CHEMISTRY

THEORY

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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 1/12th the mass of an atom of C-12.

② relative isotopic mass : the mass of an isotope relative to 1/12th 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 1/12th 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.

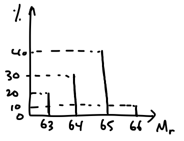
1.2 The Mole and Avogadro's constant

→ define Avogadro's constant, N_A, as the number of atoms in 12g of ^{12}C (= 6.02×10^{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.



*recall that

$A_r = \Sigma(\% \times M_r)$

i.e. $0.2 \times 63 + 0.3 \times 64 + 0.4 \times 65 + 0.1 \times 66$

$= 64.4$.

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

$\Rightarrow C_xH_y + (x+\frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

② composition by mass

to calculate :

1) tabulate M_r of desired formula / elem.
2) tabulate M_r of whole molecule
3) 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: (from formulae & eq<u>n</u>s)

① reacting masses
→ always convert to moles 1st!

② V of gases (e.g. combustion of hydrocarbons)
→ $V = 24n$ in rtp, $V = 22.4n$ in stp

③ V & conc. of solutions
→ $n = cV$ (*V is in dm^3, 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 = $\frac{1}{1840}$, 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 negligable mass.

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

*nucleon # = $n(n) + n(p)$
charge = $n(p) - |n(e^-)|$

2.2 The Nucleus Of The Atom

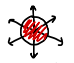
→ recognise isotopes are versions of an element — they have the same proton number, but different nucleon / neutron number.

→ use the symbolism ^A_ZX for isotopes;
Z is atomic number, A is nucleon number.

2.3 Electrons: Energy Levels, Atomic Orbitals, Ionisation Energy

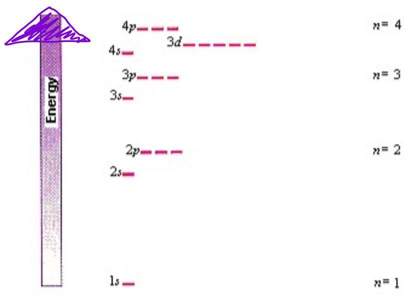
→ know your subshells

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] $3d^{10} 4s^1$ not $3d^9 4s^2$
⇒ half / filled 3d subshell more stable.

→ 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 ; N
→ as ↑n(p), ↑NC
↑F bw p & e^-, ∴ ↑ΔH_i

② distance of e^- from nucleus ; D
→ as ↑dist, ↓F bw p & e^-,
∴ ↓ΔH_i

③ shielding effect of inner e^- S
→ caused by full inner shells.
→ ↑shielding, ↓F bw p & e^-
→ ∴ ↓ΔH_i

⇒ successive ionisation energies ↑, because F bw remaining e^- and p ↑

→ you should be able to infer the electronic configuration & position in the PT (grp, prd), 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:

1s → 2s → 2p → 3s → 3p → 4s → 3d → 4p

→ elect. config. notation:

1) $1s^2 2s^2 2p^6$ etc.
2) dots-and-boxes notation

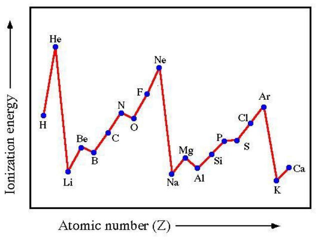
⥮	⥮	⥮ ⥮ ⥮	↿	(e.g. Na.)
1s	2s	2p	3s	

i) lone, before pair
ii) fill up successive subshells
iii) each box max 2 e^- w/ opp. spins

→ appreciate use of short-hand (e.g. [Ne])

→ realise that ionisation energies, ΔH_i, are usually positive ; because stripping an e^- away is endothermic.

→ trends of ionisation energies:



1) down a group, ↓ΔH_i
→ ↑shielding
→ ↑dist. from nucleus
→ both factors outweigh ↑NC

2) across a period, (generally) ↑ΔH_i
→ ↑NC
→ ↓dist. from nucleus bc ↓atomic size

exceptions:

3) Be→B, Mg→Al (ΔH_i ↓)
Be: [He] $2s^2$
B : [He] $2s^2 2p$
Mg: [Ne] $3s^2$
Al: [Ne] $3s^2 3p^1$
⇒ new subshell
→ ↑dist. from nucleus
→ ↑shielding
→ both factors outweigh ↑NC

4) N→O, P→S (ΔH_i ↓)
N: [He] ⥮ ↿ ↿ ↿
O: [He] ⥮ ⥮ ↿ ↿
⇒ pair of e^-
→ ↑repulsive F

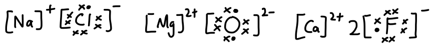
P: [Ne] ⥮ ↿ ↿ ↿
S: [Ne] ⥮ ⥮ ↿ ↿

3 Chemical Bonding

3.1 Ionic Bonding

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

i.e.
NaCl MgO CaF_2

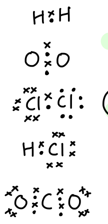


3.2 Covalent Bonding

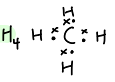
→ define **covalent bonding** as the electrostatic attraction between nuclei and localised shared pairs of electrons.

→ describe the **covalent bonds** in:

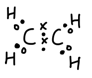
① H_2
② O_2
③ Cl_2
④ HCl
⑤ CO_2



⑥ CH_4



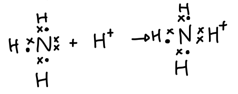
⑦ C_2H_4



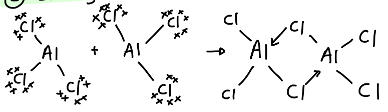
→ define **dative covalent / co-ordinate bonds** as a covalent bond, but both of the e^- in the pair derive from the same atom.

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

① $NH_3 + H^+ \rightarrow NH_4^+$



② $2AlCl_3 \rightarrow Al_2Cl_6$



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

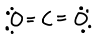
① **σ bonds** formed by **s-s** overlap
② **π bonds** formed by **p-p** overlap

→ **Single bonds** : **1 σ,**
→ **double bonds** : **1 σ, 1 π**
→ **triple bonds/ 2 double bonds** : **1 σ, 2 π**

① **sp^3** : **single**
② **sp^2** : **double**
③ **sp** : **triple** or **two doubles**

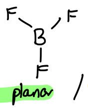
→ you must also be able to explain the **shapes**, & **bond ∡**, in the following:

① CO_2



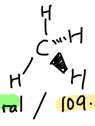
linear / **180°** / **2BP**

⑤ BF_3



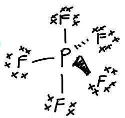
trigonal planar / **120°** / **3BP**

② CH_4



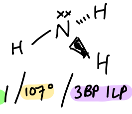
tetrahedral / **109.5°** / **4BP**

⑥ PF_5



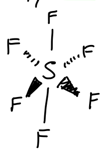
trigonal bipyramidal / **120°, 90°** / **5BP**

③ NH_3



trigonal pyramidal / **107°** / **3BP 1LP**

⑦ SF_6



octahedral / **90°** / **6BP**

④ H_2O

bent/ non-linear / **104.5°** / **2BP 2LP**

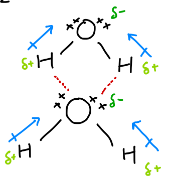
→ you should be able to use the above to predict the **bond angles** in **compounds**.

3.3 Intermolecular Forces, Electronegativity & Bond Properties

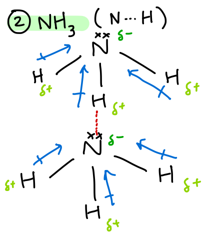
→ describe **hydrogen bonding** as an intermolecular bond, resulting from an electrostatic attraction between a proton, H^+, and an electronegative atom.

Examples:

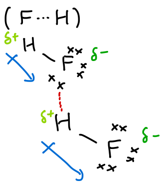
① H_2O (O⋯H)



② NH_3 (N⋯H)



③ HF (F⋯H)



*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 **Von 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:

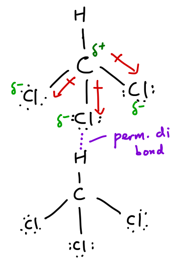
① **↓ bond length**, **↓** reactivity
⇒ ↑ FoA bw nuclei & e^-

② **↑ bond energy**, **↓** reactivity
⇒ ↑ E needed to break bond(s)

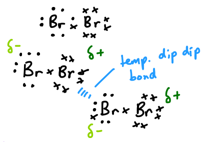
③ **↑ polarity**, **↑** reactivity
⇒ less even distribution of electrons
⇒ ↑ bond length
⇒ ↓ FoA bw nuclei & e^-

Examples *at a particular pt in time

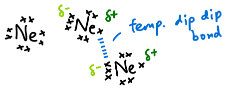
① $CHCl_3$ (l)



② Br_2 (l)

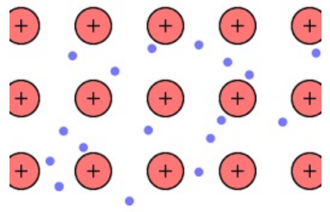


③ grp $18_{(l)}$ e.g. $Ne_{(l)}$



3.4 Metallic Bonding

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



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

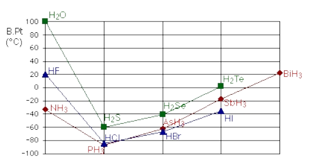
② **covalent**
→ low MP & BP ; if polar will be higher
→ solubility dependent on polarity of it & polarity of solvent (p⋅⋅p, np⋯np)
→ low density ; if polar will be higher
→ variable polarity

③ **metallic**
→ high MP & BP ; many strong metallic bonds
→ insoluble ; but some react
→ usually high density ; exceptions grp I metals

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

④ **hydrogen bonding**

1) **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 $p \geq 3$) **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**

→ define **surface tension** as the elastic tendency of the surface of a liquid which minimises its surface area.

→ define **viscosity** as a measure of a liquid's resistance to gradual deformation by stress.

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 °K or °C+273

From this, you can infer that

$$M_r = \frac{MRT}{pV}$$

(where M = mass, in g)

→ recall that at very high pressures and very low temperatures
1) intermolecular forces become significant
⇒ ↓ dist.
⇒ ↓ KE (for ↓ temp)
2) ratio of molecular size and gas volume becomes significantly high

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.

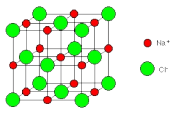
④ vapour pressure: the pressure exerted by a gas in an (thermo-dynamic) equilibrium with its liquid form state, at a given temperature.
→ caused by particles hitting the walls of the container.

4.3 The Solid State: Lattice Structures

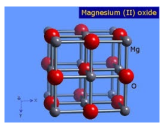
→ describe the structures of the compounds below:

4.3.1 Ionic Compounds

1) NaCl



2) MgO

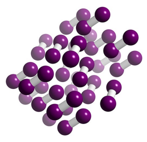


→ exist as giant ionic structures / ionic lattices
→ cubic
→ strong elec-static attraction between oppositely charged ions
→ coordination number (max # of atoms bonded to central atom) is 6

*MP of MgO more than MP of NaCl
→ ↑ charge density
→ ↑ bond strength

4.3.2 Simple Covalent Compounds

1) Iodine, I_2

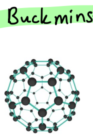


→ face centred cubic; cube of I_2 with another molecule at the centre of each face

⇒ 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

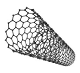
2) Buckminsterfullerene, C_{60}



→ simple spherical
→ w/ bond angles 120° & 108°
→ pentagons & hexagons
→ sp^2

Properties
① Low 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

3) Nanotubes

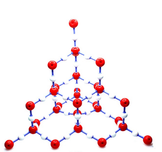


→ hexagonally arranged C atoms, bent into a cylindrical shape
→ w/ bond ∡ 120°
→ sp^2 hybridisation
→ simple

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

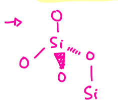
4.3.3 Giant Molecular Compounds

1) Silicon (IV) oxide, SiO_2



Silica

→ giant molecular tetrahedral structure
→ sp^3 hyb
→ bond ∡: 109.5°

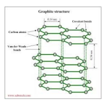


*each Si atom bonded to 4 O,
each O atom bonded to 2 Si.

Properties
① High melting point
→ many strong covalent bonds throughout structure
② Insoluble in all solvents
③ Poor conductor of electricity
→ absence of mobile charged particles throughout structure
④ Hard
→ strong covalent C-C bonds throughout structure

*
→ you must also realise the melting point of diamond is lower than the MP of graphite.
⇒ dia hyb = sp^3, gra = sp^2
⇒ ∴ dia: 25% s, 75% p
gra: 33.$\bar{3}$% s, 66.$\bar{6}$% p
⇒ ↑ s character, ↓ bond length, ∴ ↑ FoA bw nuclei & bonded pair of e^-
∵ orbital is closer to nucleus

2) Graphite



→ C atoms are arranged in planar layers, and showcases a hexagonal structure.
→ sp^2 hyb
→ 120° bond ∡

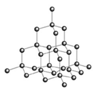
Properties
① Lubricating
→ layers can slide past each other easily
② High melting point
→ presence of many strong C-C bonds
→ a lot of thermal energy needed to break bonds
③ Insoluble in all solvents
④ Good electrical conductor
→ due to "cloud" of delocalised electrons between layers.

3) Graphene

→ single layer of graphite
→ giant hexagonal structure
→ sp^2 hyb
→ bond ∡ of 120°

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
⑤ Very strong
→ extensive network of covalent bonds

4) Diamond

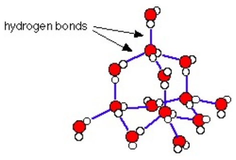


→ giant tetrahedral structure
→ bond ∡: 109.5°
→ hybridisation: sp^3

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

4.3.4 Hydrogen Bonded Compounds

→ ice

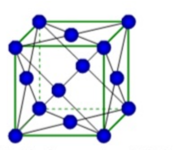


→ crystalline hexagonal structure
→ each water molecule is hydrogen bonded to 4 others (from the intermolecular FoA bw the H in one molecule and the O in the other)

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



Cubic face centered (fcc)

→ consists of a giant regular metallic lattice of positive metal cations
→ surrounded by a sea of delocalised electrons
→ structure of copper is a "face centred cubic" / fcc

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

*exceptions: grp I metals

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

Chapter 5:
Chemical Energetics

What is ENTHALPY?

→ a measure of the energy stored in a system.

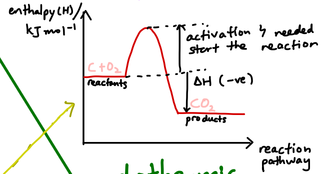
The relative enthalpies of a system differ between before and after a reaction.
This results in the gain or loss of enthalpy, signified by the enthalpy change $\boxed{(\Delta H)}$

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

exothermic

a chemical reaction that releases energy to its surroundings

$\rightarrow \Delta H < 0$



- combustion
  - eg $C + O_2 \rightarrow CO_2$
- oxidation of carb
- crystallisation & precipitation

*exot reactions are energetically ↑ stable.
- products ↓H
  ∴ ↑ stability

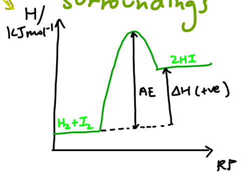
(this is why most chemical reactions are exo in nature)

endothermic

a chemical reaction that absorbs energy from the surroundings

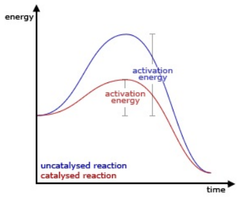
- decomposition
- photosynthesis
- dissolving NH_4^+ salts in H_2O

reaction pathway diagrams



ENTHALPY PROFILE DIAGRAMS w/ CATALYST

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



TYPES OF ENTHALPY CHANGES

① STANDARD ENTHALPY CHANGE OF FORMATION / ΔH_f^{θ}

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

eg $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H_f^{\theta} = -286\ kJ\ mol^{-1}$

$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(aq)} \quad \Delta H_f^{\theta} = -393\ kJ mol^{-1}$

- the ΔH_f^{θ} of an element in its normal physical state $= 0$
- $\begin{cases} \text{if } \Delta H_f^{\theta} < 0, & \text{compound is more stable than constituent elements.} \\ \text{if } \Delta H_f^{\theta} > 0, & \text{compound is less stable than constituent elements.} \end{cases}$

*θ indicates ΔH in standard conditions, i.e.
T= 298K, P=1.01×10⁵Pa =1atm,
each subst involved in normal physical state

*there are three elements in which their eqⁿs can be applied to both ΔH_f^{θ} & ΔH_c^{θ}

① $S + O_2 \rightarrow SO_2$
② $C + O_2 \rightarrow CO_2$
③ $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

② STANDARD ENTHALPY CHANGE OF COMBUSTION / ΔH_c^{θ}

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

eg $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \quad \Delta H_c^{\theta} = -297\ kJ mol^{-1}$

$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)} \quad \Delta H_c^{\theta} = -1411\ kJ mol^{-1}$

$S_{8(s)} + 8O_{2(g)} \rightarrow 8SO_{2(g)}$

*ΔH_c^{θ} is always negative

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

eg C_3H_8O

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

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

*C oxid. # not necessarily $\mathbb{Z}$

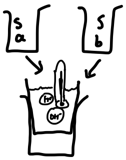
③ STANDARD ENTHALPY CHANGE OF NEUTRALISATION / ΔH_n^θ

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

eg $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$ $\Delta H_n^\theta = -57.1\ kJ\ mol^{-1}$

* ΔH_n^θ is always negative

*out of { HCl, HNO_3, H_2SO_4, H_3PO_4 ★



STRONG ACIDS & ALKALIS

⇒ $\Delta H_n^\theta \equiv -57.1\ kJ\ mol^{-1}$

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^θ is constant.

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

WEAK ACIDS & ALKALIS

⇒ $\Delta H_n^\theta > -57.1\ kJ\ mol^{-1}$

eg $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ $\Delta H = -54.0\ kJ\ mol^{-1}$

this is bc, besides the reaction bw H^+ & OH^-, ΔH_n^θ will also involve other enthalpy terms involved in ionising the weak acid

ΔH_1 : $H^+ + OH^- \rightarrow H_2O$

ΔH_2 : $CH_3COOH \rightarrow CH_3COO^- + H^+$

(heat released is used to complete the ionisation of the weak acid / base)

(weak acid / bases only ionise partially)

*less exothermic.

④ STANDARD ENTHALPY CHANGE OF SOLUTION / ΔH_{sol}^θ

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

eg $NaCl_{(s)} + aq \rightarrow NaCl_{(aq)}$ or $Na^+ + Cl^-$

∞ dilute -> all solute can be dissolved;
don't measure under supersaturated solution.
(presence of ppt)

* ΔH_{sol}^θ 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}^θ

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

eg $Na(s) \rightarrow \underline{Na}(g)$ $\Delta H_{at}^\theta = +109\ kJ\ mol^{-1}$

$\frac{1}{2}O_2(g) \rightarrow \underline{O}(g)$ $\Delta H_{at}^\theta = +248\ kJ\ mol^{-1}$

-> ensure product only has 1 mole (in eqⁿ)

* ΔH_{at}^θ 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

eg $Na_2S_2O_3 + 5H_2O \rightarrow Na_2S_2O_3 \cdot 5H_2O$ $\Delta H^\theta = -55.0\ kJ\ mol^{-1}$

* ΔH^θ 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

eg $Br_2 \rightarrow 2Br$ $\boxed{E(Br-Br)}$ $\Delta H^\theta = +193\ kJ\ mol^{-1}$

the E accompanies the reaction.

ie strength of covalent bond.

*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

×3 > ×2 > ×1

ie $N \equiv N$ > $O=O$ > $H-H$

* ↑E_B, ↓reactivity
(e.g. N_2)

② Bond length

-> distance bw the nuclei of the two atoms joined by covalent bonds

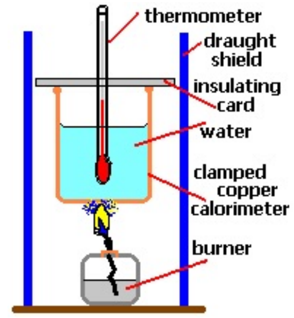
* -> dependent on size of atom :

↑ atomic size;
↑ BL;
↓ orbital overlap;

∴ ↓ BE.

EXPERIMENTAL DETERMINATION OF ENTHALPY CHANGES

Basic Calorimeter Set



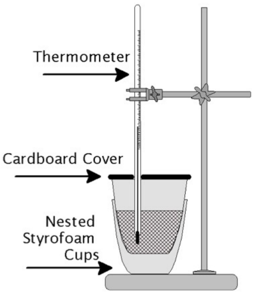
(combustion)

→ used to measure temperature change caused by a reaction

Errors

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

Diagram of a Calorimeter



(neutralisation)

Mathematical Eq^n^s for ΔH

① $Q = -mc\Delta T$ (Q = heat absorbed / produced) * "–" is important!

m = mass of solution / g

→ only mass of solvent / solution

→ for ALL aq sol : $1\,cm^3 \equiv 1\,g$

c = spec. heat cap of H_2O / $4.18\,J\,g^{-1}\,°C^{-1}$

ΔT = change of temp. *not compulsory to chg bw °K or °C

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

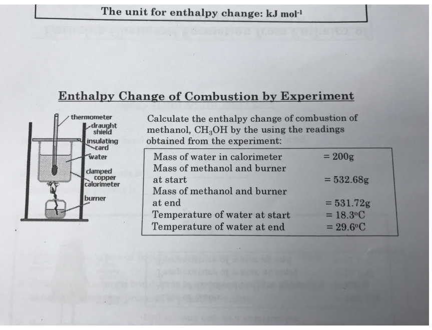
*answer must have :

① sign (ex / end)

② value

③ unit ($kJ\,mol^{-1}$)

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 the 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	= 29.6°C

$Q = -mc\Delta T$

$= -(\underline{200} \times 4.18 \times 11.3)$ mass of H_2O

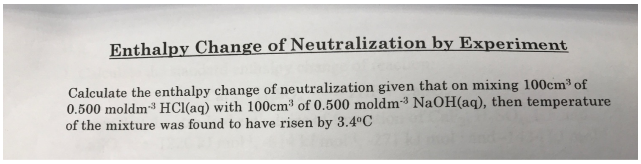
$= -9446.8\,J$

$m_{CH_3OH\ burned} = 0.96\,g$: $M_r = 32.0\,g\,mol^{-1}$

$\therefore n = \dfrac{0.96}{32} = 0.03\,mol.$

$\Delta H = \dfrac{-9446.8}{0.03} = -315\,kJ\,mol^{-1}.$

ΔH_n° by experiment



Enthalpy Change of Neutralization by Experiment

Calculate the enthalpy change of neutralization given that on mixing 100cm³ of 0.500 moldm⁻³ HCl(aq) with 100cm³ of 0.500 moldm⁻³ NaOH(aq), then temperature of the mixture was found to have risen by 3.4°C

$200\,cm^3$: $m = 200\,g$

$Q = -mc\Delta T$

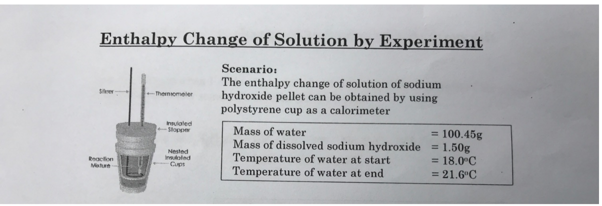
$= -(200 \times 4.18 \times 3.4)$

$= -(2842.4)\,J$

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

$\Delta H = -56.8\,kJ\,mol^{-1}.$ ✓

ΔH_{sol}° 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

$Q = -mc\Delta T$

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

$= -1511.57\,J$

$\Delta H = \dfrac{-1.51157\,kJ}{1.50 / (22.99 + 16 + 1)}$

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

*experimental value of ΔH_c is less accurate than ΔH_n

① Heat lost 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.

* ↑ BE, ↑ strength of bond
* bond breaking is endo, bond forming is exo

$$\begin{tikzcd} A+B \arrow[rr, "\Delta H"] \arrow[dr, "\Delta H_1"'] & & C \\ & X \arrow[ur, "\Delta H_2"'] & \end{tikzcd}$$

$\Delta H = \Delta H_1 + \Delta H_2.$

ΔH_f from ΔH_c

$$\begin{tikzcd} \text{elements} + O_2 \arrow[rr, "\Delta H_r"] & & \text{compound formed} + O_2 \\ & \text{combustion products} \arrow[ul, "\Delta H_1"] \arrow[ur, "\Delta H_2"'] & \end{tikzcd}$$

① Write balanced eq^n^ 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

$$\begin{tikzcd} \text{anhyd salt} \arrow[rr, "\Delta H_{hyd}"] \arrow[dr, "\Delta H_1"'] & & \text{hyd salt} \arrow[dl, "\Delta H_2"] \\ & \text{dil. aq sol of salt} & \end{tikzcd}$$

*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. electroplating)
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
② reduction : gain in e^- → ↓ ox.# / ↓ O
} OIL RIG
oxidation is loss reduction is gain

③ oxidising agent : e^- acceptor, reduces species → eg $H_2 + \underline{I_2} \rightarrow 2HI$ ($H \rightarrow H^+ + e^-$)
→ acidified $KMnO_4$ & $K_2Cr_2O_7$, H_2O_2, halogens (oxidants)

④ reducing agent : e^- donator, oxidises species → eg $\underline{H_2} + I_2 \rightarrow 2HI$ ($I + e^- \rightarrow I^-$)
→ $Na_2S_2O_3$ (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)

$$2S_2O_3{}^{2-}{}_{(aq)} + I_2 \rightarrow S_4O_6{}^{2-}{}_{(aq)} + 2I^-$$

→ iodine acts as the weak oxidising agent (by oxidising thiosulfate (S_2O_3) into tetrathionate (S_4O_6) ions)

→ 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 colorless solution (all I_2 ionised)

Usually, starch indicator is added to achieve a sharper end pt.

☆ blue-black → colorless.

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

$$MnO_4{}^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

→ 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 solution permanent pale pink. (why?

rules for working out oxidation numbers

① All neutral atoms have an oxidation num. (O_N) of 0. ie Mg, Fe, H_2, O_2, S_8

② For simple ions, the O_N is the same as the ionic charge

ie Na^+, Mg^{2+}, Al^{3+},
G1 G2 G13
Cl^-, O^{2-}, N^{3-}
G17 G16 G15

③ In a neutral molecule, ΣO_N = zero.

ie Al_2O_3 : $2Al^{3+}$ & $3O^{2-}$
$\therefore 2(+3) + 3(-2) = 0$.

④ In a polyatomic ion :

eg NH_4^+
$x + 4(1) = 1$
$\therefore x = -3$.

⑤ In complex ionic compounds:

eg NH_4NO_3

split into component ions : → NH_4^+ NO_3^-

then compare : $x+4(1) = 1$ $y+3(-2) = -1$
$x = -3$ $y = 5$.

However, there are EXCEPTIONS

a) H has an oxidation state of −1 in Group 1 metal hydrides. eg in KH and NaH

b) O has an O_N of +1 in peroxides eg in H_2O_2

c) O in compounds w/ more ≤-ve atom (ie F_2O)
→ since F has an oxid. state of −1, and is more ≤-ve, O has an O_N of +2.

d) Halogenic compounds w/ more ≤-ve atoms (ie FCl)
→ the more electronegative element gets the −1 oxidation state.

balancing chemical equations : methods

① balancing eqns for redox reactions in acidic solution.

for instance, balance :

$Cr_2O_7^{2-}{}_{(aq)} + HNO_{2(aq)} \rightarrow Cr^{3+}{}_{(aq)} + NO_3^-{}_{(aq)}$.

* some half equations are given in the DATA BOOKLET.

Steps :

i) Write the half equations.

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$
$HNO_2 \rightarrow NO_3^-$

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

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
$HNO_2 \rightarrow NO_3^-$

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

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
$HNO_2 + H_2O \rightarrow NO_3^-$

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

$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+$

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

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^-$

vi) Multiply by an appropriate factor

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (×1)
$3HNO_2 + 3H_2O \rightarrow 3NO_3^- + 9H^+ + 6e^-$ (×3)

vii) Add balanced half reactions.

$Cr_2O_7^{2-} + 14H^+ + 3HNO_2 + 3H_2O + 6e^- \rightarrow 2Cr^{3+} + 3NO_3 + 9H^+ + 7H_2O + 6e^-$
$Cr_2O_7^{2-} + 5H^+ + 3HNO_2 \rightarrow 2Cr^{3+} + 3NO_3 + 4H_2O$

important!

→ never add O_2, O atom or O^{2-} to balance oxygen.

→ never add H_2, H atom to balance hydrogen.

② balancing eq^{n}s for redox reactions in basic solution.

for instance :

$$Ag_{(s)} + Zn^{2+}_{(aq)} \rightarrow Ag_2O_{(aq)} + Zn_{(s)}$$

steps :

i) Write the half equations

$Ag \rightarrow Ag_2O$

$Zn^{2+} \rightarrow Zn$

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

$2Ag \rightarrow Ag_2O$

$Zn^{2+} \rightarrow Zn$

iii) Balance each half-reaction for oxygen by adding H_2O.

$2Ag + H_2O \rightarrow Ag_2O$

$Zn^{2+} \rightarrow Zn$

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

$2Ag + H_2O \rightarrow Ag_2O + 2H^+$

$Zn^{2+} \rightarrow Zn$

v) Balance each half-reaction for charge

$2Ag + H_2O \rightarrow Ag_2O + 2H^+ + 2e^-$

$Zn^{2+} + 2e^- \rightarrow Zn$

vi) Multiply by an appropriate factor.

$2Ag + H_2O \rightarrow Ag_2O + 2H^+ + 2e^-$

$Zn^{2+} + 2e^- \rightarrow Zn$

vii) Add balanced half-reactions

$2Ag + H_2O + Zn^{2+} + 2e^- \rightarrow Ag_2O + 2H^+ + 2e^-$

$2Ag + H_2O + Zn^{2+} \rightarrow Ag_2O + 2H^+ + Zn$

viii) Add OH^- to balance H^+

$2Ag + H_2O + Zn^{2+} + 2OH^- \rightarrow Ag_2O + 2H^+ + 2OH^- + Zn$

ix) Combine H^+ & OH^- to form water.

$2Ag + H_2O + Zn^{2+} + 2OH^- \rightarrow Ag_2O + 2H_2O + Zn$

$\Rightarrow 2Ag + Zn^{2+} + 2OH^- \rightarrow Ag_2O + Zn + H_2O.$

③ balancing chemical eq^{n}s by using oxidation numbers.

eg copper (II) oxide reacts with NH_3 to produce Cu, N_2 and H_2O.

steps :

i) write the unbalanced eq^{n} and identify the atoms which ΔO_N

$CuO + NH_3 \rightarrow Cu + N_2 + H_2O$

$CuO \rightarrow Cu$

$2NH_3 \rightarrow N_2$

ii) deduce the ox. no charge

$CuO \rightarrow Cu$ $\quad +2 \rightarrow 0$ $\quad -2$

$2NH_3 \rightarrow N_2$ $\quad -6 \rightarrow 0$ $\quad +6$

iii) balance the O_N charges

$3CuO \rightarrow 3Cu$ $\quad \Delta O_N = -6$

$2NH_3 \rightarrow N_2$ $\quad \Delta O_N = +6$

*always consider the mole !
ie $2N^{3-} = -6$ (O_N)

iv) add half eq^{n}s

$3CuO + 2NH_3 \rightarrow 3Cu + N_2$

v) balance the remaining atoms → oxygen, hydrogen.

$3CuO + 2NH_3 \rightarrow N_2 + 3Cu \boxed{+3H_2O}$

Chapter 7: Equilibria

REVERSIBLE REACTIONS

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

$H_2 + I_2 \boxed{\rightleftharpoons} 2HI$

$CuSO_4 \cdot 5H_2O \boxed{\rightleftharpoons} CuSO_4 + 5H_2O$

$Hb + 4O_2 \boxed{\rightleftharpoons} Hb \cdot 4O_2$

→ we can use activation energy data to determine whether a reaction is reversible.
  - → if AE(↑↑)↑↑, backword 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 = conc. of products   *BUT [reactants] ≠ [products] !

③ reactants continously being converted to products, and vv

④ only occurs in closed system.

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

eg $Fe^{3+} + SCN^- \rightleftharpoons [Fe(SCN)]^{2+}$

a) if c_{SCN^-} ↑, eq shifts to (→)
  - → to remove extra SCN^-
  - → observation: redder solution

b) if c_{SCN^-} ↓, eq shifts to (←)
  - → to replace lost SCN^-
  - → observation: paler (red) solution

② Pressure (only affects g reactions)

eg¹ $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

a) when ↑P, eq shifts (→)   *focus on the gases in the eq, and ignore everyt else

Why? → to produce ↓ n of g
  → to ↓P

hence: resultant mixture ↑SO_3, ↓SO_2, O_2

b) when ↓P, eq shifts (←)

Why? → to produce ↑ n of g
  → to ↑P

hence: resultant mixture ↑SO_2, O_2, ↓SO_3

eg² $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

→ if no Δ in # of n 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

eg $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H = -94.9\ kJmol^{-1}$

a) when T↑, pos of eq (←)

why? → endothermic reaction favoured
  → to remove extra heat ↯
  → result has ↑SO_2, O_2, ↓SO_3.

b) when T↓, pos of eq (→)

why? → exothermic reaction favoured
  → to replace lost heat ↯
  → result has ↓SO_2, O_2, ↑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.

