

units: $\text{mol}^{-4} \text{dm}^{-12}$

(ii) The numerical value of K_{sp} is 1.25×10^{-3} at 298 K. Use this value to calculate $[Ag^{+}]$ in a saturated solution of Ag_3PO_4 .

$$[Ag^{+}] = x \Rightarrow [PO_4^{3-}] = \frac{1}{3}x \rightarrow \text{molar ratio is } 3:1.$$

$$\Rightarrow K_{sp} = x^3 \cdot \frac{1}{3}x^3$$

$$1.25 \times 10^{-3} = \frac{1}{3}x^6$$

$$\therefore [Ag^{+}] = 1.3915 \times 10^{-5} \text{ mol dm}^{-3}$$

$$= 1.39 \times 10^{-5} \text{ mol dm}^{-3}$$

Ex 2

The solubility of calcium ethanedioate, CaC_2O_4 , is $6.65 \times 10^{-5} \text{ g dm}^{-3}$ at 298 K.

(i) Write an expression for the solubility product, K_{sp} , of CaC_2O_4 . Include its units.

$$CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$$

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

units: $\text{mol}^{-2} \text{dm}^{-6}$

(ii) Calculate the numerical value of K_{sp} of CaC_2O_4 at 298 K. Give your answer in standard form to two significant figures.

$$CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$$

$$\Rightarrow K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

$$= \frac{(6.65 \times 10^{-5})^2}{(40)(120)(40)} \text{ mol}^{-2} \text{dm}^{-6}$$

$$= 2.69 \times 10^{-9} \text{ mol}^{-2} \text{dm}^{-6}$$

$$= 2.7 \times 10^{-9} \text{ (2sf)}$$

★ have to convert into mol dm^{-3} !!

$$(\text{g dm}^{-3} = \frac{\text{mol dm}^{-3}}{m_r})$$

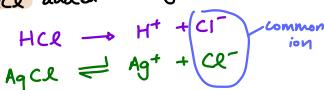
COMMON ION EFFECT

If a dissolved salt is exposed to a solution which shares a common ion with it, its solubility decreases.

↳ We coin this the "common ion effect".

↳ due to ↓ solubility, precipitation will occur.

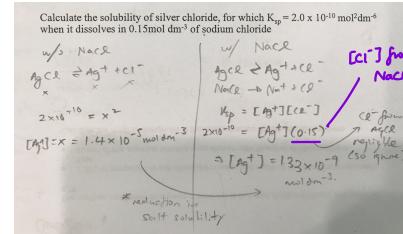
e.g. HCl added to $AgCl$



④ When HCl added:

- $[Cl^-] \uparrow$
- (by Le Chatelier's principle) eq shifts to left
- so $[Ag^+] \downarrow$ so $K_{sp} \downarrow$
- so solubility decreases.

Using common ion effect in questions



USES OF K_{sp}

Generally, K_{sp} is used to determine the "saturation point" for a solution.

e.g. K_{sp} of $BaCO_3$ = $5.5 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$.

If $[Ba^{2+}][CO_3^{2-}] = 5.5 \times 10^{-10}$, saturated

If $[Ba^{2+}][CO_3^{2-}] < 5.5 \times 10^{-10}$, can add more

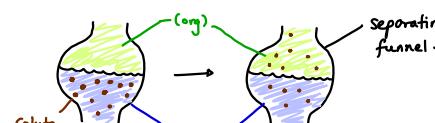
If $[Ba^{2+}][CO_3^{2-}] > 5.5 \times 10^{-10}$, precipitation occurs.

PARTITION COEFFICIENTS, K_{pc}

The partition coefficient is the ratio of the concentrations / amounts of solute in two immiscible solvents at equilibrium.

$$K_{pc} = \frac{[X \text{ in organic}]}{[X \text{ in aqueous}]}$$

VISUALISATION BY ILLUSTRATION



The solute undergoes the equilibrium ref:

$$X_{(\text{aq})} \rightleftharpoons X_{(\text{org})}$$

⇒ if X is more soluble in (aq), then the eq will shift to the left, and vice versa.

↳ it follows that K_{pc} is a measure of deducing the relative solubilities of the solute in each of the solutions.

If $K_{pc} > 1 \Rightarrow [org] > [aq]$

⇒ solute more soluble in organic solvent.

If $K_{pc} < 1 \Rightarrow [aq] > [org]$

⇒ solute more soluble in aqueous solvent.

If $K_{pc} = 1 \Rightarrow [aq] = [org]$

⇒ solute equally soluble in both solvents.

USING K_{pc} IN QUESTIONS

Ex 1. The partition coefficient of organic compound H between dichloromethane and water is 4.75. 2.0 g of compound H was dissolved in water and made up to 100 cm³ in a volumetric flask. 50 cm³ of this aqueous solution were shaken with 10 cm³ of dichloromethane. Calculate the mass of compound H that was extracted into the dichloromethane.

$$K_{pc} = \frac{[X_{\text{org}}]}{[X_{\text{aq}}]}$$

$$4.75 = \frac{(1.25-x)}{x} \rightarrow \# \text{ of moles in (a)} = \frac{(1.25-x)}{10}$$

$$\frac{(1.25-x)}{10} \rightarrow V_{\text{org}}$$

$$\left(\frac{x}{50} \right) \rightarrow \# \text{ of moles in (aq)}$$

$$\Rightarrow x = 0.61.$$

USES OF K_{pc}

K_{pc} can be used as a quantitative measure of the separation of different components in a mixture during chromatography.

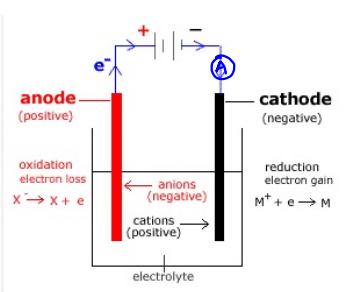
Chapter 20:

Electrochemistry

ELECTROLYSIS

💡 Electrolysis is the decomposition of a compound by an electric current.

THE ELECTROLYTIC CELL



💡 The main components of an electrolysis cell are:

- ① Electrolyte — a molten/aqueous ionic compound which is decomposed during electrolysis
- ② Electrodes — made from metal/graphite (must be conductors)
- ③ Power supply (d.c.)
- ④ Ammeter — measure current

ELECTROLYSIS ON MOLTEN ELECTROLYTES

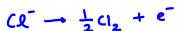
💡 In a molten electrolyte, there are only 2 ions.

eg NaCl:

→ at the cathode (-), reduction occurs:



→ at the anode (+), oxidation occurs:



ELECTROLYSIS ON AQUEOUS ELECTROLYTES

💡 For aqueous electrolytes, we have to factor in the presence of H_2O .

What is discharged?

eg NaCl(aq).

For the cathode (-):

→ compare E^θ of cation with E^θ of water.

If $E^\theta_{\text{cat}} > E^\theta_{\text{water}}$ ⇒ cation's products discharged.
If $E^\theta_{\text{cat}} < E^\theta_{\text{water}}$ ⇒ H_2 discharged.

For the anode (+):

→ compare E^θ of anion with E^θ of water.

If $E^\theta_{\text{an}} < E^\theta_{\text{water}}$ ⇒ anion's products discharged.

If $E^\theta_{\text{an}} > E^\theta_{\text{water}}$ ⇒ O_2 discharged.

cathode:
 $\text{Na}^+ + \text{e}^- \rightarrow \text{Na} \quad E^\theta = -2.71\text{V}$

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad E^\theta = -0.83\text{V}$

$-0.83\text{V} > -2.71\text{V}$

so $\underline{\underline{\text{H}_2}}$ discharged.

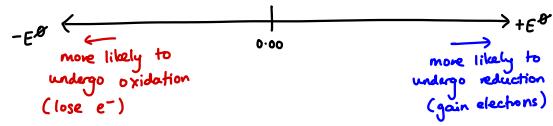
anode:
 $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^- \quad E^\theta = +1.23\text{V}$

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad E^\theta = +1.36\text{V}$

$+1.23\text{V} < +1.36\text{V}$

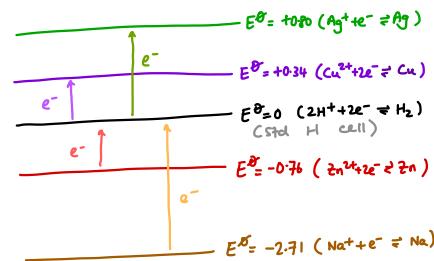
so $\underline{\underline{\text{O}_2}}$ discharged.

THE INFLUENCE OF E^θ ON EASE OF DECOMPOSITION



Why?

We can use a potential diagram to illustrate this.



④ Cu and Ag have +ve E^θ values, so electrons "want to flow" from the zero potential mark. ⇒ so they favour reduction.

④ Conversely, Zn and Na have -ve E^θ values, so electrons "want to flow" to the zero potential mark. ⇒ so they favour oxidation.

THE EFFECT OF ION CONCENTRATION ON ELECTROLYSIS (AQUEOUS ELECTROLYTES)

💡 If an ion is present at a sufficiently high concentration, it can be discharged even if water should be discharged given the E^θ values.

↳ only viable IF the difference between competing ions' E^θ is less than 0.30V.

conc = 1M
(concentrated)

cathode: abundance of $\underline{\underline{\text{H}_2\text{O}}}$, and E^θ values within 0.30V.

⇒ $\underline{\underline{\text{H}_2}}$ discharged

anode: abundance of $\underline{\underline{\text{H}_2\text{O}}}$

⇒ $\underline{\underline{\text{O}_2}}$ discharged

eg ZnCl_2 (aq)

cathode: $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn} \quad E^\theta = -0.76$
 $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad E^\theta = -0.83$

$E^\theta_{\text{Zn}} > E^\theta_{\text{H}_2\text{O}}$ ∴ $\underline{\underline{\text{Zn}}}$ discharged

anode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad E^\theta = +1.23$
 $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^- \quad E^\theta = +1.36$

$E^\theta_{\text{H}_2\text{O}} < E^\theta_{\text{Cl}_2}$ ∴ $\underline{\underline{\text{O}_2}}$ discharged

cathode: abundance of $\underline{\underline{\text{Zn}^{2+}}}$, values within 0.30V.

⇒ $\underline{\underline{\text{Zn}}}$ discharged.

anode: abundance of $\underline{\underline{\text{Cl}^-}}$,

⇒ $\underline{\underline{\text{O}_2}}$ discharged.

FURTHER EXAMPLES

Use relevant information from the Data Booklet to identify the substances formed at the anode and at the cathode when aqueous solution(s) of the following compounds are electrolysed.

compound	product at anode	product at cathode	(+) negative
1) AgF	O_2^-	Ag	
2) $\text{FeSO}_4/\text{H}_2\text{O}$	O_2	Fe, H_2	
3) MgBr_2	Br_2	H_2	

1) $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ (0.80)
 $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)
 $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (+0.83)

2) $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$ (-0.49)
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (0.00)

3) $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$ (-2.38)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (-0.83)

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (+1.23)

QUANTITATIVE ELECTROLYSIS

FARADAY's 1ST LAW OF ELECTROLYSIS

Faraday's 1st Law of Electrolysis states that the mass of a substance liberated during electrolysis is directly proportional to the quantity of electricity (charge) passing through it.

$$\hookrightarrow \text{ie } \boxed{\Delta M \propto \Delta Q.}$$

Factors that affect Δm

By the eqn in the proof, we can see that

$$\boxed{\Delta M \text{ or } \left(\frac{I M_r \Delta t}{q} \right)}$$

and it hence follows that Δm is affected by:

- ① I , the magnitude of the d.c
- ② M_r , the molar mass
- ③ Δt , the time the current passes through
- ④ q , the charge on one ion.

