UNIT 1 : INORGANIC CHEMISTRY.

ELECTROMAGNETIC RADIATION & ATOMIC SPECTRA

Radiation

- Electromagnetic radiation can be described in terms of waves and characterised in terms of wavelength and/or frequency.

→ $\boxed{c = f\lambda}$

- Radiation ordered in λ on the E.M spectrum.
- Wavelengths of visible li usually in nanometers (nm, $\times 10^{-9}$ m).

↳ PHOTONS

→ E.M radiation can also behave as a particle, a photon of light, and is said to have a dual nature.

→ Light (E.M radiation) behaves as a particle when it is absorbed or emitted by matter.

It carries quantised energy proportional to the frequency of radiation

→ $\uparrow f \uparrow E$

Energy from 1 photon:

$$\boxed{E = hf}$$

Energy from 1 mol photons:

$$\boxed{E = Lhf}$$

→ E in kJ mol^{-1}

Emission & Absorption

- When energy is transferred to atoms, e^- within the atoms may be promoted to higher energy levels.
- An atom emits a photon of light energy when an excited electron moves from a higher energy level to a lower energy level.

↳ The light energy emitted by an atom produces a spectrum that is made up of discrete (quantised) energy levels. This provides direct evidence for the existence of these energy levels.

SPECTRA

Each element in a sample produces characteristic emission and absorption spectra. Can be used to identify an element.

→ In absorption spectroscopy, E.M radiation is directed at an atomised sample. Radiation is absorbed as e^- promoted to higher energy levels.

Absorption spectrum is produced by measuring how intensity of light varies with wavelength.

→ In emission spectroscopy, high temps are used to excite e^- within atoms. As e^- drop to lower energy levels, photons are emitted.

Emission spectrum is produced by measuring the intensity of light emitted/absorbed.

- In atomic spectroscopy, the conc. of an element within a sample is related to the intensity of light emitted or absorbed.

ATOMIC ORBITALS, E^- CONFIG, & PERIODIC TABLE

Electrons

The discrete lines observed in atomic spectra can be explained if e^-, like photons, have properties of both particles AND waves.

→ e^- behave as standing (stationary) waves in an atom. These are waves that vibrate in time but do not move in space

→ There are different size & shape of standing waves around the nucleus – known as orbitals.

→ Shapes are s, p, d, f

- e^- have fixed amounts of energy called quanta.

Electron Configuration

Electrons within atoms are arranged according to:

① THE AUFBAU PRINCIPLE

→ Electrons fill orbitals in order of increasing energy (aufbau means 'building up' in German).

② HUND'S RULE

→ When degenerate orbitals are available, e^- each fill singly, keeping their spins parallel before spin pairing starts.

Quantum Numbers.

- It is possible to describe any e^- in an atom using four quantum numbers...

→ the principle quantum number n indicates the main energy level the e^- is in.

→ the angular momentum quantum number, l determines the shape of the subshell and can have values from zero to $n-1$.

- 0 = s subshell
- 1 = p subshell
- 2 = d subshell
- 3 = f subshell.

→ the magnetic quantum number, m_l determines the orientation of the orbital and can have values between $-l$ and $+l$.

→ the spin magnetic quantum number, m_s, determines the direction of spin and can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$.

③ THE PAULI EXCLUSION PRINCIPLE

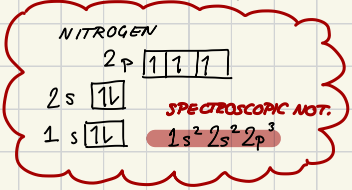
→ No 2 electrons in one atom can have the same set of 4 quantum numbers.

→ ∴ no orbital can hold more than 2 e^- and both must have opposite spins.

cont.

→ In an isolated atom, the orbitals within each subshell are degenerate (have the same energy).

- The relative energies corresponding to each orbital can be represented diagrammatically using orbital box notation, e.g:



SPECTROSCOPIC NOT: $1s^2 2s^2 2p^3$

Shape

VSEPR THEORY.

↳ 'Valence shell electron pair repulsion' theory.

- Can be used to predict the shapes of molecules and polyatomic ions.

NUMBER OF e^- PAIRS.

$$\frac{\text{no. of valence } e^- \text{ on central atom} + \text{no. of atoms attached.}}{2}$$

→ +1 to numerator for every -ve charge.

→ -1 for every +ve charge.

ELECTRON PAIR SHAPES.