HABER PROCESS

→ $N_2 + 3H_2 \rightleftharpoons \boxed{2NH_3}$ $\Delta H = -92\ kJ\ mol^{-1}$

conditions: not necessary to memorize values.

① ↑↑ pressure of (60 – 250 atm)
  - → to shift eq (→)
  - *↑↑↑ p is costly to maintain.

② ↑↑½ temp. of 300 – 500 °C
  - → if ↑↑² T, yield of NH_3 ↓ (altho ↑ rate)
  - → if ↓↓ T, rate ↓ (altho yield ↑)
  - → this temp is used mainly to speed up the reaction.

③ Fe / Fe_2O_3 catalyst
  - → to ↑ rate
  - → by providing an alternative path of lower E_a.

④ Removal of NH_3 thru condensation
  - → to ↑ yield NH_3.

uses of NH_3 IRL:

① Nitrogenous fertilisers
② HNO_3
③ Explosives
④ Refrigerant
⑤ Cleaning agents
⑥ Nylon

CONTACT PROCESS

→ the creation of $H_2SO_{4(aq)}$.

steps:

① $S + O_2 \rightarrow SO_2$

② $2SO_2 + O_2 \boxed{\rightleftharpoons} 2SO_3$ $\Delta H = -197\ kJ\ mol^{-1}$

③ $H_2SO_{4(l)} + SO_{3(g)} \rightarrow H_2S_2O_{7(l)}$

④ $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

conditions for ②:

i) 1-2 atm pressure
  - → when ↑p, eq (→) ∴ ↑ yield of SO_3
  - Then why p just above std atm?
  - → ↑↑K_p even at this p
  - → eq ↑↑(→)
  - → app. of ↑p requires ↑↑cost

ii) 400 - 450°C temp
  - → ↑ yield, while not significantly affecting rate

iii) V_2O_5 catalyst
  - → to ↑ rate by providing an alternative path of ↓E_a

iv) Air used to burn S, must be as pure as possible   *no pollutants. why? → will take up the "active site" of catalyst.
  - → to prevent catalyst "poisoning"

SIMILARITIES BW HABER & CONTACT EQ REACTIONS

① Both products are redox

② Both result in higher yield of products when pressure increased. {eq (→)}

③ Forward reactions are exothermic

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 $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

② Heterogenous eq

→ reactions in which reactants & products are in different states

eg $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

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 eq^n stoichiometry.

→ in the form $\frac{\text{products}}{\text{reactants}}$.

* applied to all eq reactions

* except solids

Why? → solids cannot be quantified by conc.

eg¹ $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$$\Rightarrow K_c = \frac{[NH_3]^{②}}{[N_2][H_2]^3}$$

# of n of NH_3.

conc. of NH_3

conc of N_2

conc. of H_2

$$*\text{unit} = \frac{(mol\ dm^{-3})^2}{(mol\ dm^{-3})^4} = mol^{-2}\ dm^{6}$$

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

*unit is very important!

eg² $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

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

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

$[K_c] = [1]$ ∴ no unit

eg³ $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

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

$[K_c] = mol\ dm^{-3}$.

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.

eg¹ $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

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

* 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.

eg¹ $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

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

eg² $N_{2(g)} + H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

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

eg³ $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

$$K_p = \frac{P^4_{H_2}}{P^4_{H_2O}} = \frac{[Pa]^4}{[Pa]^4} = [1]$$

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

MEANING OF "K"

- $K >> 1$ ⇒ eq (→) ∴ favour products.
- $K << 1$ ⇒ eq (←) ∴ favour reactants.

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

$$K_p = \frac{\left(\frac{n_c}{n_T} \times p\right)\left(\frac{n_d}{n_T} \times p\right)}{\left(\frac{n_A}{n_T} \times p\right)\left(\frac{n_B}{n_T} \times p\right)^2}$$

FACTORS THAT AFFECT EQUILIBRIUM CONSTANT POSITION

① Concentration ✗

eg $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

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

→ if more HI added, pos of eq (→)

→ hence [HI]↓, $[H_2, I_2]$↑

→ at the end, eq restored

→ so conc does not change the EC.

② Pressure ✗

eg $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

→ if pressure increases, all conc. ↑ as V ↓

→ but since K_c is a ratio, it remains unchanged.

→ so pressure also does not ΔEC.

③ Temperature ✓

$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ ΔH is +ve

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

→ if T↑, sys fav. endo.

∴ eq shifts right.

→ ∴ $[H_2, I_2]$↑, [HI]↓

∴ K_c ↑.

→ so temperature does affect the EC.

BRØNSTED-LOWRY THEORY OF ACIDS & BASES

→ in water, (Arrhenius def^n)

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 def^n:

① An acid donates a proton;

② A base accepts a proton.

eg $HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

HCl gives a proton to H_2O.

→ 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.

AMPHOTERIC COMPOUNDS

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

eg $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

CONJUGATE ACIDS & BASES

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

eg $HCl_{(g)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$

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 I 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.

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.
eg mol dm^{-3} s^{-1}, mol g^{-1}s^{-1}

FACTORS AFFECTING RATE

COLLISION THEORY

→ in order to react with other °p, the resultant °p 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 ⌃ w/ ϟ > E_a ↑.

CATALYSTS

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

HETEROGENEOUS CATALYSTS

→ a type of catalyst, where the catalyst occupies a different phase from the reaction mixture.

→ often (g) ⌃ acting on (s) catalyst surface.

→ based on "adsorption" theory:

1) diffusion to surface
2) adsorption
3) reaction
4) desorption
5) diffusion away from surface.

*process by which (s) hold ⌃ of a (g) or (l) or solute as a thin film.

→ key insights :

① Minute amts 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 $N_2 + 3H_2 \rightleftharpoons 2NH_3$
② V_2O_5, in $2SO_2 + O_2 \rightleftharpoons 2SO_3$.
③ Transition elements in catalytic converters:

(rhodium, Rh) $2CO + 2NO \rightarrow 2CO_2 + N_2$

(palladium, Pd or platinum, Pt) $2CO + O_2 \rightarrow 2CO_2$.

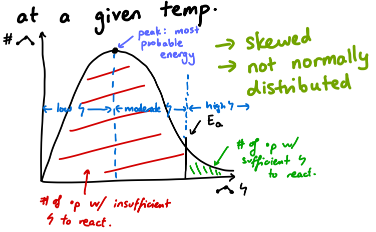
Factors :

① Concentration

→ ↑ conc, ↑ rate
→ as ↑ freq. of coll. bw °p
*NOT ↑ eff. collisions! →

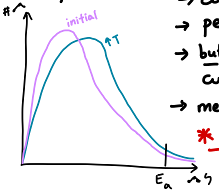
③ Temperature

Boltzmann Dist$^{\underline{n}}$ graph :
a graph showing the dist$^{\underline{n}}$ of energies of the °p in a sample at a given temp.



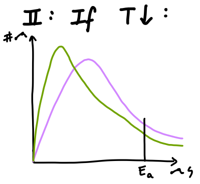
→ skewed
→ not normally distributed

I: If T↑ :



→ curve shifts (→)
→ peak ↓
→ but total area under curve & E_a ☰.
→ mean ⌃ ϟ ↑.
*→ proportion of molecules with energy > E_a increases

II: If T↓ :



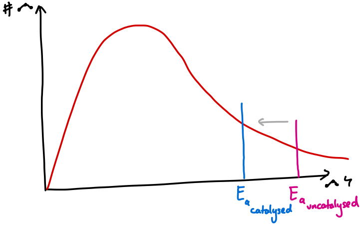
→ curve shifts (←)
→ peak ↑
→ total area under curve & E_a ☰
→ mean ⌃ ϟ ↓.
→ ⌃ w/ energy > E_a proportionally decreases.

Why does ↑T ↑rate?
→ ave. KE of °p ↑
→ more collisions
→ more successful collisions
→ more molecules possess molecular ϟ ≥ E_a.

② Pressure

→ ↑P, ↑ rate
→ ⌃ brought closer tgt, ∴ ↑ freq. of coll. bw ⌃
→ only applicable to (g) reactions

④ Catalyst



→ catalysts (generally) increase the rate of reaction by providing an alternative mechanism of ↓ E_a ⟹

→ ∴ ↑ ⌃ w/ suff. ϟ to react
→ ∴ ↑ freq. of successful collisions.

⑤ Surface Area

→ the larger the size of reacting °p, the ↓ the total SA & contact bw reacting ⌃.

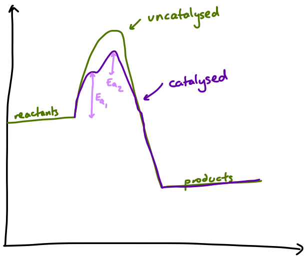
→ ∴ ↓ rate of reaction.

ACTIVATION ENERGY

→ the minimum energy that colliding °p 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 A + B → C
C + D → 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

$$\Rightarrow S_2O_8{}^{2-}{}_{(aq)} + 2I^-{}_{(aq)} \xrightarrow{Fe^{3+}_{(aq)}} 2SO_4{}^{2-}{}_{(aq)} + I_{2(aq)}$$

mechanism:

a) $2Fe^{3+}{}_{(aq)} + 2I^-{}_{(aq)} \rightarrow 2Fe^{2+}{}_{(aq)} + I_{2(aq)}$

b) $2Fe^{2+}{}_{(aq)} + S_2O_8{}^{2-}{}_{(aq)} \rightarrow 2Fe^{3+}{}_{(aq)} + 2SO_4{}^{2-}{}_{(aq)}$

② Oxides of nitrogen & acid rain

$\Rightarrow SO_{2(g)} + NO_{2(g)} \rightarrow SO_{3(g)} + NO_{(g)}$

$NO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{2(g)}$

$SO_3 + H_2O \rightarrow H_2SO_4$ (?)

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.

- specific characteristics

→ more efficient than inorg. cat.

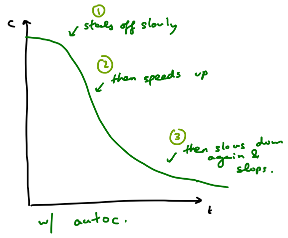
→ no byproducts formed

→ optimum conditions: 37°C, pH 7, atm. p

AUTOCATALYST

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

eg $2MnO_4{}^- + 5C_2O_4{}^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$



why?

1) ↓↓ amt of cat.

2) ↑↑ amt of cat.

3) ↓↓ conc. of reactant.

Chapter 9: Chemical Periodicity (Period 3)

WHAT ARE P3 ELEMENTS?

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

PERIODIC PATTERN OF ATOMIC RADII

covalent radius → calc by 1st identifying the dist bw 2 nuclei of the same type of bonded atom, then ÷2

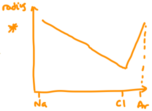
VdW radius → calc by 1st identifying the dist bw 2 nuclei of the same type of atom that are not chem bonded, then ÷2

→ higher than ar ∵ no overlap of e^- clouds.

- atomic radius decreases as you go across the period.

Why?
1) #p ↑, ∴ NC↑
2) Hence ↑ FoA on outer shell e^-
3) note: shielding ⊟

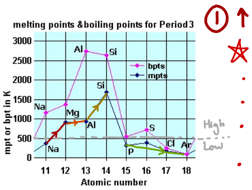
atomic radius



→ sudden jump in atomic radius in Ar
→ as Ar = VdW radius.

PERIODIC PATTERNS OF MELTING POINTS.

* MP ≤ 500°K ⇒ low
MP > 500°K ⇒ high



① ↑MP from Na to Mg

☆ Strength of metallic bonding ↑

- ↓ cation size
- ↑ # of delocalised e^-
- ∴ ↑ FoA bw cations & sea of delocalised e^-
- ↑ ϟ needed to break metallic bonding in Mg, compared to Na

② ↓(↑) in MP from Mg to Al: ⇒ not required for exam

- difference in cation size bw Mg^{2+} & Al^{3+} is less than diff bw Na^+ & Mg^{2+}.
- attraction bw e^- too strong to fully delocalise all 3 e^- in Al

③ Sharp ↑ in MP of Si

☆ Because it exists as a giant molecular structure, held tgt by strong covalent bonds

④ ↓ in MP across non-metal group

- S exists as S_8, P as P_4 & Cl as Cl_2
- 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.

PERIODIC PATTERNS OF IONIC RADII

① comparison between ions and atoms

☆ CATIONS (Na^+, Mg^{2+}, Al^{3+})

- cations have a smaller ionic radius than their respective neutral atoms.

Why?
1) lost e^- (⇒ complete outer shell lost)
2) remaining e^- more tightly bound to nucleus by p

☆ ANIONS (Cl^-, S^{2-}, P^{3-})

- anions have a larger ionic radius than their respective neutral atoms.

Why?
1) gained e^- (⇒ full outer shell of e^-)
2) ↑ repulsion bw e^-

② comparison among cations

☆ From $Na^+ \rightarrow Si^{4+}$, $P^{3-} \rightarrow Cl^-$, ionic radius decreases.

ionic radius larger.

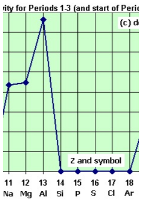
Why?
* ions in these "groups" are ISOELECTRONIC (grps of atoms/ions w/ ⊟ # of e^-)
2) ↑#p ⇒ ↑NC
3) hence, outermost e^- in 2nd principal shell attracted closer to nucleus.

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.

→ ϟ 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 S_8, P_4 & Cl_2.

PERIOD 3 OXIDES

REACTIONS OF P3 ELEMENTS WITH O_2.

Na $4Na + O_2 \rightarrow 2Na_2O_{(s)}$
- bright yellow flame
- white solid (Na_2O)

Mg $2Mg + O_2 \rightarrow 2MgO_{(s)}$
- bright white flame
- white solid (MgO)

Al $4Al + 3O_2 \rightarrow 2Al_2O_{3(s)}$
- bright white flame
- white solid (Al_2O_3)

Si $Si + O_2 \rightarrow SiO_{2(s)}$
- white flame
- white solid (SiO_2)

P (excess O_2) $P_4 + 5O_2 \rightarrow P_4O_{10(s)}$
(limited O_2) $P_4 + 3O_2 \rightarrow P_4O_{6(s)}$
- yellow or white flame
- white fumes (P_4O_{10})

S $S + O_2 \rightarrow SO_{2(g)}$
- blue flame
- toxic fumes (SO_2)

* Cl & Ar do not react with O_2!

OXIDES OF P3 ELEMENTS

Element	Bonding	Acid/Base Nature	MP
Na → Na_2O (+1)	giant ionic	strong base (pH=13)	high (1132°C)
Mg → MgO (+2)	giant ionic	weak base (pH = 9)	high (2852°C)
Al → Al_2O_3 (+3)	giant ionic (w/ some covalent character)	amphoteric (pH = 7)	very high (2072°C)
Si → SiO_2 (+4)	giant molecular	v. weakly acidic	very high (1713°C)
P → P_4O_6 (+3) → P_4O_{10} (+5)	simple molecular	strongly acidic (pH= 2)	low (360°C)
S → SO_2 (+4) → SO_3 (+6)	simple molecular	strongly acidic (pH = 2)	low (−72°C)
Cl → Cl_2O_5 (+5) → Cl_2O_7 (+7)			

REACTIONS OF OXIDES WITH WATER

- $Na_2O + H_2O \rightarrow 2NaOH$
- $MgO + H_2O \rightarrow Mg(OH)_2$

} used to relieve gastric pain (neut. HCl)

($O^{2-} + H_2O \rightarrow 2OH^-$)

- $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
- $SO_2 + H_2O \rightarrow H_2SO_3$ ($H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$)
- $SO_3 + H_2O \rightarrow H_2SO_4$
- $SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$
- $SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$

- Al_2O_3 does not react w/ water. However, it is amphoteric:

(→) $Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$

(→) $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$

- SiO_2 does not react w/ water. But it reacts w/ hot, conc. NaOH:

⇒ $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$.

PERIOD 3 CHLORIDES

REACTION OF P3 ELEMENTS WITH Cl_2

Na
- $Na + \frac{1}{2}Cl_2 \rightarrow NaCl$
- yellow flame
- white solid.

Mg
- $Mg + Cl_2 \rightarrow MgCl_2$
- white solid

Al
- $2Al + 3Cl_2 \rightarrow Al_2Cl_6$
- white solid

↳ as (s), aluminium chloride exists as $AlCl_3$ & Al_2Cl_6 (dep. on hyd. state)

↳ at T = 180–200°C (pressure dependent), sublimination occurs: aluminium chloride is converted into Al_2Cl_6.

↳ as T↑, these dimers break up into $AlCl_3$ ^.

Si
- $Si + 2Cl_2 \rightarrow SiCl_4$
- colourless liquid forms

P
- (excess Cl_2) $P_4 + 10Cl_2 \rightarrow 4PCl_5$ → colourless solid
- (ltd Cl_2) $P_4 + 6Cl_2 \rightarrow 4PCl_3$ → colourless (l)
- yellow or white flame
- white fumes

S
- $2S + Cl_2 \rightarrow S_2Cl_2$
- orange pungent liquid

CHLORIDES OF P3 ELEMENTS

	NaCl	$MgCl_2$	$AlCl_3$ (anhyd) Al_2Cl_6 (hyd)	$SiCl_4$	PCl_5	S_2Cl_2
Structure	giant ionic		simple molecular			
When added to H_2O...	white solids dissolve to form colourless solutions		react to yield white fumes of HCl			
pH	7	6.5	3	2	2	2
Oxidation #	+1	+2	+3	+4	+5	+1

REACTION OF CHLORIDES WITH WATER

① $NaCl + aq \rightarrow Na^+ + Cl^-$

② $[Mg(H_2O)_6]^{2+} \rightarrow [Mg(H_2O)_5OH]^+ + H^+$ (pH = 6.5)

→ complex ion will undergo polarisation, releasing an hydrogen ion

$MgCl_2 + aq \rightarrow Mg^{2+} + 2Cl^-$

③ $Al_2Cl_6 + 12H_2O \rightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$

$[Al(H_2O)_6]^{3+} \rightarrow [Al(H_2O)_5OH]^{2+} + H^+$ → due to the ↑↑ charge ρ of water ^

$AlCl_3 \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

④ $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl_{(g)}$

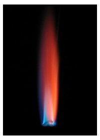
⑤ $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl_{(g)}$

Chapter 10: Group 2

→ alkaline earth metals
→ outershell config of ns^2
→ reactive metals w/ low 4-tivity.

FLAME TESTS


Mg - bright white


Ca - brick red


Sr - scarlet / red


Ba - apple green

PROPERTIES

METALLIC RADIUS

↳ half of the dist. bw 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 + O_2

💡 ALL G2 metals burn in O_2 to yield white solid metal monoxides.

$2X_{(s)} + O_{2(g)} \rightarrow 2XO_{(s)}$

METAL + ACIDS

HCl : $X_{(s)} + 2HCl_{(aq)} \rightarrow XCl_{2(aq)} + H_{2(g)}$

★ H_2SO_4: $X_{(s)} + H_2SO_{4(aq)} \rightarrow XSO_{4(aq/s)} + H_{2(g)}$

*the solubility of G2 sulfates decreases down the group

$BeSO_4$ } (aq)
$MgSO_4$
$CaSO_4$ } (s)
$SrSO_4$
$BaSO_4$

METAL OXIDES

MgO - slightly soluble in H_2O (pH = 9)
CaO, SrO, BaO } dissolve in H_2O to yield an alkaline solution (pH = 10-13)

★ pH of group 2 oxides ↑, ↓ the grp.

why? • H_2O solubility of group 2 hydroxides ↑, ↓ the grp
• hence more OH^- ionises

$Mg(OH)_2$ (s)
$Ca(OH)_2$ (s/aq)
$Sr(OH)_2$ (aq)
$Ba(OH)_2$ (aq)

* $Ca(OH)_2$ is technically partially soluble in H_2O. For exam, say it is INSOLUBLE.

THERMAL DECOMPOSITION OF G2 NO_3^- & CO_3^{2-}

★ nitrates: $M(NO_3)_2 \rightarrow MO + 2NO_2 + \frac{1}{2}O_2$

*brown poisonous (g) observed

★ carbonates: $MCO_3 \rightarrow MO + CO_2$

* effervescence observed

→ therm. stab. of CO_3 ↑ down the group. → why?

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

⇒ $MgCO_3$, $CaCO_3$ } can be decomp. by bunsen flame
$SrCO_3$, $BaCO_3$ } cannot.

REACTIVITY (ABILITY TO REDUCE)

★ ↑, ↓ the grp.

why? • desp ↑ NC
• ↑ shielding from inner e^-
• ↑ atomic radius
• ↓ FoA bw nucl. & outershell e^-
• so ↑ easier to ionise.

METAL OXIDE + ACIDS

① HCl · $XO_{(s)} + 2HCl \rightarrow XCl_{2(aq)} + H_2O_{(l)}$

② H_2SO_4: $XO_{(s)} + H_2SO_{4(aq)} \rightarrow XSO_{4(s/aq)} + H_2O_{(l)}$

③ HNO_3 : $XO_{(s)} + 2HNO_{3(aq)} \rightarrow X(NO_3)_{2(aq)} + H_2O_{(l)}$

METAL OXIDE + H_2O

*most G2 oxides react w/ H_2O to form metal hydroxides:

$XO + H_2O \rightarrow X(OH)_2$

SOLUBILITIES OF GRP II HYDROXIDES

$Mg(OH)_2$ — insoluble
$Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$ } soluble

* water solubility ↑, ↓ the grp
↳ so pH ↑, ↓ the grp
why? → ↑ OH^- present.

* $Ca(OH)_2$ appears as a white suspension.

APPLICATIONS OF G2 METALS

★ $CaCO_3$ — "building" rocks — blocks — expensive tiles — cement

★ CaO (quickline) — roasted w/ clay to form cement

★ $Ca(OH)_2$ (limewater) — used in agriculture to treat acidic soils.

METAL + H_2O

★ Mg reacts differently with H_2O, depending on its temperature.

i) at 15°C : $Mg_{(s)} + 2H_2O_{(l)} \rightarrow Mg(OH)_{2(s)} + H_{2(g)}$

→ effervescence of a colourless gas

ii) at 70°C : $Mg_{(s)} + H_2O_{(g)} \rightarrow MgO_{(s)} + H_{2(g)}$

↳ exam expl : $Mg(OH)_2$ is decomposed into MgO at ↑ θ

★ Ca reacts more readily with cold water :

$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$

↳ Ca dissolves
↳ cloudy white suspension of $Ca(OH)_2$
↳ effervescence of a colourless gas

SOLUBILITIES OF G2 SO_4^-

★ solubilities decrease ↓ the group.

$MgSO_4$ — soluble
$CaSO_4$, $SrSO_4$, $BaSO_4$ } insoluble

→ jst rmb $BaSO_4$ is insoluble.

Chapter 11: Group 17

PHYSICAL PROPERTIES

PHYSICAL STATES

F_2 rtp: colourless gas
BP: −188°C
MP: −220°C

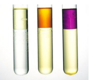
Cl_2 rtp: green gas
BP: −35°C
MP: −101°C

Br_2 rtp: red-brown liquid
(brown as vapour)
BP: 59°C
MP: −7°C

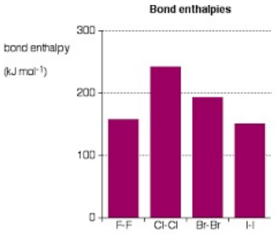
I_2 rtp: purple-black solid
(violet as vapour)
BP: 184°C
MP: 114°C

*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



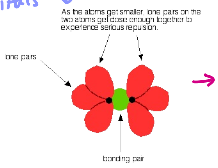
☆ decreases from Cl_2 to I_2

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?

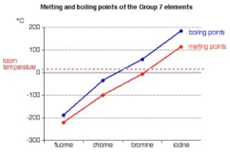
→ atomic rad. of F is too small.

→ 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 bw the bond pair & the nuclei.

MP/BP / VOLATILITIES OF HALOGENS



☆ ↑ down the group

Why? → $n(e^-)$ ↑ w/ ↑ atomic #
→ strength of VdW F ↑
→ ↑ ϟ req. to overcome FoA bw 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
→ ∴ ↓ |FoA| bw p in nucleus & outer e^-
→ shielding effect ↑ down the grp
→ despite ↑NC

→ we can identify the reactivity by observing the displacement reactions.

	Cl_2	Br_2	I_2
+ NaCl	—	—	—
+ NaBr	→ NaCl + Br_2	—	—
+ NaI	→ NaCl + I_2	→ NaBr + I_2	—

REACTIONS WITH H_2 and it's desc.

eq^n …

$H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$ explosive reaction even in cool, dark conditions

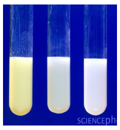
$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ explosive reaction in sunlight

$H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$ reacts slowly upon heating

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ forms an equilibrium upon heating.

TEST FOR HALIDE IONS

☆ reaction between acidified silver nitrate and halide compounds yields a ppt



① AgCl — white ppt
— readily soluble in NH_3
($AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$)

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

③ AgI — pale yellow ppt
— insoluble in NH_3 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/ H_2
→ ↓ bond energy

① $2HI \rightarrow I_2 + H_2$
→ 20% of sample decomposes to release purple fumes, at 430°C
* if a hot glass rod is placed in HI, decomposition immediately occurs

② $2HBr \rightleftharpoons Br_2 + H_2$
→ at 430°C, 10% of HBr decomposes to release red-brown fumes

③ HF & HCl do not decompose up to 1500°C.

REACTION OF HALIDE IONS WITH CONC. H_2SO_4

- Cl^- $NaCl_{(s)} + H_2SO_{4(l)} \rightarrow HCl_{(g)} + NaHSO_{4(s)}$
  — white fumes of HCl produced

Why?
→ conc. H_2SO_4 is not a strong enough oxidising agent to oxidise Cl^- into Cl_2
or Cl^- are not strong enough reducing agent to reduce H_2SO_4

- Br^- $NaBr_{(s)} + H_2SO_{4(l)} \rightarrow HBr_{(g)} + NaHSO_{4(s)}$
  $2HBr_{(g)} + H_2SO_{4(l)} \rightarrow Br_{2(g)} + SO_{2(g)} + 2H_2O_{(l)}$
  — reddish brown of Br_2 produced

Why?
→ Br^- are strong enough reducing agents to reduce H_2SO_4
($2Br^- \rightarrow Br_2 + 2e^-$)
($H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$)

- I^- $NaI_{(s)} + H_2SO_{4(l)} \rightarrow \boxed{HI}_{(g)} + NaHSO_{4(s)}$ all of it will be oxidised to I_2

happen at the same time.
1. $2HI_{(g)} + H_2SO_{4(l)} \rightarrow I_{2(g)} + SO_{2(g)} + 2H_2O_{(l)}$
2. $6HI_{(g)} + H_2SO_{4(l)} \rightarrow 3I_{2(g)} + S_{(s)} + 4H_2O_{(l)}$
3. $8HI_{(g)} + H_2SO_{4(l)} \rightarrow 4I_{2(g)} + H_2S_{(g)} + 4H_2O_{(l)}$

— for all : purple (g) of I_2 observed
— for (2.) : S seen as a yellow ppt
— for (3.) : H_2S has a pungent smell resembling rotten eggs.

Why?
→ I^- are strong enough reducing agents to reduce H_2SO_4.
→ in fact, it can reduce it in three steps:
- $H_2SO_4 \rightarrow SO_2$ (+6 → +4)
- $SO_2 \rightarrow S$ (+4 → 0)
- $S \rightarrow H_2S$ (0 → −2)

* any residue of HI will be contaminated by $S_{(s)}$.

*We can use H_3PO_4 to prepare HI.
Why? → weaker acid than H_2SO_4.

REACTION OF Cl_2 w/ $NaOH_{(aq)}$

☆ Cl_2 reacts differently w/ NaOH depending on the temp.

- with cold $NaOH_{(aq)}$ — 15°C

$$\underset{0}{\boxed{Cl_2}} + 2NaOH \longrightarrow \underset{-1}{NaCl} + \underset{+1}{NaClO} + H_2O$$

- with hot $NaOH_{(aq)}$ — 70°C

$$\underset{0}{\boxed{3Cl_2}} + 6NaOH \longrightarrow \underset{-1}{5NaCl} + \underset{+5}{NaClO_3} + 3H_2O$$

→ more vigorous redox reaction

when Cl_2 reacts with alkalis, they undergo disproportionation.

USES OF HALOGENS AND ITS COMPOUNDS

CHLORINE (AND ITS COMPOUNDS)

1) Chlorination of H_2O

(→) $Cl_{2(aq)} + H_2O_{(l)} \rightarrow HCl_{(aq)} + HClO_{(aq)}$

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

$HClO \rightarrow HCl + [O]$

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)

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(tetrafluroethene), ie teflon

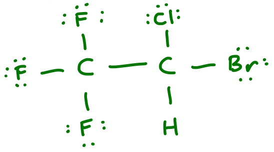
→ commonly used as a non-stick coating on pans.

Why? → C-F bond ϟ is ↑↑

→ so ↑↑ thermal stability.

Br_2, F_2 & Cl_2

→ anesthetics with the chemical name of 2-bromo-2-chloro-1,1,1-trifluroethane (chalothane)



Why? → due to high bond ϟ 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 ⇈ ϟ needed to break it.

→ N_2 does not react with O_2 under atmospheric conditions.

Why? → ↑ bond ϟ in N_2
→ ↑ E_a in reaction
→ endot. reaction

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

→ the ⇈ T & p in car engines provides enough ϟ to break the bonds, & provides E_a for the reaction.

FORMATION OF ACID RAIN

☆ NO_2 is a pollutant as it catalyses the formation of SO_3 from SO_2.

$$SO_{2(g)} + NO_{2(g)} \rightarrow SO_{3(g)} + NO_{(g)}$$

$$NO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow NO_{2(g)}$$

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

$$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$$

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 ↑ water loss and ↑ susceptibility to plant diseases
4) - ↓ 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

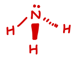
Exists as:

cations (exists in a cation)

① NH_4^+

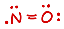
neutral molecule

① NH_3



- polar
- trigonal pyramidal
- 107°

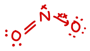
② NO



- polar
- colourless gas
- 180°
- linear

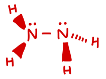
*has a radical: an atom w/ a single unpaired e^-

③ NO_2



- polar
- bent, 117°

④ N_2H_4 (hydrazine)



- fossil fuels for rockets
- trigonal pyramidal at N
- 107°

anions

① NO_3^-

② NO_2^-

NITROGEN DIOXIDE

☆ NO_2 naturally occurs.

How?

① Lightning provides the Ea for the reaction bw N_2 & O_2

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$$

② NO will further oxidise into NO_2

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

③ NO_2 dissolves in water to form HNO_3.

$$2NO_{2(g)} + H_2O_{(l)} + \tfrac{1}{2}O_{2(g)} \rightarrow 2HNO_{3(aq)}$$

☆ NO_2 is also created via man-made sources.

① Nitrogen oxides are formed from fuel combustion in car engines under ⇈ p, T

② Produced in power stations & furnaces.

NH_3 & NH_4^+ COMPOUNDS

☆ NH_3 is manufactured via the Haber process:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

→ NH_3 is a weak alkali in (aq):

$$\underbrace{NH_3 + H_2O \rightleftharpoons NH_4^+}_{\text{p acceptor}} + OH^-$$

☆ NH_4^+ compounds can easily be identified by heating it with a stronger alkali (ie 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)

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

☆ NH_3 uses:

1) involved in the production of nitrogenous fertilisers through reactions with acids.

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

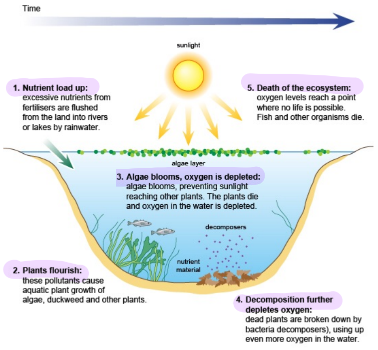
$$3NH_3 + H_3PO_4 \rightarrow (NH_4)_2PO_4$$

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.

☆ 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.
   → 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

Main constituents of exhaust fumes.

☆ CARBON MONOXIDE

→ formed from incomplete combustion of fuels
  → exposure to CO reduces the absorping ability of red blood cells
  → as haemoglobin has higher affinity to CO compared to O_2.

☆ SULFUR DIOXIDE

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

☆ NITROGEN DIOXIDE

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

☆ UNBURNT HYDROCARBONS

→ global dimming
  → gradual reduction in the amt of global direct irradiance at the Earth's surface
  → due to ↑ presence of aerosol ·p in atm, caused by pollution / dust / volcanic eruptions
  → that reflect sunlight back into space.