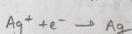
USING FIL TO SOLVE PROBLEMS

Exa 1

1. Calculate the mass of silver deposited at the cathode when a current of 0.5A is passed through a solution of silver nitrate for 15 minutes.

$$Q = It = Ne \quad \therefore N = \frac{Q}{e} = \frac{0.5(1.6 \times 10^{-19})}{1.6 \times 10^{-19}} = 2.8125 \times 10^{21}.$$

$$\Rightarrow n = \frac{N}{N_A} = \frac{2.8125 \times 10^{21}}{6.02 \times 10^{23}} = 4.671 \times 10^{-3}.$$



$$\therefore n_{\text{Ag}} = 4.671 \times 10^{-3}.$$

$$\begin{aligned} M_{\text{Ag}} &= n M_r \\ &= 4.671 \times 10^{-3} \times 107.9 \\ &= 0.504100 \\ &= 0.504g. \end{aligned}$$

Proof: $\Delta Q (= I \Delta t) = \Delta N (q_e)$

time current was passed through.
charge on an electron
number of particles
charge on one ion ($+1, +2, +3$ etc.)

magnitude of current.
Hence, $I \Delta t = (N)(q_e)$
 $\Rightarrow I \Delta t = (n \cdot N_A)(q_e)$
number of moles.
Avogadro's constant

$\Rightarrow I \Delta t = \Delta n (q_e)$
Faraday's constant, F in chemistry.
 $F = N_A \cdot e$
"L" is used for Avogadro's constant

Hence, $\boxed{\Delta Q = I \Delta t = \frac{qF}{M_r} \Delta M.}$

SOLVING FOR N_A , AVOGADRO'S CONSTANT, USING AN ELECTROLYTIC METHOD

Recall, from F1L, that

$$\Delta Q = I \Delta t = \frac{qF}{M_r} \Delta M.$$

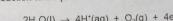
$$\text{Hence, } F = N_A e = \frac{I M_r \Delta t}{q \Delta M},$$

$$\text{or } \boxed{N_A = \frac{I M_r \Delta t}{q \Delta M \cdot e}.}$$

we can devise an experiment to determine N_A using this result.

Exa 2

When a current of 1.2A was passed through dilute sulfuric acid for 20 minutes, it was found that 130cm^3 of oxygen, measured at 25°C and 1atm , was collected at the anode. The following reaction takes place:



Use these data and data from the Data Booklet to calculate a value for the Avogadro constant, N_A , by calculating

$V = 24\text{L}$

$$\begin{aligned} 1. &\text{ the number of moles of oxygen produced,} \\ 2. &\text{ the number of moles of electrons needed for this,} \\ 3. &\text{ the number of coulombs passed,} \\ 4. &\text{ the number of electrons passed,} \\ 5. &\text{ the number of electrons in one mole of electrons (L).} \end{aligned}$$

$$(1) (for O_2) \frac{V - nRT}{2L} = n(8.31)(25+27) \quad (3) Q = It = 1.2(30 \times 60) = 2160 \text{ C}$$

$$(10 \times 10^{-3})(130 \times 10^{-6}) = n(8.31)(25+27) \quad \therefore n_{O_2} = 5.30 \times 10^{-2}.$$

$$(2) n_{O_2} = n_e = 1:4$$

$$2160 = N(1.6 \times 10^{-19}) \quad \therefore n_e = 5.20 \times 10^{-3} \times 4 = 2.1208 \times 10^{-2}.$$

$$(4) Q = Ne$$

$$2160 = N(1.6 \times 10^{-19}) \quad \therefore N = 1.35 \times 10^{22}.$$

$$(5) \frac{N}{N_A} = n \quad (N_A = L) \quad \therefore N_A = L = 6.37 \times 10^{22} \text{ mol}^{-1}$$

$$\frac{1.35 \times 10^{22}}{N_A} = 2.1208 \times 10^{-2} \quad \therefore N_A = 6.37 \times 10^{22} \text{ mol}^{-1}$$

Exa 2

An oxide of iron dissolved in an inert solvent is electrolysed for 2.0 hours using a current of 0.800A . The electrolysis products are iron and oxygen. The mass of iron produced is 1.11g .

Calculate the oxidation number of Fe in the oxide of iron. Show all your working.

$$Q = It = Ne \quad \therefore n_e = \frac{It}{e} = \frac{I}{N_A e}.$$



$$\therefore n_{\text{Fe}^{x+}} = \frac{1}{x} \frac{It}{e} = \frac{I}{x N_A e} \quad \text{oxidation number of Fe} = +3 \quad [3]$$

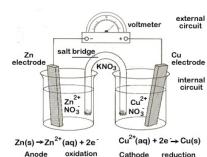
$$\frac{1}{x} \frac{0.800(2 \times 3600)}{9.64 \times 10^4} = \frac{1.11}{558}$$

$$x = 3.0037 \dots$$

$$x = 3.$$

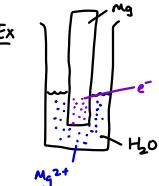
THE ELECTROCHEMICAL CELL

DIAGRAM (EXAMPLE)



The electrochemical cell consists of 2 half-cells in separate compartments, joined by a salt bridge.
When the 2 half cells are joined by a wire:
→ electrons travel from the cell with the lower E° value to the cell with the higher E° value.

EQUILIBRIUM POINT OF VIEW IN A HALF CELL

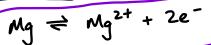


↳ this results in a build-up of electrons onto the metal, which is surrounded by the +ve Mg^{2+} cations.

↳ some of these cations may be attracted enough to join back with the electrons to form neutral Mg atoms.

In the half cell, there is a tendency for Mg atoms to shed electrons and dissolve, leaving behind the e^- onto the metal.

↳ this results in the formation of a dynamic equilibrium, when the rate of dissociation = rate of recombination.



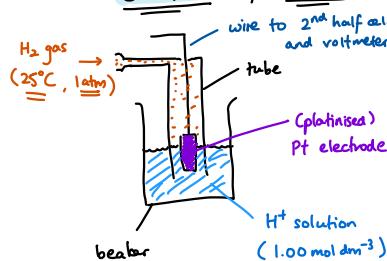
↳ meanwhile, each half cell gains an electric potential, which is dependent on the position of the equilibrium.

↳ note this E° cannot be measured directly.

THE STANDARD HYDROGEN ELECTRODE

The standard hydrogen electrode (SHE) is used as a reference electrode to measure E° in electrochemical experiments.

↳ it is always taken to have an E° value of 0.00V.



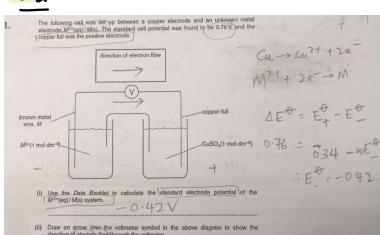
* note the conditions of the gas and solution!

Why a Pt electrode is used:

- 1) Pt is inert;
- 2) Pt has moderate surface binding energy with H;
- 3) Pt is a catalyst in the reaction with H.

EXAMPLES

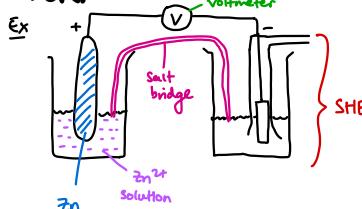
Ex1



(1) Use the data sheet to calculate the standard electrode potential of the M^{2+}/M redox system.

(2) Draw an arrow (use the voltmeter symbol) to show the direction of electron flow through the voltmeter.

COMBINING HALF CELLS TO FORM AN EC CELL.



The voltmeter reading is the difference between the E° of the two cells.

$$E_{\text{cell}} = E^\circ_{\text{anode}} - E^\circ_{\text{cathode}}$$

$$= E^\circ_{\text{cathode}} + E^\circ_{\text{anode}}$$

By this, a defn of E° can be formed:

↳ the "standard electrode potential" of a half cell is the pd produced when the half cell is connected to a standard hydrogen electrode under standard conditions ($25^\circ C$, 1 atm, $[H^+] = 1.00\text{ mol dm}^{-3}$)

STANDARD CELL POTENTIAL

Standard cell potential is the pd between 2 half-cells under standard conditions

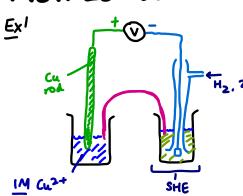
($25^\circ C$ and 1 atm; $[all\ solutions] = 1.00\text{ mol dm}^{-3}$)

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

+ if $E^\circ_{\text{cell}} < 0$, the reaction is not feasible.

MEASURING E°

HALF CELLS CONTAINING METALS & METAL IONS



At cathode (-): $2H^+ + 2e^- \rightarrow H_2$ $E^\circ = 0.00V$

At anode (+): $Cu \rightleftharpoons Cu^{2+} + 2e^-$ $E^\circ = +0.34V$

$$\Rightarrow E^\circ_{\text{cell}} = +0.34 - (+0.00)$$

$$= +0.34V$$

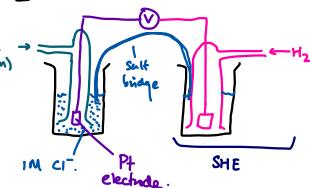
shown on voltmeter.

* reduction half cell should ALWAYS be on the right.

HALF CELLS CONTAINING NON-METALS AND NON-METAL IONS

In non-metal half cells, we use Pt wires & foil as electrodes.

Ex3



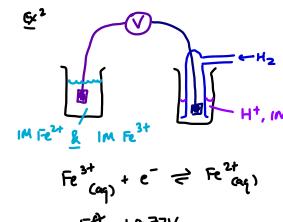
At cathode (-): $2H^+ + 2e^- \rightarrow H_2$ $E^\circ = 0.00V$

At anode (+): $Cl_2 + 2e^- \rightarrow 2Cl^-$ $E^\circ = +1.36V$

$$\Rightarrow E^\circ_{\text{cell}} = (+1.36V) - (0.00V)$$

$$= +1.36V$$

HALF CELLS CONTAINING IONS OF THE SAME ELEMENT BUT DIFFERENT OXIDATION STATES.



$$E^\circ = +0.77V$$

CELL DIAGRAM

A cell diagram is a shorthand method for describing an electrochemical cell.

Notation:

(electrode for cathode) | (cathode constituents) || (anode constituents) | (electrode for anode).

Using the above examples:

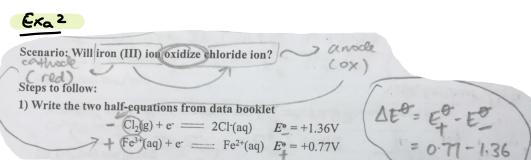
Ex1 $Pt(s) | H_2(g), 2H^+(aq) || Cu^{2+}(aq) | Cu(s)$

Ex2 $Pt(s) | H_2(g), 2H^+(aq) || Cl_2(g), 2Cl^-(aq) | Pt(s)$

Ex3 $Pt(s) | H_2(g), 2H^+(aq) || Fe^{3+}, Fe^{2+}(aq) | Pt(s)$

* State symbols and molecularity is important!

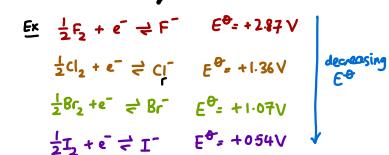
* Put lowest oxidation numbered compound next to the electrode.



negative so not feasible.

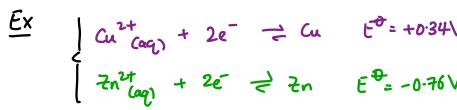
WHAT DOES E^\ominus TELL US?

A MEASURE OF THE REDUCING/
OXIDISING ABILITY OF AN
ELEMENT / ION



From F_2 to I_2 , E^\ominus decreases.
Hence, they are less likely to undergo reduction;
so, the reducing strength of the halogens decreases down the group.