Lone e^- pairs are -vely charged and are arranged to minimise repulsion and maximise seperation.

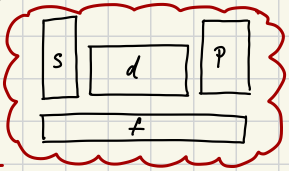
→ Electron pair repulsions dec. in the order:

non bonding/non bonding > non bonding/bonding > bonding/bonding.

Periodic Table

- The periodic table is subdivided into 4 blocks (s, p, d & f), corresponding to the outer e^- configuration within these blocks.

↳



IONISATION ENERGY.

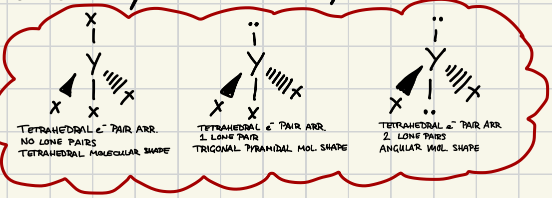
- The variation in first, second, and subsequent ionisation energies (for the first 36 elements) can be explained in terms of the relative stability of their subshell electron configurations.

Anomalies in general trends for ionisation energy (i.e decreasing down a group and increasing across a period) can be explained by considering the electronic configurations.

↳ There is a special, high stability associated with half-filled and fully filled subshells. More stable the electronic configuration, higher ionisation energy.

MOLECULAR SHAPES

- Shapes of molecules or polyatomic ions are determined by the shapes adopted by atoms based on the arrangements of electron pairs. For example:



TRANSITION METALS

Electron Configuration

- The d-block transition metals are elements with an incomplete d subshell in at least one of their ions.
- The filling of the d orbitals follows the Aufbau principle, with the exception of Chromium and Copper.

↳ These exceptions are due to the special stability associated with the d subshell being half filled or completely filled.

$d^1, d^2, d^3, d^5, d^5, d^6, d^7, d^8, d^{10}, d^{10}$ →

- When atoms from the first row of the transition metals form ions, it is the 4s electrons that are lost first rather than the 3d electrons.

Ligands & Complexes

- Ligands are negative ions or molecules with non bonding pairs of electrons that they donate to a central metal ion to form dative covalent bonds.

↳ both e⁻ in covalent bond come from the same atom.

- Ligands can be classified by how many attractions they form with a central metal ion, e.g

→ Monodentate = 1 attraction, Bidentate = 2 attractions, etc.

- Total number of bonds attached to the central metal ion is known as the coordination number.

Oxidation Number

An element is said to be in a particular oxidation state when it has a specific oxidation number.

Oxidation numbers can be det. by:

→ uncombined elements have an ox no. 0

→ ions containing single atoms have ox. no. same as the charge on the ion.

→ in most of it's compounds, O has ox no -2.

→ in most of its compounds, H has ox no. +1.

→ sum of all ox no. in a neutral compound is 0.

→ the sum of all ox no. in a polyatomic ion must be equal to the charge on the ion.

TRANSITION METAL OX NOs.

- A transition metal can have different oxidation states in its compounds
- Compounds of the same transition metals in different oxidation states may have different colours.

→ Oxidation – inc. in ox no.

→ Reduction – dec. in ox no.

- Compounds containing metals in high ox. states are often oxidising agents. low ox states are often reducing agents.

NAMING COMPLEXES

Names & formulae are written in accordance w/ IUPAC rules:

- If the complex is a salt, name of +ve ion comes 1st.
- Name of complex is 1 word, ligands 1st.
- Name of ligand has prefix to show number. e.g "di" for 2. Names are put alphabetically (ignoring prefix)
- Metal name is followed by ox no. in brackets.
- If complex is -ve, metal ends in ate.

cont.

NAMING COMPLEXES → EXAMPLES

$[Co\underline{Cl}(NH_3)_5]^+$

Must be written in alphabetical order of symbol, too.
Part joined to metal comes first (i.e NH_3, not H_3N).

→ Pentaamminechloridocobalt(II)

$K_3^{3+}[V(CN)_6]^{3-}$

→ Potassium hexacyanidovanadate (III)

NAMES OF COMMON LIGANDS.

-ve ions:

bromide, Br^- → bromido
chloride, Cl^- → chlorido
cyanide, CN^- → cyanido
hydroxide, OH^- → hydroxido
oxalate, $C_2O_4^{2-}$ → oxalato
nitrite, NO_2^- → nitrito.

neutral molecules:

ammonia, NH_3 → ammine
carbon monoxide, CO → carbonyl.
water, H_2O → aqua.