→ photochemical smog
  → smog produced when UV reacts w/ nitrogen oxides in the atmosphere.

→ the 3 main pollutants that are present in car engine exhaust gases are SO_2, CO, & NO_2.

can be NO, or oxides of N.

→ exhaust fumes also contain $H_2O_{(g)}$ & CO_2.
Why? → common products formed through fossil fuel combustion.

☆ N_2 occupies the ⇈ prop. in exhaust fumes.
→ due to unreactivity.

CATALYTIC CONVERTERS

→ used to remove the 3 main pollutants.
→ contains:

① Pt, Pd
$$\begin{cases} 2CO + O_2 \rightarrow 2CO_2 \\ C_xH_y + (x+\frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \end{cases}$$

② Rh — $2CO + 2NO \rightarrow 2CO_2 + N_2$

☆ catalytic converters are not perfect, however:

→ toxic gases not removed until the catalytic converter is warmed up
→ 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 : NO

→ just rmb bc

N
S
C
↓ decreasing reactivity.

Chapter 13:
Intro to Organic Chemistry

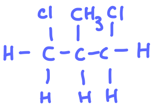
UTILISING STRUCTURAL FORMULAS

↳ shows how the atoms are bonded to each carbon atom in the 

* L → R

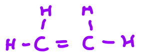
* show C=C bonds in the formula.

examples

1) 

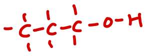
*brackets indicate we are "substituting" groups into the formula.

⇒ $CH_2(Cl)CHC(CH_3)CH_2(Cl)$

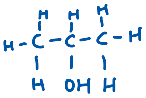
2) 

⇒ $H_2C=CH_2$.

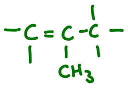
*only for "C=C" do we have to show.

3) propanol 

⇒ $CH_3CH_2CH_2OH$

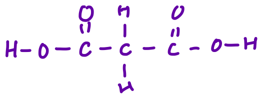
4) propan-2-ol 

⇒ $CH_3CH(OH)CH_3$

5) but-2-ene 

⇒ $H_2C=C(CH_3)CH_3$

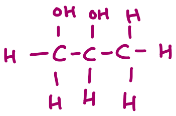
6) ethanoic acid CH_3COOH

7) propane dioic acid : 

di – two

oic acid – carboxylic acid

⇒ $HOOCCH_2COOH$

8) propan-1,2-diol 

⇒ $CH_2(OH)CH(OH)CH_3$

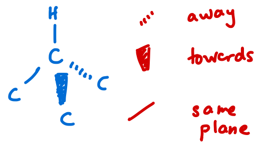
DISPLAYED FORMULAE

→ shows both the relative placing of atoms & the number of bonds between them.

*ALL bonds shown!

STEREOCHEMICAL FORMULAE

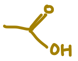
→ shows the shape of a molecule as well as the # of atoms of each element & the bonds.

eg 

SKELETAL FORMULAE

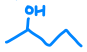
→ a simplified representation of an organic structure

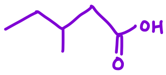
→ the displayed formula — BUT! ALL C atoms & C–H bonds ONLY are omitted.

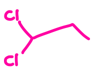
ethanoic acid : 

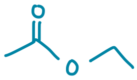
① butane : 

② 2,3-dimethylhexane : 

③ pentan-2-ol 

④ 3-methyl pentanoic acid 

⑤ 1,1-dichloropropane 

⑥ ethyl ethanoate 

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 ↑
5) similar / like chemical properties.

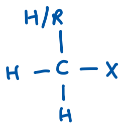
HS	FG
alkane →	"C–C"
alkene →	"C=C"
halogenoalkane →	primary / secondary / tertiary halogenalkane
alcohol →	primary / secondary / tertiary alcohol
carboxylic acid →	carboxylic acid
aldehyde →	aldehyde
ketone →	ketone

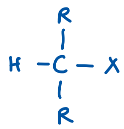
FUNCTIONAL GROUP

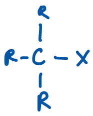
→ an atom / groups of atoms in an organic molecule that

*determine the characteristic reactions of a homologous series.

"ORDER" OF A MOLECULE

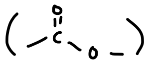
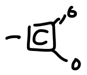
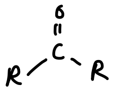
☆ primary: 

☆ secondary: 

☆ tertiary : 

R : alkyl chains (CH_3, CH_2CH_3 etc)

X : functional group (–OH, –COOH etc)

functional group	characteristic	shape / bond ∠	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? → H bond bw 
6) carboxylic acids	contains -COOH (suffix = -oic acid)	trigonal planar / 120° (at $\overset{O}{\overset{\|}{\boxed{C}}}-O-H$)	
7) esters 	formed by reaction bw alcohol & carboxylic acid.	trigonal planar / 120° (at )	
8) aldehydes	contains $(H/_{R}-\overset{O}{\overset{\|}{C}}-H)$ (suffix : -al)	trigonal planar / 120°	
9) ketones	contains  (suffix : -one)	trigonal planar / 120°	• not necessarily same R • first member is propanone • for pentanone and up, you have to indicate where the "-one" is.

NAMING COMPOUNDS

$\underbrace{\text{3-chloro}}_{\text{prefix}}\underbrace{\text{prop}}_{\text{stem}}\underbrace{\text{an}}_{\text{stem suffix}}\underbrace{\text{al}}_{\text{suffix}}$

STEM

→ # of atoms in **LONGEST** carbon chain.

*not necessarily the most "visible" one.

1 → meth-
2 → eth-
3 → prop-
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-
$CH_2CH_2CH_3$ → propyl-
Cl → chloro
Br → bromo
-OH → hydroxy

RULES!

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.

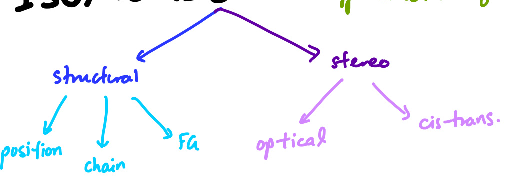
④ ☆ Priorities in parent chain numbering:

Prefix → stem-suffix → suffix
(↓↓) (↑↑)

	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



CHAIN

↳ isomers differ in their C skeleton.

eg

POSITION

↳ different positions of FG

↳ same C skeleton, same homologous series, same FGs.

eg

FUNCTIONAL GROUP

↳ isomers have different FGs

↳ different chemical & physical properties.

eg

(aldehyde)

(ketone)

OPTICAL

→ exist as 2 non-superimposable images

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

→ characteristics of chiral ^:
1) optically active
2) displays a pair of non-superimposable optical isomers / enantiomers.

→ n chiral centres ⇒ 2^n optical isomers

→ optical isomers have like physical & chemical properties.

cis has ↑BP than trans.

→ cis is polar, trans isn't

→ cis has perm. dip-dip F & VdW ; trans only VdW

trans has ↑MP than cis.

→ cis have "U" shape, trans have straighter shape

→ ∴ better packing / arrangement.

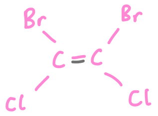
→ ∴ stronger IMF.

GEOMETRICAL (CIS-TRANS)

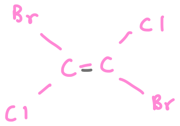
↳ arises due to restricted rotation from presence of 2x bonds

★ each C atom on either end of the 2x bond must be bonded to 2 non-identical FGs.

(2 FGs)

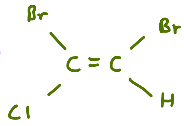


cis

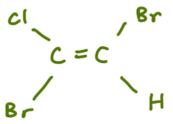


trans

(3 FGs)

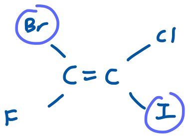


cis

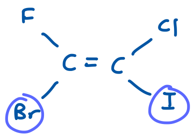


trans

(4 FGs)



trans



cis

★ for 4 FGs: analyse p #.
→ identify ↑↑ FG on LHS, and RHS.

★ Racemic mixture:

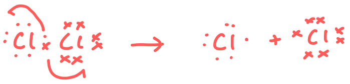
→ mixture that contains = amts of each optical isomer

→ optically inactive.

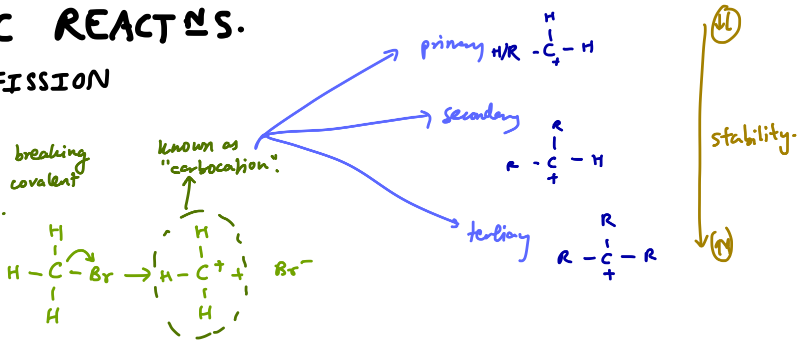
TYPES OF ORGANIC REACT$^{\underline{N}}$S.

HOMO vs HETEROLYTIC FISSION

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



HETEROLYTIC → uneven breaking of a covalent bond.



why?

1) alkyl are e⁻ donating groups (+ve inductive effect)
2) ∴ ↑ # of alkyl grps attached, ↓ Qρ
3) ↑ stability.

NUCLEOPHILE v ELECTROPHILE

NUCLEOPHILE ↓ donator of a pair of e⁻

↳ ☆ not all nucleophiles are -vely charged!

eg OH^-, CN^-, NH_3

ELECTROPHILE ↓ receiver / acceptor of a pair of e⁻.

↳ strongly attracted to alkenes & benzenes.

eg NO_2^+, Cl_2, Br_2.

Chapter 14: Alkanes

→ general formula: C_nH_{2n+2}

TRENDS IN PHYSICAL PROPERTIES

1) BP in aliphatic alkanes ↑, 目↓
   - ↳ # of VdW F ↑
   - ↳ as # of e^- ↑

2) Non-polar
   - ↳ soluble in non-polar solvents (eg CCl_4)
   - ↳ insoluble in polar solvents (eg H_2O)

ALKANE REACTIONS

COMBUSTION

O_2 supply	→ reaction
excess	$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow \underline{nCO_2} + (n+1)H_2O$
ltd	$C_nH_{2n+2} + \left(\frac{2n+1}{2}\right)O_2 \rightarrow \underline{nCO} + (n+1)H_2O$
v. ltd	$C_nH_{2n+2} + \left(\frac{n+1}{2}\right)O_2 \rightarrow \underline{nC} + (n+1)H_2O$

☆ recap: consequences of CO:

1) global dimming
2) photochemical smog

FREE-RADICAL SUBST<u>N</u>

💡 Alkanes undergo subst<u>n</u> reactions w/ halogens.

eg $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

* it is a redox react<u>n</u>!

Mechanism

① Initiation:

<u>Homolytic fission</u> of <u>Cl-Cl bond</u> from <u>UV light</u> generates <u>2 free radicals</u>. $Cl_2 \rightarrow 2Cl\cdot$

② Propagation:

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

eg $CH_3CH_3 + Cl\cdot \rightarrow CH_3CH_2\cdot + HCl$

$CH_3CH_2\cdot + Cl{-}Cl \rightarrow CH_3CH_2Cl + Cl\cdot$

⋮

③ Termination

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

eg $H\cdot + \cdot H \rightarrow H_2$

$CH_3\cdot + Cl\cdot \rightarrow CH_3Cl$

⋮

CHEMICAL PROPERTIES

→ generally unreactive.

Why?

1) C-H bond ϟ ↑↑²
2) ↓↓² ϟ-tivity diff. b/w C & H
   - ↳ non-polar bond
   - ↳ too charge neutral to attract nucleophile or electrophile.

CRACKING

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

eg $C_{16}H_{34} \xrightarrow{☆} \boxed{C_8H_{18} +}\ C_8H_{16}$

(diesel) (gasoline)

- types:

1) thermal — ↑↑ 🌡, ↑↑ P
2) catalytic — ↑↑ 🌡, suitable catalyst (SiO_2, Al_2O_3, Pt, zeolite, pumice, ceramic)

- Mechanism:

① Initiation

Two free rad. are formed through homolytic fission.

eg $CH_3CH_3 \rightarrow 2CH_3\cdot$

② Propagation

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

$CH_3\cdot + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2\cdot$

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

eg $CH_3CH_2\cdot \rightarrow CH_2{=}CH_2 + H\cdot$

③ Termination

i) Recombination: two radicals combine to form 1 larger ^

eg $CH_3\cdot + CH_3CH_2\cdot \rightarrow CH_3CH_2CH_3$

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

eg $CH_3\cdot + CH_3CH_2\cdot \rightarrow CH_4 + CH_2{=}CH_2$

SOURCES OF ALKANES

💡 alkanes can be harvested from <u>crude oil</u>.

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

two methods:

1) (physical) fractional distillation
   → the sep. of a mixture into its fractions by <u>BP</u>.
2) (chemical) cracking

- applications:

1) fulfill ↑↑ demand for gasoline frac.
2) cracking yields ↓↓BP alkenes, which are <u>reactive</u>.
   ↳ hence these can be converted into a variety of compounds, eg plastics.

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? → 2 fewer e^- (than alkane)
→ ∴ ↓VdW F

SOLUBILITY

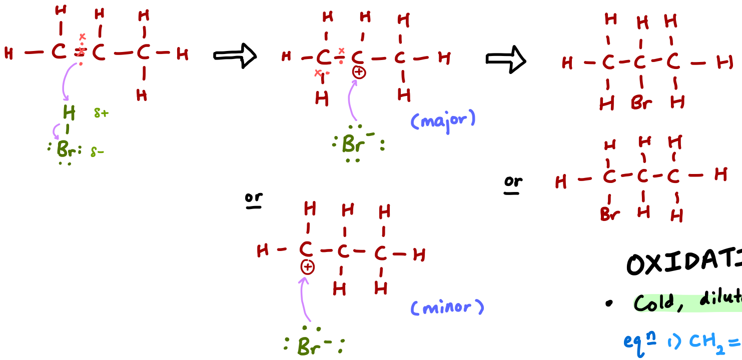
→ non-polar.
- soluble in non-polar solvents (eg CCl_4)
- insoluble in polar solvents (eg H_2O)

ELECTROPHILIC ADDITION OF HX (aq)

conditions room temp
reagent conc. sol. of HX
product halogenoalkanes

ex. eqⁿs 1) $CH_3CH=CH_2 + HBr \rightarrow CH_3CH_2CH_2Br$ (minor)
$\rightarrow CH_3CHBrCH_3$ (major)

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.
↳ addition rctⁿ where a π bond is broken and converted into 2 σ bonds.

→ C=C rich in e^-
⇒ attract electrophiles.

ADDITION OF H_2 (g)

conditions high temp, Ni catalyst or rtp, Pt catalyst
reagent H_2
product alkane

ex. eqⁿs 1) $CH_2=CH_2 + H_2 \rightarrow CH_3CH_3$

2)


ℹ Ni is preferred over Pt, despite needing ↑T to function.
Why? → Ni ↓$ & ↑abund. than Pt
→ so ↑↑ Ni can be used.
→ even if some Ni poisoned, enough Ni remains for reaction catalysis.

ADDITION OF H_2O (g)

conditions 330°C, 6MPa, H_3PO_4 catalyst
reagent H_2O (g)
product alcohols

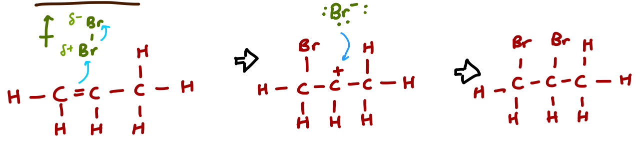
ex. eqⁿ $CH_2=CH_2 + H_2O \rightarrow CH_3CH_2OH$

ELECTROPHILIC ADDITION OF HALOGENS (Br_2)

- Br_2 in organic solvent, eg CCl_4

conditions room temp
product halogenoalkane
eqⁿ $CH_2=CH_2 + Br_2 \rightarrow BrCH_2CH_2Br$

mechanism



- Br_2 in H_2O, ie bromine water

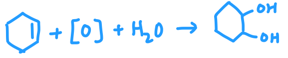
conditions room temp
products halogenoalkane & alcohol
→ specialised test for alkenes.

OXIDATION WITH ACIDIFIED $KMnO_4$ (aq)

↱ oxidising agent.

- Cold, dilute $KMnO_4$

eqⁿ 1) $CH_2=CH_2 + H_2O + [O] \rightarrow HOCH_2CH_2OH$

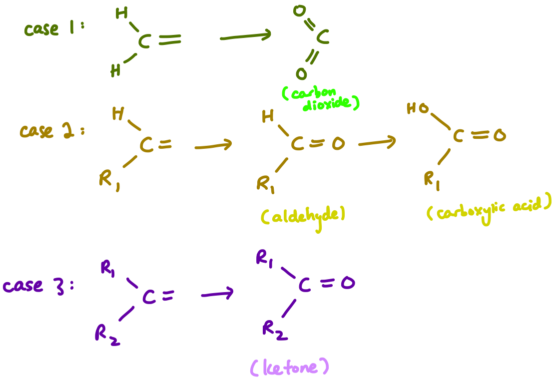
2)


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$^{\underline{n}}$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.

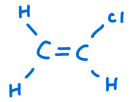
conditions <u>either</u> ↑↑^{2} P
<u>or</u> Ziegler-Natta catalyst

eq$^{\underline{n}}$ $nC_2H_4 \rightarrow -[C_2H_4]-_n$

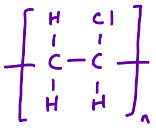
Examples of addition polymers

① PVC (poly (chloroethene))

monomer



polymer



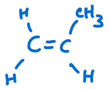
② Poly (ethene) : high vs low density

high
- very little branching along HC chains
- ↑↑ MP & strength (↑↑ VdW. ↑↑SA)
- ↑↑ density

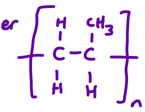
low
- high # of branch chains
- ↓↓ MP & strength (↓↓ VdW, ↓↓ SA)
- ↓↓ density

③ Poly (propene)

monomer



polymer



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

uses
1) meshes for medical uses

Disadvantages of using poly (alkene) plastics

① Disposal

↳ poly (alkenes) exist as large ^

↳ 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 <u>CO</u> (incomplete combustion)

↳ for CN^- containing polymers, <u>HCN</u> is released

↳ for Cl^- containing polymers. <u>HCl</u> is released

↳ HCl is thermally stable.

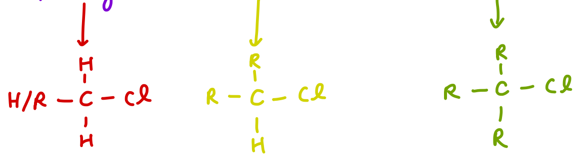
Chapter 16: Halogenoalkenes

Halogenoalkanes are halogen derivatives of alkanes.

ex : CH_3CH_2Cl , $CH_3CHBrCH_3$

Classification

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



Physical properties

☆ Their BP ↑ than alkenes & alkanes

why? → presence of pdd F & tdid F
perm. dip. dip — temp dip. induced dip. / VdW

→ alkenes & alkanes only have weak VdWF

CHEMICAL RCT^{N}S OF HALOGENOALKANES

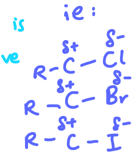
Most rct^{n}s of halogenoalkanes are nucleophilic subst^{n}s.

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

Why does this happen?

→ bc carbon-halogen bond is polar, as halogen is ↑ δ-ve than C.

ie :



☆ Heating under reflux.

Why?

1) allows & to be kept ⊟ at BP, to ↑ rate

2) prevent evaporation of volatile organic compounds

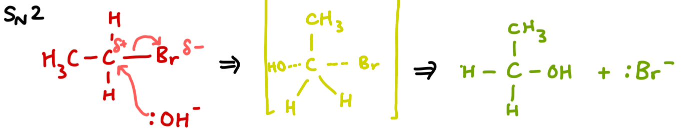
3) ensure full rct^{n} bw halogenoalkanes & reactants.

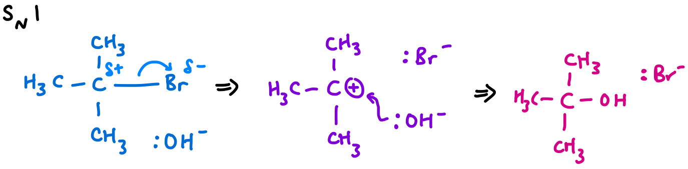
NUCLEOPHILIC SUBST^{N} W/ OH^-.

reagent	NaOH or KOH (aq)
conditions	heat under reflux
product	alcohol

ex eq^{n} $CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$

Mechanism of nuc subst^{n} w/ OH^-





Rates of nucleophilic subst^{n}

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

⇒ any halide ions formed will form ppt.

decreasing rate ↓	ppt observed...
CH_3CH_2I	immediately
CH_3CH_2Br	after 2 mins
CH_3CH_2Cl	after 10 mins
CH_3CH_2F	after a very long time

☆ a similar rct^{n} to nuc subst^{n} can be done by adding hot water.

↳ hydrolysis.

eg $CH_3CH_2Br + H_2O \rightarrow CH_3CH_2OH + HBr$

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

*

S_N2	vs	S_N1
- 1° & 2°		- 2° & 3°
- 1 step (transition)		- 2 step (intermediate)

ELIMINATION

reagent	ethanolic NaOH or KOH (dissolved in ethanol)
condition	heat under reflux
product	alkene

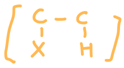
ex eq^{n} $CH_3CHBrCH_2CH_3 + OH^- \rightarrow CH_3CH=CHCH_3 + Br^-$

☆ can elimination be done?

req :

↳ neighbouring C w/ H.

ie

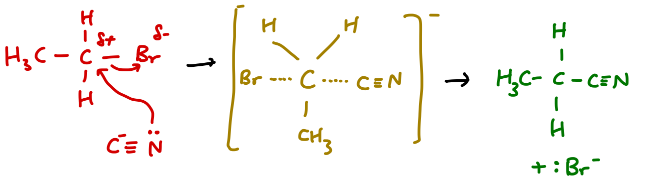


NUCLEOPHILIC SUBST^{N} W/ CN^- IONS

reagent	ethanolic CN^- (KCN)
conditions	heat under reflux
product	nitriles ($C\equiv N$)

ex eq^{n} : $CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$

mechanism :

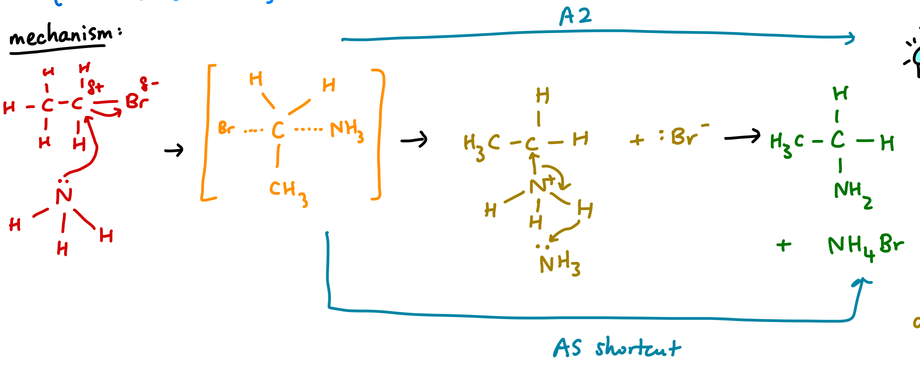


NUCLEOPHILIC SUBST^{N} W/ NH_3

reagent	ethanolic NH_3
condition	heat in sealed tube
product	amines ($-NH_2$)

ex eq^{n} $CH_3CH_2Br + NH_3 \rightarrow CH_3CHNH_2COOH + HCl$

mechanism:



uses of nucl. subst^{n} 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.

① acidic hydrolysis

reagent	HCl (aq)
conditions	heat & reflux
rct^{n}	$CH_3CH_2CN + HCl + 2H_2O \rightarrow CH_3CH_2COOH + NH_4Cl$

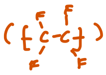
② alkaline hydrolysis

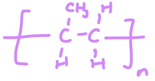
reagent	NaOH (aq)
conditions	heat under reflux
ex eq^{n}s	$CH_3CH_2CN + NaOH + H_2O \rightarrow CH_3CH_2COONa + NH_3$ (sodium ethanoate) $CH_3CH_2COONa + HCl \rightarrow CH_3CH_2COOH + NaCl$

HALOGENOALKANES IN OUR WORLD

applications of halogenoalkanes:

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

2) teflon ( $\left(\left[\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}\right]\right)$) as non-stick lining of pans

3) PVC used in food packaging (replacement: polypropylene, or  $\left[\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\right]_n$)

4) CCl_4 as solvents

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

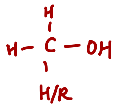
Chapter 17: Alcohols, Carboxylic Acids and Esters

ALCOHOLS

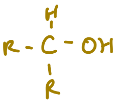
Alcohols contain one or more **-OH** groups.

⇒ gen formula: $C_nH_{2n+1}OH$

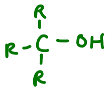
Classification


$H-\underset{H/R}{\overset{H}{C}}-OH$

primary (1°)


$R-\underset{R}{\overset{H}{C}}-OH$

secondary (2°)


$R-\underset{R}{\overset{R}{C}}-OH$

tertiary (3°)

PHYSICAL PROPERTIES

① Less volatile than alkenes or alkanes

why? → presence of H bonds in ^

② H_2O solubility

⇒ solubility ↓ as C chain ↑

why? → non-polarity ↑

→ H bond less significant.

CHEMICAL REACTIONS

① Combustion

(excess O_2) $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

→ clean blue flame seen

(ltd O_2) $CH_3CH_2OH + O_2 \rightarrow 2C + 3H_2O$

→ yellow flame

→ soot produced.

② Reaction with Na

Although alcohol is neutral, it can react with metals.

$CH_3CH_2OH + Na \rightarrow CH_3CH_2ONa + \frac{1}{2}H_2$

sodium ethanoate

- white solid

⇒ a redox rct^n^

③ Elimination

reagent : H_2SO_4 / H_3PO_4 / Al_2O_3 → acts as oxidising / dehydrating agent

conditions : heat (170°C)

product : alkene & water

☆ to occur: neighbouring C must have H present.

*elimination w/ 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

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

$CH_3CH_2OH + HCl \rightarrow CH_3CH_2Cl + H_2O$

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

iii) Phosphorous halides

a) PCl_5

reagent : PCl_5 (solid)

condition : rtp

$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + \boxed{HCl} + \boxed{POCl_3}$

b) PCl_3 / Br_3 / I_3

⇒ condition: (Cl_3) heat

(Br_3/I_3) warm

$3CH_3CH_2OH + PCl_3 \rightarrow 3CH_3CH_2Cl + \boxed{H_3PO_3}$.

iv) $SOCl_2$ (best one)

⇒ condition: warm at rtp

$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + \boxed{SO_2}$

Why is this the best?

⇒ byproducts are gaseous

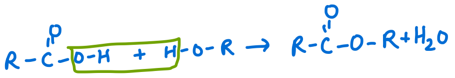
⇒ so distillation not req to obtain halogenoalkane.

⑤ Esterification

reagent : alcohol & carboxylic acid

condition : heat under reflux w/ conc H_2SO_4

product : ester + H_2O


$R-\overset{O}{\overset{\|}{C}}-\boxed{O-H + H}-O-R \rightarrow R-\overset{O}{\overset{\|}{C}}-O-R + H_2O$

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.

☆ Since tertiary alcohols cannot be oxidised,

⇒ this is a test that can distinguish between 3° & (1°, 2°) alcohols.

⑦ Triiodomethane reaction (iodoform)

This test specifically tests for the presence of $CH_3CH_2(OH)-$ in the compound.

⇒ oxidation reaction

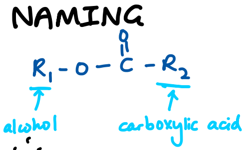
reagent : alkaline I_2

condition : warm

product : CHI_3 (yellow ppt)

ESTERS

NAMING



$R_1-O-C(=O)-R_2$

Ester name = _____yl ______oate.
(alcohol) (acid)

PHYSICAL PROPERTIES

① Partially soluble in water

② Liquid at rtp

③ Fruity aroma

☆ applications IRL:
- artificial flavourings
- perfumes
- nail varnish remover
- solvent

CHEMICAL REACTIONS

① Hydrolysis

☆ key: water.

a) Acidic

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

$CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + HOCH_3$

b) Alkaline

reagent: $NaOH$ (dil)
conditions: heat under reflux
product: salt + alcohol
↓
acid

$CH_3COOCH_3 + NaOH \rightarrow CH_3COONa + HOCH_3$

$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$

CARBOXYLIC ACIDS

Carboxylic contain **–COOH** in their ^.

PHYSICAL PROPERTIES

① Simple aliphatic acids exist as **(l)** in rtp.

② High BP & solubility
⇒ 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

$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$

$CH_3CHO + [O] \rightarrow CH_3COOH$

② Hydrolysis of nitriles (–C≡N)

reagents: **HCl** (dil)
conditions: heat under reflux

$CH_3CH_2CN + 2H_2O \rightarrow CH_3CH_2COOH + NH_3$

$NH_3 + HCl \rightarrow NH_4Cl$.

CHEMICAL REACTIONS

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

However, they also undergo a few more:

① Reduction

reagent: $LiAlH_4$ in dry ether
condition: rtp
products: alcohols

$CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$.

② Substitution with halides

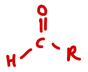
(see alcohols) → PCl_5
→ PCl_3 / Br_3 / I_3
→ $SOCl_2$

⇒ product: acyl chloride

$C-C(=O)Cl$

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 perm. dip-dip F bw 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!

CHEMICAL REACTIONS

REDUCTION

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

⇒ $LiAlH_4$ in dry ether, or → rtp

⇒ $NaBH_4$ in alkaline & (aq), or → warm

⇒ H_2 w/ Ni or Pt catalyst. → ☆ if excess: both C=C broken & carbonyl reduced.

if limited: only C=C broken.

$CH_3CH_2CHO + 2[H] \rightarrow CH_3CH_2CH_2OH$

$CH_3COCH_3 + 2[H] \rightarrow CH_3CH(OH)CH_3$

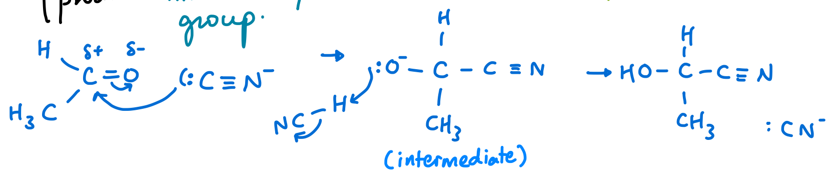
☆ NUCLEOPHILIC ADDITION W/ HCN

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 → why? ⇒ HCN only stable under this temp

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

⇒ condition: rtp

⇒ result: orange ppt

note:
1) condensation process
2) applicable for both aldehydes & ketones

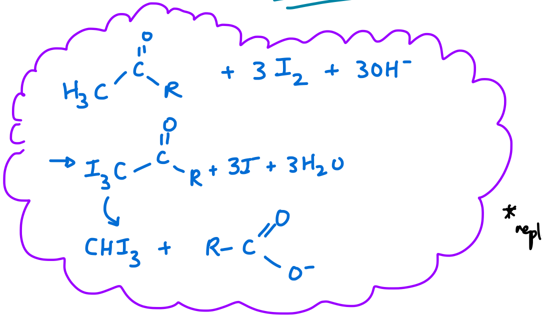
② Tri-iodomethane (iodoform) reaction

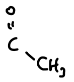
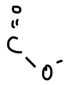
The iodoform reaction tests specifically for the group CH_3CO-.

reagent: alkaline solution of I_2

condition: warm

product: CHI_3 (yellow ppt)



*replace the  with 

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: $Cu^{2+} \rightarrow Cu^{+}$

② Tollen's reagent

⇒ $AgNO_3 + NaOH + NH_3$
(ie alkaline $AgNO_3$)

idea: $Ag^{+} \rightarrow Ag$

⇒ condition: warm

⇒ observation: Silver ppt

③ via conventional oxidising agents
(ie $K_2Cr_2O_7$ & $KMnO_4$)

⇒ condition: heat

IR SPECTROSCOPY

IR Spectroscopy is a method used to determine the <u>functional groups</u> <u>present</u> in a compound.

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.

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

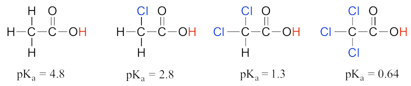
Chapter 26: Carboxylic Acids and Their Derivatives

ACIDITY OF CARBOXYLIC ACIDS

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

① The number of e^- withdrawing groups

⇒ ↑ # of grps, ↑ acidity.



(↑pKa, ↓acidity)

Why?