THE DIRECTION OF ELECTRON FLOW



$$\therefore E^\ominus_{cell} = E^\ominus_+ - E^\ominus_-$$

For $E^\ominus_{cell} > 0$ (so feasible reaction), E^\ominus_+ must be 0.34V and E^\ominus_- must be -0.76V (otherwise $E^\ominus_{cell} = -1.10V (< 0)$).

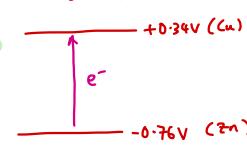
so anode is Cu, and cathode is Zn.



overall eqn is



Energy diagram:



* e^- always moves from "-ve" to "+ve."

∴ electrons flow from Zn half cell to Cu half cell.

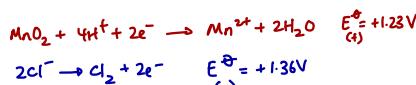
LIMITATIONS OF PREDICTIONS OF REACTION FEASIBILITY WITH E^\ominus VALUE.

Some reactions may not be feasible, despite the fact that the E^\ominus_{cell} predicts it is, and v.v.

Here are several reasons why:

NON-STANDARD REACTION CONDITIONS

Ex The reaction between MnO_2 and Cl^-



However, this reaction can occur by heating MnO_2 w/ conc. HCl.

but these are non-standard conditions.

Overall reaction:



$$E^\ominus_{cell} = E^\ominus_+ - E^\ominus_-$$

$$= 1.23 - 1.36$$

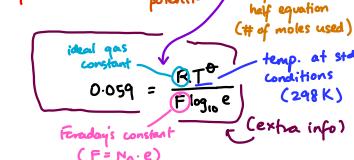
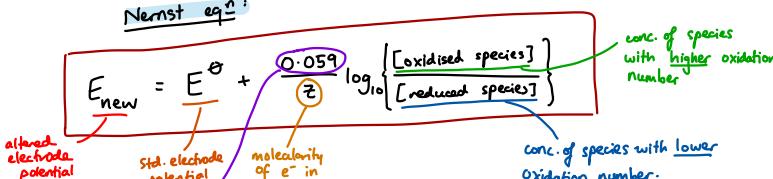
$$= -0.13 (< 0)$$

∴ reaction should not be feasible.

THE NERNST EQUATION

Under non-standard reaction conditions, the electrode potential of a reaction can change.

∴ we can calculate this altered E using the Nernst eqn:



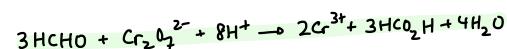
HALF CELL WHICH CONTAINS NON-METAL AND METAL ION

Ex Calculate E of Cl_2/Cl^- half cell if $[Cl^-] = 0.10$, and $E^\ominus = +1.36$.

[oxidised species] not given, so equate it to 1.
 $Cl_2 + 2e^- \rightarrow 2Cl^- \quad z=2$
 $\Rightarrow E = E^\ominus + \frac{0.059}{2} \log_{10} \left(\frac{1}{[Cl^-]} \right)$
 $= +1.36 + \frac{0.059}{2} \log_{10} \left(\frac{1}{0.1} \right)$
 $= +1.3895$
 $= +1.39$.

REACTION HAS HIGH E_a

Ex Reaction between methanol and dichromate ions



$E^\ominus_{cell} = +1.27V$ (so reaction should be feasible.)

However, at room temperature, there is no reaction (high E_a). Heating is required to initiate the reaction.

QUALITATIVE ANALYSIS OF HOW ION CONCENTRATION AFFECTS ELECTRODE POTENTIAL.

Ex $Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\ominus = -0.76$

If $[Zn^{2+}] > 1$, eq shifts to the left

∴ E^\ominus decreases.
Likewise, if $[Zn^{2+}] < 1$, eq shifts to the right
∴ E^\ominus increases.

* use the original equilibrium eqn from data booklet.

HALF CELL WITH METAL AND METAL ION

Ex Calculate E of Cu/Cu^{2+} half cell, where $[Cu^{2+}] = 0.001M$, and $E^\ominus = +0.34V$.

[reduced species] not given, so we assume it is "normal" (ie equal to 1.)



$$\Rightarrow E = E^\ominus + \frac{0.059}{2} \log_{10} \left(\frac{Cu^{2+}}{0.001} \right)$$

$$= +0.34 + \frac{0.059}{2} \log_{10} (0.001) = +0.2515$$

HALF CELL WHICH CONTAIN IONS OF THE SAME ELEMENTS IN DIFFERENT OXIDATION STATES

Ex Calculate the E for the Fe^{2+}/Fe^{3+} half cell if $[Fe^{2+}] = 0.20$, and $E^\ominus = +0.77$.



$$E = E^\ominus + \frac{0.059}{1} \log_{10} \left(\frac{1}{[Fe^{2+}]} \right)$$

$$= +0.77 + 0.059 \log_{10} \left(\frac{1}{0.20} \right)$$

$$= +0.81123V$$

$$= +0.81V$$

CELLS AND BATTERIES

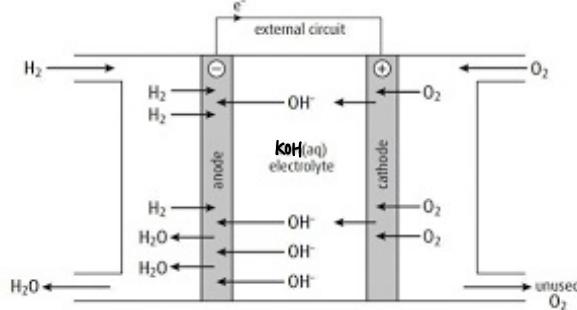
Many different batteries and cells rely on electrochemistry to provide power.

H₂/O₂ FUEL CELLS

A "fuel cell" is an electrochemical cell in which a fuel oxidises at one electrode and oxygen gains electrons at the other electrode.

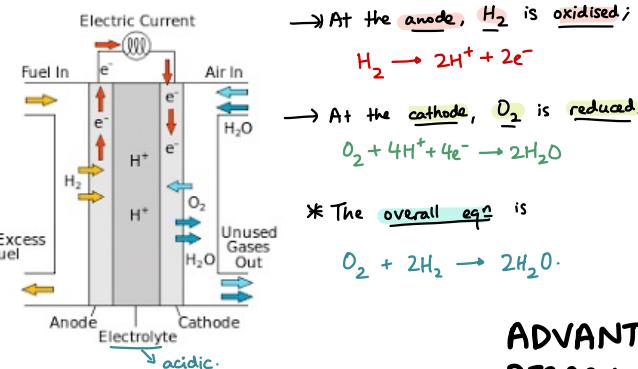
(+) A H₂/O₂ cell requires a continuous supply of H₂ and O₂.

ALKALINE H₂/O₂ FUEL CELL



* A high concentration of the electrolyte (NaOH or KOH) is used to increase the rate of the reaction.

ACIDIC H₂/O₂ FUEL CELL



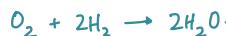
→ At the anode, H₂ is oxidised;



→ At the cathode, O₂ is reduced;



* The overall eqn is



ADVANTAGES & DISADVANTAGES OF H₂/O₂ FUEL CELLS

- Advantages:
 - ① Lesser pollution (only byproduct is H₂O)
 - ② Efficient
 - ③ Can use atmospheric H₂ if fuel H₂ runs out
- Disadvantages:
 - ① High cost in manufacturing electrodes / membrane
 - ② Ineffective at low temperature (reliant on rate)
 - ③ H₂ is manufactured using fossil fuels.

NICKEL-METAL HYDRIDE BATTERIES

Nickel metal hydride batteries (NiMH) are rechargeable batteries, mainly used for small home cells. (eg "AA").

MECHANISM (EXTRA INFO)

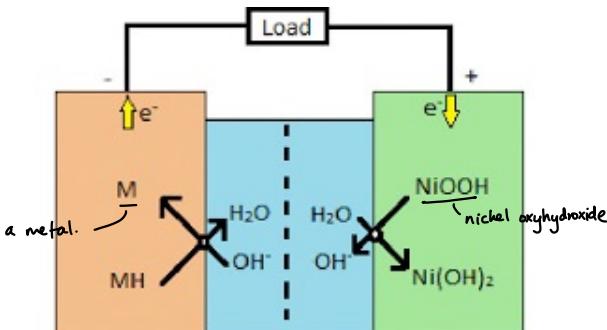
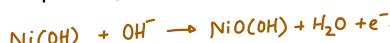


Fig. 4. Scheme representing the overall cell discharge reaction:

→ Ni reacts with the OH⁻ ions to form Ni(OH)₂, and this is oxidised to form NiO(OH);



→ The metal M is reduced to form its hydride, MH;



* The overall eqn is



★ ADVANTAGES AND DISADVANTAGES

Advantages:

- ① Environmentally friendly. (can be recycled)
- ② High capacity.

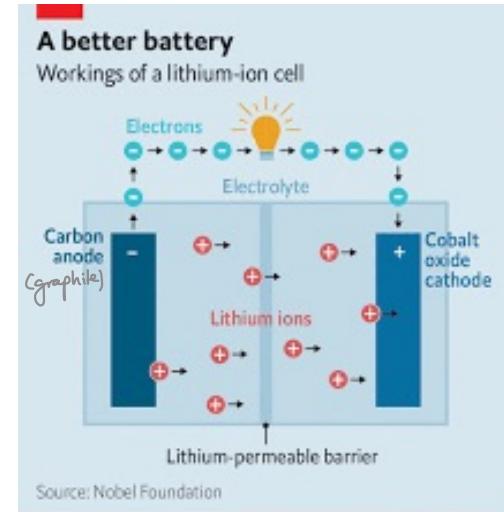
Disadvantages:

- ① Limited service life
- ② High self-discharge (loss in charge even if electrodes not connected to an external circuit).

LITHIUM-ION RECHARGEABLE BATTERIES

Lithium ion batteries (LIB) are usually used in portable electronics and electric vehicles.

MECHANISM (EXTRA INFO)



★ ADVANTAGES AND DISADVANTAGES

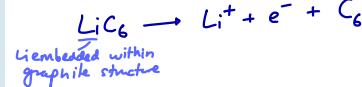
Advantages:

- ① High energy density
- ② Low self-discharge

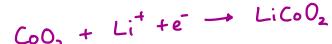
Disadvantages:

- ① High cost
- ② Protection needed when charging (unsafe if overcharged)

→ At the anode, lithium cations are liberated from the graphite electrode, denoted as C_6 :



→ At the cathode, the lithium cations are "received" by the cobalt oxide substrate:



→ The overall eqn is:



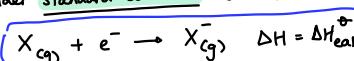
The Economist

Chapter 19: Further Chemical Energetics

ELECTRON AFFINITY

STANDARD 1ST EA, $\Delta H_{\text{ea1}}^{\circ}$

The standard 1st electron affinity is the enthalpy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous -1 ions under standard conditions (25°C, 1 atm).



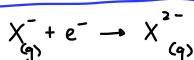
* $\Delta H_{\text{ea1}}^{\circ}$ is (generally) exothermic;

↳ neutral atom has incomplete valence electron shell, so

↳ there is attraction between it and the electron (to fill the shell, so more stable).

STANDARD 2ND EA, $\Delta H_{\text{ea2}}^{\circ}$

Similarly, $\Delta H_{\text{ea2}}^{\circ}$ is the enthalpy change when one mole of electrons are added to one mole of gaseous -1 ions to form one mole of gaseous -2 ions under standard conditions.