Coloured Complexes.

- In a complex of a transition metal, d orbitals are no longer degenerate.

This is due to ligands approaching, and bonding to the metal, repelling orbitals lying along the axes.

→ Occurs in octahedral complexes.

d orbitals are split up, so some now have more energy.

→ The difference in energy between the split d-orbitals depends on ligand, ox no. and transition metal.

COLOUR.

Colours of many transition metal complexes can be explained in terms of d to d transitions.

Electrons in one of the lower energy d orbitals can be promoted to a d orbital of higher energy by absorbing photons of a certain energy ($E=hf$ / $E=Lhf$).

→ If light of one colour is absorbed, then the complementary colour will be observed (use colour wheel.)

Catalysts

- Transition metals & their compounds can act as catalysts.

HETEROGENEOUS CATALYSTS.

→ In a different state to the reactants, usually solids.

→ Adsorbs reactants onto active sites and weakens bonds, which lowers the activation energy. The reactants then collide, react, and leave the active site for more reactants to be adsorbed.

↳ like enzymes in biology!

HOMOGENEOUS CATALYSTS.

→ In the same state as the reactants.

→ Work by a change in oxidation state, which is thought to allow activated complexes to form. This can provide reaction pathways with lower activation energy.

UNIT 2: PHYSICAL CHEMISTRY.

EQUILIBRIUM

↳ a chemical rxn is at equilibrium when the composition of the reactants and products remains constant indefinitely

→ not necessarily equal!

Equilibrium Constant

The equilibrium constant, K, characterises the equilibrium composition of the rxn mixture.

→ For the general reaction:

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

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

no units!

conc. @ equilibrium

→ always products over reactants!

Value of K indicates position of equilibrium.

- $K > 1$ ⇒ products favoured, right
- $K = 1$ ⇒ conc. products = reactants.
- $K < 1$ ⇒ reactants favoured, left.

NOTE: In homogeneous rxns (everything same state), take all reactants and products into account.

In heterogeneous rxns (different states), solids and liquids are given a value of 1, so effectively are not included in equilibrium expression.

EFFECTS ON K.

Temperature is the only thing that can affect K:

→ For endothermic reactions, inc. temp. inc. K, higher yield of products.

→ For exothermic reactions, inc. temp. dec. K, lower yield of products.

Equilibrium of Water.

In water and aqeous solutions, there is an equilibrium between water molecules and hydronium (hydrogen) and hydroxide ions.

$$H_2O(l) \rightleftharpoons \underbrace{H_3O^+}(aq) + OH^-(aq)$$

hydronium ion, $H^+(aq)$.

Water is amphoteric, i.e it can react as both an acid and a base.

The dissociation constant for the ionisation of water is K_w. It also varies with temperature.

$$K_w = [H_3O^+][OH^-]$$

@ 25°C/298K $K_w = 1\times10^{-14}$

→ pH SCALE.

The relationship between pH and hydrogen ion conc. is given by:

$$pH = -\log_{10}[H_3O^+] \;/\; [H_3O^+] = 10^{-pH}$$

In water and aqueous solutions with a pH value of 7 the conc. of H_3O^+ and OH^- are both 1×10^{-7} @ 25°C/298K.

→ If the conc. of H_3O^+/OH^- is known, the conc. of the other ion can be calculated using K_w or:

$$pH + pOH = 14$$

Acids & Bases.

The Bronsted-Lowry definition of acids and bases states that:

→ An acid is a proton donator

→ A base is a proton acceptor.

For every acid, there is a conjugate base, formed by the loss of a proton.

For every base, there is a conjugate acid, formed by the gain of a proton.

↳ STRONG VS. WEAK ACIDS.

Strong acids are completely dissociated into ions in aqueous solution.

→ Nitric acid, sulfuric acid, and hydrochloric acid are all strong acids.

Weak acids are only partially dissociated into ions in aqueous solution, forming an equilibrium.

→ Weak acids in databook!
e.g ethanoic acid

↳ STRONG VS. WEAK BASES.

Strong bases are completely dissociated into ions in aqueous solution.

→ Solutions of metal hydroxides are strong bases.

Weak bases are only partially dissociated into their ions in aqueous solution, forming an equilibrium.

→ Ammonia and amines are examples of weak bases. → in databook!