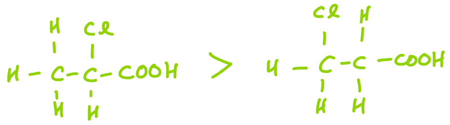
→ e^- withdrawing grp weakens O–H bond

→ it also stabilises the carboxylate ion ($R-\overset{O}{\overset{\|}{C}}-O^-$) by allowing delocalisation of e^- around $-COO^-$ group.

☆ basically, it depolarises the $C-O^-$ bond, making it less suspectible to attacks by H^+.

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

⇒ ↑ dist, ↓ acidity

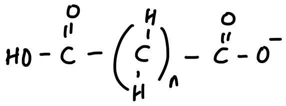


$$H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-COOH > H-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-COOH$$

Why? – the C–O bond is less polarised

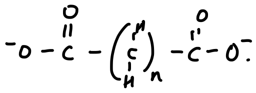
- because influence of e^--withdrawing group is less.

Also,



$$HO-\overset{O}{\overset{\|}{C}}-\left(\overset{H}{\underset{H}{C}}\right)_n-\overset{O}{\overset{\|}{C}}-O^-$$

is more stable than



$$^-O-\overset{O}{\overset{\|}{C}}-\left(\overset{H}{\underset{H}{C}}\right)_n-\overset{O}{\overset{\|}{C}}-O^-.$$

Why? → ϟ-static attr. b/w H+ & −1 is less than ϟ-static attr. b/w H+ & −2.

OXIDATION OF SELECTED CARBOXYLIC ACIDS

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

METHANOIC ACID — HCOOH

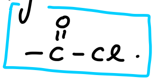
⇒ $HCOOH + [O] \rightarrow CO_2 + H_2O$

ETHANEDIOIC ACID — HOOCCOOH

⇒ $HOOCCOOH + [O] \rightarrow 2CO_2 + H_2O$

ACYL CHLORIDES

Acyl chlorides have the FG



$$\boxed{-\overset{O}{\overset{\|}{C}}-Cl\,.}$$

FORMATION OF ACYL CHLORIDES

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)
(rtp) $RCOOH + PCl_5 \rightarrow RCOCl + \underline{HCl} + \underline{POCl_3}$

② PCl_3
(heat) $3RCOOH + PCl_3 \rightarrow 3RCOCl + \underline{H_3PO_3}$

③ $SOCl_2$
(rtp) $RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$

NAMING ACYL CHLORIDES

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

eg ethanoic acid → ethanoyl chloride
propanoic acid → propanoyl chloride etc.

PHYSICAL PROPERTIES

(a) Colourless (l)
(b) id-id F & perm.d-d F exist b/w ^
(c) ↑ BP than halogenoalkanes.

Why? → ↑ |perm. d-d F|.
∵ C connected to 2 δ-ve grps.

RELATIVE EASE OF HYDROLYSIS OF ACYL, ALKYL & ARYL CHLORIDES

R-COCl R-Cl

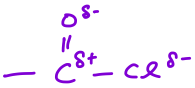
Acyl chlorides > alkyl chlorides > aryl chlorides.

Why?
- C attached to 2 δ-ve atoms
- so ↑ δ^+ on C
- so ↑ 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 ↑ difficulty to hydrolyse.

CHEMICAL REACTIONS

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



$$-\overset{O^{\delta-}}{\overset{\|}{C^{\delta+}}}-Cl^{\delta-}$$

⇒ hence, it is susceptible to nucleophilic attack, in which it undergoes the following general reaction,

$$RCOCl + HZ \rightarrow RCOZ + HCl.$$

where Z is a nucleophile.

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

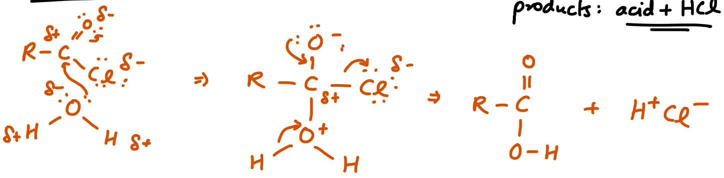
① Hydrolysis of Acyl Chlorides

Recall that hydrolysis describes the "breaking down" of a ^ by H_2O.

(rtp) $RCOCl_{(l)} + H_2O_{(l)} \rightarrow \underline{\underline{RCOOH}}_{(aq)} + \underline{\underline{HCl}}_{(g)}$

products: $\underline{\underline{\text{acid} + HCl}}$.

Mechanism



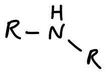
Chapter 27:
Organic Nitrogen Compounds

AMINES

Functional group:

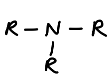
⇒ 1° (primary): $R-NH_2$

2° (secondary):



$R-\overset{H}{N}-R$

3° (tertiary):



$R-\underset{R}{N}-R$

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.
eg methanamine

CH_3-NH_2	methan amine
$CH_2CH_3-NH_2$	ethan amine
$(CH_3)_2NH$	N-methyl methanamine
$CH_3CH_2NHCH_3$	N-methyl ethanamine
$(CH_3)_3N$	N,N,N- trimethanamine

(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)

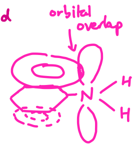
Hence:

basicity of alkylamine > basicity of ammonia > basicity of phenylamine

Why? - alkyl group is e⁻ donating
- so LP is "pushed away" and hence is more "available" to H^+

$\overset{\delta+}{R}-\overset{\delta-}{\ddot{N}H_2}$

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 ↑ → BP ↑ (because id-id F ↑)
when chain length ↑ → solubility ↓ (due to H bonding bw H_2O ^ & amine ^)

*$1°_{BP} > 2°_{BP} > 3°_{BP}$.

less polar than 1°.

only perm. dip-dip F. no H bonds.

*amines have ↓BP than alcohols.

Why? → O more electronegative than N
→ so strength of H bonds ↑↑ in alcohols.

FORMATION OF AMINES

NUCLEOPHILIC SUBSTN OF HALOGENOALKANES W/ NH3 (AS)

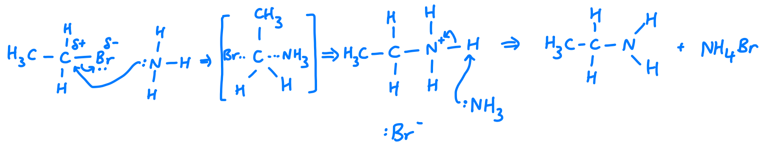
Reagent : ethanolic NH_3
Condition : heat in sealed tube

Note: we add excess NH_3 to prevent the formation of 2°/3° amines.

(halogenoalkanes can react w/ amines)

example: $CH_3Cl + NH_3 \longrightarrow CH_3NH_2 + HCl$
$(NH_3 + HCl \longrightarrow \underline{NH_4Cl})$

mechanism:



NUCLEOPHILIC SUBSTN OF HALOGENOALKANES W/ CN⁻, FOLLOWED BY REDUCTION.

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

(2nd step) reagent: $LiAlH_4$ in dry ether
or H_2 over Ni catalyst (at 140°C)

example:

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

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

CHEMICAL REACTIONS

REACTION W/ H2O

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

e.g.

$CH_3NH_2 + H_2O \rightleftharpoons \underbrace{CH_3NH_3^+}_{\text{methylammonium ion}} + OH^-$

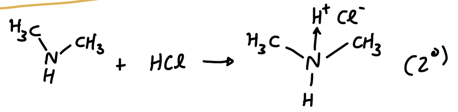
(this shows it is a weak base)

NEUTRALISATION OF ACIDS

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

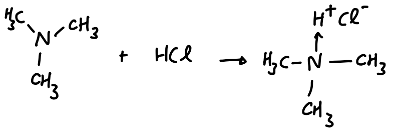
e.g.¹ $CH_3NH_2 + HCl \longrightarrow \underbrace{CH_3NH_3^+Cl^-}_{\text{methylammonium chloride}}$ (1°)

e.g.²



(2°)

e.g.³

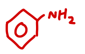


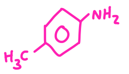
(3°)

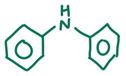
PHENYLAMINES

Phenylamines are compounds with a benzene ring containing a $-NH_2$ group.

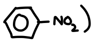
NOMENCLATURE


phenyl amine


4-methyl phenylamine


diphenylamine

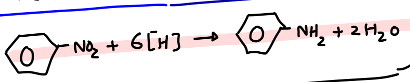
FORMATION OF PHENYLAMINES

Phenylamines form through reduction of nitrobenzene compounds. ()

reagent : Sn + conc. HCl. followed by $NaOH^-$

condition : heat

example:



$$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$$

DIAZOTISATION

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

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

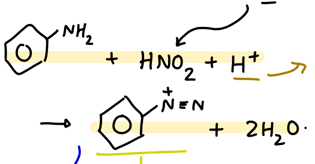
Step 1: Creation of the benzenediazonium ion

reagents : $NaNO_2$, HCl

condition : temp. < 10°C.

why?
↳ $NaNO_2$ is unstable.
↳ so prepared in situ.

⇒ $NaNO_2 + HCl \rightarrow NaCl + HNO_2$.



$$C_6H_5NH_2 + HNO_2 + H^+ \rightarrow C_6H_5\overset{+}{N}\equiv N + 2H_2O$$

acidic solution!

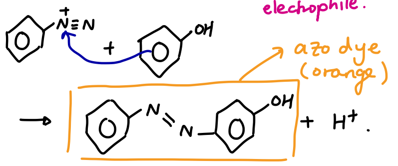
benzenediazonium ion.

Step 2: Coupling reaction

reagent : phenol in alkaline condition.

condition: $NaOH_{(aq)}$

example:



* the ion can act as an electrophile.

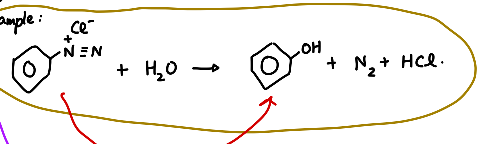
* the ion will be substituted onto the 4th position of the phenol. If it is occupied, it will occupy the 2nd or 6th pos instead.

Reaction of diazonium salts

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

reagent : H_2O at temp. > 60°C. ("boil in hot water")

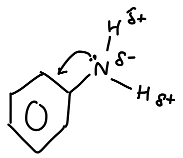
example:



$$C_6H_5\overset{+}{N}\equiv N\,Cl^- + H_2O \rightarrow C_6H_5OH + N_2 + HCl.$$

CHEMICAL REACTIONS

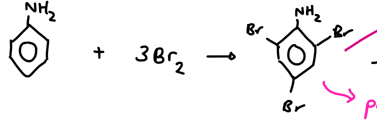
Since $-NH_2$ is an electron-donating group, the e^- density of the benzene ring increases, making it more susceptible to electrophilic attack.



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

↳ hence, it can undergo electrophilic substitution.

REACTION WITH Br_2 (aq)

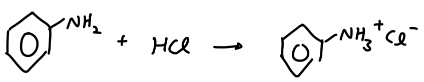


$$C_6H_5NH_2 + 3Br_2 \rightarrow C_6H_2Br_3NH_2 + 3HBr$$

while ppt.

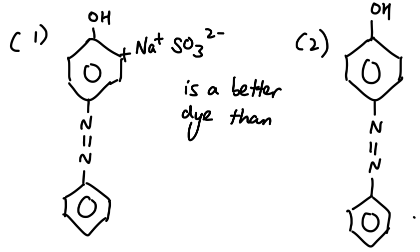
pos 2,4,6 (refer to data booklet).

REACTION WITH HCl



$$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^+Cl^-$$

Take note:



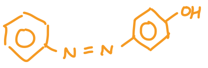
(1) is a better dye than (2).

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

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.

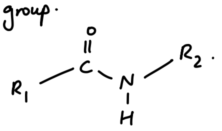
$$R\text{-}NH_2 + HNO_2 \rightarrow R\text{-}OH + N_2 + H_2O$$

☆ this is also a test to differentiate 1°, 2° & 3° amines.

(1° : N_2 produced
2° : coloured salt
3° : solution (salt is soluble))

AMIDES

Amides have the functional group.



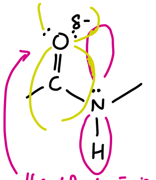
PHYSICAL PROPERTIES

Amides exist as solids at rtp, and are water soluble:

↳ this is due to the extensive H bonding bw molecules.

Amides are also pH - neutral.

↳ this is because the presence of an e^--withdrawing O atom makes the LP of e^- on N unavailable to accept H^+.



the LP of e^- is delocalised into the orbitals; this makes it stable.

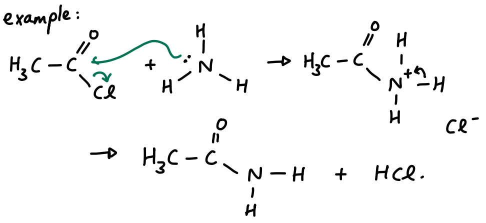
FORMATION OF AMIDES

ACYL CHLORIDE + CONC. NH_3

reagent: NH_3 (conc)
condition: rtp

*type of reaction: condensation / nucleophilic substitution

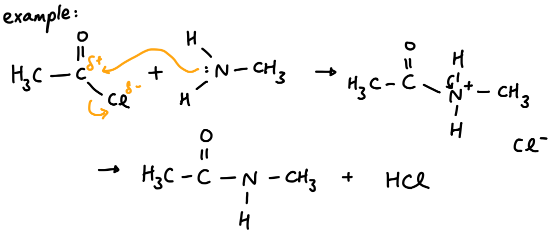
example:



ACYL CHLORIDE + 1° AMINE

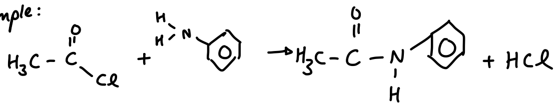
reagent: 1° amine
condition: rtp

example:



ACYL CHLORIDE + PHENYLAMINE

example:



CHEMICAL REACTIONS

HYDROLYSIS

Amides can be hydrolysed, resulting in a carboxylic acid and ammonia.

*if alkali used, salt of carb. acid is produced.

I Acid hydrolysis

reagent: dilute acid eg $HCl_{(aq)}$
condition: heat under reflux.

II Alkaline hydrolysis

reagent: dilute alkali eg $NaOH_{(aq)}$
condition: heat under reflux.

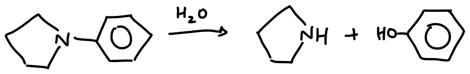
example:

(acid) $CH_3CONHCH_3 \ (+ \ H^+) \longrightarrow CH_3COOH + CH_3NH_2$

wd or excess H^+, the respective ammonium ion can be formed; eg $CH_3NH_3^+$

(alkali) $CH_3CONHCH_3 \ (+ \ OH^-) \longrightarrow CH_3COONa + CH_3NH_2$

diagrams



REDUCTION

Amides can be reduced to form amines.

reagent / condition: $LiAlH_4$ in dry ether.

example: $CH_3CONH_2 + 4[H] \longrightarrow CH_3CH_2NH_2 + H_2O$

DIFFERENTIATING AMINE VS AMIDE COMPOUNDS.

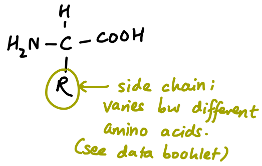
As amide compounds are pH-neutral, but amine compounds are pH-basic, we can use red litmus paper as a test.

⇒ amines: paper turns blue
amides: no reaction

AMINO ACIDS

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

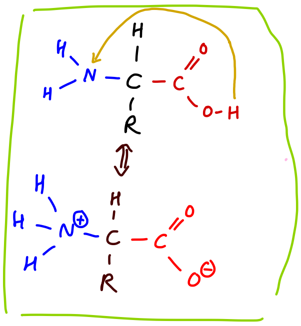
Structure:



ZWITTERION CHARACTERISTIC OF AMINO ACIDS

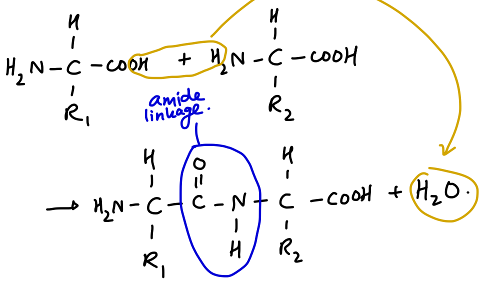
Due to the presence of both a basic ($-NH_2$) and acidic ($-COOH$) FG, each molecule can react with itself.

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



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

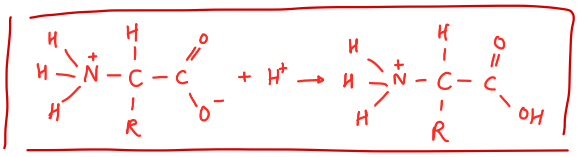
BUFFER SOLUTION PROPERTY OF AMINO ACIDS

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

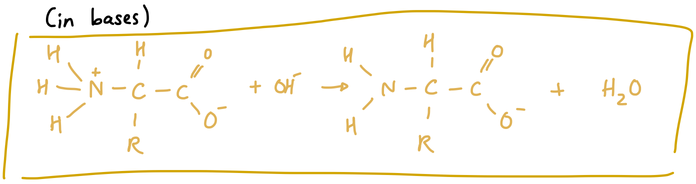
↳ a solution that resists changes in pH when a small amount of an acid/base is added.

(A2 phys chem)

(in acids)



(in bases)

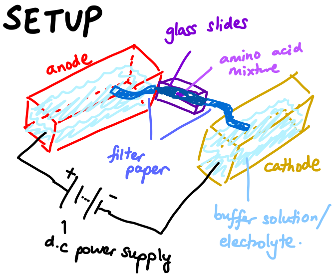


PAPER ELECTROPHORESIS

Paper electrophoresis is an analytical technique used to separate, identify and purify proteins.

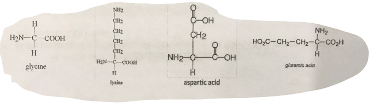
(it is similar to "paper chromatography")

SETUP

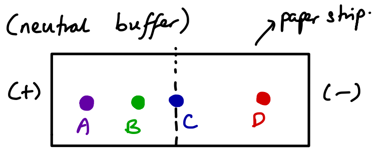


EXAMPLE

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



(neutral buffer)



Observations:

① Spot C is glysine.
why? → no net ionic charge.

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

③ Spot A is aspartic acid. B is glutamic acid.
Why? → 1) Both have a charge of −1.
2) But A is farther away than B ∴ $RMM_A < RMM_B$.

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 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.

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

1) Temperature;
2) Magnitude of p.d applied;
3) RMM / size of ^; and
4) Charge (magnitude).

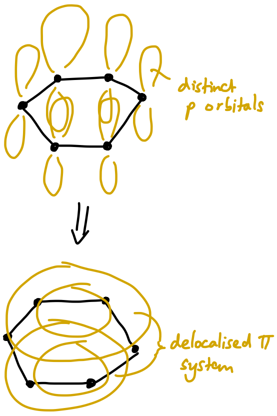
☆ Note:

① in an acidic buffer, none of the $-COOH$ groups would ionise;
↳ 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;
↳ hence all the amino acids will have a −ve charge, and move towards the cathode (+).

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

① All C display sp^2 hybridisation

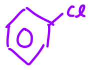
② Bond angle = 120°

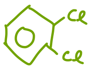
③ All of the C---C bonds have equal length

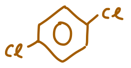
NOMENCLATURE

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


benzene


chlorobenzene


1,2 - dichlorobenzene


1,4 - dichlorobenzene

PRECEDENCE OF NOMENCLATURE

precedence decreases (upper will become suffix etc)

FG	prefix	suffix
- COOH (acid)	-	-oic acid
- COO - (ester)	-	(-yl) -oate
- COCl (acyl halide)	-	- oyl halide
- CONH - (amide)	-	- amide
- C≡N (nitrile)	cyano-	- 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
- X (halide)	fluoro/ chloro/ bromo/ iodo -	-
- NO_2 (nitrous)	nitro -	-

CHEMICAL REACTIONS OF BENZENE

Alkenes and benzenes undergo wildly different chemical reactions.

ELECTROPHILIC SUBSTITUTION OF HALOGENS

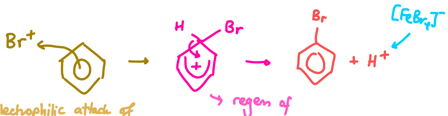
Case 1 "just" benzene

reactant: molten bromine / chlorine gas

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

mechanism:

$Br_2 + FeBr_3 \rightarrow Br^+ + [FeBr_4]^-$



electrophilic attack of bromine cation on benzene ring

→ regen of catalyst + benzene ring

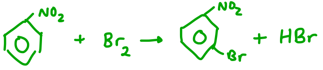
case 2 benzene w/ e⁻ withdrawing group (eg $-NO_2$, $-NH_3$, $-CN$) → more stable than benzenes:
- electron density decreases
- lower reactivity
- less susceptible to electrophilic attack

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

reactant: molten bromine / chlorine

condition: heat with anhyd $FeBr_3$ / $AlBr_3$

example:



☆ in data booklet:
(LH) e⁻ donating
(RH) e⁻ withdrawing

case 3 benzene with e⁻ donating group (eg -OH, -alkyl, $-NH_2$, -Cl) → less stable than benzenes:
- lone pairs on atoms connected to ring delocalise into π structure
- electron density increases
- increased reactivity
- more susceptible to electrophilic attack

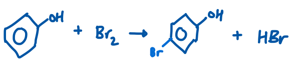
special cases. (2,4)

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

reactant: aqueous bromine / chlorine.

condition: heat with $FeBr_3$ / $AlBr_3$

example:

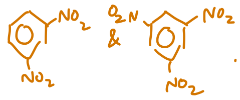


☆ hence aqueous bromine is enough to start the reaction.

ELECTROPHILIC SUBSTN OF NO_2

For $-NO_2$ to be substituted, we need to create NO_2^+ cations.

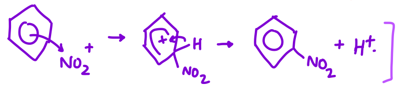
★ further nitration leads to 1,3 - and 1,3,5 nitrobenzenes, ie



reactant: conc. HNO_3 & H_2SO_4
condition: heat under reflux at 55°C

mechanism:

$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$
$H_2NO_3^+ \rightarrow H_2O + NO_2^+$.
] formation of NO_2^+. (neutralisation reaction)



] substn.

$H^+ + HSO_4^- \rightarrow H_2SO_4$.] regeneration of catalyst.

FRIEDEL-CRAFTS REACTION

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

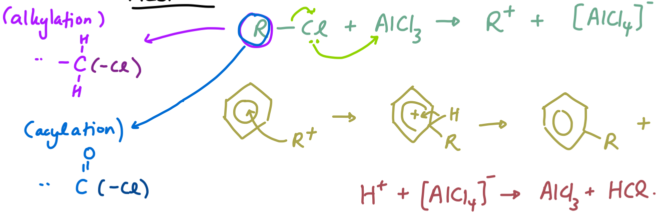
↳ Two types:

① alkylation (alkyl)
② acylation (contains  , ie -COOH, -COHek)

*type of reaction: electrophilic substitution.

reactant: halogenoalkane (alkylation), acyl chloride (acylation)
condition: heat w/ $AlCl_3$ catalyst.

mechanism:



$R-Cl + AlCl_3 \rightarrow R^+ + [AlCl_4]^-$] formation of "R" cation.

R^+ → H R → R + H^+.

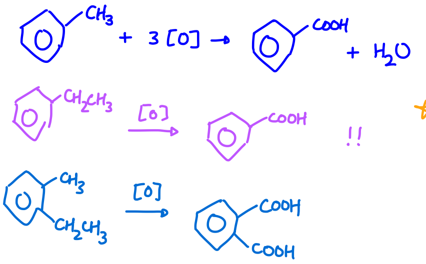
$H^+ + [AlCl_4]^- \rightarrow AlCl_3 + HCl$.

OXIDATION IN THE SIDE CHAIN

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

reactant: $KMnO_4/H^+$ or $KMnO_4/OH^- + H_2SO_4$
condition: heat under reflux

example:



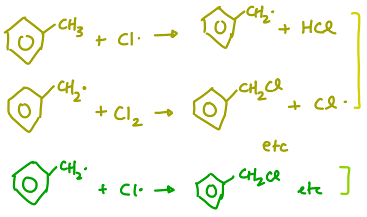
★ LHS is ethyl, but RHS is still -COOH !!

FREE-RADICAL SUBSTITUTION OF METHYL SIDE CHAIN

reactant: Cl_2
condition: UV light

mechanism:

$Cl-Cl \rightarrow 2Cl\cdot$] initiation



] propagation

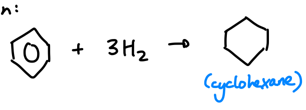
] termination

HYDROGENATION OF THE BENZENE RING

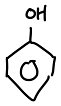
The benzene ring, under certain conditions, can undergo an addition reaction with H_2.

reactant: H_2 (g)
condition: heat at 200°C & 30atm in the presence of Ni

reaction:



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 aryle compounds.

Why? → H bonding bw molecules.

H_2O SOLUBILITY

Benzenes are only slightly soluble in water.

Why? → large non-polar benzene ring
→ desp. H bonding w/ H_2O molecules.

ACIDITY

acidity of carboxylic acid > acidity of phenol > acidity of H_2O > acidity of alcohols.

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

$H_2O \rightarrow H^+ + OH^-$

$CH_3CH_2OH \rightarrow CH_3CH_2O^- + H^+$

① Why acid > phenol?

- $C=O$ bond has a negative inductive 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 > H_2O?

- 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^+.

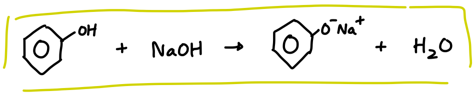
③ Why alcohols < H_2O?

- 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 decreases.
- so pos of eq shifts to the left, leading to lesser formation of H^+.

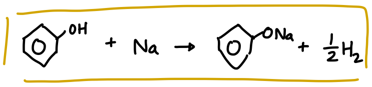
* key idea: talk about the weakening of O-H bond or stabilisation of anion.

CHEMICAL REACTIONS

NEUTRALISATION



REACTION W/ METAL



☆ phenols are not shong enough to react with carbonates.

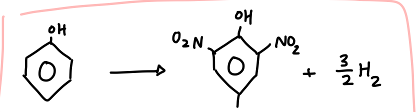
ELECTROPHILIC SUBSTITUTION

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/ NO_2

reactant: dilute / conc. HNO_3
condition: room temperature

reaction:



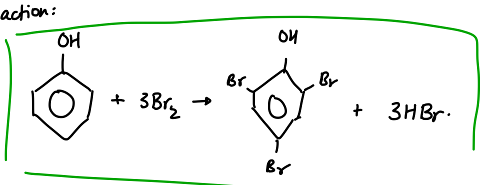
(2,4,6 - trinitrophenol)

W/ Br_2

reactant: Br_2 (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.

reagent: $FeCl_3$ (or $AlCl_3$)

phenol: purple colour

alcohol: nothing

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 : **J K^{-1} mol^{-1}**

(ΔS : entropy change)

STANDARD MOLAR ENTROPY

"Standard molar entropy" is the **entropy** of **one mole of substance** in its **standard state** under **standard conditions** (298 K, 1.01×10^5 Pa)

↳ symbol : $S^{\ominus}$ ($\Delta S^{\ominus}$ if changing)

☆ as **all** substances have entropy, $S^{\ominus}$ is **always positive**!

RELATIONSHIP BETWEEN SPONTANEITY AND ENTROPY

A reaction is **spontaneous** if $\boxed{\Delta S^{\ominus} > 0}$.

FACTORS THAT AFFECT A SYSTEM'S ENTROPY

CHANGE IN PHASE

$$\boxed{S_{solid} < S_{liquid} < S_{gas}}$$

Why? It has to do with the **arrangement** of the ·p in the phases ;

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

(liquid)
- irregular arrangement
- ·p slide past each other

(gas)
- irreguler 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 :

$S_{CaCO_3} < S_{CaO}$ ($CaCO_3$ has more "shit" than CaO)

$S_{C_2H_6} < S_{C_2H_4}$ (C_2H_6 is a bigger molecule than C_2H_4)

$S_{Na_2O} > S_{MgO}$ (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? → ·p have more vibrational energy

CHANGE IN HARDNESS

Harder substances have **lower entropy**.

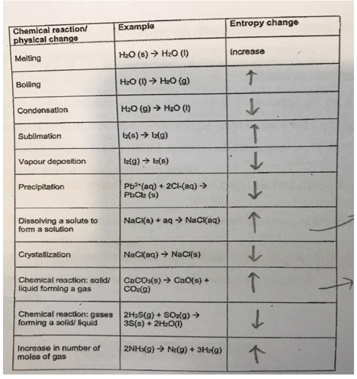
(eg $S_{diamond} < S_{graphite}$)

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	$H_2O (s) \rightarrow H_2O (l)$	Increase
Boiling	$H_2O (l) \rightarrow H_2O (g)$	↑
Condensation	$H_2O (g) \rightarrow H_2O (l)$	↓
Sublimation	$I_2(s) \rightarrow I_2(g)$	↑
Vapour deposition	$I_2(g) \rightarrow I_2(s)$	↓
Precipitation	$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2 (s)$	↓
Dissolving a solute to form a solution	$NaCl(s) + aq \rightarrow NaCl(aq)$	↑
Crystallization	$NaCl(aq) \rightarrow NaCl(s)$	↓
Chemical reaction: solid/ liquid forming a gas	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	↑
Chemical reaction: gases forming a solid/ liquid	$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$	↓
Increase in number of moles of gas	$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$	↑

CALCULATING TOTAL ENTROPY CHANGE

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

$$\Rightarrow \boxed{\Delta S_{total}} = \boxed{\Delta S_{system}} + \boxed{\Delta S_{surroundings}}$$

total entropy change

(disorder of everything else not involved in system, eg test tube, solvent etc)

total entropy change of the system;

$\Delta S_{sys} = S_{products} - S_{reactants}$

entropy of products

entropy of reactants.

total entropy change of the surroundings:

$$\Delta S_{sur} = \frac{-\Delta H_r}{T}$$

energy change of reaction

☆(have to ×1000 because convert into J mol⁻¹

temperature (in °K)

☆ note the minus sign!

$\Delta H > 0 : \Delta S_{sur} < 0$ (endo)

$\Delta H < 0 : \Delta S_{sur} > 0$ (exo)

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↑, ΔS_{sys} ↑.

Hence, since ΔS_{sys} $\boxed{=}$, ΔS_{total} ↑.

⇒ more feasible.

(for exothermic reaction) as T↑, ΔS_{sys} ↓.

Hence, since ΔS_{sys} $\boxed{=}$, ΔS_{total} ↓.

⇒ less feasible.

* Hence, the feasibility of endo rctⁿs increases, and the feasibility of exo rctⁿs decreases, as temperature ↑.

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

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

temp in °K!!

☆ must ÷1000 bc unit of ΔG is kJ mol⁻¹.

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.

symbol: G (ΔG: change; ΔG^{θ}: std. change)

unit: kJ mol⁻¹

EFFECT OF TEMPERATURE CHANGE ON FEASIBILITY.

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

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.

Chapter 22: Reaction Kinetics

RATE EQUATION

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

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

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

rate of reaction

rate constant (unit dep on rctⁿ)

conc. of A

"order" of [A]

conc. of B

"order" of [B]

☆ only includes reactants that affect the rate.

☆ rate eqⁿs can only be determined theoretically !

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

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

eg for $N_2 + 3H_2 \rightleftharpoons 2NH_3$, rate eqⁿ is

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

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 $\propto [H_2]^2$ ⟶ order of $[H_2]$ is $\underline{\underline{2}}$

↳ rate $\propto [NO]$ ⟶ order of $[NO]$ is $\underline{\underline{1}}$

$$\boxed{\text{overall order} = \text{sum of orders of reactants in eq}^{n}}$$

so overall order of rctⁿ above $= 2+1$
$= \underline{\underline{3}}$.

HALF LIFE

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

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

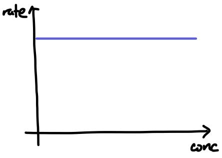
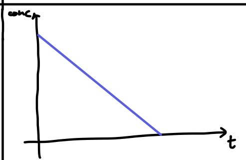
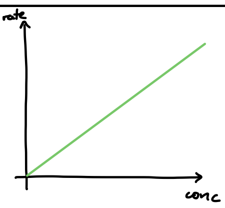
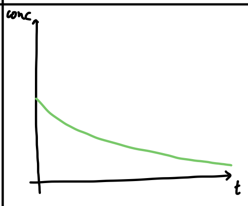
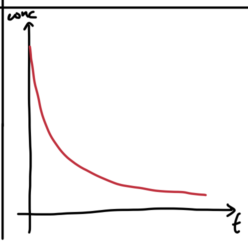
MOLECULARITY

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

↳ deduced from mechanism of reaction.

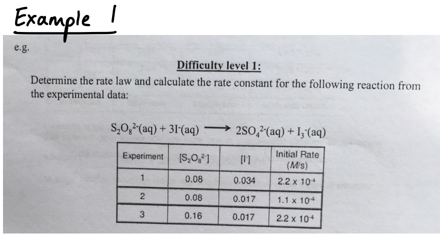
☆ experimentally determined.