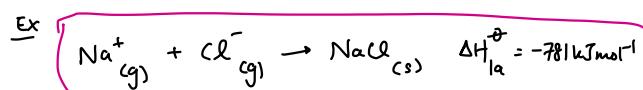


* $\Delta H_{\text{ea2}}^{\circ}$ (and $\Delta H_{\text{ea3}}^{\circ}$) are often endothermic;

↳ energy is required to overcome the electrostatic repulsion between the electron and the anion (like charges repel)

LATTICE ENERGY

The lattice energy is the enthalpy change when one mole of a solid ionic compound is formed from its gaseous ions under standard conditions.



* Lattice energies are always exothermic as it requires the formation of bonds.

FACTORS WHICH AFFECT LATTICE ENERGY

① Ion size

As ion size increases, LA becomes less exothermic.

↳ size increases implies

↳ cationic radius increases

↳ so charge density = $\frac{\text{charge}}{\text{volume}}$ decreases

↳ so electrostatic attraction between ions decreases

② Charge on the ions

As ionic charge increases, LA becomes more exothermic.

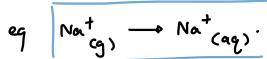
↳ greater charge means

↳ greater charge density

↳ so electrostatic attraction between ions increases.

STANDARD ENTHALPY CHANGE OF HYDRATION, $\Delta H_{\text{hyd}}^{\circ}$

$\Delta H_{\text{hyd}}^{\circ}$ is the enthalpy change when 1 mole of specified gaseous ions dissolves in sufficient water to form a very dilute solution under standard conditions.



* $\Delta H_{\text{hyd}}^{\circ}$ is always exothermic.

Why? → formation of ion-dipole bonds.

FACTORS WHICH AFFECT $\Delta H_{\text{hyd}}^{\circ}$

① Ionic charge

↳ as charge increases

↳ charge density increases

↳ ion-dipole bond with H_2O molecules gets stronger

↳ so $\Delta H_{\text{hyd}}^{\circ}$ is more exothermic.

② Ionic size

↳ as size increases

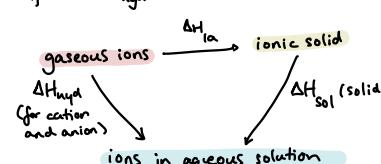
↳ charge density decreases

↳ ion-dipole bond with H_2O molecules gets weaker

↳ so $\Delta H_{\text{hyd}}^{\circ}$ is less exothermic.

DETERMINATION OF $\Delta H_{\text{hyd}}^{\circ}$

We can use an energy method to find $\Delta H_{\text{hyd}}^{\circ}$.

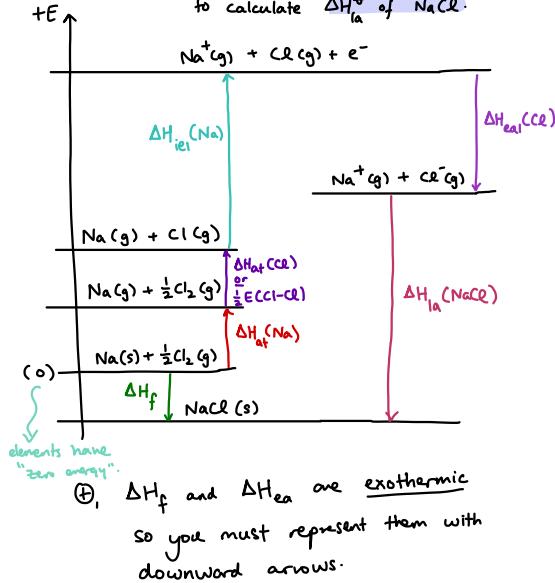


BORN-HABER CYCLE

A Born-Haber cycle is an energy level diagram, primarily used to find enthalpy changes that cannot be measured directly. (e.g. lattice energy).

CONSTRUCTING A BH CYCLE

Worked example: construct an energy cycle diagram to calculate ΔH_{la}° of NaCl.



Using Hess' law:

$$|\Delta H_f| + |\Delta H_{at}| + |\Delta H_{iel}(\text{Cl}_2)| + |\Delta H_{iel}(\text{Na})| = |\Delta H_{el}(\text{Cl})| + |\Delta H_{la}(\text{NaCl})|$$

(using data)

$$411 + 107 + 494 + 121 = 355 + |\Delta H_{la}|$$

$$\therefore \Delta H_{la} = (-)778 \text{ kJ mol}^{-1}$$

If the final moles of the reaction $\neq 1$, then multiply ΔH with the appropriate molarity factor.

EXPLANATION OF THE PROPERTIES OF GROUP 2 USING ENTHALPY.

TREND OF THERMAL STABILITY OF GROUP 2 NITRATES / CARBONATES

From MgX to BaX , thermal stability increases.

- cation size increases;
- so charge density decreases;
- so anion suffers less distortion/polarisation
- the C-O bond in carbonate / N-O bond in nitrate is less polarised
- so less likely to decompose into CO_2 / NO_2

TREND OF SOLUBILITY OF GROUP 2 SULFATES

From MgSO_4 to BaSO_4 , solubility decreases.

- both ΔH_{la} and ΔH_{hyd} are less exothermic down the group.
- however, ΔH_{la} becomes less exothermic by relatively smaller values than ΔH_{hyd} .

$$\Delta H_{la} \propto \frac{q_+ \cdot q_-}{r_+ - r_-} \rightarrow \text{size of } \text{SO}_4^{2-} \gg \text{size of cation}$$

\rightarrow so decrease in ΔH_{la} is relatively smaller.

$$\Delta H_{sol} = \Delta H_{hyd} - \Delta H_{la}$$

so ΔH_{sol} decreases down the group.

TREND OF SOLUBILITY OF GROUP 2 HYDROXIDES DOWN THE GROUP

From Mg(OH)_2 to Ba(OH)_2 , solubility increases.

- both ΔH_{la} and ΔH_{hyd} are less exothermic down the group.
- but ΔH_{la} becomes less exothermic by relatively larger values than ΔH_{hyd} .
- $\Delta H_{la} \propto \frac{q_+ \cdot q_-}{r_+ - r_-}$ → size of $\text{OH}^- \ll$ size of cation.
 \rightarrow so decrease in ΔH_{la} is relatively larger.

$$\Delta H_{sol} = \Delta H_{hyd} - \Delta H_{la}$$

so ΔH_{sol} increases down the group.

Chapter 24: Transition Elements

A transition element is a d-block element that forms one or more stable ions with an incomplete d subshell.

Although all transition elements are d-block, not all d-block elements are transition elements:

① Scandium, Sc (only forms Sc^{3+})
electron configuration of Sc: $[\text{Ar}]3d^14s^2$
 $\therefore e^-$ configuration of Sc^{3+} : $[\text{Ar}]$ or $[\text{Ne}]2s^23p^6$
 \Rightarrow ion has no electrons in its 3d subshell, so cannot be a transition element.

② Zinc, Zn (only forms Zn^{2+})
electron configuration of Zn: $[\text{Ar}]3d^{10}4s^2$
 $\therefore e^-$ configuration of Zn^{2+} : $[\text{Ar}]3d^{10}$.
 \Rightarrow ion has a full 3d subshell, so cannot be a transition element.

PHYSICAL PROPERTIES

HIGHER MELTING POINTS (THAN Ca)

In Ca, only 4s e^- involved in metallic bonding, but in transition metals, 3d e^- are also involved in metallic bonding.
 \hookrightarrow hence number of delocalised electrons in the "sea" increases
 \hookrightarrow so stronger metallic bonds.

HIGH ELECTRICAL CONDUCTIVITY

Due to the sea of delocalised electrons (which are mobile and can carry charge), transition metals are good conductors of electricity.

METALLIC RADIUS?

Compared with Ca, transition metals have a smaller metallic radius:
 \hookrightarrow due to greater nuclear charge
 \hookrightarrow so force on electrons increases

Compared with each other, the metallic radii for transition elements remain roughly the same.
 \hookrightarrow this is because the slight increase in nuclear charge is counteracted by the increase in inner electron shielding (as valence e^- added to 3d).

DENSITY?

Compared with Ca, transition metals have greater densities.
 \hookrightarrow due to greater Ar and smaller radii
 \hookrightarrow note $\rho = \frac{M}{V}$ ($M \uparrow$, $V \downarrow$)

Densities increase across the period:
 \hookrightarrow relatively same atomic size
 \hookrightarrow atomic number increases.

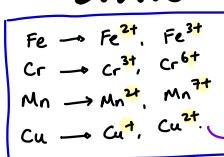
Ex: Co: $[\text{Ar}]3d^74s^2$ (inner shielding ↑)
 Ni: $[\text{Ar}]3d^84s^2$ (so size same)
 compared to
 Al: $[\text{Ne}]3s^23p^1$ (shielding same)
 Si: $[\text{Ne}]3s^23p^2$ (↑ proton number (so size ↓))

CHEMICAL PROPERTIES

Transition metals display four main characteristics:

DISPLAY VARIOUS OXIDATION STATES

Due to the close proximity in energy of the 4s and 3d electrons, transition metals can form ions of different oxidation states, but with roughly the same magnitude of stability.

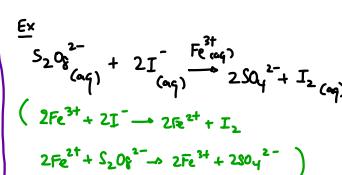


+2 is the most common oxidation number (this is obtained when the 2 4s e^- are lost from the atoms).
 exception: Cu.
 Recall e^- config is $[\text{Ar}]3d^{10}4s^1$. So it can form a stable ion of +1.

CAN ACT AS CATALYSTS.

HOMOGENEOUS

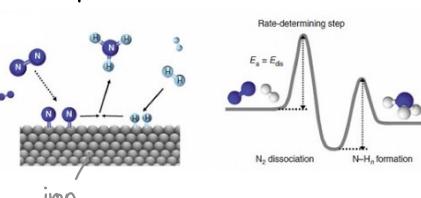
Transition metals are good homogeneous catalysts due to them being able to exist in multiple stable ions with variable oxidation states.



HETEROGENEOUS

Due to the presence of partially filled d orbitals, transition elements can provide a surface for the adsorption/desorption of reactant molecules.

Ex The catalysis of the Haber process using Fe



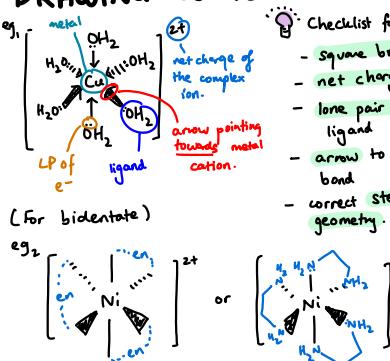
LIGANDS AND COMPLEX FORMATION

A complex ion is an ion formed when ligands datively bond to a central metal cation.

A ligand is a molecule or ion with one or more lone pairs of electrons available to form dative covalent bonds to a transition metal atom/cation.

→ generally, 2, 4 or 6 ligands will combine with one metal cation.

DRAWING COMPLEX IONS



NOMENCLATURE

- Identify all the identities of all the ligands present and the number of ligands present.
- Determine the corresponding prefix:
- Determine the root name:
 - if complex is a cation, it has the usual metal name.
 - otherwise, add -ate to it. (see table for understanding).
- Calculate the oxidation number of the cation. (net charge - charge on ligands).

SHAPE OF A COMPLEX ION.

The "coordination number" of a complex ion is the number of dative covalent bonds formed to the central metal ion.