↳ WEAK ACID/BASE EQUILIBRIA.

e.g weak acid, ethanoic acid.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

e.g weak base, ammonium ion.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3.$$

→ PROPERTIES OF WEAK AND STRONG ACIDS/BASES

Equimolar solutions of weak and strong acids/bases will have different properties

→ different pH

→ strong will have greater rxn rate.

→ strong will have greater conductivity

ACID DISSOCIATION CONSTANT.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}, \quad pK_a = -\log_{10} K_a.$$

pH OF WEAK ACID

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log_{10} \underbrace{c}_{\text{concentration}}.$$

ACID	BASE	SOLUBLE SALT DISSOLVES:
STRONG	STRONG	NEUTRAL
WEAK	STRONG	ALKALINE
STRONG	WEAK	ACIDIC.

Buffers.

A buffer solution: pH stays constant when a small amount of acid, base, or water is added

ACID BUFFER.

An acid buffer consists of a solution of a weak acid and one of its salts made from a strong base.

→ The weak acid provides H_3O^+ when these are removed by adding a small amount of base.

→ The salt of the weak acid provides the conjugate base, which can absorb excess H_3O^+ when adding a small amount of acid.

→ Both the salts and the weak acid will be diluted by the same amount when adding water so pH doesn't change.

↳

BASIC BUFFER.

A basic buffer consists of a solution of a weak base and one of its salts made from a strong acid.

- → The weak base removes excess H_3O^+ when a small amount of acid is added.
- → The conjugate acid provided by the salt supplies hydrogen ions when these are removed by adding a small amount of base.

pH OF AN ACIDIC BUFFER SOL.

$$pH = pK_a - \log_{10} \frac{[acid]}{[salt]}.$$

Indicators

Indicators are weak acids for which the dissociation can be represented as:

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

→ In aqueous solution, the colour of an acid indicator is distinctly different from that of its conjugate base.

The acid indicator dissociation constant is represented as K_{IN} and is given by the following expression:

$$K_{IN} = \frac{[H_3O^+][In^-]}{[HIn]}.$$

COLOUR OF INDICATORS.

- → Determined by the ratio of $[HIn]$ to $[In]^-$
- → The theoretical point at which colour change occurs is when $[H_3O^+] = K_w$
- → The colour change is assumed to be distinguishable when $[HIn]$ and $[In^-]$ differ by a factor of 10.
- → The pH range over which a colour change occurs can be estimated by the expression:

$$pH = pK_{IN} \pm 1.$$

REACTION FEASABILITY

Enthalpy

The standard enthalpy of formation, ΔH°, is the enthalpy change when one mole of a substance is formed from its elements in their standard states.

→ The standard state of a substance is its most stable state at a pressure of 1 atmosphere and at a specified temperature, usually taken as 298K (25°C).

The standard enthalpy of a reaction can be calculated from the standard enthalpies of formation of its reactants and products.

$$\Delta H^\circ = \Sigma \Delta H^\circ_f (\text{products}) - \Sigma \Delta H^\circ_f (\text{reactants}).$$

Free Energy.

Change in free energy gives us information about a reaction. Can be found by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ.$$

A 'feasible' reaction is one that tends towards the products rather than the reactants. This does not give any indication of the rate.

→ $\Delta G^\circ < 0$ - reaction is feasible

→ $\Delta G^\circ > 0$ - reaction is not feasible.

The standard free energy change for a reaction can be calculated from the standard free energies of formation of the reactants and products using the relationship:

$$\Delta G^\circ = \Sigma \Delta G^\circ (\text{products}) - \Delta G^\circ (\text{reactants})$$

@equilibrium, $\Delta G = 0$. A reaction will proceed spontaneously until the composition is reached where $\Delta G = 0$.

Entropy.

The entropy (S) of a system is a measure of the degree of disorder of the system → greater disorder, greater entropy.

Solids have low disorder and gases have high disorder.

Entropy increases as temperature increases.

→ 2ND LAW OF THERMODYNAMICS.

The total entropy of a reaction system and its surroundings always increases for a spontaneous process.

→ Heat energy released by a rxn increases entropy of surroundings

→ Heat energy absorbed by a rxn decreases entropy of surroundings

3RD LAW OF THERMODYNAMICS.

The entropy of a perfect crystal @0K is zero.

The standard entropy of a substance is the entropy of a substance in its standard state.

Change in entropy for a rxn:

$$\Delta S^\circ = \Sigma S^\circ (\text{products}) - \Sigma S^\circ (\text{reactants})$$

KINETICS

Rate.