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 rate = k			half-life decreases over time
One	rate ∝ conc of reactant rate = k[A]			half-life stays the same over time. $\boxed{T_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}}$
two	rate ∝ conc of reactant squared rate = $k[A]^2$			half-life increases over time.

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:

$S_2O_8^{2-}(aq) + 3I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$

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 → $[S_2O_8^{2-}]$ $\boxed{=}$; $[I^-]$ (÷2), rate ÷2

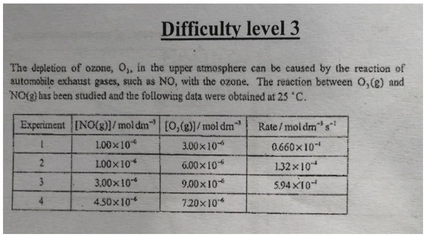
so order of $[I^-] = 1$

E2, E3 → $[S_2O_8^{2-}]$ (×2), rate ×2 ($[I^-]$ $\boxed{=}$)

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

⇒ rate eqn 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 °C.

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

O_3 eeasy to determine. (use method from E1)

known order of NO

$$\left(\frac{e3}{e2}\right) \Rightarrow \frac{rate_f}{rate_i} = \left(\frac{[O_3]_f}{[O_3]_i}\right)^m \left(\frac{3.00\times10^{-6}}{1.00\times10^{-6}}\right)^{\underline{1}}$$

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

$$1.5 = 1.5^m \quad \Rightarrow \underline{\underline{m=1}}.$$

KINETICS & REACTION MECHANISMS

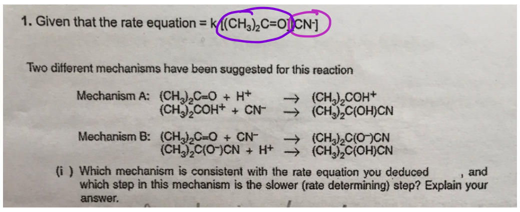
Many reactions happen in many steps. We call this the "reaction mechanism".

↳ 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.

VERIFICATION OF POSSIBLE MECHANISMS FROM KINETIC DATA



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

Two different mechanisms have been suggested for this reaction

Mechanism A: $(CH_3)_2C{=}O + H^+ \rightarrow (CH_3)_2COH^+$
$(CH_3)_2COH^+ + CN^- \rightarrow (CH_3)_2C(OH)CN$

Mechanism B: $(CH_3)_2C{=}O + CN^- \rightarrow (CH_3)_2C(O^-)CN$
$(CH_3)_2C(O^-)CN + H^+ \rightarrow (CH_3)_2C(OH)CN$

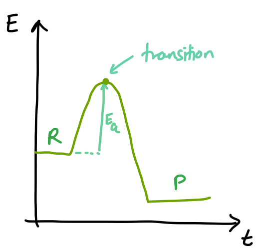
(i) Which mechanism is consistent with the rate equation you deduced , and which step in this mechanism is the slower (rate determining) step? Explain your answer.

mechanism B. Why?

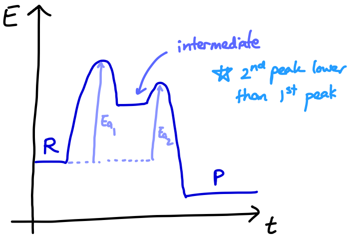
→ 1st rctn has both reactants in rate eqn

→ so, 1st rctn is slowest rctn.

REACTION PROFILE

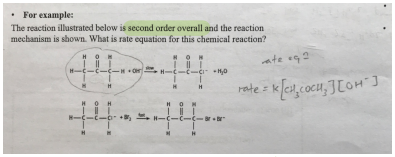


one-step



multi-step

PREDICTION OF ORDER FROM MECHANISM



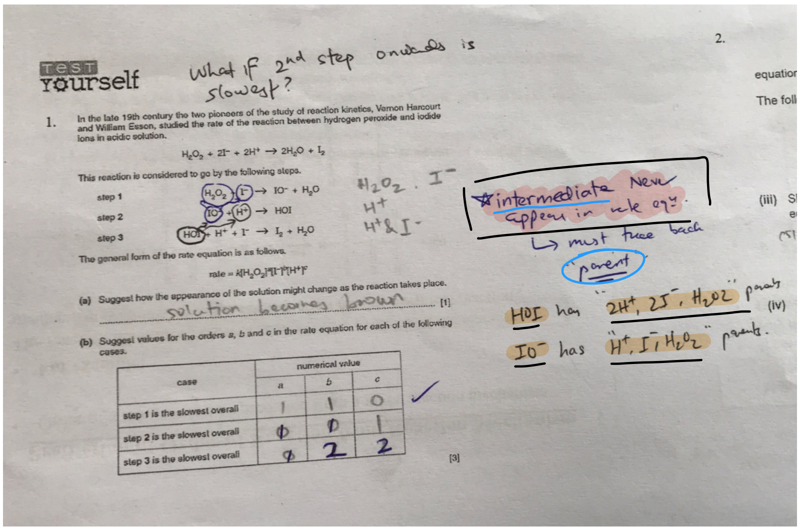
- **For example:**

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

rate eqn

rate $= k[CH_3COCH_3][OH^-]$

order for both = 1. (only solution)



TEST yourself

What if 2nd step onwards is slowest?

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

$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$

This reaction is considered to go by the following steps.

step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$ — H_2O_2. I^-

step 2 $IO^- + H^+ \rightarrow HOI$ — H^+

step 3 $HOI + H^+ + I^- \rightarrow I_2 + H_2O$ — H^+ & I^-

The general form of the rate equation is as follows.

rate $= k[H_2O_2]^a[I^-]^b[H^+]^c$

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

solution becomes brown [1]

(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

✓ [3]

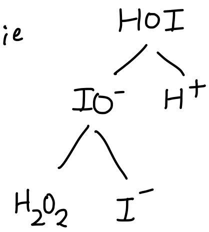
☆ intermediate Never appear in rate eqn.

↳ must trace back "parent"

HOI has "2H⁺, 2I⁻, H₂O2" parents

IO⁻ has "H⁺, I⁻, H₂O₂" parents.

ie



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 rate $= k[H_2O_2][I^-][H^+]$.

Alternatively, if step 3 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 $\underline{2}$;

ie rate $= [H^+]^2[I^-]^2[H_2O_2]$.

CATALYSIS

Recap: catalysis can be divided into two categories:

homogenous

① The iodine-peroxodisulfate reaction

$S_2O_8^{2-}{}_{(aq)} + 2I^-{}_{(aq)} \xrightarrow{Fe^{3+}} 2SO_4^{2-}{}_{(aq)} + I_2$

☆ can't occur w/o catalyst ∵ anions repel each other

mechanism:

$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$

$2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$

② The decomposition of hydrogen peroxide

$2H_2O_{2(aq)} \xrightarrow{I^-} 2H_2O_{(g)} + O_{2(g)}$

③ The formation of acid rain

$SO_2 + \frac{1}{2}O_2 \xrightarrow{NO_2} SO_3$

heterogenous

① Haber process

$N_2 + 3H_2 \underset{}{\overset{Fe}{\rightleftharpoons}} 2NH_3$

② Contact process

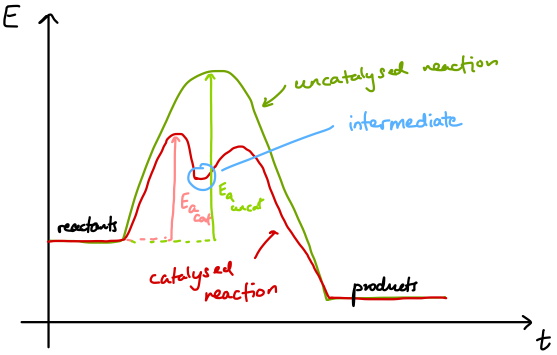
$2SO_2 + O_2 \overset{V_2O_5}{\rightleftharpoons} 2SO_3$

③ Transition elements in catalytic converter

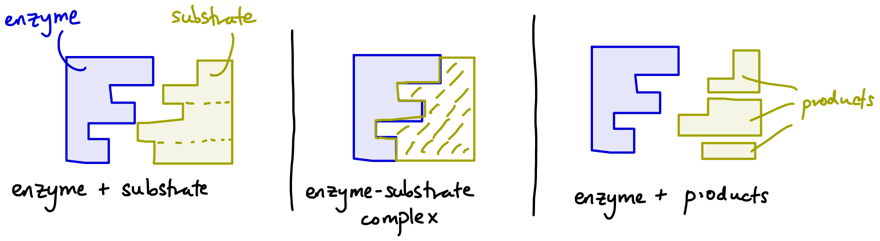
$2CO + 2NO \xrightarrow{Rh} 2CO_2 + N_2$

$2CO + O_2 \xrightarrow{Pt/Pd} 2CO_2$

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 ;

$$\boxed{k = Ae^{-\frac{E_a}{RT}}}$$

activation energy (in $J\,mol^{-1}$!!)

kelvin temperature

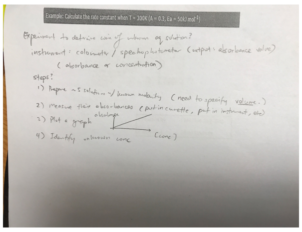
rate constant

freq factor (constant)

e (2.718..)

gas constant (8.31)

EXPERIMENT TO DETERMINE CONC OF UNKNOWN SOLUTION



Example: Calculate the rate constant when T = 300K (A = 0.3, Ea = 50kJ mol^{-1})

Experiment to determine conc of unknown aq solution?

instrument : colorimeter / spectrophotometer (output : absorbance value)

(absorbance ∝ concentration)

steps?

1) Prepare ~5 solutions w/ known molarity (need to specify volume.)
2) measure their absorbances (put in cuvette, put in instrument, etc)
3) Plot a graph
4) Identify unknown conc

Chapter 21:
Further Aspects of Equilibria

IONIC PRODUCT OF WATER (K_w)

K_w = equilibrium constant for the ionisation of water

$H_2O \rightleftharpoons H^+ + OH^-$ $\Delta H = +58\ kJ\,mol^{-1}$

⇒ K_w is given by the formula

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

⊕ Relation between K_w & T

↳ if $\boxed{T\uparrow}$, eq shifts to right, so $\boxed{K_w \uparrow}$.

pH

pH is given by the eq$^{\underline{n}}$

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

pH OF PURE WATER

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

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

Then, the pH of pure water, at rtp, is equal to $-\log_{10}(10^{-7}) = ⑦$.

pH OF STRONG ACIDS

* Assumptions → $[H^+]$ from H_2O is negligible
→ $[H^+] = [H^+]$ from acids.

Examples

① $0.001\ mol\ dm^{-3}$ HCl

$HCl \rightarrow H^+ + Cl^-$

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

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

$\therefore pH = -\log_{10}[H^+]$
$= -\log_{10}(0.001)$
$= 3$.

② $0.10\ mol\ dm^{-3}$ H_2SO_4

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

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

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

$\therefore pH = -\log_{10}[H^+]$
$= -\log_{10}(2 \cdot 0.10)$
$= 0.70$.

BUT

★ as T ↑, K_w ↑.

Then $[H^+]$ ↑. (so $-\log_{10}[H^+]$ ↓).

Hence,

the pH decreases when T increases.

pH OF STRONG BASES

* Assumptions → $[OH^-] = [OH^-]$ from base
→ $[OH^-]_{H_2O}$ negligible

Examples

① $2.0\ mol\ dm^{-3}$ NaOH

$NaOH \rightarrow Na^+ + OH^-$

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

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

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

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

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

Alternative method:
$pH + pOH = 14$
$\therefore pH = 14 - pOH$
$= 14 + \log_{10}(2)$
$= 14.3$.

So $pH = -\log_{10}[H^+]$
$= -\log_{10}(5.00 \times 10^{-15})$

$pH = 14.3$.

ACID DISSOCIATION CONSTANT, K_a

K_a provides a measure of the extent to which an acid is dissociated.

↳ for the acid HX $\rightleftharpoons H^+ + X^-$,

K_a is given by

$$\boxed{K_a = \frac{[H^+][X^-]}{[HX]}}$$

Note that $\boxed{pK_a = -\log_{10} K_a}$.

⊕ Example of use

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

* $[H^+] = [X^-]$ $\therefore$ $K_a = \frac{[H^+]^2}{[HX]}$

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

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

$\therefore pH$
$= -\log_{10}\sqrt{0.18 \times 10^{-5}}$
$= 2.8723$
$= \underline{\underline{2.9}}$.

RELATION BETWEEN K_a & pH

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

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

BUFFER SOLUTION

Buffer solutions are solutions that resist changes in its pH when small amounts of acids / bases are added.

↳ either acidic or alkaline

weak acid + salt of acid

(eg $CH_3COOH + CH_3COO^-Na^+$)

($pH < 7$)

weak base + salt of base

(eg $NH_3 + NH_4Cl$)

($pH > 7$)

MECHANISM OF BUFFER SOLUTIONS

ACIDIC

In an acidic buffer solution:

- the weak acid is partially ionised, & — eg $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
- the salt is fully ionised. $CH_3COO^-Na^+ \rightarrow CH_3COO^- + Na^+$.

⊕ if a small amt of acid is added

↳ eq shifts to the left;

↳ added H^+ reacts with excess CH_3COO^-

↳ so pH does not change significantly

$CH_3COO^- + H^+ \rightarrow CH_3COOH$

⊕ if a small amt of alkali is added

↳ eq shifts to the right;

↳ added OH^- reacts with excess CH_3COOH

↳ so pH does not change significantly

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

ALKALINE

In an alkaline buffer solution:

- the weak alkali is partially ionised: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
- the salt is fully ionised: $NH_4Cl \rightarrow NH_4^+ + Cl^-$

⊕ small amt of acid added:

↳ eq shifts to right

↳ H^+ reacts with NH_3

↳ pH does not change significantly

$H^+ + NH_3 \rightarrow NH_4^+$

⊕ small amt of alkali added:

↳ eq shifts to the left

↳ OH^- reacts with NH_4^+

↳ pH does not change significantly

$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

APPLICATIONS OF BUFFER SOLUTION

Many industrial & biological systems are sensitive to minute changes in pH.

↳ a buffer solution is a good method of maintaining pH.

CARBONATE BUFFER SYSTEM

$\boxed{CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-}$

⊕ If H^+ added ⇒ eq shifts to left

$HCO_3^- + H^+ \rightarrow H_2CO_3$

⊕ If OH^- added ⇒

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

PHOSPHATE BUFFER SYSTEM

$\boxed{H_2PO_4^- \rightleftharpoons H^+ + HPO_4^-}$

⊕ If H^+ is added ⇒ eq shifts to left

$H^+ + HPO_4^{2-} \rightarrow H_2PO_4^-$

⊕ If OH^- is added ⇒

$OH^- + H_2PO_4^- \rightarrow HPO_4^{2-} + H_2O$

pH OF BUFFER SOLUTION

In an acidic buffer, recall that the acid partially ionises and the salt fully ionises:

$HA \rightleftharpoons H^+ + A^-$

$NaA \rightarrow Na^+ + A^-$.

★ two assumptions:

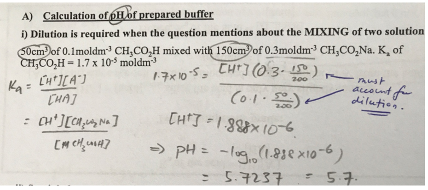
① $[A^-]$ from acid negligible

② $[HA] = [HA]_{initial}$ because negligible ionisation of acid.

Also recall that acid $K_a = \frac{[H^+][A^-]}{[HA]}$ ⇒ $\boxed{\therefore K_a \text{ of acid} = \frac{[H^+][salt]}{[acid]}}$

↳ we can use this to determine the acid's pH.

SAMPLE PROBLEMS



A) Calculation of pH of prepared buffer

i) Dilution is required when the question mentions about the MIXING of two solution

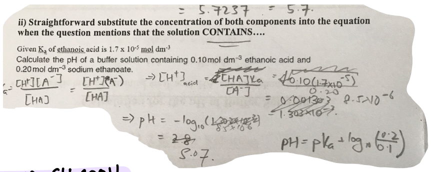
50cm³ of 0.1moldm⁻³ CH_3CO_2H mixed with 150cm³ of 0.3moldm⁻³ CH_3CO_2Na. K_a of $CH_3CO_2H = 1.7 \times 10^{-5}$ moldm⁻³

$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+][CH_3CO_2Na]}{[\cancel{M}\ CH_3COOH]}$

$1.7 \times 10^{-5} = \frac{[H^+](0.3 \cdot \frac{150}{200})}{(0.1 \cdot \frac{50}{200})}$ ← must account for dilution.

$[H^+] = 1.888 \times 10^{-6}$

$\Rightarrow pH = -\log_{10}(1.888 \times 10^{-6}) = 5.7237 = 5.7.$



= 5.7237 = 5.7.

ii) Straightforward substitute the concentration of both components into the equation when the question mentions that the solution CONTAINS….

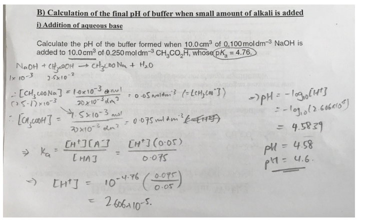
Given K_a of ethanoic acid is 1.7×10^{-5} mol dm⁻³

Calculate the pH of a buffer solution containing 0.10 mol dm⁻³ ethanoic acid and 0.20 mol dm⁻³ sodium ethanoate.

$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+](A^-)}{[HA]} \Rightarrow [H^+]_{acid} = \frac{[HA]K_a}{[A^-]} = \frac{0.10(1.7 \times 10^{-5})}{0.20} = \cancel{0.00130}\ 8.5 \times 10^{-6}$ ~~$= 1.303 \times 10^{-3}$~~

$\Rightarrow pH = -\log_{10}(\cancel{1.303 \times 10^{-3}}\ 8.5 \times 10^{-6}) = \cancel{2.8}\ 5.07.$

$pH = pK_a + \log_{10}\left(\frac{0.2}{0.1}\right)$



B) Calculation of the final pH of buffer when small amount of alkali is added

i) Addition of aqueous base

Calculate the pH of the buffer formed when 10.0 cm³ of 0.100 mol dm⁻³ NaOH is added to 10.0 cm³ of 0.250 mol dm⁻³ CH_3CO_2H, whose $pK_a = 4.76$.

$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$

1×10^{-3} $\quad 2.5 \times 10^{-3}$

$\therefore [CH_3COONa] = \frac{1.0 \times 10^{-3} \text{ mol}}{20 \times 10^{-3} \text{ dm}^3} = 0.05 \text{ moldm}^{-3}$ $(= [CH_3COO^-])$

$(2.5-1) \times 10^{-3}$

$\therefore [CH_3COOH] = \frac{1.5 \times 10^{-3} \text{ mol}}{20 \times 10^{-3} \text{ dm}^3} = 0.075 \text{ mol dm}^{-3}$

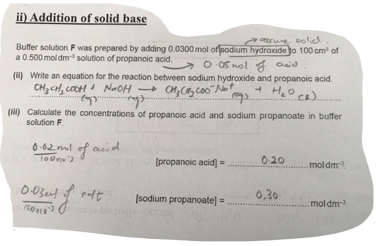
$\Rightarrow K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+](0.05)}{0.075}$

$\Rightarrow [H^+] = 10^{-4.76}\left(\frac{0.075}{0.05}\right) = 2.606 \times 10^{-5}.$

$\Rightarrow pH = -\log_{10}[H^+] = -\log_{10}(2.606 \times 10^{-5}) = 4.5839$

pH = 4.58

pH = 4.6.



ii) Addition of solid base

Buffer solution **F** was prepared by adding 0.0300 mol of sodium hydroxide to 100 cm³ of a 0.500 mol dm⁻³ solution of propanoic acid. → assume solid. → 0.05 mol of acid.

(ii) Write an equation for the reaction between sodium hydroxide and propanoic acid.

$CH_3CH_2COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_3CH_2COO^-Na^+_{(aq)} + H_2O_{(l)}$

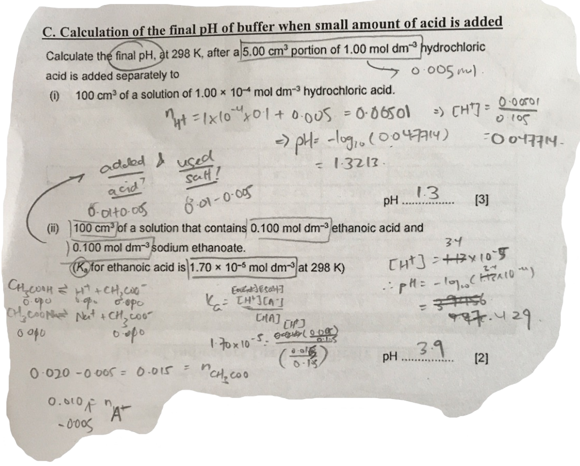
(iii) Calculate the concentrations of propanoic acid and sodium propanoate in buffer solution **F**.

$\frac{0.02 \text{ mol}}{100 \times 10^{-3}}$ of acid

[propanoic acid] = 0.20 mol dm⁻³

$\frac{0.03 \text{ mol}}{100 \times 10^{-3}}$ of salt

[sodium propanoate] = 0.30 mol dm⁻³



C. Calculation of the final pH of buffer when small amount of acid is added

Calculate the final pH, at 298 K, after a 5.00 cm³ portion of 1.00 mol dm⁻³ hydrochloric acid is added separately to → 0.005 mol.

(i) 100 cm³ of a solution of 1.00 × 10⁻⁴ mol dm⁻³ hydrochloric acid.

$n_{H^+} = 1 \times 10^{-4} \times 0.1 + 0.005 = 0.00501 \Rightarrow [H^+] = \frac{0.00501}{0.105} = 0.047714.$

$\Rightarrow pH = -\log_{10}(0.047714) = 1.3213.$

pH 1.3 [3]

added acid? & used salt!

0.01+0.005 $\quad$ 0.01-0.005

(ii) 100 cm³ of a solution that contains 0.100 mol dm⁻³ ethanoic acid and 0.100 mol dm⁻³ sodium ethanoate.

(K_a for ethanoic acid is 1.70 × 10⁻⁵ mol dm⁻³ at 298 K)

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

0.010 $\quad$ 0.010 $\quad$ 0.010

$CH_3COONa \rightarrow Na^+ + CH_3COO^-$

0.010 $\quad$ 0.010

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

$1.70 \times 10^{-5} = \frac{[H^+](\frac{0.005}{0.105})}{(\frac{0.015}{0.105})}$

$[H^+] = \cancel{1.7}\ 3.4 \times 10^{-5}$

$\therefore pH = -\log_{10}(3.4 \times 10^{-5})$

= [illegible].429.

pH 3.9 [2]

$0.020 - 0.005 = 0.015 = n_{CH_3COO}$

$0.010 + ... = n_{A^+}$ −0.005

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.

SELECTING A SUITABLE INDICATOR

Each indicators "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	acid → alkali colour change
methyl orange	3.2 − 4.4	red → yellow
bromophenol blue	2.8 − 4.6	yellow → blue
phenolphthalein	8.2 − 10.0	colourless → pink

MECHANISM

$HIn \rightleftharpoons H^+ + In^-$

in acidic solution
→ eq shifts to left
→ $[In^-]\downarrow$, $[HIn]\uparrow$

in basic solution
→ eq shifts to right
→ $[In^-]\uparrow$, $[HIn]\downarrow$

two distinct colours

TITRATION CURVES

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

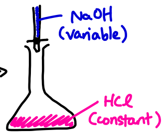
DRAWING TITRATION CURVES

#1 STRONG ACID + STRONG BASE

Ex 25cm^3 of 0.1M HCl w/ 50cm^3 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.

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

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

$= -\log_{10}(0.10) = 1.0$.

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

$HCl + NaOH \rightarrow NaCl + H_2O$.

$n_{HCl} = 25\times10^{-3} \times 0.1 = 2.5\times10^{-3}$.

$\therefore n_{NaOH} = 2.5\times10^{-3}$. $\quad \therefore V_{NaOH} = \frac{n}{c} = \frac{2.5\times10^{-3}}{0.1}$

$= 25\times10^{-3}\,dm^3$

$= 25cm^3$.

Step 4 Identify final pH.

$n_{HCl} = 2.5\times10^{-3}mol. \Rightarrow n_{H^+} = 2.5\times10^{-3}$.

$\Rightarrow n_{NaOH} = 50\times10^{-3} \times 0.1 = 5.0\times10^{-3}mol$.

$\therefore n_{OH^-}$ left $= 5.0\times10^{-3} - 2.5\times10^{-3}$

$= 2.5\times10^{-3}mol$.

$\therefore [OH^-] = \frac{2.5\times10^{-3}}{(50+25)\times10^{-3}}$ — V of both acid + alkali

$= 0.0333$.

$\rightarrow K_w = [H^+][OH^-] = 1.00\times10^{-14}$

$\therefore [H^+] = \frac{1.00\times10^{-14}}{[OH^-]}$

$= \frac{1.00\times10^{-14}}{0.0333}$

$= 3.0030\times10^{-13}$.

$\rightarrow$ final $pH = -\log_{10}(3.0030\times10^{-13})$

$= 12.5224$

$= 12.5$.

☆ 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,

final $pH = -\log_{10}[H^+] = -\log_{10}\frac{k_w}{[OH^-]}$

$= -\log_{10}\frac{10^{-14}}{0.1}$

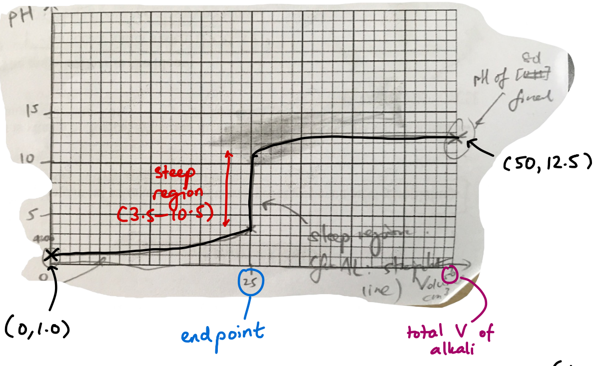
$= 13.0$ (instead of 12.5.)

Step 5 Identify the steep region.

The steep region is where a sharp increase in pH is observed, and where the indicator changes colour.

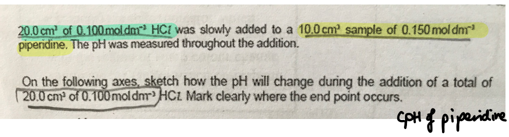
For this reaction, the steep region is $\boxed{3.5 - 10.5}$.

Step 6 Draw the curve.



#2 STRONG ACID + WEAK BASE

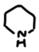
Ex



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 piperidine. 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.

(pH of piperidine = 11.9

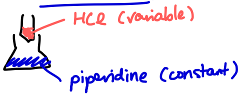


)

Method is the same as case #1

However, note the steep region is $\boxed{3.5 - 7.5}$.

(step 1)



(step 2) $pH_i = 11.9$ (given)

(step 3) $n_{base} = 0.150 \times (10\times10^{-3}) = 1.50\times10^{-3}$.

$\therefore n_{H^+} = 1.50\times10^{-3}$ $\because$ 1:1 mole ratio

$\therefore V_{HCl} = \frac{n}{c} = \frac{1.50\times10^{-3}}{0.10} = 15\times10^{-3}\,dm^3$

$= 15cm^3$.

(step 4) After all H^+ added,

$n_{H^+} = 0.100 \times (20\times10^{-3})$

$= 2.0\times10^{-3}$.

$\Rightarrow n_{H^+}$ remaining $= 2.0\times10^{-3} - 1.50\times10^{-3}$

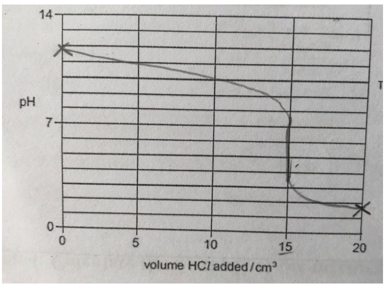
$= 5.00\times10^{-4}$

$\therefore [H^+] = \frac{5.00\times10^{-4}}{(20+10)\times10^{-3}} = 0.01666$.

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

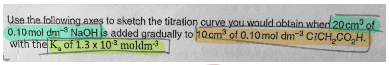
$= 1.78$.

(step 6)



#3 WEAK ACID + STRONG BASE

Ex

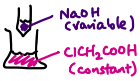


Use the following axes to sketch the titration curve you would obtain when 20 cm³ of 0.10 mol dm⁻³ NaOH is added gradually to 10 cm³ of 0.10 mol dm⁻³ ClCH₂CO₂H. with the Kₐ of 1.3 x 10⁻³ moldm⁻³

Steep region: $\boxed{7.5 - 11}$

Method:

(step 1)



(step 2: pH_i)

We can calculate $[H^+]$ from K_a;

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

$$\therefore [H^+] = \sqrt{K_a[HA]}$$

$$= \sqrt{(1.3\times10^{-3})(0.10)} = 0.0114017.$$

$$\therefore pH_i = -\log_{10}(0.0114017)$$

$$= \underline{\underline{1.94}}.$$

(step 3: V_{endp})

$$n_{ClCH_2COOH} = (10\times10^{-3})\times0.10$$

$$= 1.0\times10^{-3}.$$

$$CH_2ClCOOH + NaOH \longrightarrow CH_2ClCOO^-Na^+ + H_2O$$

$$\therefore n_{NaOH} = 1.0\times10^{-3}$$

$$\therefore V_{NaOH} = \frac{n}{c} = \frac{1.0\times10^{-3}}{0.10} = 10\times10^{-3}\,dm^3$$

$$= \underline{\underline{10\,cm^3}}.$$

(step 3.5) Calculation of V used at half end point ($V = \frac{1}{2}V_{endp}$)

At the half end point, $[salt] = [acid]$.

Hence, as K_a of a buffer sol. $= \frac{[H^+][salt]}{[acid]}$,

we see that $K_a = [H^+]$, or $pH = pK_a$;

$$\Rightarrow pH_{1/2} = -\log_{10}(1.3\times10^{-3})$$

$$= 2.88605$$

$$= \underline{\underline{2.89}}.$$

$$V_{1/2} = \frac{10\,cm^3}{2}$$

$$= \underline{\underline{5\,cm^3}}.$$

(step 4: pH_f)

After all OH^- added,

$$n_{OH^-\,total} = (20\times10^{-3})\times0.10$$

$$= 2.0\times10^{-3}.$$

$$\Rightarrow n_{OH^-\,excess} = 2.0\times10^{-3} - 1.0\times10^{-3}$$

$$= 1.0\times10^{-3}.$$

$$\therefore [OH^-] = \frac{1.0\times10^{-3}}{(20+10)\times10^{-3}} = 0.03333.$$

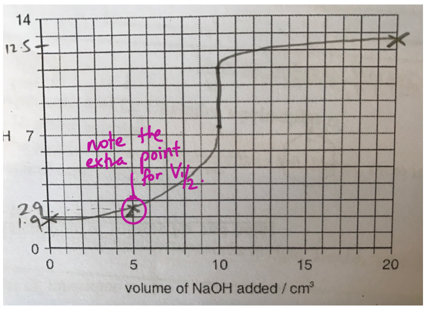
$$\Rightarrow [H^+] = \frac{K_w}{[OH^-]} = \frac{1\times10^{-14}}{0.0333}$$

$$= 3.003\times10^{-13}.$$

$$\therefore pH = -\log_{10}(3.003\times10^{-13})$$

$$\underline{\underline{pH_f = 12.5}}.$$

(step 6)



#4 WEAK ACID + WEAK BASE

For this case, the steep region is too faint to be detected by any indicator.

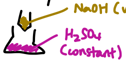
(extra info)

#5 POLYBASIC ACIDS

For polybasic acids, there are <u>2 or more</u> endpoints.

<u>Ex</u> $20\,cm^3$ of $0.1M\ H_2SO_4$ titrated w/ $0.1M$ NaOH

(step 1)



(step 2: pH_i)

$$[H_2SO_4] = 0.1$$

$$\therefore [H^+] = 0.1\ \underline{\underline{\times 2}}$$

diprotic!

$$= 0.2.$$

$$\therefore pH_i = -\log_{10}(0.2)$$

$$= 0.7.$$

(step 4: pH_f)

no V of NaOH given so assume inf V.

$$[OH^-] = 0.1$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]}$$

$$= \frac{10^{-14}}{0.1}$$

$$= 10^{-13}.$$

$$\therefore pH_f = -\log_{10}(10^{-13})$$

$$= 13.$$

(step 3) Identify the two endpoint volumes

H_2SO_4 undergoes a two step neutralisation process w/ NaOH:

$$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O \quad ①$$

$$NaHSO_4 + NaOH \longrightarrow \underline{Na_2SO_4} + H_2O. \quad ②$$

↳ each stage has its own endpoint.