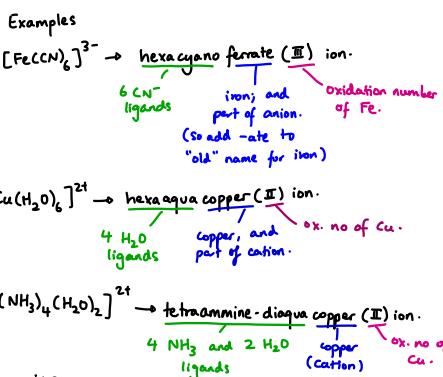
→ the magnitude of this determines the shape of the complex ion:

coordination # = 2 → linear (eg $[\text{AgCl}_2]^+$)

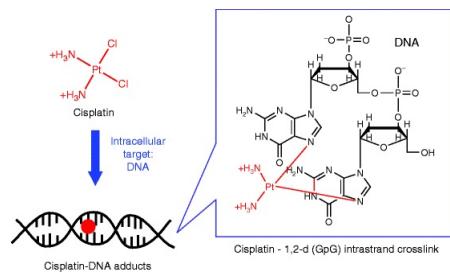
coordination # = 4 → tetrahedral (eg $[\text{CuCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$)

coordination # = 4 → square planar (eg $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (platin))

coordination # = 6 → octahedral (eg $[\text{Cr}(\text{OH})_6]^{2-}$)



THE USE OF CIS-PLATIN IN CANCER TREATMENT



- Mechanism:
- Cis-platin diffuses through the cell membrane via passive diffusion and active transport.
 - Once in the nucleus, the cisplatin binds to two guanine bases in DNA; it accomplishes this by losing its Cl⁻ atoms in exchange for the N atoms of the target guanines. *why? N more electronegative, so more stable.
 - This binding induces the binding of high-mobility group (HMG) proteins, which cause breaks in the DNA strand.
 - This leads to replication and transcription inhibition, cell cycle arrest and eventually cell death.

TYPES OF LIGANDS

MONODENTATE

Monodentate ligands contain one lone pair of electrons that can form a dative covalent bond with a metal atom/cation.

e.g. $\text{H}_2\text{O}^{\cdot-}$, $\text{NH}_3^{\cdot-}$, :X^- (halide), :CN^- .

In order for a molecule to be a ligand, the lone pair of e⁻ must be located at the "central" atom.

This is why BF_3 ($\text{B}^{\ddagger\ddagger}$) is NOT a ligand. (LP of e⁻ not at B).

Otherwise the ligand would be unstable. The exception to this rule is NO_3^- , which can function as a ligand even though the LP of electrons is not located at the central N atom.



BIDENTATE

Bidentate ligands contain two lone pairs of electrons that each can form a dative covalent bond with a metal atom/cation.

e.g. $\begin{array}{c} \text{O} \\ | \\ \text{C}-\text{C} \\ | \\ \text{O} \end{array}$ (or "ox")

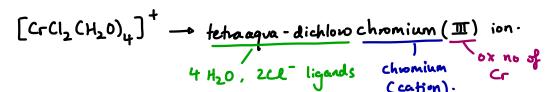
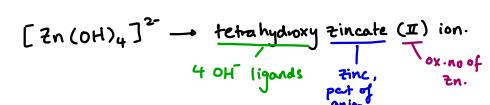
ethanedioate ion

$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2$ (or "en")

The complex ions formed from bidentate ligands are very stable.

In order for a molecule to be a bidentate ligand, the 2 lone pairs must be positioned on different atoms. This is why H_2O cannot be a bidentate ligand, even though it has 2 lone pairs of e⁻.

Impossible to force the 2 e⁻ clouds to a sufficient angle to match the "slots" on the metal atom.

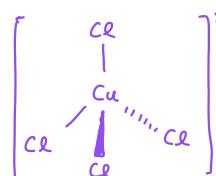


Diagrams

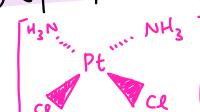
① Linear



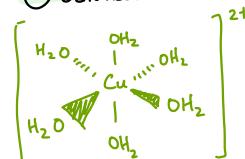
② Tetrahedral



③ Square planar



④ Octahedral



remember to show the stereochemistry / molecular geometry clearly!

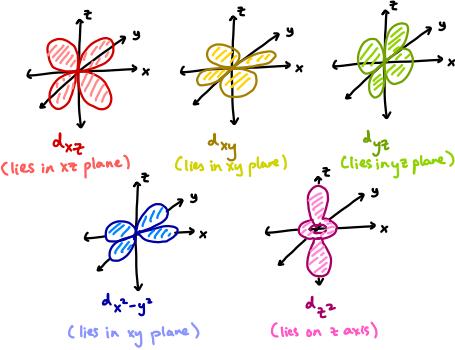
Polarity of cis-platin vs trans-platin

Cis-platin is polar, trans-platin is not.

→ Cl atoms on same side in cis-platin.

BONDING IN COMPLEX IONS.

THE SHAPES OF d ORBITALS.

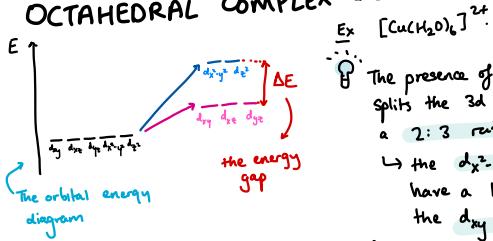


Q: d_{xy} , d_{xz} and d_{yz} are located between axes, whereas $d_{x^2-y^2}$ and d_{z^2} are located along axes.
↳ to show this, you remove the "coordinate axis" if the orbital "lies" on the axis. (as shown).

HOW THE ENERGY LEVEL CHANGES AFTER LIGAND BONDING.

Q: Before ligand bonding, all the five 3d orbitals are degenerate. (they possess the same energy level). However, after ligand bonding, the 3d orbitals split.

OCTAHEDRAL COMPLEX ION

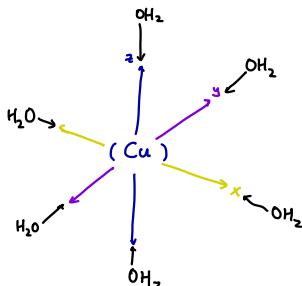


Why? → ② Ligands have lone pairs of electrons:

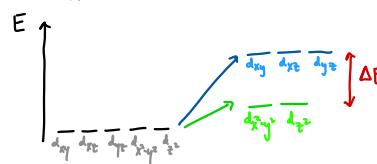
↳ e^- in $d_{x^2-y^2}$ & d_{z^2} "point" towards incoming ligands, but e^- in d_{xy} , d_{xz} and d_{yz} point between the incoming ligands.

↳ so the $d_{x^2-y^2}$ and d_{z^2} subshells experience greater inter-electron repulsion with the LP of e^- on the ligands. (so they are at a higher "energy level").

Q: The presence of the 6 ligands splits the 3d orbitals into a 2:3 ratio:
↳ the $d_{x^2-y^2}$ and d_{z^2} orbitals have a higher energy level than the d_{xy} , d_{xz} and d_{yz} orbitals.



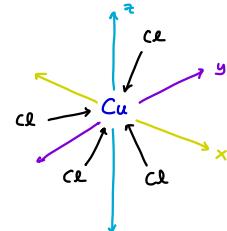
TETRAHEDRAL COMPLEX ION



Why? → ① Again, the ligands have a lone pair of electrons.

↳ BUT, the ligands bond between the axes, which is where d_{xy} , d_{xz} and d_{yz} are located.

↳ so, it is these 3 orbitals that experience greater interelectrostatic repulsion with the lone pair of electrons on ligands.



EX $[\text{Cu}(\text{Cl}_4)]^{2-}$

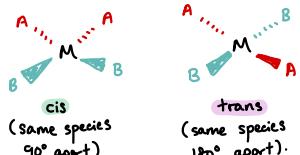
The presence of ligands for a tetrahedral complex ion splits the d orbitals into a 3:2 ratio, with now the d_{xy} , d_{yz} and d_{xz} orbitals being at a higher energy level.

STEREOISOMERISM OF TRANSITION METAL COMPLEXES

Note: tetrahedral → no stereoisomers
square planar → cis-trans stereoisomers
octahedral → both cis-trans and optical stereoisomers.

SQUARE PLANAR COMPLEX ION

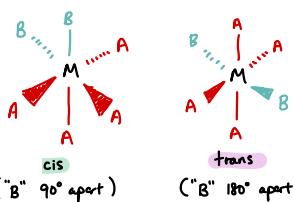
Q: Square planar complex ions can only form geometric isomers.



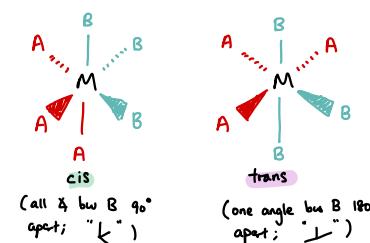
OCTAHEDRAL COMPLEX ION

GEOMETRIC ISOMERISM

case 1 $[\text{MA}_4\text{B}_2]$ (e.g. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$) (A, B = mono)



case 2 $[\text{MA}_3\text{B}_3]$ (e.g. $[\text{Cr}(\text{OH})_3\text{CH}_2\text{O}_3]$)



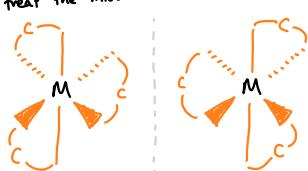
* note that these are just a few examples.

(Exam can ask about harder material).

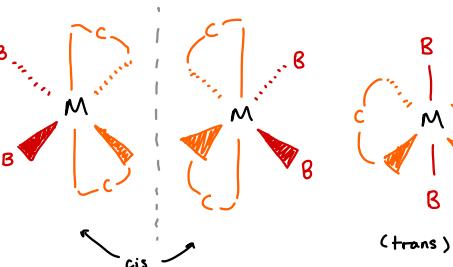
* make sure, for each stereoisomer, you cannot "rotate" it to obtain a previous stereoisomer.

OPTICAL ISOMERISM

case 1 $[\text{MC}_3]$ (C = bidentate)
* treat the middle "line" as a mirror.



case 2 $[\text{MB}_2\text{C}_2]$



Chapter 28: Polymerisation

CONDENSATION

POLYMERISATION POLYAMIDES

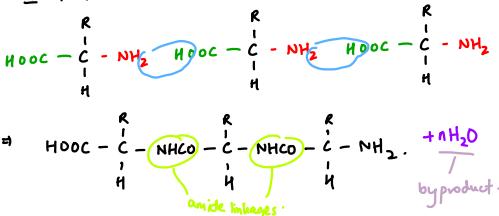
Condensation polymerisation is the polymerisation that occurs between monomers that contain two different functional groups, capable of reacting with each other, resulting in the liberation of a small molecule (e.g. H_2O).

* polyamides (and polyesters) are synthetic polymers.

TYPE I VS TYPE II POLYMERISATION

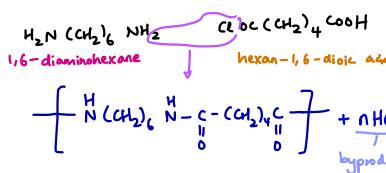
Type I: the two functional groups are present within one molecule.

Ex Amino acids



Type II: the two functional groups are present in 2 different molecules.

Ex Nylon 6,6: both monomers have 6 carbon atoms



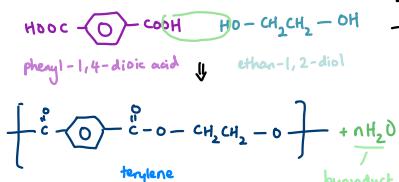
POLYESTERS

* advantage of polyesters: they are biodegradable.

Polyesters are polymers whose monomers are bonded together via ester ($-\text{C}-\text{O}-$) links.

TERYLENE

Terylene is formed from phenyl-1,4-dioic acid and ethan-1,2-diol.



(+) Condition

- heat at 280°C
- w/ Sb_2O_3 (Antimony (III) oxide)
as catalyst.