The rate of a rxn normally depends on the concentrations of the reactants.
Orders of reaction are used to relate the rate of a reaction to the reactant species.
→ The order of a reaction can only be determined from experimental data.

RATE EQUATION.

for a reaction

$$A + B \rightarrow C + D.$$

$$\text{rate} = k[A]^a[B]^b$$

rate constant

order of reactants

Reactions usually occur by a set of steps called a 'mechanism'. The rate of reaction depends on the slowest step, the 'rate determining step'

⇒ ORDER OF REACTANTS.

- 0 order → doubling [A] has no effect on rate.
- 1st order → doubling [A] doubles rate.
- 2nd order → doubling [A] quadruples rate.
- 3rd order → doubling [A] 8x rate.

→ The overall order of a reaction is the sum of the orders of a reaction. i.e $k = [A]^a[B]^b$, overall order $= a + b$.

UNIT 3: ORGANIC CHEMISTRY AND INSTRUMENTAL ANALYSIS.

SYNTHESIS

Bond fission"

When an organic rxn takes place, bonds in the reactant molecules are broken and bonds in the product molecules are made.

Process of bond breaking is known as bond fission.

There are 2 types of bond fission:

→ ① HOMOLYTIC FISSION

- Normally occurs when non-polar covalent bonds are broken.
- Occurs when each atom retains one e^- from the bond – bond breaks evenly.
- Results in the formation of 2 neutral radicals

→ Rxns involving homolytic fission tend to result in the formation of very complex mixtures of products, so have a low yield and are hard to control – making them unsuitable for organic synthesis.

→ ② HETEROLYTIC FISSION

- Normally occurs when polar covalent bonds are broken.
- Occurs when one atom retains both e^- from the covalent bond, bond breaks unevenly.

→ Better suited for organic synthesis as tend to result in far fewer products than homolytic fission.

→ MOVEMENT OF e^-

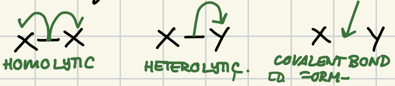
→ notation also used for mechanisms

Movement of e^- during bond fission/making can be represented using arrows according to the following rules:

→ single-headed arrow (⇀) means 1 e^-. double-headed (→) means a pair.

→ tail of arrow (start) shows source of e^-.

→ head of arrow shows destination.



Nucleophiles & Electrophiles

→ NUCLEOPHILES.

Species attracted to full/partial +ve charge. Electron rich, so donate e^-. May be -ve ions or molecules with a lone pair, e.g Cl^-, OH^-, NH_3, or H_2O.

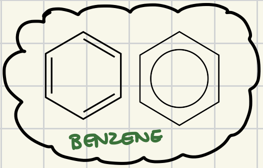
→ ELECTROPHILES.

Species attracted to full/partial -ve charge. Electron deficient, so accept e^-. May be +ve ions or other electron deficient molecules, e.g. H^+.

REACTION TYPES.

→ TYPES OF REACTIONS.

→ ① Substitution



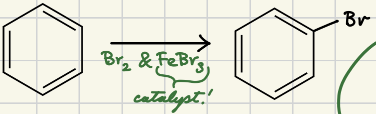
↳ ELECTROPHILLIC SUB.

Benzene (C_6H_8) is a very stable molecule, due to the ring of delocalised e^-. This means it will not take part in addition reactions, but can undergo electrophillic substitution.

→ Halogenation.

+ $AlCl_3$ / $FeCl_3$ for Cl or $AlBr_8$ / $FeBr_3$ for bromination.

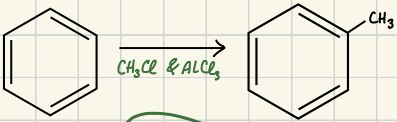
e.g.



→ Alkylation

+ haloalkane and $AlCl_3$.

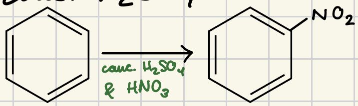
e.g.



→ Nitration

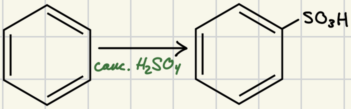
+ conc. H_2SO_4 and HNO_3.

e.g.



→ Sulfonation

Conc. H_2SO_4.



↳ FREE RADICAL SUB.