For ① →

$$n_{H_2SO_4} = (20\times10^{-3})\times0.1$$

$$= 2.0\times10^{-3}.$$

1:1 $\therefore n_{NaOH} = 2.0\times10^{-3}.$

$$\Rightarrow V_1 = \frac{n}{c} = \frac{2.0\times10^{-3}}{0.1}$$

$$= 20\times10^{-3}\,dm^3$$

$$V_1 = 20\,cm^3.$$

For ② →

$$n_{H_2SO_4} = 2.0\times10^{-3}$$

$$n_{NaOH} = 2.0\times10^{-3}$$

$$\therefore V = 20\,cm^3 + \underbrace{20\,cm^3}_{\text{from ①}}$$

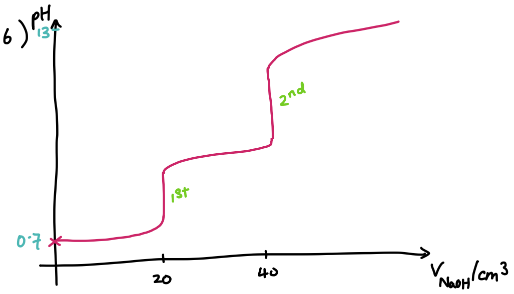
$$\downarrow$$

$$\therefore V_2 = 40\,cm^3$$

(step 5) Just remember the <u>1st steep region</u> is <u>shorter</u> than the <u>2nd steep region</u>.

(① ~ 3pH
② ~ 5pH)

(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

⊕ For the compound

$$X_pY_{q(s)} \rightleftharpoons pX^{q+}_{(aq)} + qY^{p-}_{(aq)},$$

the solubility product is given by

$$\boxed{K_{sp} = [X^{q+}]^p[Y^{p-}]^q.}$$

Examples

$AgCl \rightleftharpoons Ag^+ + Cl^-$ $K_{sp} = [Ag^+][Cl^-]$

$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$ $K_{sp} = [Ca^{2+}][OH^-]^2$

$Ag_3PO_4 \rightleftharpoons 3Ag^+ + PO_4^{3-}$ $K_{sp} = [Ag^+]^3[PO_4^{3-}]$

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

$$HCl \longrightarrow H^+ + \underbrace{Cl^-}_{\text{common ion}}$$

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

⊕ When HCl added:

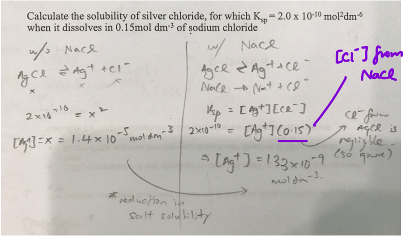
→ $[Cl^-]$ ↑

→ (by Le Chatelier's principle) eq shifts to left

→ so $[Ag^+]$ ↓ so K_{sp} ↓

→ so solubility decreases.

Using common ion effect in questions



Calculate the solubility of silver chloride, for which $K_{sp} = 2.0 \times 10^{-10}$ mol²dm⁻⁶ when it dissolves in 0.15mol dm⁻³ of sodium chloride

w/o NaCl

$AgCl \rightleftharpoons Ag^+ + Cl^-$

x x x

$2\times10^{-10} = x^2$

$[Ag^+] = x = 1.4 \times 10^{-5}$ mol dm⁻³

w/ NaCl

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$NaCl \rightarrow Na^+ + Cl^-$

$K_{sp} = [Ag^+][Cl^-]$

$2\times10^{-10} = [Ag^+](0.15)$

$\Rightarrow [Ag^+] = 1.33\times10^{-9}$ mol dm⁻³.

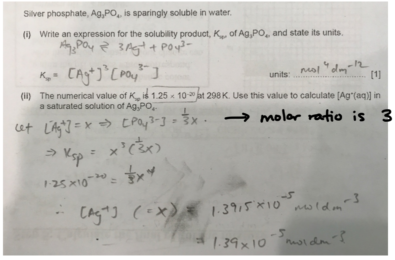
$[Cl^-]$ from NaCl

Cl^- from AgCl is negligible (so ignore)

* reduction in salt solubility

USING K_{sp} IN PROBLEMS

Exa 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: mol⁴ dm⁻¹² [1]

(ii) The numerical value of K_{sp} is 1.25×10^{-20} at 298 K. Use this value to calculate $[Ag^+(aq)]$ in a saturated solution of Ag_3PO_4.

let $[Ag^+] = x \Rightarrow [PO_4^{3-}] = \frac{1}{3}x$. → molar ratio is 3:1.

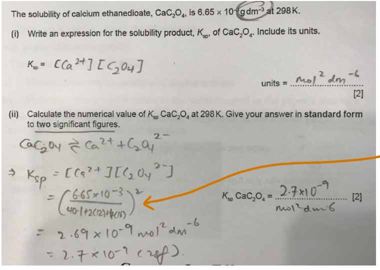
$\Rightarrow K_{sp} = x^3(\frac{1}{3}x)$

$1.25\times10^{-20} = \frac{1}{3}x^4$

$\therefore [Ag^+] (=x) = 1.3915\times10^{-5}$ mol dm⁻³

$= 1.39\times10^{-5}$ mol dm⁻³

Exa 2



The solubility of calcium ethanedioate, CaC_2O_4, is 6.65×10^{-3} g dm⁻³ at 298 K.

(i) Write an expression for the solubility product, K_{sp}, of CaC_2O_4. Include its units.

$K_{sp} = [Ca^{2+}][C_2O_4]$

units = mol² dm⁻⁶ [2]

(ii) Calculate the numerical value of K_{sp} CaC_2O_4 at 298 K. Give your answer in standard form to two significant figures.

$CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$

$\Rightarrow K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$

$= \left(\frac{6.65\times10^{-3}}{40.1+2(12)+4(16)}\right)^2$

$= 2.69\times10^{-9}$ mol² dm⁻⁶

$= 2.7\times10^{-9}$ (2sf).

K_{sp} CaC_2O_4 = 2.7×10^{-9} mol²dm⁻⁶ [2]

★ have to convert into mol dm⁻³ !!

$\left(\text{gdm}^{-3} = \frac{\text{mol dm}^{-3}}{M_r}\right)$

USES OF K_{sp}

Generally, K_{sp} is used to determine the "saturation point" for a solution.

eg K_{sp} of $BaCO_3$ = 5.5×10^{-10} mol² dm⁻⁶.

If $[Ba^{2+}][CO_3^{2-}] = 5.5\times10^{-10}$, saturated

If $[Ba^{2+}][CO_3^{2-}] < 5.5\times10^{-10}$, can add more

If $[Ba^{2+}][CO_3^{2-}] > 5.5\times10^{-10}$, precipitation occurs.

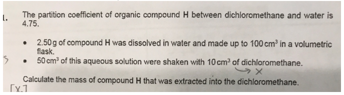
PARTITION COEFFICIENTS, K_{pc}

The partition coefficient is the ratio of the concentrations / amounts of solute in two immiscible solvents at equilibrium.

$$= \; K_{pc} = \frac{[X \text{ in organic}]}{[X \text{ in aqueous}]}$$

USING K_{pc} IN QUESTIONS

Ex



1. The partition coefficient of organic compound H between dichloromethane and water is 4.75.
   - 2.50 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.

$$K_{pc} = \frac{[X_o]}{[X_{aq}]}$$

$$4.75 = \frac{\left(\frac{1.25-x}{10}\right)}{\left(\frac{x}{50}\right)}$$

$1.25-x$ → # of moles in (o)

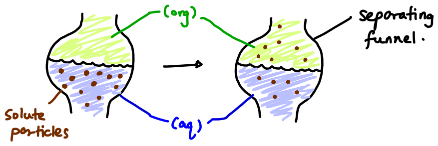
10 → $V_{(o)}$

x → # of moles in (aq)

50 → $V_{(aq)}$

$\Rightarrow x = \underline{\underline{0.61}}.$

VISUALISATION BY ILLUSTRATION



The solute undergoes the equilibrium rxn

$$X_{(aq)} \rightleftharpoons X_{(org)}.$$

⇒ 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 $K_{pc} > 1$ ⇒ [org] > [aq]

⇒ solute more soluble in organic solvent.

If $K_{pc} < 1$ ⇒ [aq] < [org]

⇒ solute more soluble in aqueous solvent.

If $K_{pc} = 1$ ⇒ [aq] = [org]

⇒ solute equally soluble in both solvents.

USES OF K_{pc}

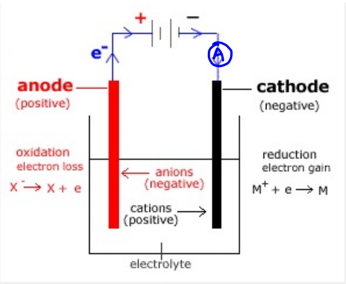
K_{pc} can be used as a quantitative measure of the separation of different components in a mixture during chromatography

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.
$Na^+ + e^- \rightarrow Na$

→ at the anode (+), oxidation occurs.
$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

ELECTROLYSIS ON AQUEOUS ELECTROLYTES

For aqueous electrolytes, we have to factor in the presence of H_2O.

What is discharged?

- For the cathode (−):
  ⇒ compare $E^\ominus$ of cation with $E^\ominus$ of water.
  If $E^\ominus_{cat} > E^\ominus_{water}$ ⇒ cation's products discharged.
  If $E^\ominus_{cat} < E^\ominus_{water}$ ⇒ H_2 discharged.

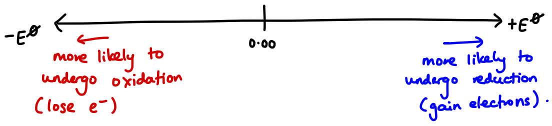
eg NaCl (aq).

cathode:
$Na^+ + e^- \rightarrow Na$ $E^\ominus = -2.71V$.
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^\ominus = -0.83V$.
$-0.83V > -2.71V$
so H_2 discharged.

- For the anode (+):
  ⇒ compare $E^\ominus$ of anion with $E^\ominus$ of water.
  If $E^\ominus_{an} < E^\ominus_{water}$ ⇒ anion's products discharged.
  If $E^\ominus_{an} > E^\ominus_{water}$ ⇒ O_2 discharged.

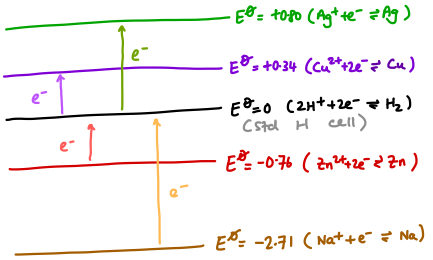
anode:
$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ $E^\ominus = +1.23V$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^\ominus = +1.36V$
$+1.23V < +1.36V$
so O_2 discharged.

THE INFLUENCE OF $E^\ominus$ ON EASE OF DECOMPOSITION



Why?

We can use a potential diagram to illustrate this.



⊕ Cu and Ag have +ve $E^\ominus$ values, so electrons "want to flow" from the zero potential mark.
⇒ so they favour reduction.

⊕ Conversely, Zn and Na have −ve $E^\ominus$ 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 $E^\ominus$ values.

↳ only viable IF the difference between competing ions' $E^\ominus$ is less than 0.30V.

eg $ZnCl_2$ (aq)

conc = 1M (normal)

cathode: $Zn^{2+} + 2e^- \rightarrow Zn$ $E^\ominus = -0.76$
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^\ominus = -0.83$
$E^\ominus_{Zn} > E^\ominus_{H_2O}$ ∴ Zn discharged

anode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^\ominus = +1.23$
$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E^\ominus = +1.36$
$E^\ominus_{H_2O} < E^\ominus_{Cl_2}$ ∴ O_2 discharged

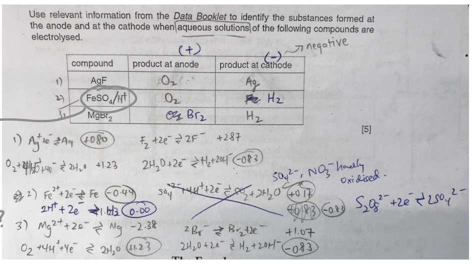
conc = 10M (concentrated)

cathode: abundance of H_2O, and $E^\ominus$ values within 0.30V.
⇒ H_2 discharged
anode: abundance of H_2O
⇒ O_2 discharged

conc = 0.01M (dilute)

cathode: abundance of Zn^{2+}, values within 0.30V.
⇒ Zn discharged.
anode: abundance of Cl^-,
⇒ Cl_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 solutions of the following compounds are electrolysed.

	compound	product at anode (+)	product at cathode (−) → negative
1)	AgF	O_2	Ag
2)	$FeSO_4$/H^+	O_2	~~Fe~~ H_2
3)	$MgBr_2$	~~O_2~~ Br_2	H_2

[5]

1) $Ag^+ + e^- \rightleftharpoons Ag$ +0.80　$F_2 + 2e^- \rightleftharpoons 2F^-$ +2.87
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23　$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ −0.83

2) $Fe^{2+} + 2e^- \rightleftharpoons Fe$ −0.44　~~$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$ +0.17~~
$2H^+ + 2e^- \rightleftharpoons H_2$ 0.00　−0.83　$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$
SO_4^{2-}, NO_3^- hardly oxidised.

3) $Mg^{2+} + 2e^- \rightleftharpoons Mg$ −2.38　$2Br^- \rightleftharpoons Br_2 + 2e^-$ +1.07
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23　$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ −0.83

why H^+ important?

⇒ $2H^+ + 2e^- \rightleftharpoons H_2$ used instead of $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$, diff $E^\ominus$ values

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.

↳ ie $\boxed{\Delta M \propto \Delta Q}$.

Factors that affect Δm

By the eq^n in the proof, we can see that

$$\boxed{\Delta M \propto \left(\frac{I m_r \Delta t}{q}\right)}$$

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.

Proof: $\Delta Q\ (= I\Delta t) = \Delta N \cdot (qe)$

magnitude of current.
time current was passed through.
charge on an electron
number of particles
charge on one ion (+1, +2, +3 etc)

Hence, $I\Delta t = (\Delta N)(qe)$

$\Rightarrow I\Delta t = (\Delta n \cdot N_A)(qe)$

number of moles.
Avogadro's constant

$\Rightarrow I\Delta t = \Delta n(qF)$

$= \frac{\Delta M}{m_r} \cdot qF$

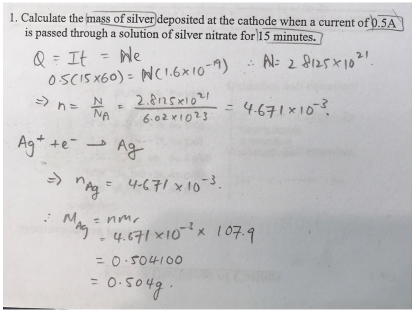
Faraday's constant, $F = N_A \cdot e$

★ in chemistry, "L" is used for Avogadro's constant

Hence, $\boxed{\Delta Q = I\Delta t = \frac{qF}{m_r}\Delta M.}$

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.

$Q = It = Ne$ $\quad \therefore N = 2.8125\times10^{21}$.

$0.5(15\times60) = N(1.6\times10^{-19})$

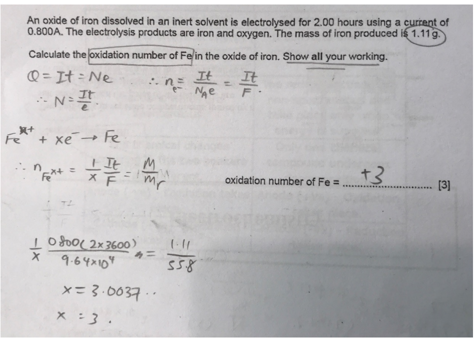
$\Rightarrow n = \frac{N}{N_A} = \frac{2.8125\times10^{21}}{6.02\times10^{23}} = 4.671\times10^{-3}$.

$Ag^+ + e^- \rightarrow Ag$

$\Rightarrow n_{Ag} = 4.671\times10^{-3}$.

$\therefore M_{Ag} = nm_r$
$= 4.671\times10^{-3}\times 107.9$
$= 0.504100$
$= 0.504g$.

Exa 2



An oxide of iron dissolved in an inert solvent is electrolysed for 2.00 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.

$Q = It = Ne$ $\quad \therefore n_{e^-} = \frac{It}{N_A e} = \frac{It}{F}$.

$\therefore N = \frac{It}{e}$.

$Fe^{x+} + xe^- \rightarrow Fe$

$\therefore n_{Fe^{x+}} = \frac{1}{x}\frac{It}{F} = \frac{M}{m_r}$

oxidation number of Fe = ... +3 .... [3]

$\frac{1}{x}\frac{0.800(2\times3600)}{9.64\times10^4} = \frac{1.11}{55.8}$

$x = 3.0037..$

$x = 3$.

SOLVING FOR N_A, AVOGADRO'S CONSTANT, USING AN ELECTROLYTIC METHOD

Recall, from F1L, that

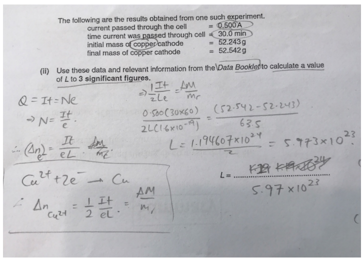
$\Delta Q = I\Delta t = \frac{qF}{m_r}\Delta M$.

Hence, $F = N_A e = \frac{I m_r \Delta t}{q\,\Delta M}$,

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 1



The following are the results obtained from one such experiment.

current passed through the cell = 0.500 A
time current was passed through cell = 30.0 min
initial mass of copper cathode = 52.243 g
final mass of copper cathode = 52.542 g

(ii) Use these data and relevant information from the *Data Booklet* to calculate a value of L to **3 significant figures.**

$Q = It = Ne$

$\Rightarrow N = \frac{It}{e}$.

$\therefore (\Delta n)_{e} = \frac{It}{eL}$.

$Cu^{2+} + 2e^- \rightarrow Cu$

$\therefore \Delta n_{Cu^{2+}} = \frac{1}{2}\frac{It}{eL} = \frac{\Delta M}{m_r}$

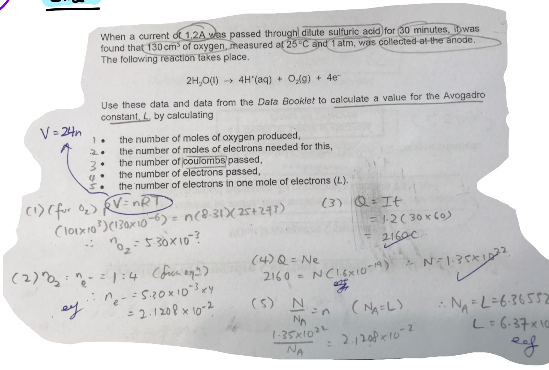
$\Rightarrow \frac{1}{2}\frac{It}{Le} = \frac{\Delta M}{m_r}$

$\frac{0.500(30\times60)}{2L(1.6\times10^{-19})} = \frac{(52.542-52.243)}{63.5}$

$L = \frac{1.194607\times10^{24}}{2} = 5.973\times10^{23}$.

L = ~~1.19 1.19×10^24~~ 5.97×10^{23}

Exa 2



When a current of 1.2A was passed through dilute sulfuric acid for 30 minutes, it was found that 130 cm³ of oxygen, measured at 25 °C and 1 atm, was collected at the anode. The following reaction takes place.

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$$

Use these data and data from the *Data Booklet* to calculate a value for the Avogadro constant, L, by calculating

1. the number of moles of oxygen produced,
2. the number of moles of electrons needed for this,
3. the number of coulombs passed,
4. the number of electrons passed,
5. the number of electrons in one mole of electrons (L).

$V = 24n$

(1) (for O_2) $pV = nRT$
$(101\times10^3)(130\times10^{-6}) = n(8.31)(25+273)$
$\therefore n_{O_2} = 5.30\times10^{-3}$.

(2) $n_{O_2} : n_{e^-} = 1:4$ (from eq^n)
ecf $\therefore n_{e^-} = 5.30\times10^{-3}\times4$
$= 2.1208\times10^{-2}$.

(3) $Q = It$
$= 1.2(30\times60)$
$= 2160C$.

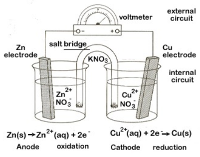
(4) $Q = Ne$
$2160 = N(1.6\times10^{-19})$ ecf $\therefore N = 1.35\times10^{22}$.

(5) $\frac{N}{N_A} = n$ $(N_A = L)$
$\frac{1.35\times10^{22}}{N_A} = 2.1208\times10^{-2}$

$\therefore N_A = L = 6.36552$
$L = 6.37\times10$
ecf

THE ELECTROCHEMICAL CELL

DIAGRAM (EXAMPLE)



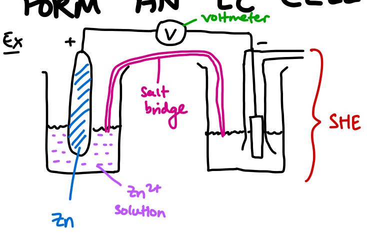
The electrochemical cell consists of **2 half-cells** in seperate compartments, joined by a **salt bridge**.

When the 2 half cells are **joined by a wire**:

→ electrons travel **from** the cell with the **lower $E^\ominus$ value** **to** the cell with the **higher $E^\ominus$ value**.

COMBINING HALF CELLS TO FORM AN EC CELL.

Ex



The **voltmeter reading** is the **difference between** the **$E^\ominus$** of the **two cells**;

$$\boxed{E_{cell} = E^\ominus_{anode} - E^\ominus_{cathode}.}$$

$$= E^\ominus_{+} - E^\ominus_{-}$$

By this, a defⁿ of $E^\ominus$ 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°C**, **1atm**, **$[H^+] = 1.00 \text{ mol dm}^{-3}$**)

The **salt bridge** is used to allow the **ions to move**, to ensure **charges are balanced**.

↳ usually made from **KNO_3**.

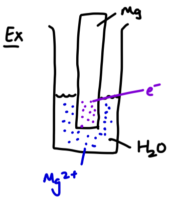
Why? → **all K compounds** are **soluble**

→ **all nitrate compounds** are **soluble**

→ so **no ppt will form with any ions that contact it**.

EQUILIBRIUM POINT OF VIEW IN A HALF CELL

Ex



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 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**.

↳ this results in the formation of a **dynamic equilibrium**, when the **rate of dissociation** = **rate of recombination**.

$$\boxed{Mg \rightleftharpoons Mg^{2+} + 2e^-}$$

↳ meanwhile, each half cell gains an **electric potential**, which is **dependent** on the **position** of the **equilibrium**.

↳ note this $E^\ominus$ **cannot** be **measured directly**.

STANDARD CELL POTENTIAL

Standard cell potential is the **pd** between **2 half-cells** **under standard conditions** (**25°C** and **1atm**; **[all solutions] = 1.00 moldm^{-3}**)

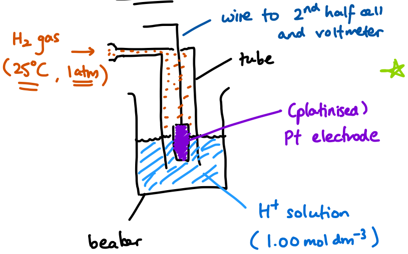
↳ $$\boxed{E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}.}$$

⊕ if **$E^\ominus_{cell} < 0$**, the reaction is **not feasible**.

THE STANDARD HYDROGEN ELECTRODE

The standard hydrogen electrode (SHE) is used as a **reference electrode** to **measure** **$E^\ominus$** in electrochemical experiments.

↳ it is **always** taken to have an **$E^\ominus$ value** of **0.00V**.



★ note the conditions of the gas and solution!

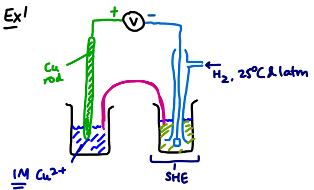
Why a Pt electrode is used:

1) Pt is **inert**;
2) Pt has **moderate surface binding energy** with **H**;
3) Pt is a **catalyst** in the reaction with **H**.

MEASURING $E^\ominus$

HALF CELLS CONTAINING METALS & METAL IONS

Ex¹



At **cathode** (−): $2H^+ + 2e^- \rightleftharpoons H_2$ **$E^\ominus = 0.00$**

At **anode** (+): $Cu \rightleftharpoons Cu^{2+} + 2e^-$ **$E^\ominus = +0.34$.**

$$\Rightarrow E^\ominus_{cell} = +0.34 - (+0.00)$$

$$= +0.34.$$

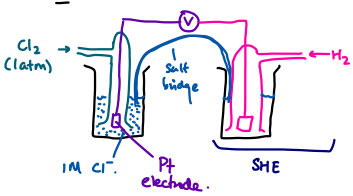
shown on Voltmeter.

★ **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 (−)**: $2H^+ + 2e^- \rightleftharpoons H_2$ **$E^\ominus = 0.00V$**

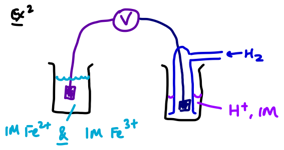
At **anode (+)**: $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ **$E^\ominus = +1.36V$**

$$\Rightarrow E^\ominus_{cell} = (+1.36V) - (0.00V)$$

$$= +1.36V.$$

HALF CELLS CONTAINING IONS OF THE SAME ELEMENT BUT DIFFERENT OXIDATION STATES.

Ex²



$$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$$

$$E^\ominus = +0.77V.$$

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 $Pt_{(s)} \mid H_{2(g)}, 2H^+_{(g)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

Ex2 $Pt_{(s)} \mid H_{2(g)}, 2H^+_{(g)} \parallel Cl_{2(g)}, 2Cl^-_{(aq)} \mid Pt_{(s)}$

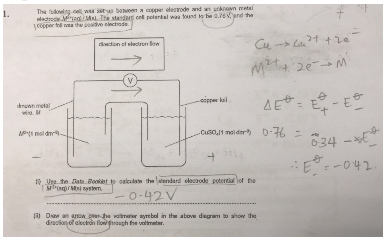
Ex3 $Pt_{(s)} \mid H_{2(g)}, 2H^+_{(g)} \parallel Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} \mid Pt_{(s)}$

* **State symbols** and **molecularity** is important!

* Put **lowest oxidation numbered compound next to the electrode**

EXAMPLES

Exa 1



1. The following cell was set up between a copper electrode and an unknown metal electrode $M^{2+}(aq)/M(s)$. The standard cell potential was found to be 0.76 V, and the copper foil was the positive electrode.

(i) Use the *Data Booklet* to calculate the standard electrode potential of the $M^{2+}(aq)/M(s)$ system.

−0.42V

(ii) Draw an arrow over the voltmeter symbol in the above diagram to show the direction of electron flow through the voltmeter.

$Cu \rightarrow Cu^{2+} + 2e^-$

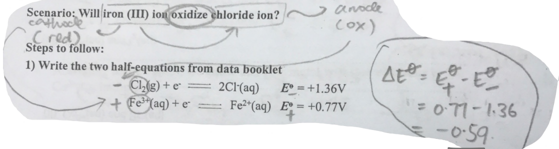
$M^{2+} + 2e^- \rightarrow M$

$\Delta E^\ominus = E^\ominus_+ - E^\ominus_-$

$0.76 = 0.34 - E^\ominus_-$

$\therefore E^\ominus_- = -0.42.$

Exa 2



Scenario: Will iron (III) ion oxidize chloride ion?

cathode (red)

anode (ox)

Steps to follow:

1) Write the two half-equations from data booklet

− $Cl_2(g) + e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus_- = +1.36V$

+ $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E^\ominus_+ = +0.77V$

$\Delta E^\ominus = E^\ominus_+ - E^\ominus_-$

$= 0.77 - 1.36$

$= -0.59$

negative so not feasible.

WHAT DOES $E^\ominus$ TELL US?

A MEASURE OF THE REDUCING/ OXIDISING ABILITY OF AN ELEMENT / ION

Ex $\frac{1}{2}F_2 + e^- \rightleftharpoons F^-$ $E^\ominus = +2.87\,V$

$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$ $E^\ominus = +1.36\,V$

$\frac{1}{2}Br_2 + e^- \rightleftharpoons Br^-$ $E^\ominus = +1.07\,V$

$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$ $E^\ominus = +0.54\,V$

decreasing $E^\ominus$

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

Ex
$$\begin{cases} Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu & E^\ominus = +0.34\,V \\ Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn & E^\ominus = -0.76\,V \end{cases}$$

$E^\ominus_{cell} = E^\ominus_+ - E^\ominus_-$.

For $E^\ominus_{cell} > 0$ (so feasible reaction), $E^\ominus_+$ must be 0.34 V and $E^\ominus_-$ must be −0.76V

(otherwise $E^\ominus_{cell} = -1.10V\ (<0)$).

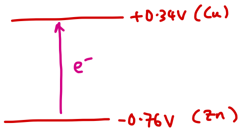
⇒ so anode is Cu, and cathode is Zn.

⇒ half eq^n^s are $\begin{cases} Zn \rightarrow Zn^{2+} + 2e^- . \\ Cu^{2+} + 2e^- \rightarrow Cu . \end{cases}$

⇒ overall eq^n^ is

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$.

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^-

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ $E^\ominus_{(+)} = +1.23\,V$

$2Cl^- \rightarrow Cl_2 + 2e^-$ $E^\ominus_{(-)} = +1.36\,V$

Overall reaction:

$MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O + Cl_2$.

$$E^\ominus_{cell} = E^\ominus_+ - E^\ominus_-$$
$$= 1.23 - 1.36$$
$$= -0.13\ (<0).$$

∴ reaction should not be feasible.

⊕ However, this reaction can occur by heating MnO_2 w/ conc. HCl.

↳ but these are non standard conditions.

REACTION HAS HIGH E_a

Ex Reaction between methanal and dichromate ions

$3HCHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3HCO_2H + 4H_2O$

$E^\ominus_{cell} = +1.27\,V$ (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 $Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$.

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 eq^n^ from data booklet.

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 eq^n^:

$$\boxed{E_{new} = E^\ominus + \frac{0.059}{z}\log_{10}\left\{\frac{[\text{oxidised species}]}{[\text{reduced species}]}\right\}}$$

altered electrode potential

std. electrode potential

molecularity of e^- in half equation (# of moles used)

conc. of species with higher oxidation number

conc. of species with lower oxidation number.

$$\boxed{0.059 = \frac{RT^\ominus}{F\log_{10}e}}$$

ideal gas constant

temp. at std conditions (298 K)

Faraday's constant ($F = N_A \cdot e$)

(extra info)

HALF CELL WITH METAL AND METAL ION

Ex Calculate E of Cu/Cu²⁺ half cell, where $[Cu^{2+}] = 0.001M$, and $E^\ominus = +0.34V$.

"re" "ox"

[reduced species] not given, so we assume it is "normal" (ie equal to 1.)

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ ∴ $z = 2$.

$$\Rightarrow E = E^\ominus + \frac{0.059}{2}\log_{10}[Cu^{2+}].$$

"oxidised" species (higher oxidation #)

$$= +0.34 + \frac{0.059}{2}\log_{10}(0.001) = \underline{\underline{+0.2515}}.$$

HALF CELL WHICH CONTAINS NON-METAL AND NON-METAL ION

Ex Calculate E of Cl_2/Cl^- half cell if $[Cl^-] = 0.10$, and $E^\ominus = +1.36$.

"ox" "re"

[oxidised species] not given, so equate it to 1.

$Cl_2 + 2e^- \rightarrow 2Cl^-$ ∴ $z = 2$.

$$\Rightarrow E = E^\ominus + \frac{0.059}{2}\log_{10}\left(\frac{1}{[Cl^-]}\right)$$
$$= +1.36 + \frac{0.059}{2}\log_{10}\left(\frac{1}{0.1}\right)$$
$$= +1.3895$$
$$= \underline{\underline{+1.39}}.$$

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 $E^\ominus = +0.77$.

$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$ ∴ $z = 1$.

$$E = E^\ominus + \frac{0.059}{1}\log_{10}\left(\frac{1}{[Fe^{2+}]}\right)$$
$$= +0.77 + 0.059\log_{10}\left(\frac{1}{0.20}\right)$$
$$= +0.81123V$$
$$= +0.81V.$$

CELLS AND BATTERIES

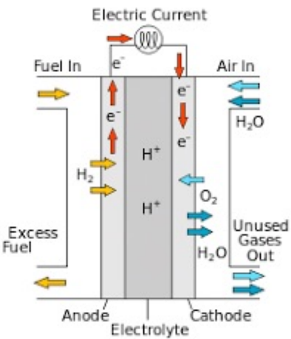
Many different batteries and cells rely on electrochemistry to provide power.

H_2/O_2 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 H_2/O_2 cell requires a continuous supply of H_2 and O_2.

ACIDIC H_2/O_2 FUEL CELL



acidic.