(+) Applications

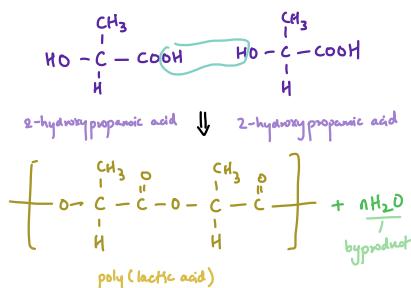
→ can be mixed with natural fibre to produce a variety of fabrics.

* polyesters cannot be used to package acidic food, e.g. vinegar:
→ ester linkage hydrolysed in acidic solutions.

POLY(LACTIC ACID)/ PLA

→ formed from lactic acid (2-hydroxypropanoic acid).

* lactic acid can be manufactured by the fermentation of corn starch and sugar.



(+) Applications

- degradeable packing materials
- meshes for medical implants

(+) Limitations

- low melting point, softens around $60^\circ\text{C} - 80^\circ\text{C}$
→ cannot be used for hot drinks.

DIFFERENCES BETWEEN ADDITION AND CONDENSATION POLYMERS.

Functional group on monomer vs. FG on polymer

Difference in EF b/w polymer and monomer

Elimination of molecules?

Condensation

different
(contains amide/ester linkages)

different
(removal of small molecule)

yes
(generally $\text{HCl}/\text{H}_2\text{O}$)

Addition

the same

none

none

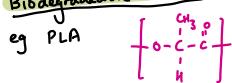
DESIGNING "USEFUL" POLYMERS (ENVIRONMENT AND CONSUMER FRIENDLY)

DEGRADEABLE PLASTICS

Photodegradeable Plastics

- Photodegradeable plastics incorporate $C=O$ bonds into their structure.
- $\hookrightarrow C=O$ bonds can be broken easily upon the absorption of UV radiation.
- \hookrightarrow this leads to a greater decomposition rate of the polymer.

Biodegradeable Plastics \rightsquigarrow esters



- The ester linkages in PLA can be easily hydrolysed, either - under acidic / alkaline conditions, or - in the presence of an enzyme (esterase).
- \hookrightarrow the resultant lactic acid can then be easily metabolised into CO_2 and H_2O by organisms.

NON-SOLVENT BASED ADHESIVES (GLUES)

- Traditionally, solvent-based adhesives are used; in these, ester-based solvents (eg CH_3COOCH_3) are used to dissolve a polymer that will serve as an adhesive. Subsequently, the solvents are evaporated.
- \hookrightarrow however, these have some disadvantages:
 - solvents are flammable; and
 - some organic solvents are harmful to our health.

Hence, we have started to use non-solvent based adhesives instead.

Epoxy resin



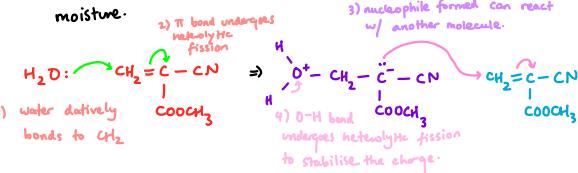
- Epoxy resins are thermosetting; they form an extensive network of covalent cross-links within their structure.

Advantage:

- Extremely strong
- Heat resistant.

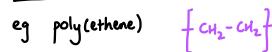
Super glue

- formed from the addition polymerisation of $CH_2=C(CN)COOCH_3$, in the presence of moisture.



Thermosoftening Plastics (Thermoplastics)

* addition polymers only.



- Thermosoftening plastics are plastics that soften (and eventually melt) on heating.
- \hookrightarrow during heating, eventually enough energy is supplied to overcome the weak id-id forces between long chain molecules.

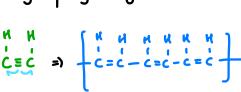
Thermosetting Plastics

* much stronger than thermosoftening plastics.

- In the manufacture of thermosetting plastics, covalent bonds are made between the original polymer chains to give a cross-linked structure, effectively creating one gigantic molecule.
- \hookrightarrow significantly more heat must be supplied to break the strong covalent bonds.
- \hookrightarrow instead of softening / melting, thermosetting plastics tend to blacken (but remain solid).

CONDUCTING POLYMERS

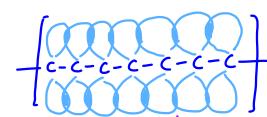
eg poly(ethyne) / poly(acetylene)



** The C backbone of the polymer is conjugated;

\hookrightarrow consists of alternating $C=C$ and $C-C$ bonds.

- Conducting polymers can conduct electricity due to the presence of a long chain of delocalised/mobile electrons.



formed from $C=C$ in conjugated backbone.

④ molecular geometry requirement: planar molecule

\hookrightarrow so p-orbitals overlap with each other.

- advantages of conducting polymers:
 - more resistant to corrosion
 - more lightweight / less dense
 - more malleable

LOW-DENSITY AND HIGH DENSITY POLY(ETHENE) / LDPE & HDPE.

Structure: LDPE
high number of branched chains

melting point: lower

densities: lower

HDPE
very little branching

higher

higher \rightarrow HDPE has a greater surface area for the formation of id-id forces between polymers.

\rightarrow HDPE polymers are more tightly packed with each other

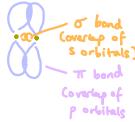
applications: 1) plastic bags

- plastic pipes
- plastic milk bottles

* specific to addition polymers.

* π bond is broken during homolytic fission.

Why? $\rightarrow \sigma$ bonds are closer to the nucleus than π bonds \rightarrow so σ bonds are stronger than π bonds.



④ molecular geometry requirement: planar molecule

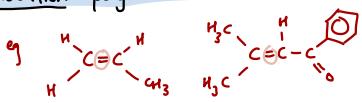
\hookrightarrow so p-orbitals overlap with each other.

- advantages of conducting polymers:
 - more resistant to corrosion
 - more lightweight / less dense
 - more malleable

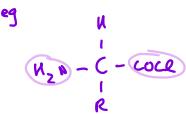
POLYMER DEDUCTIONS

#1 RECOGNISING THE TYPE OF POLYMERISATION FROM THE MONOMERS GIVEN.

If a monomer contains a double bond, there is a high possibility it undergoes addition polymerisation.

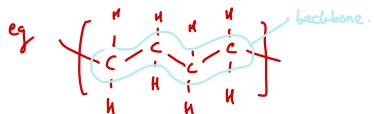


If a monomer/s contain two different functional groups at the end of the monomer/s, there is a high possibility it undergoes condensation polymerisation.

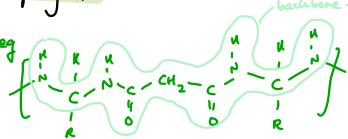


#2 RECOGNISING THE TYPE OF POLYMERISATION FROM THE POLYMER.

If the polymer "backbone" contains only C atoms, the polymer is an addition polymer.



If the polymer "backbone" contains amide / ester links, the polymer is a condensation polymer.



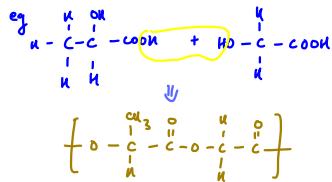
#4 IDENTIFICATION OF MONOMERS FROM CONDENSATION POLYMER

Steps:

- Identify the small molecules that are given off during the polymerisation reaction
- Then, replace them on the reactive functional groups on the monomers.

COPOLYMERISATION

Copolymerisation refers to the polymerisation of two or more different monomers.

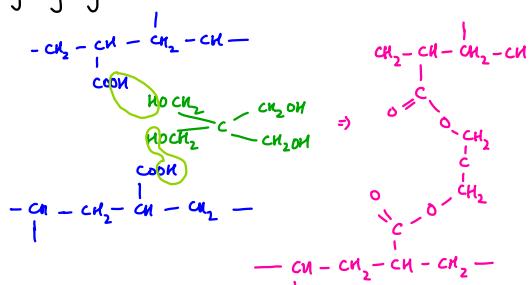


CROSS-LINKED POLYMERS

Cross-linked polymers are formed when the polymer chains can join with each other.

Condition: presence of side group on chain that can link to other chains

eg hydrogel



Advantage:

- Harder
- Stronger
- More flexible.

PROTEINS

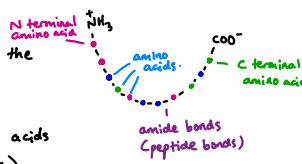
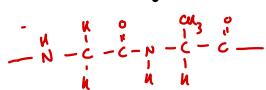
Proteins are formed through the polymerisation of amino acids, making them polyamides / polypeptides.

PROTEIN STRUCTURE

PRIMARY

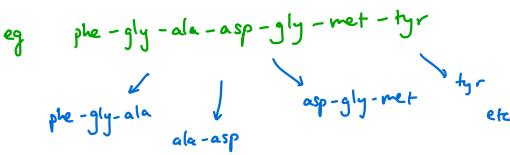
The "primary" structure consists of the amino acid sequence / chain.

Drawing: pick two random amino acids and draw. (eg. Gly, Ala)



HYDROLYSIS OF PROTEINS

Under acidic or alkaline conditions, peptide bonds in proteins can be hydrolysed, resulting in a mixture of polypeptide fragments.



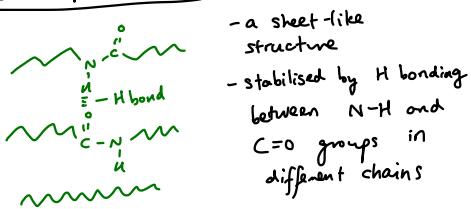
SECONDARY

The secondary structure of a protein is the regular structural arrangement stabilised by hydrogen bonding between the N-H group of one peptide bond and the C=O group of another.

① Alpha helix

- a rod-like structure
 - stabilised by H bonding between N-H group and C=O group
- * H bonds formed are parallel with the "long" axis of the helix.

② Beta-pleated sheet



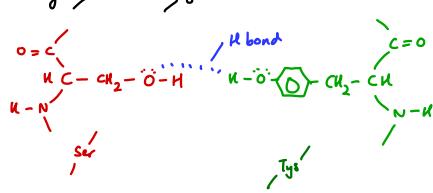
TERTIARY

The tertiary structure of a protein is the coiling / folding of it due to interactions between side chains on amino acids, giving it its overall 3D shape.

Drawing: select two interactions from below.

① H bonding

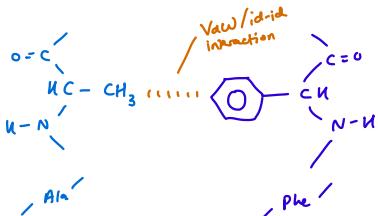
eg. ser and tyr



③ id-id forces

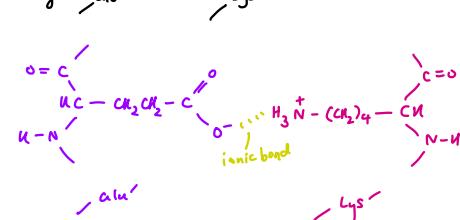
eg. Ala' & phe'

* occurs between 2 non-polar groups.



② Ionic bond

eg. glu' and lys'

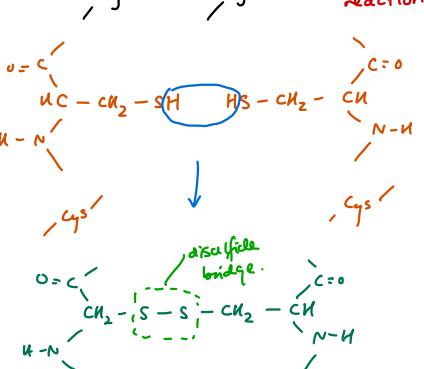


* formed between ionised acid and ionised base chain.

④ Disulfide bridges

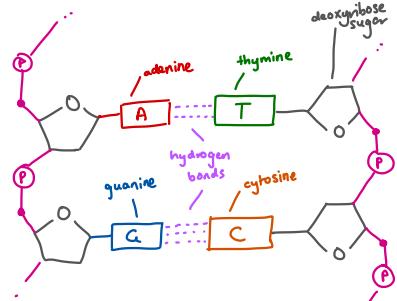
ONLY , cys' and , cys' .