- Alkanes can undergo free radical sub. rxns but due to the high reactivity of free radicals these rxns can be difficult to control. They tend to produce a mixture of products so are not that useful for synthesising specific molecules.

→ often in the presence of UV light!

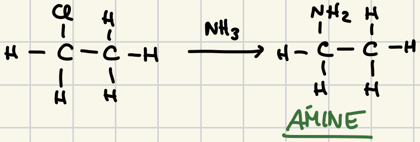
NUCLEOPHILLIC SUB.

↳ NUCLEOPHILLIC SUB.

Haloalkanes are compounds in which one or more H atoms in an alkane have been replaced by a halogen atom. A.K.A alkyl halides. Undergo nucleophillic sub. because the electronegativity of the halogen puts a δ+ charge on the carbon atom.

→ + AMMONIA (NH_3)

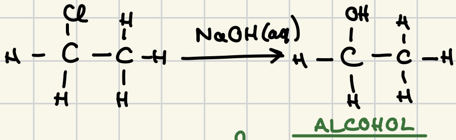
e.g



→ +AQ ALKALI

e.g NaOH(aq)

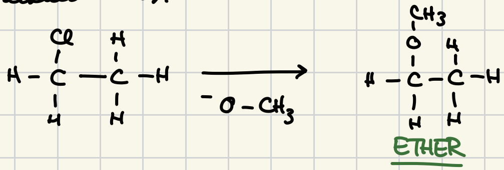
e.g



→ + ALKOXIDE (^-O-R)

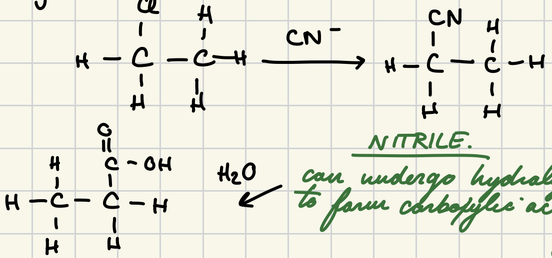
(an alkoxide can be made by reacting alcohol w/ alkali metal).

e.g



→ + CYANIDE (CN^-)

e.g

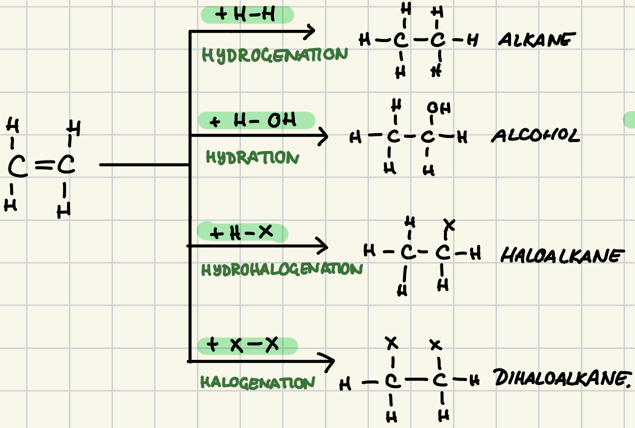


can undergo hydrolysis to form carboxylic acid.

→ ② Addition

- A small molecule is added across the double bond of an alkene.

i.e.



MARKOVKINOV'S RULE.

When H-X is added to an asymmetrical alkene, the most favourable (major) product occurs when the H atom attaches to the C with the greatest no. of H atoms already attached, as this involves the most stable carbocation.

③ ELIMINATION

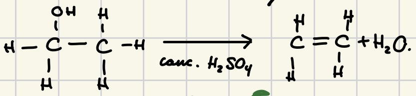
③ Elimination

The 'reverse' of addition. Atoms are removed from an organic molecule and a double bond forms.

DEHYDRATION.

- The removal of water from an alcohol.
- Catalysed by:
  - → conc. sulfuric acid.
  - → conc. phosphoric acid.
  - → aluminium oxide.

e.g.

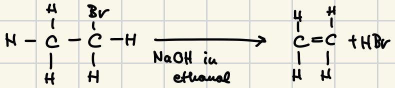


$$\mathrm{H-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \xrightarrow[\text{conc. } H_2SO_4]{} \overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}} + H_2O}$$

DEHYDROHALOGENATION.

- Removing a halogen atom from a haloalkane.
- Requires the presence of a strong alkali (e.g NaOH) dissolved in ethanol.

e.g



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-H \xrightarrow[\text{NaOH in ethanol}]{} \overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}} + HBr}$$

④ Condensation

The combination of 2 molecules to form one larger molecule, with the elimination of a small molecule (usually water).

e.g Acid + Alcohol → Ester + water.