→ At the anode, H_2 is oxidised;

$H_2 \longrightarrow 2H^+ + 2e^-$

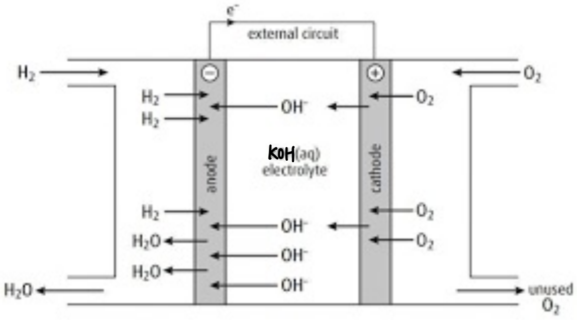
→ At the cathode, O_2 is reduced;

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

∗ The overall eqⁿ is

$O_2 + 2H_2 \longrightarrow 2H_2O.$

ALKALINE H_2/O_2 FUEL CELL



→ At the anode, H_2 is oxidised;

$H_2 \longrightarrow 2H^+ + 2e^-$

→ At the cathode, O_2 is reduced;

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

∗ The overall eqⁿ is

$O_2 + 2H_2 \longrightarrow 2H_2O.$

☆ A high concentration of the electrolyte ($NaOH$ or KOH) is used to increase the rate of the reaction.

ADVANTAGES & DISADVANTAGES OF H_2/O_2 FUEL CELLS

Advantages:

① Lesser pollution (only byproduct is H_2O)

② Efficient

③ Can use atmospheric H_2 if fuel H_2 runs out

Disadvantages:

① High cost in manufacturing electrodes / membrane

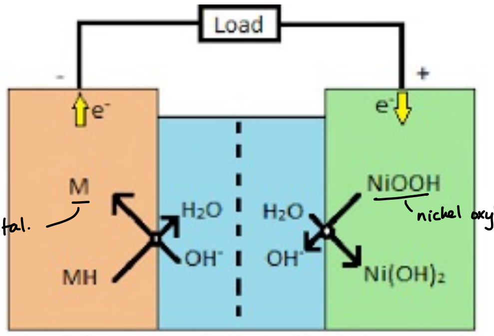
② Ineffective at low temperature (reliant on rate)

③ H_2 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)



a metal.

nickel oxyhydroxide

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 $NiO(OH)$;

$Ni(OH)_2 + OH^- \longrightarrow NiO(OH) + H_2O + e^-.$

→ The metal M is reduced to form its hydride, MH;

$M + H_2O + e^- \longrightarrow MH + OH^-$

∗ The overall eqⁿ is

$Ni(OH)_2 + M \longrightarrow NiO(OH) + MH.$

☆ ADVANTAGES AND DISADVANTAGES

Advantages:

① Environmentally friendly. (can be recycled)

② High capacity.

Disadvantages:

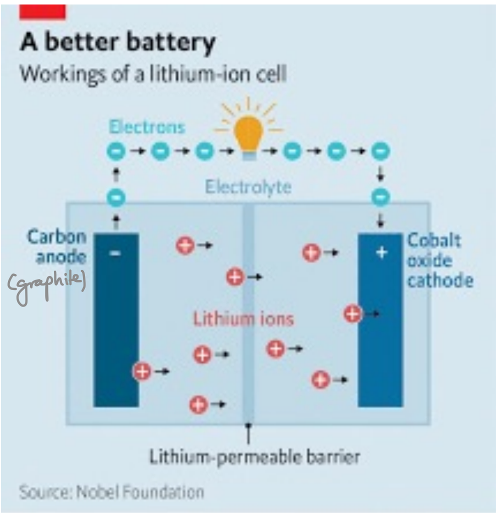
① Limited service life

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)



Source: Nobel Foundation

The Economist

→ At the anode, lithium cations are liberated from the graphite electrode, denoted as C_6;

$$LiC_6 \longrightarrow Li^+ + e^- + C_6$$

Li embedded within graphite structure

→ At the cathode, the lithium cations are "received" by the cobalt oxide substrate;

$$CoO_2 + Li^+ + e^- \longrightarrow LiCoO_2.$$

→ The overall eqⁿ is:

$$LiC_6 + CoO_2 \longrightarrow C_6 + LiCoO_2$$

ADVANTAGES AND DISADVANTAGES

Advantages:

① High energy density
② Low self-discharge

Disadvantages:

① High cost
② Protection needed when charging (unsafe if overcharged)

Chapter 19: Further Chemical Energetics

ELECTRON AFFINITY

STANDARD 1ST EA, $\Delta H^{\ominus}_{ea1}$

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 anions under standard conditions (25°C, 1atm).

$$\boxed{X_{(g)} + e^- \longrightarrow X^-_{(g)} \quad \Delta H = \Delta H^{\ominus}_{ea1}}$$

* $\Delta H^{\ominus}_{ea1}$ 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, $\Delta H^{\ominus}_{ea2}$

Similarly, $\Delta H^{\ominus}_{ea2}$ 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.

$$\boxed{X^-_{(g)} + e^- \longrightarrow X^{2-}_{(g)}}$$

* $\Delta H^{\ominus}_{ea2}$ (and $\Delta H^{\ominus}_{ea3}$) 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.

Ex

$$\boxed{Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \quad \Delta H^{\ominus}_{la} = -781\,kJmol^{-1}}$$

* 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, $\Delta H^{\ominus}_{hyd}$

$\Delta H^{\ominus}_{hyd}$ is the enthalpy change when 1 mole of specified gaseous ions dissolves in sufficient water to form a very dilute solution under standard conditions.

eg $\boxed{Na^+_{(g)} \longrightarrow Na^+_{(aq)}}$

* ΔH_{hyd} is always exothermic.

Why? → formation of ion-dipole bonds.

FACTORS WHICH AFFECT ΔH_{hyd}

* specify whether cationic or anionic.

① Ionic charge

↳ as charge increases

↳ charge density increases

↳ ion-dipole bond with H_2O molecules gets stronger

↳ so ΔH_{hyd} is more exothermic.

② Ionic size

↳ as size increases

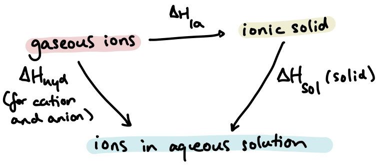
↳ charge density decreases

↳ ion-dipole bond with H_2O molecules gets weaker

↳ so ΔH_{hyd} is less exothermic.

DETERMINATION OF $\Delta H^{\ominus}_{hyd}$

We can use an energy method to find $\Delta H^{\ominus}_{hyd}$.



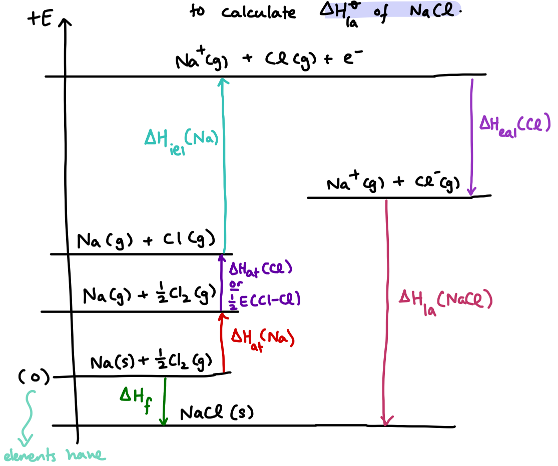
BORN-HABER CYCLE

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.



⊕₁ ΔH_f and ΔH_{ea} are exothermic so you must represent them with downward arrows.

Using Hess' law:

remember $\frac{1}{2}E(Cl-Cl)$ can also be used for this.

$$\boxed{|\Delta H_f| + |\Delta H_{at}| + |\Delta H_{at}(Cl_2)| + |\Delta H_{iel}(Na)| = |\Delta H_{eal}(Cl)| + |\Delta H_{la}(NaCl)|.}$$

(using data)

$$411 + 107 + 494 + 121 = 355 + |\Delta H_{la}|$$

$$\therefore \Delta H_{la} = (-)778\ kJmol^{-1}!$$

⊕₂ If the final moles of the reaction ≠ 1, then multiply ΔH with the appropriate molecularity 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}.

↳ $\boxed{\Delta H_{la} \propto \frac{q_+ \cdot q_-}{r_+ - r_-}}$ → size of SO_4^{2-} >> size of cation

↳ 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}.

↳ $\boxed{\Delta H_{la} \propto \frac{q^+ \cdot q^-}{r_+ - r_-}.}$ → size of OH^- << size of cation.

↳ 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: $[Ar]3d^14s^2$
∴ e^- configuration of Sc^{3+}: $[Ar]$ or $[Ne]3s^23p^6$
⇒ 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: $[Ar]3d^{10}4s^2$
∴ e^- configuration of Zn^{2+}: $[Ar]3d^{10}$.
⇒ ion has a full 3d subshell, so cannot be a transition element.

PHYSICAL PROPERTIES

HIGHER MELTING POINTS (THAN Ca)

1 In Ca, only 4s e^- involved in metallic bonding, but in transition metals, 3d e^- are also involved in metallic bonding.
↳ hence number of delocalised electrons in the "sea" increases
↳ 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?

1 Compared with Ca, transition metals have a smaller metallic radius;
↳ due to greater nuclear charge
↳ so force on electrons increases

2 Compared with each other, the metallic radii for transition elements remain roughly the same.
↳ this is because the slight increase in nuclear charge is counteracted by the increase in inner electron shielding (as valence e^- added to 3d).

eg $Co: [Ar]3d^74s^2$
↓
$Ni: [Ar]3d^84s^2$
inner shielding ↑ (so size same)

compared to
$Al: [Ne]3s^23p^1$
↓
$Si: [Ne]3s^23p^2$
shielding same
↑ proton number
(so size ↓)

DENSITY?

1 Compared with Ca, transition metals have greater densities.
↳ due to greater A_r and smaller radii
↳ note $\rho = \frac{M}{V}$. (M↑, V↓)

2 Densities increase across the period:
↳ relatively same atomic size
↳ atomic number increases.

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.

$Fe \rightarrow Fe^{2+}, Fe^{3+}$
$Cr \rightarrow Cr^{3+}, Cr^{6+}$
$Mn \rightarrow Mn^{2+}, Mn^{7+}$
$Cu \rightarrow Cu^{+}, Cu^{2+}$.

+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 $[Ar]3d^{10}4s^1$).
So it can form a stable ion of +1.

REDOX REACTIONS WITH TRANSITION ELEMENTS

When exposed to a suitable reagent, its oxidation state can change.

Ex $\underbrace{MnO_4^-}_{\text{purple/pink}} + \underbrace{5Fe^{2+}}_{\text{pale green}} + 8H^+ \rightleftharpoons Mn^{2+} + \underbrace{5Fe^{3+}}_{\text{pale brown}} + 4H_2O$

Observations :
① Initial pale green solution
② As MnO_4^- added, solution fades to (almost) colourless
③ Then, a permanent faint pink solution is observed.
④ If excess MnO_4^- added, solution becomes purple.

CAN ACT AS CATALYSTS.

HOMOGENOUS

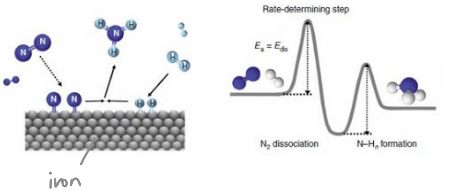
Transition metals are good homogenous catalysts due to them being able to exist in multiple stable ions with variable oxidation states.

Ex
$$S_2O_8^{2-}{}_{(aq)} + 2I^-{}_{(aq)} \xrightarrow{Fe^{3+}_{(aq)}} 2SO_4^{2-} + I_{2\,(aq)}$$
$$\left(\begin{array}{l} 2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \\ 2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-} \end{array}\right)$$

HETEROGENOUS

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

1 A complex ion is an ion formed when ligands datively bond to a central metal cation.

2 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.

⊕ A ligand is a nucleophile; it donates its electrons into the vacant orbital on the transition element, leading to the formation of dative covalent bonds and a complex ion.

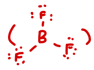
TYPES OF LIGANDS

MONODENTATE

Monodentate ligands contain one lone pair of electrons that can form dative covalent bonds with a metal atom / cation.

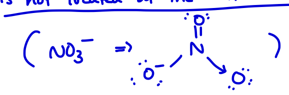
e.g. $H_2\ddot{O}$, $\ddot{N}H_3$, $:X^-$ (halide), $:CN^-$.

⊕₁ 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 () is NOT a ligand. (LP of e^- not at B).

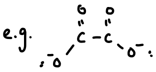
* otherwise the ligand would be unstable.

⊕₂ 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.

(NO_3^- ⇒ )

BIDENTATE

Bidentate ligands contain two lone pairs of electrons that each can form a dative covalent bond with a metal atom / cation.

e.g.  ethanedioate ion (or "ox")

$H_2\ddot{N}-(CH_2)_2-\ddot{N}H_2$ 1,2-diaminoethane (or "en")

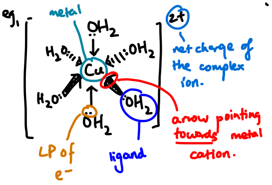
⊕₃ The complex ions formed from bidentate ligands are very stable.

⊕₄ 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.

DRAWING COMPLEX IONS

eg₁

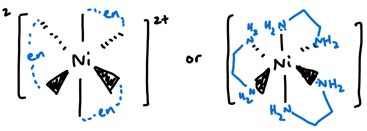


Checklist for drawing:

- square brackets
- net charge of complex
- lone pair of e^- next to ligand
- arrow to signify dative bond
- correct stereochemical geometry.

(For bidentate)

eg₂



FORMULAE

We need to write square brackets for the complex ion so we can clearly distinguish the ligands from the "outside" molecules.

eg₁ $[Cu(H_2O)_6]^{2+}$

eg₂ $[Ni(en)_3]^{2+}$

or $[Ni(H_2N(CH_2)_2NH_2)_3]^{2+}$

NOMENCLATURE

Steps:

① Identify all the identities of all the ligands present and the number of ligands present.

② Determine the corresponding prefix.

③ Determine the root name.

→ if complex is a cation, it has the usual metal name.

→ otherwise, add -ate to it. (see table for understanding).

④ Calculate the oxidation number of the cation. (net charge − charge on ligands).

Examples

$[Fe(CN)_6]^{3-}$ → hexacyano ferrate (III) ion.
- hexacyano: 6 CN^- ligands
- ferrate: iron; and part of anion. (so add -ate to "old" name for iron)
- (III): oxidation number of Fe.

$[Cu(H_2O)_6]^{2+}$ → hexaaqua copper (II) ion.
- hexaaqua: 4 H_2O ligands
- copper: copper, and part of cation.
- (II): ox. no of Cu.

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ → tetraammine-diaqua copper (II) ion.
- tetraammine-diaqua: 4 NH_3 and 2 H_2O ligands
- copper: copper (cation)
- (II): ox. no of Cu.

$[Zn(OH)_4]^{2-}$ → tetrahydroxy zincate (II) ion.
- tetrahydroxy: 4 OH^- ligands
- zincate: zinc, part of anion.
- (II): ox. no of Zn.

$[CrCl_2(H_2O)_4]^+$ → tetraaqua-dichloro chromium (III) ion.
- tetraaqua-dichloro: 4 H_2O, 2Cl^- ligands
- chromium: chromium (cation).
- (III): ox no of Cr

$[CuCl_4]^{2-}$ → tetrachloro cuprate (II) ion.
- tetrachloro: 4Cl^- ligands
- cuprate: copper, anion so add -ate.
- (II): ox no of Cu

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 $[AgCl_2]^+$)

coordination # = 4 → tetrahedral (eg $[CuCl_4]^{2-}$, $[CoCl_4]^{2-}$)
→ square planar (eg $[Pt(NH_3)_2Cl_2]$ (platin))

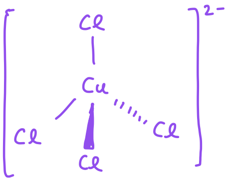
coordination # = 6 → octahedral (eg $[Cr(OH)_6]^{2-}$)

Diagrams

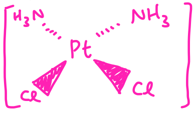
① Linear

$[Cl:\rightarrow Ag \leftarrow :Cl]^-$

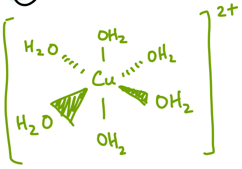
② Tetrahedral



③ Square planar

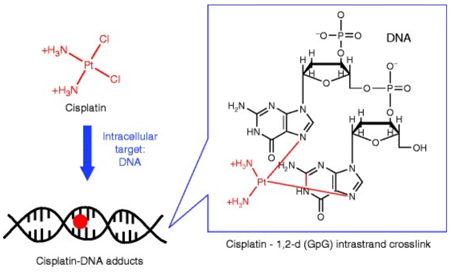


④ Octahedral



☆ remember to show the stereochemistry / molecular geometry clearly!

THE USE OF CIS-PLATIN IN CANCER TREATMENT



Mechanism:

① Cis-platin diffuses through the cell membrane via passive diffusion and active transport.

② 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.

③ This binding induces the binding of high-mobility group (HMG) proteins, which cause kinks (breakages) in the DNA strand.

④ This leads to replication and transcription inhibition, cell cycle arrest and eventually cell death.

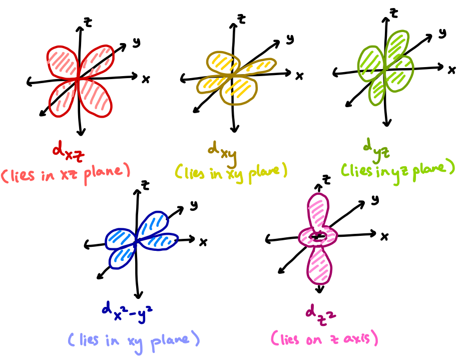
Polarity of cis-platin vs trans-platin

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.



d_{xy}, d_{xz} and d_{yz} are located between axises, whereas $d_{x^2-y^2}$ and d_{z^2} are located along axises.

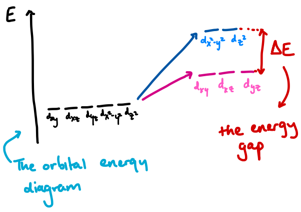
↳ to show this, you remove the "coordinate axis" if the orbital "lies" on the axis. (as shown).

HOW THE ENERGY LEVEL CHANGES AFTER LIGAND BONDING.

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



Ex $[Cu(H_2O)_6]^{2+}$.

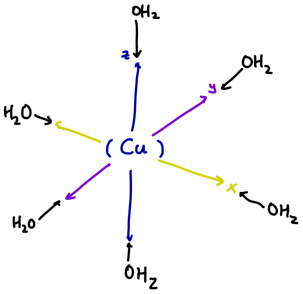
The presence of the 6 ligands splits the 3d orbitals into a 2 : 3 ratio;

↳ 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.

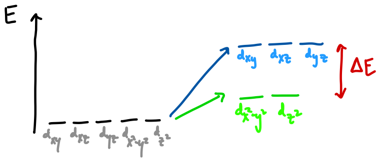
why? → ⊕ Ligands have lone pairs of electrons.

↳ 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 highe "energy level").



TETRAHEDRAL COMPLEX ION



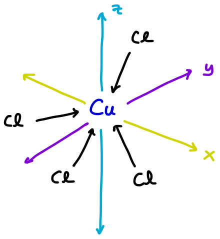
Ex $[CuCl_4]^{2-}$

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.

Why? → ⊕ Again, the ligands have a lone pair of electrons.

↳ BUT, the ligands bond between the axises, which is where d_{xy}, d_{xz} and d_{yz} are located.

↳ so, it is these 3 orbitals that experience greater interelectron repulsion with the lone pair of electrons on ligands.

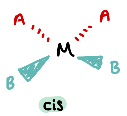


STEREOISOMERISM OF TRANSITION METAL COMPLEXES

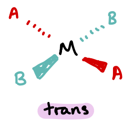
Note: tetrahedral → no stereoisomers
square planar → cis-trans stereoisomers
octahedral → both cis-trans and optical stereoisomers.

SQUARE PLANAR COMPLEX ION

Square planar complex ions can only form geometric isomers.



cis
(same species 90° apart)

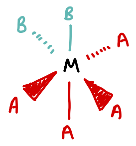


trans
(same species 180° apart).

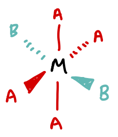
OCTAHEDRAL COMPLEX ION

GEOMETRIC ISOMERISM

case 1 $[MA_4B_2]$ (eg $[Co(NH_3)_4Cl_2]^+$) (A, B : mono)

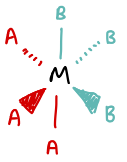


cis
("B" 90° apart)

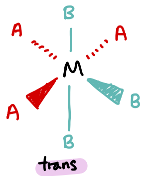


trans
("B" 180° apart)

case 2 $[MA_3B_3]$ (eg $[Cr(OH)_3(H_2O)_3]$)



cis
(all ∡ bw B 90° apart; "k")



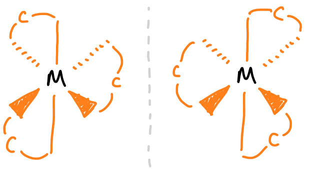
trans
(one angle bw B 180° apart; "⊥")

☆ note that these are just a few examples. (Exam can ask about harder material).

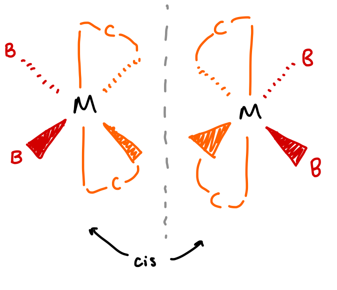
OPTICAL ISOMERISM

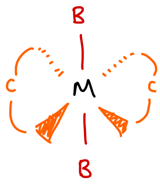
case 1 $[MC_3]$ (C= bidentate)

*treat the middle "line" as a mirror.



case 2 $[MB_2C_2]$





(trans)

☆ make sure, for each stereoisomer, you cannot "rotate" it to obtain a previous stereoisomer.

LIGAND SUBSTITUTION/ EXCHANGE.

Ligands in a complex ion can be exchanged, wholly or partially, for other ligands.

↳ substitution will occur if a complex ion is exposed to a stronger ligand.

SUBSTITUTION WITH (CONC) Cl^-

COPPER

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

octahedral blue — tetrahedral yellow solution

COBALT

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O.$$

octahedral pink — tetrahedral blue solution

⊕ Cl^- can come from NH_4Cl or HCl.

1. All ligand substitutions are equilibrium reactions.
2. Why can $6H_2O$ ligands fit into the ions, but only $4Cl^-$?
   ↳ H_2O is smaller than Cl^-.
3. How to reverse the reaction?
   ↳ dilute the solution;
   ↳ $[H_2O]$ ↑ so eq shifts to the left.

STABILITY CONSTANTS, K_{stab}

A stability constant is an equilibrium constant for the formation of a complex ion in solution.

⊕ The greater the value of K_{stab}, the more stable the complex ion is.

$$K_{stab} = \frac{[\text{formed complex ion}]}{[\text{reactants}]}$$

eg $[Cu(H_2O)_6{}^{2+}] + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O.$

$$K_{stab} = \frac{[[Cu(NH_3)_4(H_2O)_2]]}{[[Cu(H_2O)_6]^{2+}][NH_3]^4}$$

*molecularity of NH_3.

*exclude the "kicked out ligand" (H_2O).

SUBSTITUTION WITH NH_3.

ADDITION OF LIMITED NH_3 / NaOH

When limited NH_3, or NaOH, is added, a precipitation / acid-base reaction occurs:

$$[X(H_2O)_6]^{2+} + 2OH^- \longrightarrow [X(OH)_2(H_2O)_4] + 2H_2O.$$

neutral molecule. (most stable)

☆ remember,

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$.

origin of OH^- ions in eqⁿ.

⊕ Why is it a neutralisation reaction?

↳ $[X(H_2O)_6]^{2+}$ dissociates partially:

$$[X(H_2O)_6]^{2+} \rightleftharpoons [X(H_2O)_5(OH)]^+ + H^+.$$

↳ the highly positive central cation polarises the O–H bond, weakening it. (It easily undergoes fission to liberate H^+.)

ADDITION OF EXCESS NH_3

When excess NH_3 is added, a ligand substitution occurs:

COPPER

$$[Cu(OH)_2(H_2O)_4] + 4NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+} + 2OH^-$$

octahedral blue ppt — octahedral dark blue sol.

COBALT

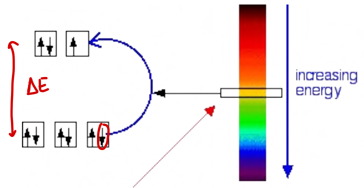
$$[Co(OH)_2(H_2O)_4] + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 4H_2O + 2OH^-$$

octahedral blue ppt — octahedral brown solution

☆ must be eq reaction!

For other elements, you can add 4 or 6 NH_3.

COLOUR OF COMPLEXES



The energy of this particular colour is just right to promote the electron.

The dative covalent bonds from ligands causes the splitting of the d-orbitals.

↳ some electrons in the lower energy level d-orbitals, after absorbing a photon, can jump to a higher level d-orbital, if $\Delta E = hf$.

↳ the colour seen is the "complement" of the colour absorbed.

COLOUR CHART

Colour	Corresponding wavelength of photon	Complement
Red	650–700nm	Green
Yellow	600nm	Purple
Green	500nm	Red
Blue	450nm	Orange
Purple	400nm	Yellow

WHY ARE SOME COMPOUNDS NOT COLOURED?

COPPER (I) SALT

Electron configuration: $[Ar]\,3d^{10}$.

↳ all orbitals occupied.

↳ so no absorption of light in the visible spectrum.

ZINC (II) SALT

Electron configuration: $[Ar]\,3d^{10}$.

↳ all orbitals occupied.

↳ so no absorption of light in the visible spectrum.

SCANDIUM (II) SALT

Electron configuration: $[Ar]$

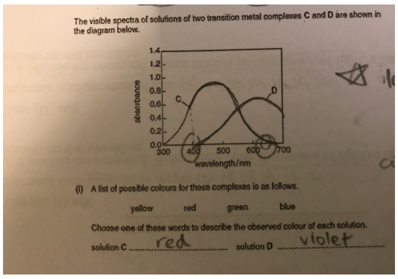
↳ there is no electron that can be promoted to a higher level when the 3d subshell is split.

S-BLOCK ELEMENTS, e.g Na

ΔE between 3s and 3p is too large to be overcome by a photon in the visible light range.

DETERMINING COLOUR OF COMPLEX USING ABSORBANCE GRAPH

The least absorbed colour is the colour of the compound.



The visible spectra of solutions of two transition metal complexes C and D are shown in the diagram below.

(i) A list of possible colours for these complexes is as follows.

yellow red green blue

Choose one of these words to describe the observed colour of each solution.

solution C ....red.... solution D ....violet....

WHAT AFFECTS THE COLOUR OF A COMPLEX ION?

NATURE OF LIGANDS

Stronger ligands will produce a larger energy gap when they datively bond to a transition metal atom.

↳ $\Delta E = \frac{hc}{\lambda}$; so as ΔE increases, λ decreases, so complex's colour is "more towards" the violet end of the spectrum.

MAGNITUDE OF ABSORBANCE

The greater the absorbance, the darker / more colour intense the compound is.

Chapter 28: Polymerisation

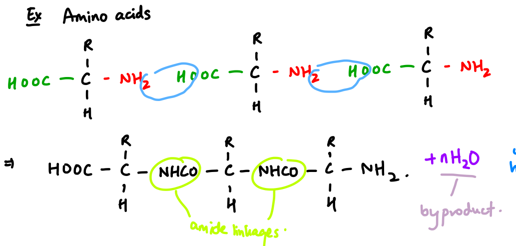
CONDENSATION POLYMERISATION

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 (eg H_2O).

TYPE I VS TYPE II POLYMERISATION

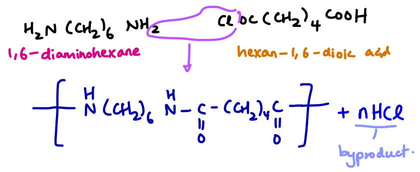
Type I: the two functional groups are present within one molecule.

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

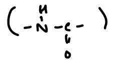


$$\left[\overset{H}{N}(CH_2)_6\overset{H}{N}-\underset{O}{\underset{\|}{C}}-(CH_2)_4\underset{O}{\underset{\|}{C}} \right] + nHCl$$

POLYAMIDES

* polyamides (and polyesters) are synthetic polymers.

Polyamides are polymers whose monomers are bonded to each other via amide $(-\overset{H}{N}-\underset{O}{\underset{\|}{C}}-)$ links.



NYLON

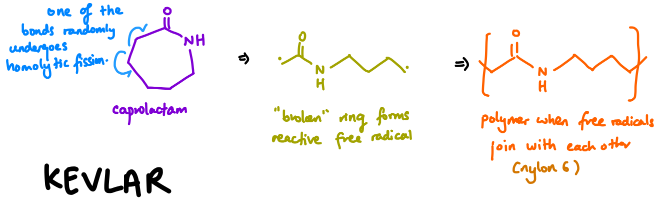
All nylon is formed from condensation polymerisation except Nylon 6.

⊕ Nylon 6,6

↳ see example to the left.

⊕ Nylon 6

↳ formed from "ring opening" polymerisation.



⊕ Physical Properties

1) High tensile strength
2) High elasticity
3) Low density

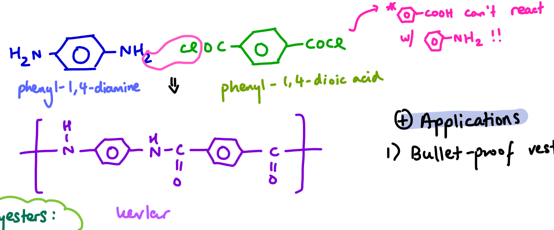
due to strong hydrogen bonds between neighbouring chains.

⊕ Applications

1) Climbing rope
2) Classical musical instruments

KEVLAR

Kevlar is formed by the polymerisation of two benzene compounds.



⊕ Properties

1) Very strong but flexible
2) Fire resistant

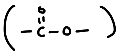
⊕ Applications

1) Bullet-proof vests

POLYESTERS

* advantage of polyesters: they are biodegradeable.

Polyesters are polymers whose monomers are bonded together via ester $(-\overset{O}{\overset{\|}{C}}-O-)$ links.

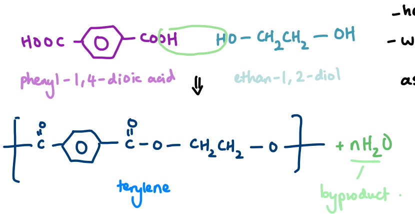


* polyesters cannot be used to package acidic food, eg vinegar:

→ ester linkage hydrolysed in acidic solutions.

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.

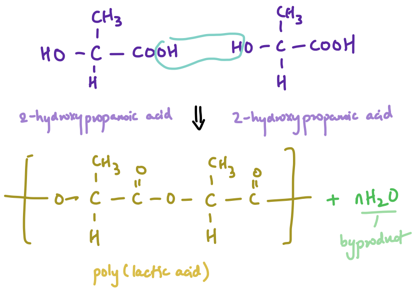
⊕ Applications

↳ can be mixed with natural fibre to produce a variety of fabrics.

POLY(LACTIC ACID)/ PLA

* lactic acid can be manufactured by the fermentation of corn starch and sugar.

↳ formed from lactic acid (2-hydroxypropanoic acid).



⊕ Applications

1) degradeable packing materials
2) meshes for medical implants

⊕ Limitations

1) Low melting point, softens around 60°C – 80°C
   ↳ cannot be used for hot drinks.

DIFFERENCES BETWEEN ADDITION AND CONDENSATION POLYMERS.

	Functional group on monomer vs. FG on polymer	Difference in EF bw polymer and monomer	Elimination of molecules?.
Condensation	different (contains amide / ester linkages)	different (removal of small molecule)	yes (generally HCl/H_2O)
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.

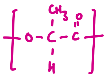
↳ C=O bonds can be broken easily upon the absorption of UV radiation.

↳ this leads to a greater decomposition rate of the polymer.

Biodegradeable Plastics

esters

eg PLA



$$-\left[O-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}\right]-$$

The ester linkages in PLA can be easily hydrolysed, either

- under acidic / alkaline conditions, or
- in the presence of an enzyme (esterase).

↳ the resultant lactic acid can then be easily metabolised into CO_2 and H_2O by organisms.

Thermosoftening Plastics (Thermoplastics)

*addition polymers only.

eg poly(ethene) $-[CH_2-CH_2]-$

Thermosoftening plastics are plastics that soften (and eventually melt) on heating.

↳ 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.

eg epoxy resins (see below)

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.

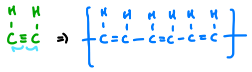
↳ significantly more heat must be supplied to break the strong covalent bonds.

↳ instead of softening / melting, thermosetting plastics tend to blacken (but remain solid).

CONDUCTING POLYMERS

*specific to addition polymers.

eg poly(ethyne) / poly(acethylene)



*π bond is broken during homolytic fission.

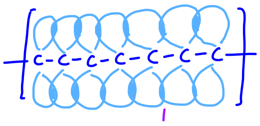
Why? → σ bonds are closer to the nucleus than π bonds

→ so σ bonds are stronger than π bonds.