* oxidation reaction.



STRUCTURE OF DNA

DNA (deoxyribonucleic acid) is formed from monomer units called nucleotides.



- ④ In DNA:
 $(AT) : (GC) = 1 : 2$.
- ⑤ A, G, T & C are planar structures:
 - A, G contain 2 rings.
 - T, C contain 1 ring.
- ⑥ There are 2 H bonds between A & T, but 3 between G & C.
- ⑦ Left and right chains are "inverted" from each other.
- ⑧ A-T & G-C are complementary bases (they always go together).

DNA REPLICATION

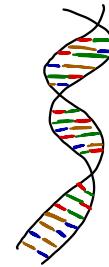
Replication: copying of DNA during cell division.

Mechanism

- ① H bonds and id-id forces between complementary bases are weak and are easily broken.
- ② This causes the DNA strands to unwind.
- ③ Nucleoside triphosphate are brought up one by one to the separated DNA chain.
- ④ Complementary bases join to form a new strand of DNA.
- ⑤ This process is catalysed by DNA ligase & DNA polymerase (I).

DOUBLE HELIX STRUCTURE

DNA is in the form of a double helix, ie two interlinked spirals.



* DNA replication is a semi-conservative replication as each newly synthesised DNA strand consists of one old DNA strand and one new DNA strand.

Chapter 29: Analytical Chemistry

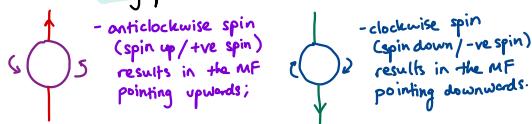
PROTON (^1H) NUCLEAR MAGNETIC RESONANCE (NMR)

^1H NMR is a technique used to find the structure of an unknown compound.

WORKING PRINCIPLE

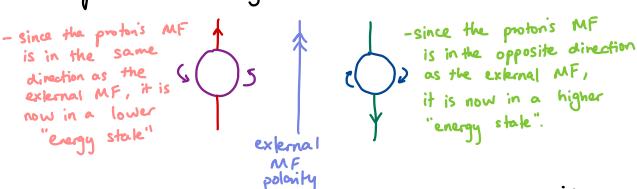
^1H NMR focuses on the hydrogen atoms in the organic compounds; in particular, we examine their "spin".

↳ this spin induces a magnetic field, whose polarity is determined by the RM rule:

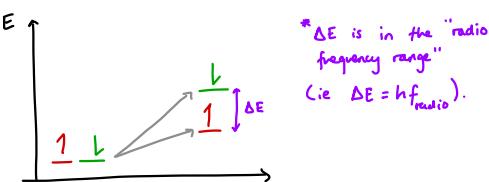


Prior to the addition of an external MF, both spin states possess the same energy level.

↳ however, upon bringing the sample into the machine, it is brought under the presence of an external magnetic field.



↳ the resultant non-degeneration of the two spin states can be shown on an energy level diagram:



Subsequently, a radio frequency pulse is applied. ↳ upon absorption of a photon, a proton with "spin up" can turn into "spin down". Then, upon relaxation, the proton emits a photon in the rf range.

↳ resonance of the proton hence occurs.

ΔE can vary depending on the groups of atoms surrounding the hydrogen.

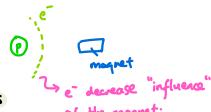
↳ by examining the specific frequency of the rf pulse needed to induce resonance, we can deduce the chemical environment of the protons.

(+) Why?

- the more electronegative the chemical environment is, the greater the magnitude of "electron deshielding".
- hence, the repulsion between the proton's MF and the external MF is greater. (for spin down).

this hence increases ΔE .

* note: $\uparrow \Delta E$, \uparrow chemical shift, &



CHEMICAL SHIFT

Chemical shift is the difference in the radio frequency required for resonance compared to standard solution. TMS (tetramethylsilane, or $\text{Si}(\text{CH}_3)_4$).

↳ TMS displays small chemical shift due to strong shielding effect from electrons.

* C-Si bond is not polarised, so H atoms are still surrounded by e⁻ clouds.

⊕ Chemical shift of TMS is set to 0.

SOLVENT

CCl₄ or CDCl₃ (D=7H) is used as a solvent as they do not contain any ^1H , which would affect the spectrum.

CHEMICAL ENVIRONMENT

The chemical environment refers to the groups of molecules attached to the C bonded with the targeted H atom.

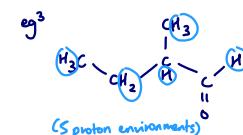
↳ The number of peaks in the spectrum equals the number of chemical environments.

6H are affected by the "same group", so same proton env.

In this, there are 2 proton environments.

eg²

In this, there are 2 proton environments.



eg³

In this, there are 2 proton environments.

eg⁴

8 of this env ↑ because it is bonded to Cl (electronegative element)

eg⁵

again, these "look out" at the same groups, so they are only counted as 1 chemical environment.

eg⁶

* sequence of "groups" matter.

RELATIVE PEAK AREA

Area under peak equals the number of H in the chemical environment.

↳ given in the spectrum.

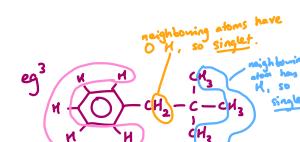
PEAK SPLITTING

In high resolution NMR, due to interference of magnetic moments, peak splitting can be observed.

↳ peak splitting indicates number of H in neighbouring atoms. → * adjacent, or "one step away" (left, right, up, down)

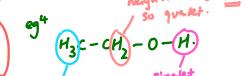
The n+1 rule

Number of H on neighbouring atom	"n+1 rule"	splitting pattern	diagram
0	1	singlet (s)	
1	2	doublet (d)	
2	3	triplet (t)	
3	4	quartet (q)	
4		quintet (quint)	
5		multiplet (m)	



H on benzene will not be split, nor split others. ⇒ so singlet.

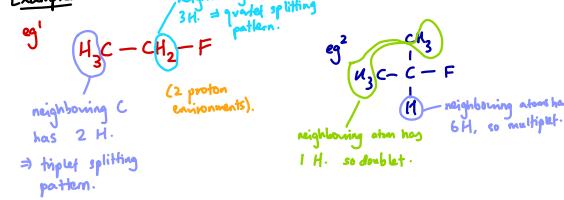
* however, in Q, splitting may be given as multiplet:



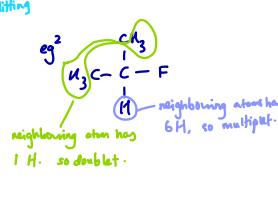
neighbour has 3H so quartet.

singlet (labile proton; see next page)

Examples

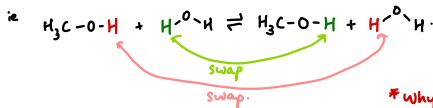


neighboring C has 2H. ↳ triplet splitting pattern.



LABILE PROTONS

O-H, N-H and S-H are labile protons; they are easily exchanged with the surrounding solvent molecules.



- ④ Labile protons will not be splitted nor will they contribute to the peak splitting of other H. (They will always exist as a singlet).

DETECTION

We can identify labile protons by adding heavy water (D_2O , where $\text{D} = {}^2\text{H}$ / deuterium).



- Since D does not get detected, the peak that stemmed from the labile proton group will disappear.

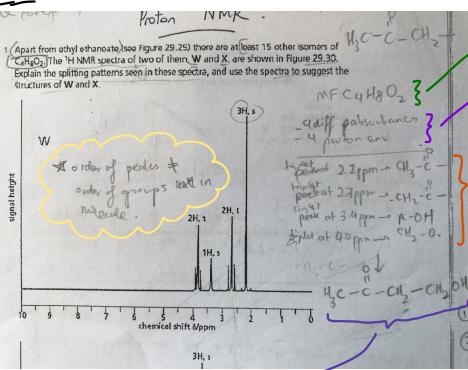
* ΔE too large to be overcome by radio freq photons.

ANALYSIS OF A NMR SPECTRUM

Exa 1

Proton NMR

Apart from ethyl ethanoate (see Figure 29.25) there are at least 15 other isomers of $\text{C}_4\text{H}_8\text{O}_2$. The ^1H NMR spectra of two of them, W and X, are shown in Figure 29.30. Explain the splitting patterns seen in these spectra, and use the spectra to suggest the structures of W and X.



- ③ Once you have determined the groups responsible for each peak, string them all together to find the molecular structure.

① look for initial data given. (molecular formula is $\text{C}_4\text{H}_8\text{O}_2$).

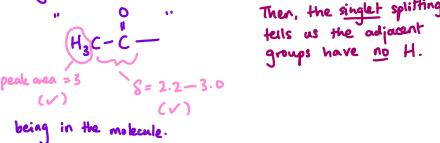
② # of peaks = # of proton environments.

③ use the peak area data, chemical shift and peak splitting to find the group responsible for the peak. (use Data Booklet).

Example: for the peak at $\delta = 2.2$ ppm;

- singlet splitting indicates neighbouring atoms has no H.
- peak area = 3 indicates group comprises of 3H.
- $\delta = 2.2$ corresponds to an "aldehyde next to C=O".

Together, these allude to the group



* try to begin analysing from the rightmost peak.

Exa 2

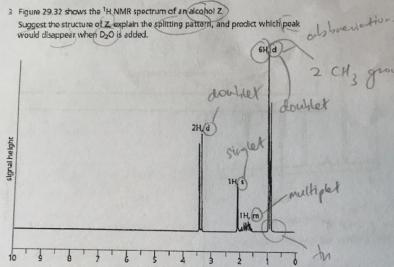


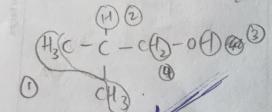
Figure 29.32 shows the ^1H NMR spectrum of molecule Z. Suggest the structure of Z, explain the splitting pattern, and predict which peak would disappear when D_2O is added.

① 2x singlet of $\delta = 0.9$ ppm $\Rightarrow -\text{CH}_3$ - solvent

② multiplet of $\delta = 1.7$ ppm $\Rightarrow -\text{CH}_2-$

③ singlet at $\delta = 2.2$ \Rightarrow alcohol (-OH)

④ doublet at $\delta = 3.5$ $\Rightarrow -\text{CH}_2-\text{O}-$



Why?
 - peak at $\delta = 2.2$ corresponds to O-H.
 - in O-H, proton is labile.
 - so upon addition of hard water, peak would disappear.

Peak at $\delta = 2.2$
 would disappear
 when D_2O is
 added.

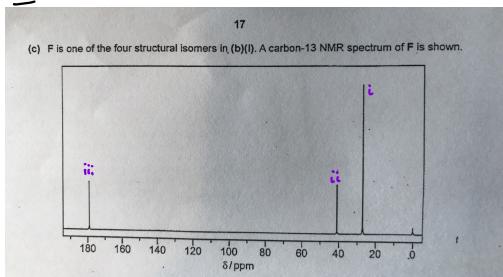
CARBON-13 (^{13}C) NUCLEAR MAGNETIC RESONANCE (NMR)

WORKING PRINCIPLE

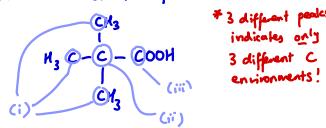
- In a random sample of carbon, 98.9% of the atoms are ^{12}C , and 1.1% of the atoms are ^{13}C .
- however, the nucleus of ^{13}C has a resultant spin, whereas the nucleus of ^{12}C does not.
- hence, the nucleus in ^{13}C can behave like a tiny magnet, similar to how the proton in ^1H acts.
- * the "theory" follows roughly the same structure as ^1H NMR.