⑤ (Acidified) Hydrolysis

Adding water to a molecule to form 2 smaller molecules in the presence of H^+ (like reverse of condensation).

e.g Ester + water → alcohol + acid.

⑥ Neutralisation

Acid + base → salt + water.

→ ⑦ Oxidation

- An increase in the oxygen to hydrogen ratio (i.e add oxygen/remove hydrogen).
- Common oxidising agents could be hot copper (II) oxide, potassium dichromate.

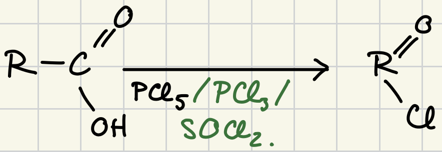
→ ⑧ Reduction

- Decrease in the O to H ratio (decrease in O/add H)
- Reducing agent - Lithium Aluminium Hydride ($LiAlH_4$)

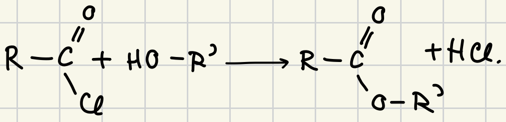
Esters

- From Higher, we know that esters can be made from the condensation of an alcohol and carboxylic acid with conc. sulfuric acid catalyst.
- But they can also be made from an alcohol and acid chloride. This is faster, irreversible, and does not require a catalyst.

→ MAKING ACID CHLORIDES:



→ MAKING AN ESTER.



Ethers

- General structure R–O–R'
- Prepared by reacting a haloalkane with an alkoxide.
- Relatively chemically inert so used for solvents.

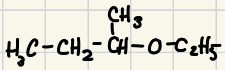
→ lower b.ps than alcohols because no hydrogen bonding between ethers

→ small ethers are soluble in water, as can form H bonds w/ water, larger ethers are insoluble.

NAMING ETHERS.

1. Identify longest chain.
2. Identify branches on longest chain.
3. Number branches, list alphabetically.
4. Longest chain not incl. O forms 2nd half of name

e.g.

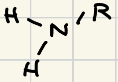


$H_3C-CH_2-CH(CH_3)-O-C_2H_5$ 2-ethoxybutane.

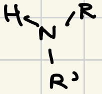
Amines

- Organic nitrogen compounds that can be thought of as derivatives of ammonia.

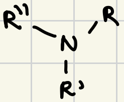
PRIMARY.



SECONDARY.



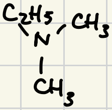
TERTIARY.



NAMING AMINES.

Alkyl branches attached to N are arranged alphabetically and amine added on the end.

e.g



ethyldimethylamine.

MAKING AMIDES.

After amines react with carboxylic acids, they form alkylammonium salts, which can then be heated to form amides.

PROPERTIES.

- Primary & secondary have H bonding so have higher b.p than tertiary amines.
- All amines with small molecular mass are soluble in water as can form H bonds.

REACTIONS.

Amines are weak bases as they dissociate in aqueous solution, the lone pair on the N accepts a proton from water, producing OH^-. This means they can react w/ acids to form salts.

e.g

$$CH_3CH_2NH_2 + NHO_3 \rightleftharpoons CH_3CH_2NH_3^{\oplus} NO_3^{-}$$

Ethylamine   Nitric acid   Ethylammonium nitrate.

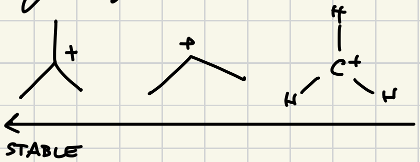
Mechanisms

→ MECHANISMS.

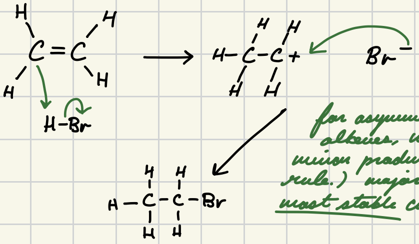
Show movement of e^-.

Carbocations

Unstable intermediate states in many organic reactions.