**The C backbone of the polymer is conjugated;

↳ 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.

⊕ molecular geometry requirement: Planar molecule

↳ so p-orbitals overlap with each other.

⊕ advantages of conducting polymers:

1) more resistant to corrosion
2) more lightweight / less dense
3) more malleable

NON-SOLVENT BASED ADHESIVES (GLUES)

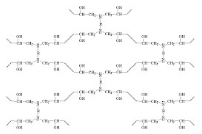
Traditionally, solvent-based adhesives are used; in these, ester-based solvents (eg CH_3COOCH_3) are used to dissolve a polymer that will serve as an adhesive. Subsequently, the solvents are evaporated.

↳ however, these have some disadvantages:

1) solvents are flammable; and
2) some organic solvents are harmful to our health.

Hence, we have started to use non-solvent based adhesives instead.

⊕ Epoxy resin



monomers: diepoxy and diamine.

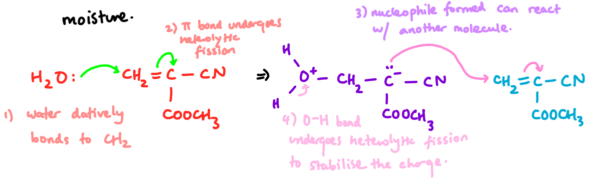
Epoxy resins are thermosetting; they form an extensive network of covalent cross-links within their structure.

Advantage:

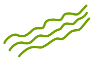
① Extremely strong
② Heat resistant.

⊕ Super glue

↳ formed from the addition polymerisation of $CH_2=C(CN)COOCH_3$, in the presence of moisture.



LOW-DENSITY AND HIGH DENSITY POLY(ETHENE) / LDPE & HDPE.

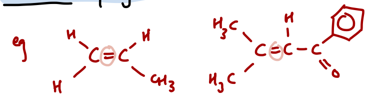
	LDPE	HDPE	
structure:	high number of branched chains 	very little branching 	
melting point:	lower	higher	→ HDPE has a greater surface area for the formation of id-id forces between polymers.
densities:	lower	higher	→ HDPE polymers are more tightly packed with each other
applications:	1) plastic bags	1) plastic pipes 2) plastic milk bottles	

POLYMER DEDUCTIONS

#1 RECOGNISING THE TYPE OF POLYMERISATION FROM THE MONOMERS GIVEN.

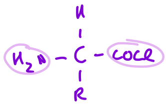
1 If a monomer contains a double bond, there is a high possibility it undergoes addition polymerisation.

eg



2 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.

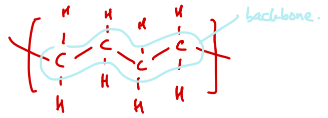
eg



#2 RECOGNISING THE TYPE OF POLYMERISATION FROM THE POLYMER.

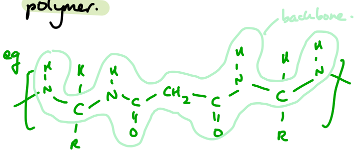
1 If the polymer "backbone" contains only C atoms, the polymer is an addition polymer.

eg



2 If the polymer "backbone" contains amide / ester links, the polymer is a condensation polymer.

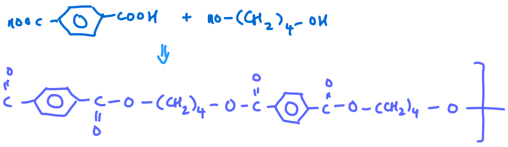
eg



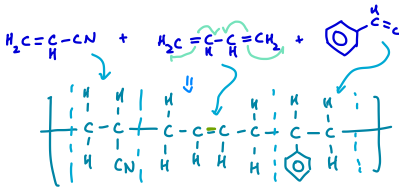
#3 IDENTIFICATION OF THE REPEAT UNIT OF A CONDENSATION POLYMER FROM GIVEN MONOMERS.

To draw:
1) Draw product formed if monomers reacted together; then
2) Take off the atoms at both ends that would be lost if another 2 monomers were to react with those groups.

eg¹



eg²

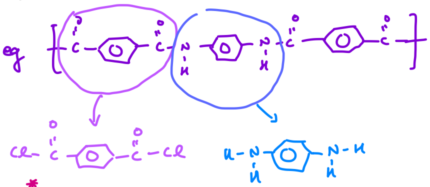


* homolytic fission of 2 "adjacent" double bonds results in creation of π bond

#4 IDENTIFICATION OF MONOMERS FROM CONDENSATION POLYMER

Steps:
1) Identify the small molecules that are given off during the polymerisation reaction
2) Then, replace them on the reactive functional groups on the monomers.

eg

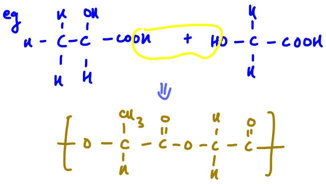


* "safer" to put –COCl than –COOH (more reactive)

COPOLYMERISATION

Copolymerisation refers to the polymerisation of two or more different monomers.

eg

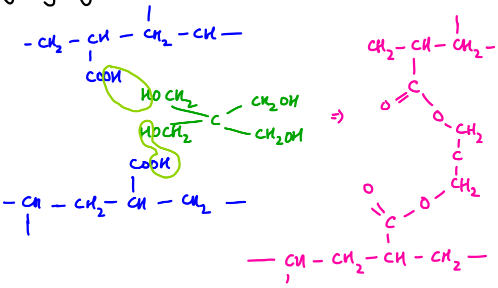


CROSS-LINKED POLYMERS

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:
1) Harder
2) Stronger
3) More flexible.

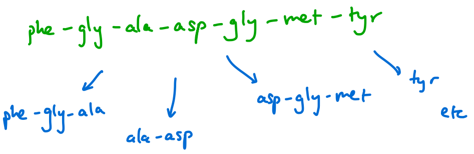
PROTEINS

Proteins are formed through the polymerisation of amino acids, making them polyamides / polypeptides.

HYDROLYSIS OF PROTEINS

Under acidic or alkaline conditions, peptide bonds in proteins can be hydrolysed, resulting in a mixture of polypeptide fragments.

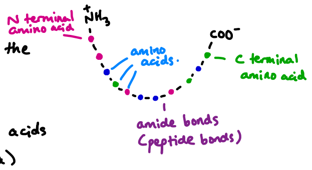
eg



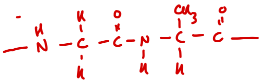
PROTEIN STRUCTURE

PRIMARY

The "primary" structure consists of the amino acid sequence / chain.



Drawing: pick two random amino acids and draw. (eg Gly, Ala)



SECONDARY

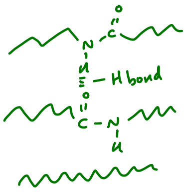
The secondary structure of a protein is the regular structural arrangement stabilised by hydrogen bonding between the N-H group of one peptide bond and the C=O group of another.

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



- a sheet-like structure
- stabilised by H bonding between N-H and C=O groups in different chains

TERTIARY

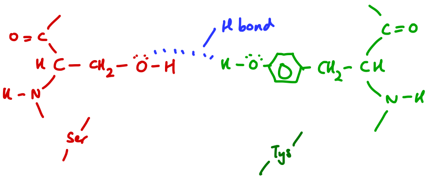
The tertiary structure of a protein is the coiling / folding of it due to interactions between side chains on amino acids, giving it its overall 3D shape.

*due to side groups, NOT between atoms on peptide links.

Drawing: select two interactions from below.

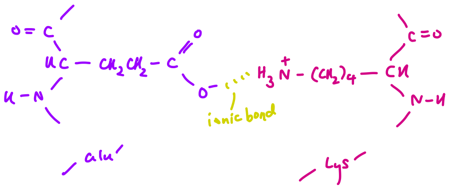
① H bonding

eg Ser and Tys



② Ionic bond

eg Glu and Lys

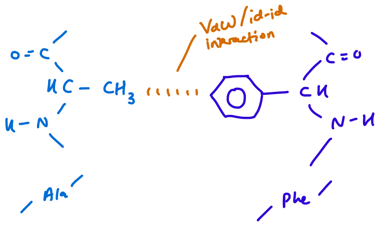


*formed between ionised acid and ionised base chain.

③ id-id forces

eg Ala & Phe

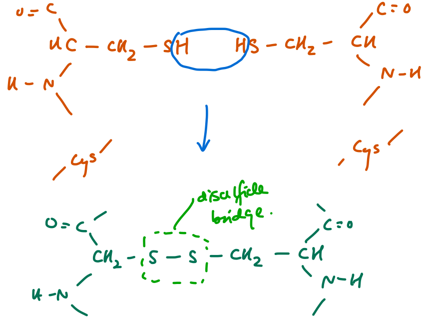
*occurs between 2 non-polar groups.



④ Disulfide bridges

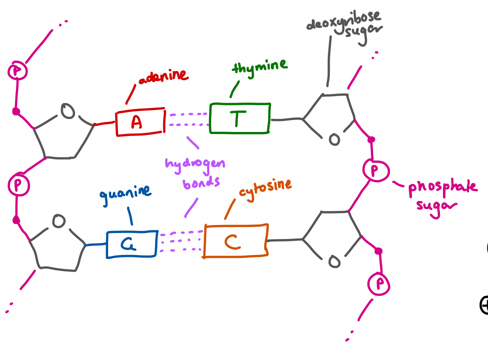
ONLY Cys and Cys.

*oxidation reaction.



STRUCTURE OF DNA

DNA (deoxyribonucleic acid) is formed from monomer units called nucleotides.



⊕$_1$ In DNA:
(AT) : (GC) = 1 : 2.

⊕$_2$ A, G, T & C are planar structures;
- A, G contain 2 rings.
- T, C contain 1 ring.

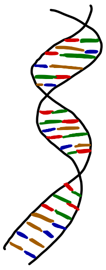
⊕$_3$ There are 2 H bonds between A & T, but 3 between G & C.

⊕$_4$ Left and right chains are "inverted" from each other.

⊕$_5$ A-T & G-C are complementary bases (they always go together).

DOUBLE HELIX STRUCTURE

DNA is in the form of a double helix, ie two interlinked spirals:



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).

* DNA replication is a semi-conservative replication as each newly synthesised DNA strand consists of one old DNA strand and one new DNA strand.

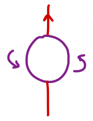
Chapter 29: Analytical Chemistry

PROTON (^1H) NUCLEAR MAGNETIC RESONANCE (NMR)

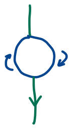
^1H NMR is a technique used to find the structure of an unknown compound.

WORKING PRINCIPLE

1. ^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 RH grip rule:



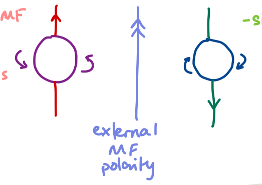
- anticlockwise spin (spin up / +ve spin) results in the MF pointing upwards;



- clockwise spin (spin down / -ve spin) results in the MF pointing downwards.

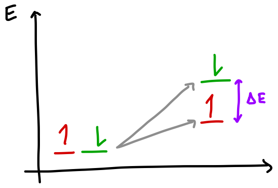
2. Prior to the addition of an external MF, both spin states possess the same energy level.
   ↳ however, upon bringing the sample into the machine, it is brought under the presence of an external magnetic field.

- since the proton's MF is in the same direction as the external MF, it is now in a lower "energy state"



- since the proton's MF is in the opposite direction as the external MF, it is now in a higher "energy state".

↳ the resultant non-degeneration of the two spin states can be shown on an energy level diagram:



*ΔE is in the "radio frequency range" (ie $\Delta E = hf_{radio}$).

3. 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 r.f range.
   ↳ resonance of the proton hence occurs.

4. ΔE can vary depending on the groups of atoms surrounding the hydrogen.
   ↳ by examining the specific frequency of the r.f pulse needed to induce the 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 : ↑ ΔE, ↑ chemical shift, δ.

↳ e^- decrease "influence" of the magnet.

CHEMICAL SHIFT

Chemical shift is the difference in the radio frequency required for resonance compared to standard solution, TMS (tetramethylsilane, or $Si(CH_3)_4$).
↳ 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.

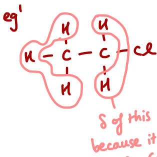
SOLVENT

CCl_4 or $CDCl_3$ ($D = {}^2_1H$) 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.

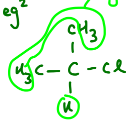
eg¹



In this, there are 2 proton environments.

δ of this env ↑ because it is bonded to Cl (electronegative element)

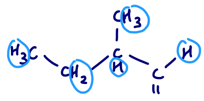
eg²



6H are affected by the "same group", so same proton env.

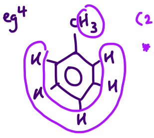
In this, there are 2 proton environments.

eg³



(5 proton environments)

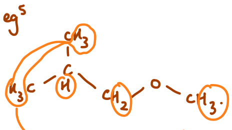
eg⁴



(2 proton environments).

*treat all the H on benzene rings as one chemical environment.

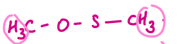
eg⁵



again, these "look out" at the same groups, so they are only counted as 1 chemical environment.

(5 proton environments).

eg⁶



(2 proton environments).
*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

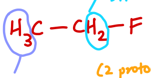
In high resolution NMR, due to interference of magnetic moments, peak splitting can be observed.
↳ peak splitting indicates number of H in neighbouring atoms. → *adjacent, or "one step away" (left, right, up, down)

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)	 1:2:1
3	4	quartet (q)	 1:3:3:1
4	5	multiplet (m)	 etc.

Examples

eg¹

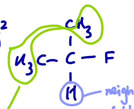


neighbouring C has 3H. ⇒ quartet splitting pattern.

neighbouring C has 2 H.
⇒ triplet splitting pattern.

(2 proton environments).

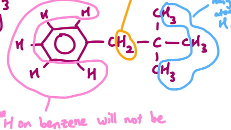
eg²



neighbouring atom has 1 H. so doublet.

neighbouring atoms has 6H, so multiplet.

eg³



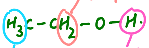
neighbouring atoms have 0 H, so singlet.

neighbouring atom has 0 H, so singlet.

*H on benzene will not be splitted, nor split others.
⇒ so singlet.

*however, in Q, splitting may be given as multiplet.

eg⁴



neighbour has 3H so quartet.

neighbour has 2H so triplet

singlet (labile proton: see next page)

LABILE PROTONS

O-H, N-H and S-H are labile protons; they are easily exchanged with the surrounding solvent molecules.

ie $H_3C-O-H + H-O-H \rightleftharpoons H_3C-O-H + H-O-H$.

swap

swap.

⊕ Labile protons will not be splitted nor will they contribute to the peak splitting of other H.

(they will always exist as a **singlet**).

* Why?

↳ Before they can establish their own MF, they are already "exchanged".

DETECTION

We can identify labile protons by adding heavy water (D_2O, where D = ^2_1H / deuterium).

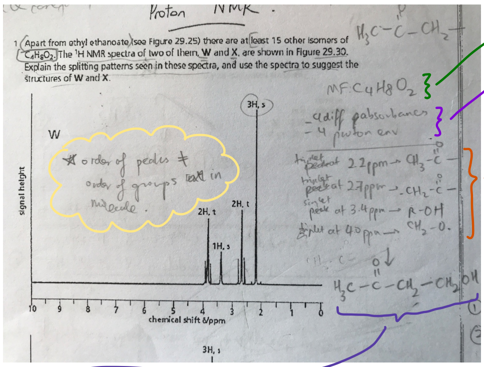
$$H_3C-O-H + D_2O \rightleftharpoons H_3C-O-D + DHO$$

↳ 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.

1 Apart from ethyl ethanoate (see Figure 29.25) there are at least 15 other isomers of $C_4H_8O_2$. 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.

☆ order of peaks ≠ order of groups ~~exist~~ in molecule.

$H_3C-C(=O)-CH_2-$

MF: $C_4H_8O_2$

- 4 diff ~~p~~ absorbances
- 4 proton env

~~triplet~~ peak at 2.2 ppm → $CH_3-C(=O)-$

triplet peak at 2.7 ppm → $-CH_2-C(=O)-$

singlet peak at 3.4 ppm → R-OH

triplet at 4.0 ppm → CH_2-O.

$H_3C-C(=O)-CH_2-CH_2OH$

⓪ : look for initial data given. (molecular formula is $C_4H_8O_2$).

① : # of peaks = # of proton environments.

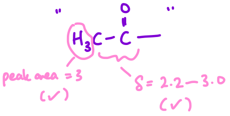
② : use the peak area data, chemical shift and peak splitting to find the group responsible for the peak. (use Data Booklet).

* try to begin analysing from the rightmost peak.

Example: for the peak at δ = 2.2 ppm;

- singlet splitting indicates neighbouring atoms has no H.
- peak area = 3 indicates group comprises of 3H.
- δ = 2.2 corresponds to an "alkyl next to C=O".

Together, these allude to the group



$$\text{"}\ H_3C-\overset{O}{\overset{\|}{C}}-\ \text{"}$$

peak area = 3 (✓)

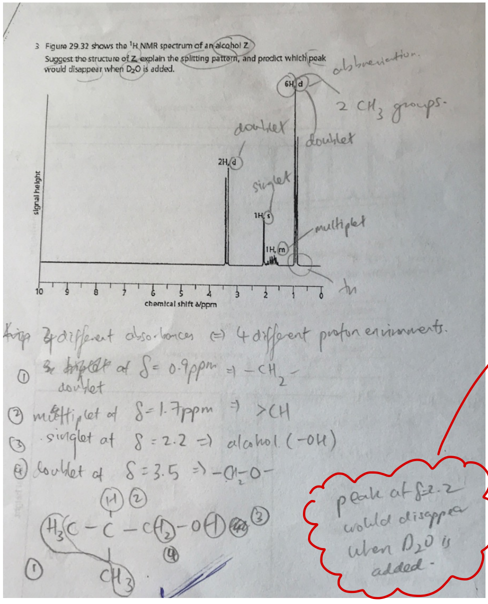
δ = 2.2 — 3.0 (✓)

being in the molecule.

Then, the singlet splitting tells us the adjacent groups have no H.

③ : Once you have determined the groups responsible for each peak, string them all together to find the molecular structure.

Exa 2



3 Figure 29.32 shows the ^1H NMR spectrum of an alcohol Z. Suggest the structure of Z, explain the splitting pattern, and predict which peak would disappear when D_2O is added.

abbreviation.

2 CH_3 groups.

doublet

doublet

singlet

multiplet

tri

~~4 ripp~~ ~~3~~ 4 different absorbances ⟺ 4 different proton environments.

① ~~3x triplet~~ doublet at δ = 0.9 ppm ⟹ $-CH_2-$

② multiplet at δ = 1.7 ppm ⟹ >CH

③ singlet at δ = 2.2 ⟹ alcohol (-OH)

④ doublet at δ = 3.5 ⟹ $-CH_2-O-$

$H_3C-CH(CH_3)-CH_2-OH$

peak at δ = 2.2 would disappear when D_2O is added.

Why?

- peak at δ = 2.2 corresponds to O-H.
- in O-H, proton is labile.
- so upon addition of hard water, peak would disappear.

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 ^{1}H acts

*the "theory" follows roughly the same structure as ^{1}H NMR.

COMPARISON TO ^{1}H NMR

There are a few notable differences between ^{1}H and ^{13}C NMR.

① Chemical shift

⊕ ^{13}C NMR δ values are larger than ^{1}H NMR δ values.

(^{1}H : 0, 1, 2 ..
^{13}C : 10, 20, ..)

*Why?
→ extent of deshielding of e^- shells in ^{13}C is greater than in ^{1}H.

(C has $6e^-$, H has $1e^-$).

② Chemical environments

⊕ In ^{13}C NMR:

Carbons that carry the same number of H, and have the same "structure" bonded to it, possess the same environment.

③ Peak splitting

⊕ There is no peak splitting due to an extremely unlikely chance ($0.012\% = (1.1\%)^2$) of getting 2 ^{13}C next to each other.

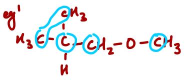
④ Peak area

⊕ 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

eg¹



4 environments.

eg²

5 environments.

*analyse ALL C on benzene.

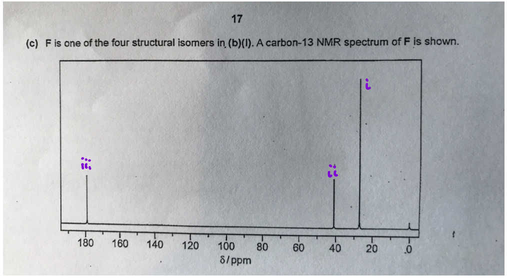
eg³

3 C environments.

*try to look for "symmetries" within the molecule.

ANALYSIS OF A ^{13}C NMR SPECTRUM

Ex



17

(c) F is one of the four structural isomers in (b)(I). A carbon-13 NMR spectrum of F is shown.

⓪ Given info:
- F is a carboxylic acid
- F has a molecular formula of $C_5H_{10}O_2$

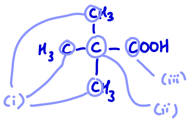
① Analyse the peaks:

(i) $\delta = 25$ → corresponds to C in alkyl.

(ii) $\delta = 40$ → corresponds to C next to carboxyl

(iii) $\delta = 180$ → corresponds to C in carboxyl.

② Deduce the structural formula:



*3 different peaks indicates only 3 different C environments!

MASS SPECTROMETER

AS: used to determine % of isotopes in an element.

A2: used to determine structure of a compound.

MASS SPECTRUM OF A COMPOUND

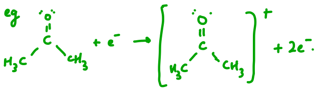
In a mass spectrophotometer, the sample is first vapourised.

↳ 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.

eg



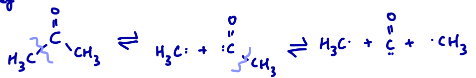
FRAGMENTATION

Molecular ions are energetically unstable, and they will break into fragments spontaneously.

↳ they do this via the homo/heterolytic fission of bonds.

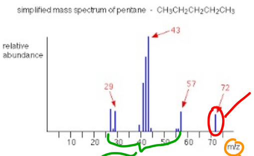
*single bonds usually break first before double/triple bonds.

eg



*a molecule can undergo fragmentation more than once.

MASS SPECTRUM



simplified mass spectrum of pentane - $CH_3CH_2CH_2CH_2CH_3$

① The rightmost (and "highest") peak is the RMM of the compound.
ie RMM of $CH_3(CH_2)_3CH_3 = 72$.

② $m/z = m$, since $z = +1$
(z = charge, m = relative molecular mass)

③ The peaks on the left are the RMM of the fragments of the molecule.

$m = 29 \rightarrow [CH_3CH_2]^+$
$m = 43 \rightarrow [CH_3CH_2CH_2]^+$
$m = 57 \rightarrow [CH_3CH_2CH_2CH_2]^+$.

*use the notation "$[\text{molecule}]^+$" to describe fragment structure.

HIGH RESOLUTION MASS SPECTROPHOTOMETER

High resolution spectrophotometers show more accurate values for isotopic mass and RMM of the ion.

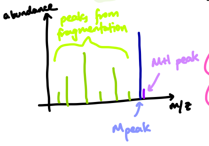
↳ this allows molecules with relatively close RMM values to be distinguished.

		low res	high res
eg	$[C_2H_7N]^+$	45	45.0578
	$[CH_3NO]^+$	45	45.0214

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 = RMM of the molecule.

↳ this is caused when one C in the molecule is ^{13}C (instead of ^{12}C).



⊕ The number of C atoms in the molecule is given by

$$N_c = \frac{100}{1.1} \times \frac{A_{M+1}}{A_M}$$

A_{M+1} → relative abundance of M+1 peak

A_M → relative abundance of M peak.

(round N_c to nearest integer.)

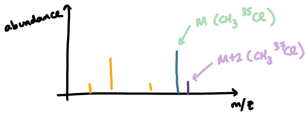
THE M+2/M+4 PEAKS

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 75% and ^{37}Cl 25%.
- Br exists as ^{79}Cl 50% and ^{81}Br 50%.

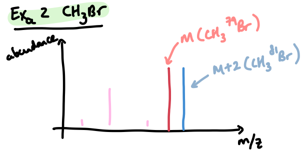
ONE Cl/Br ATOM (M+2)

Ex 1 CH_3Cl



*relative heights of M : M+2 is 3:1

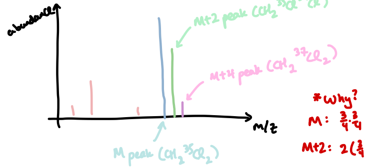
Ex 2 CH_3Br



*relative heights of M : M+2 is 1:1 .

TWO Cl/Br ATOMS (M+2, M+4)

Ex 1 CH_2Cl_2

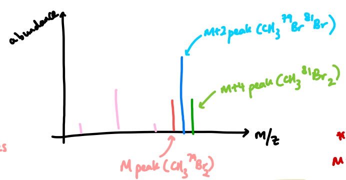


*relative heights of M : M+2 : M+4 is 9 : 6 : 1.

*Why?
M: $\frac{3}{4} \cdot \frac{3}{4} = \frac{9}{16}$
M+2: $2(\frac{3}{4})(\frac{1}{4}) = \frac{6}{16}$
M+4: $\frac{1}{4} \cdot \frac{1}{4} = \frac{1}{16}$.

probabilities for each "peak".

Ex 2 CH_2Br_2



*relative heights of M : M+2 : M+4 is 1 : 2 : 1.

*Why?
M: $\frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$
M+2: $2(\frac{1}{2} \cdot \frac{1}{2}) = \frac{1}{2}$.
M+4: $\frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$.

CHROMATOGRAPHY

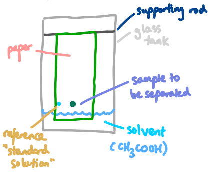
💡 Chromatography is used to identify the amino acids present in a polypeptide.

↳ 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



💡1 Mobile phase: solvent (CH_3COOH) → "non-polar"

Stationary phase: water trapped between cellulose fibres of paper. → "polar".

💡2 Essentially, paper chromatography relies on partition to seperate the mixture's components.

⊕ Partition: the separation of compounds due to their different solubilities in two solvents/phases.

💡3 ① A small spot of the solution is placed about 1cm from the paper edge.

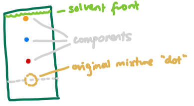
② The solvent is allowed to evaporate, allowing the solutes to be adsorbed into the paper fibres.

③ 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

💡4 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 larger distance.

*why? → more polar = less soluble in the mobile phase
= greater attractive force with H_2O molecules between fibres
= lesser distance travelled.

💡5 The resulting paper will consist of a series of dots — the components of the original mixture.
This is called a chromatogram.



IDENTIFICATION OF COMPOUNDS

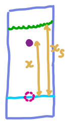
💡1 Seperated compounds can be visualised by spraying the paper with:

i) Ninhydrin — amino acids, small peptides
ii) Tollen's/Fehling's reagent — reducing sugars, e.g glucose/maltose } contain aldehyde functional group.
iii) Iodine - most other organic compounds

💡2 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.

ie



$$\boxed{R_f = \frac{x}{x_s}.}$$

*the lower the R_f, the more polar the compound is. (if mobile phase is non-polar).

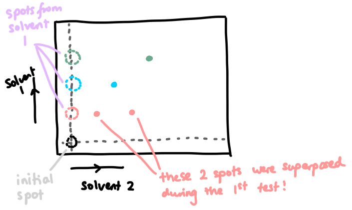
TWO WAY CHROMATOGRAPHY

💡 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.

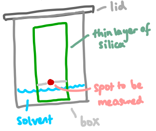
Method

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



💡1 Mobile phase: solvent → usually non-polar. (careful: some qns may say polar mobile phase).

Stationary phase: thin layer of a solid such as silica, supported on an inert base such as glass, Al foil or insoluble plastic. → usually polar.

💡2 Esentially, TLC relies on adsorption to separate the components in mixture.

⊕ Adsorption: a measure of the varying strengths of the bonds the compounds form with the stationary phase.

💡5 TLC is preferred over paper chromatography because:
1) more reproducible results
2) can be used for smaller samples.

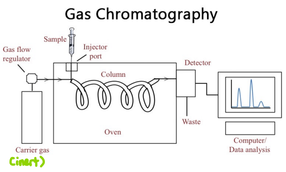
💡3 The method used roughly follows paper chromatography.

💡4 If the compound can be adsorbed (bonded) onto the solid's surface, (either through polar/H-bonded interactions, or acid-base interactions, since SiO_2 is slightly acidic) then the compound will travel a shorter distance.

polar/H-bonded → ↑ polarity, ↓ distance.

GAS-LIQUID CHROMATOGRAPHY

WORKING PRINCIPLE



💡1 Mobile phase: inert gas, eg He or N_2

Stationary phase: non-volatile liquid, eg mineral oil coated on small particles.

💡2 GL chromatography relies on partition for separation.

💡3 ① The sample is vapourised and passed through the oven with the carrier gas.

② The fractions travel through the tubing towards the detector.

travel → alternative term: elude

💡4 The higher the molecule's "volatility" (ie affinity for the stationary phase), the greater the magnitude of forces between them, and hence it will travel slower through the machine.

them → (stationary phase & molecule).

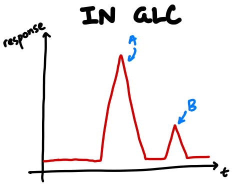
} if stationary phase is non-polar, then non-polar substances will travel slower.

💡5 Hence, the mixture's components can be distinguished via retention time (R_t):

→ the more volatile the compound is, the longer it will take to travel to the detector.

⊕ 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.

DETERMINATION OF THE % COMPOSITION OF A MIXTURE IN GLC



💡 The % composition of a compound in a mixture can be found by taking the ratio of the area of the peak corresponding to it, to the sum of all of the peak areas.

*in exam, peaks will be triangles.
So $A = \frac{1}{2}bh$.

eg

$$\% \text{ of A in mixture} = \frac{\text{peak area of A}}{\text{peak area of A,B}} \times 100\%$$

APPLICATIONS OF GLC

① Detection of drugs in athletes' blood/urine
② Detection of pesticide residues
③ Comparison of caffeine contents in coffee.

Chapter 30:
Organic Synthesis

SYNTHESIS OF CHIRAL DRUG MOLECULES

Many drugs can be obtained from natural resources;
eg 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.

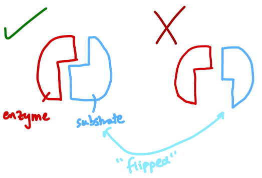
↳ this led to scientists investing lots of research into finding synthetic production methods.

ENANTIOPURE DRUGS

1 The main "requirement" during synthetic drug synthesis is the production of enantiopure drugs; ie only one optical isomer of the drug.

2 Naturally occurring drugs are also enantiopure.

Why?
① In biological systems, molecules are synthesised via enzymes.
② Since enzymes work in a lock-and-key mechanism, a molecule has to be exactly the right shape to fit the enzyme.
③ However, different arrangements around a chiral centre will force an entirely different shape on the molecule; hence, it will not fit the molecule anymore.
④ Consequently, enzyme systems only produce a single optical isomer because that is the only shape they can "work with."



3 Reasons:

1) It lowers the undesirable side-effects due to the other (harmful) enantiomer.
2) It is cheaper in the long-run, as it is a waste of money/materials to produce a drug, which only half of it is useful.
3) The patient doses can be smaller, since all of the drug is active.
4) The pure enantiomer is more potent and has better therapeutic activity.

4 Methods to synthesise an enantiopure mixture:

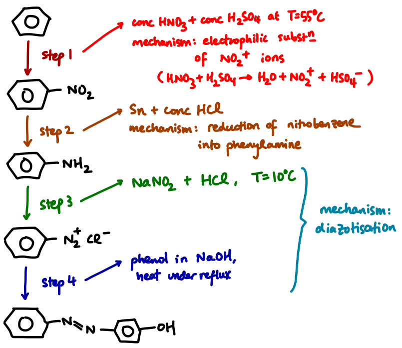
1) Chiral catalyst + enzyme
2) Chiral pool synthesis
3) Optical resolution / use of a chiral auxiliary.

SYNTHETIC ROUTES

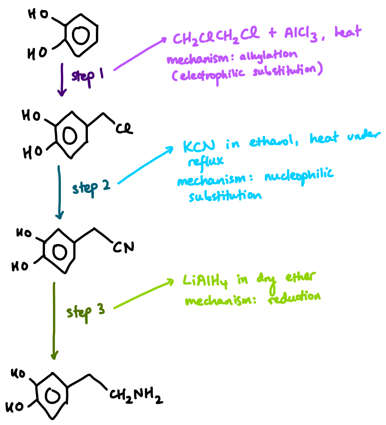
In order to synthesise a new compound, chemists tend to use a starting material extracted from a commonly raw substance, and subject it to a series of organic reactions.

* reactions are derived from AS/A2 organic chemistry.

Exa1 benzene → azo dye



Exa 2 benzenediol → dopamine



Exa 3 methylbenzene → procaine