ANALYSIS OF A ^{13}C NMR SPECTRUM

Ex



- Given info:
 - F is a carboxylic acid
 - F has a molecular formula of $\text{C}_5\text{H}_8\text{O}_2$
- Analyse the peaks:
 - (i) $\delta = 25$ → corresponds to C in alkyl.
 - (ii) $\delta = 40$ → corresponds to C next to carboxy.
 - (iii) $\delta = 180$ → corresponds to C in carboxy.
- Reduce the structural formula:
 - 3 different peaks indicates only 3 different C environments!



③ Peak splitting

- ④ There is no peak splitting due to an extremely unlikely chance (0.012% , $= (1/1.1)^2$) of getting 2 ^{13}C next to each other.

④ Peak area

- ⑤ Peak area cannot be used to determine the number of C to which it corresponds.

} do not consider peak splitting or area in ^{13}C NMR!

CHEMICAL ENVIRONMENT ANALYSIS



MASS SPECTROMETER

- A1: used to determine % of isotopes in an element.
A2: used to determine structure of a compound.

MASS SPECTRUM OF A COMPOUND

- In a mass spectrometer, the sample is first vapourised.
Subsequently, it is bombarded by high-energy electrons.

FORMATION OF MOLECULAR ION

- The high-speed electrons "knock" away one electron from the molecule, transforming it into a cation with a +1 charge.

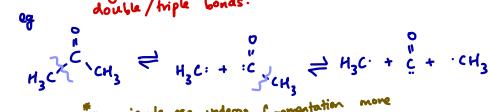


FRAGMENTATION

- Molecular ions are energetically unstable, and they will break into fragments spontaneously.

- they do this via the homo/heterolytic fission of bonds.

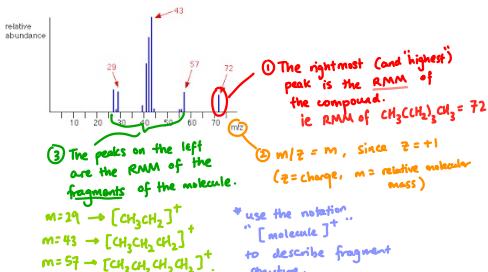
* single bonds usually break first before double/triple bonds.



* a molecule can undergo fragmentation more than once.

MASS SPECTRUM

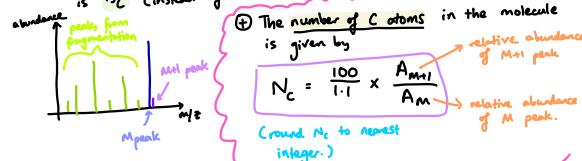
simplified mass spectrum of pentane: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



THE M+1 PEAK

- There will always be a very small peak just beyond the molecular ion peak at a mass of $M+1$, where $M = \text{RMM}$ of the molecule.

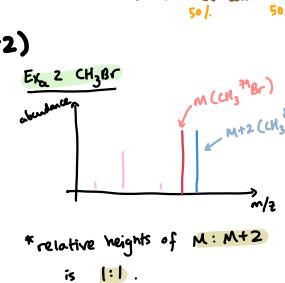
↳ this is caused when one C in the molecule is ^{13}C (instead of ^{12}C).



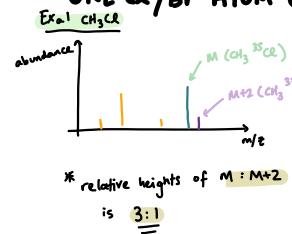
THE M+2/M+4 PEAKS

- M+2 and M+4 peaks can be observed if the compound contains one, or two, Cl or Br atoms.

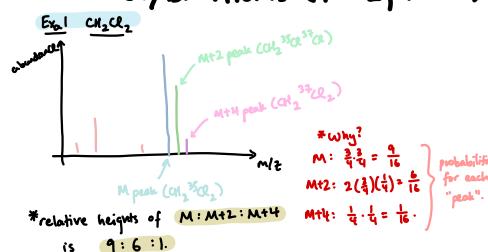
why?
- Cl exists as ^{35}Cl and ^{37}Cl : 25%
- Br exists as ^{79}Br and ^{81}Br : 50%



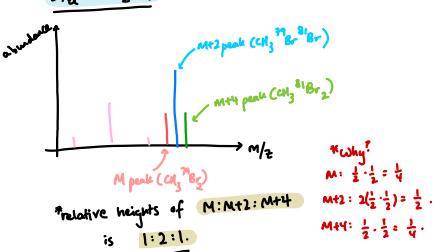
ONE Cl/Br ATOM (M+2)



TWO Cl/Br ATOMS (M+2, M+4)



Ex2 CH_3Br_2



HIGH RESOLUTION MASS SPECTROPHOTOMETER

- High resolution spectrophotometers show more accurate values for isotopic mass and RMM of the ion. This allows molecules with relatively close RMM values to be distinguished.

low res high res



CHROMATOGRAPHY

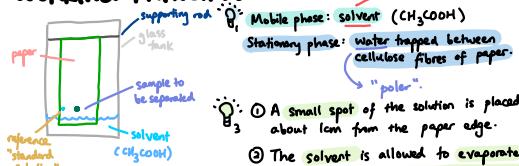
Q Chromatography is used to identify the amino acids present in a polypeptide.

↳ all chromatographic methods use the same working principle of a "mobile" phase (a liquid or gas) moving past a "stationary" phase.

Name	Mechanism	Measured value
paper chromatography	partition	R _f
thin-layer chromatography	adsorption	R _f
gas-liquid chromatography	partition	R _t

PAPER CHROMATOGRAPHY

WORKING PRINCIPLE



- Q A small spot of the solution is placed about 1cm from the paper edge.
- ③ The solvent is allowed to evaporate, allowing the solutes to be adsorbed into the paper fibres.
- ④ Capillary action draws the liquid up the sheet; as it passes the point where the spot has been adsorbed, the mixture will partition themselves between the cellulose surface and the moving solvent.

Q Essentially, paper chromatography relies on partition to separate the mixture's components.
⊕ Partition: the separation of compounds due to their different solubilities in two solvents/phases.

Q The solvent is usually less polar than the cellulose surface and its associated water layer. Hence, polar, more strongly H bonded compounds only travel a very small distance, whereas less polar and compounds with fewer H bonds travel a longer distance.

* Why? → more polar = less soluble in the mobile phase
= greater attractive force with H_2O molecules between fibres
= lesser distance travelled.

IDENTIFICATION OF COMPOUNDS

Q Separated compounds can be visualised by spraying the paper with:

- i) Ninhydrin - amino acids, small peptides
- ii) Tollen's/Fehling's reagent - reducing sugars, { contain aldehyde functional group, e.g. glucose/maltose}
- iii) Iodine - most other organic compounds

Q Different compounds travel up the paper by varying distances. We can quantify this by using the retardation/retention ratio (R_f):

⊕ R_f is the distance moved by the compound from the baseline, divided by the distance travelled by the solvent front.

$$R_f = \frac{x}{x_s}$$

* the lower the R_f , the more polar the compound is. (if mobile phase is non-polar).

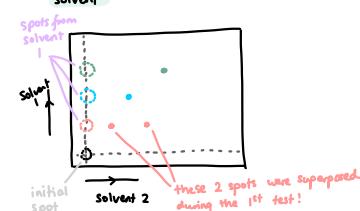
TWO WAY CHROMATOGRAPHY

Q Each compound has a characteristic R_f value in a particular solvent. However, some compounds have the same R_f value in the same solvent.

↳ when this occurs, we can use two-way chromatography to distinguish the overlapping mixtures.

Method

- ① Carry out chromatography as normal
- ② Allow the paper to dry out completely, and rotate the chromatogram by 90°.
- ③ Re-run the test, but use a different solvent.



THIN-LAYER CHROMATOGRAPHY

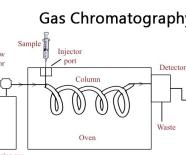
WORKING PRINCIPLE



- Q Essentially, TLC relies on adsorption to separate the components in mixture.
- ④ Adsorption: a measure of the varying strengths of the bonds the compounds form with the stationary phase.
- Q TLC is preferred over paper chromatography because:
 - 1) more reproducible results
 - 2) can be used for smaller samples.

GAS-LIQUID CHROMATOGRAPHY

WORKING PRINCIPLE



Gas Chromatography
Mobile phase: inert gas, e.g. He or N_2 .
Stationary phase: non-volatile liquid, e.g. mineral oil coated on small particles.

Q GL chromatography relies on partition for separation.

- Q The higher the molecule's "volatility" (ie affinity for the stationary phase), the greater the magnitude of force between them, and hence it will travel slower through the machine.
- Q Hence, the mixture's components can be distinguished via retention time (R_t):
- ④ Retention time: the amount of time elapsed from the injection of a sample into the chromatographic system to the detection and recording of its peak.

→ the more volatile the compound is, the longer it will take to travel to the detector.

if stationary phase is non-polar, then non-polar substances will travel slower.

DETERMINATION OF THE % COMPOSITION OF A MIXTURE IN GLC



APPLICATIONS OF GLC

- ① Detection of drugs in athletes' blood/urine
- ② Detection of pesticide residues
- ③ Comparison of caffeine contents in coffee.

* in exam, peaks will be triangles.

Chapter 30:

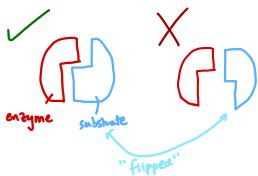
Organic Synthesis

SYNTHESIS OF CHIRAL DRUG MOLECULES

- Many drugs can be obtained from natural resources
e.g. Taxol, an anti-cancer drug, can be obtained from Pacific yew tree bark.
- however, a large amount of natural resources is required to produce a small amount of drugs.
- this led to scientists investing lots of research into finding synthetic production methods.

ENANTIOPURE DRUGS

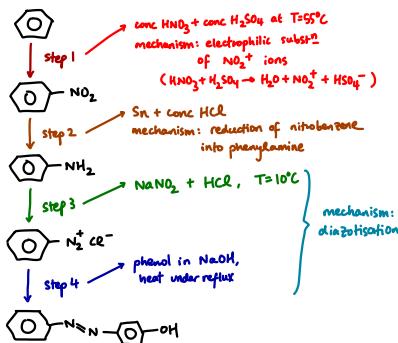
- The main "requirement" during synthetic drug synthesis is the production of enantiopure drugs; i.e. only one optical isomer of the drug.
- Naturally occurring drugs are also enantiopure.
- Why?
 - In biological systems, molecules are synthesised via enzymes.
 - Since enzymes work in a lock-and-key mechanism, a molecule has to be exactly the right shape to fit the enzyme.
 - However, different arrangements around a chiral centre will force an entirely different shape on the molecule; hence, it will not fit the molecule anymore.
 - Consequently, enzyme systems only produce a single optical isomer because that is the only shape they can "work with."



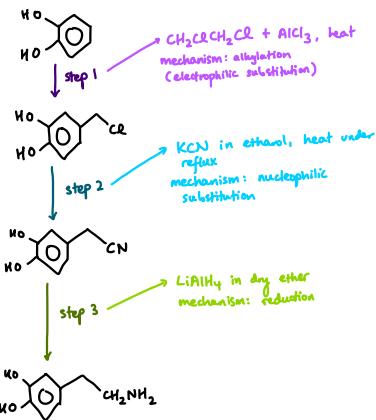
SYNTHETIC ROUTES

- In order to synthesise a new compound, chemists tend to use a starting material extracted from a commonly raw substance, and subject it to a series of organic reactions.
- * reactions are derived from AS/A2 Organic chemistry.

Ex1 benzene → azo dye



Ex2 benzenediol → dopamine



Ex3 methylbenzene → procaine