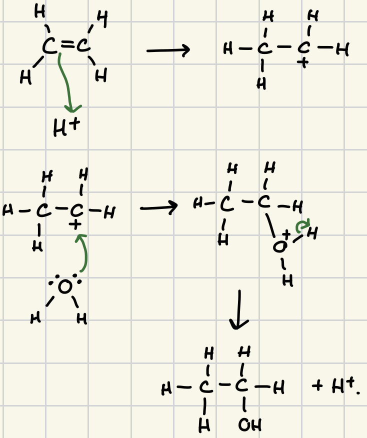
ADDING HYDROGEN HALIDES.



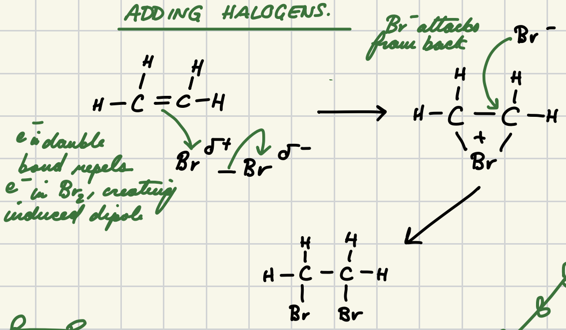
for asymmetrical alkenes, major and minor product (markovnikov's rule.) major contains most stable carbocation!

ADDING WATER.

(acid catalysed hydration).



ADDING HALOGENS.



e^- in double bond repels e^- in Br_2, creating induced dipole

Br^- attacks from back

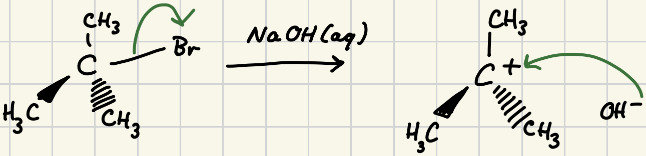
Nucleophilic Substitution Mechanisms

Haloalkanes will undergo nucleophilic substitution by one of two different reaction mechanisms: S_N1 or S_N2.

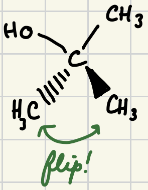
→ S_N1.

- 1 species involved in rate det. step.
- 2 step process!!

STEP 1: PRODUCES CARBOCATION → RATE DET.

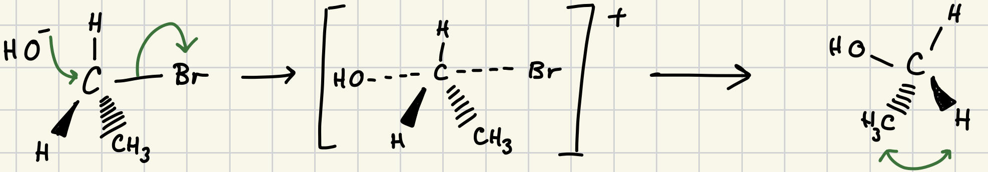


STEP 2: NUCLEOPHILE JOINS → FAST STEP.



S_N2.

- 2 species involved in rate det. step.
- 1 step process.!!



again, flip!

S_N1 OR S_N2?

Tertiary alkanes tend to act via S_N1, as it will involve a stable tertiary carbocation.
A tertiary alkane has 3 bulky alkyl groups which makes it difficult for the nucleophile to attack in S_N2. Hence secondary and primary haloalkanes proceed via S_N2 and tertiary haloalkanes will not.

MOLECULAR ORBITALS

↳ VSPER cannot explain the bonding in all compounds. Molecular orbital theory can provide an explanation for more complex molecules.

What are Molecular Orbitals?

- They form when atomic orbitals combine.

No. of mol. orbitals formed = no. of atm. orbitals combined.

The combination of 2 atomic orbitals results in the formation of a bonding molecular orbital and an antibonding molecular orbital.

↳ Bonding mol. orbital encompasses both nuclei. The attraction of the positively charged nuclei and the negatively charge e^- in the bonding molecular orbital is the basis for bonding between atoms. Each mol. orbital can hold a max. 2 e^-.

↳ THE BONDING CONTINUUM.

NON POLAR COVALENT. → bonding mol. orbital symmetrical about midpoint.

POLAR COVALENT: → bonding mol. orbital asymmetrical about the midpoint atom w/ greater electronegativity has greater share of bonding e^-.

IONIC. → extreme case of asymmetry, bonding molecular orbitals almost entirely around 1 atom → forms an ion.

σ AND π BONDS.

→ Molecular orbitals that form by end-on overlap of atomic orbitals are sigma (σ) bonds.

→ Molecular orbitals that form by side on overlap of atomic orbitals that lie perpendicular to the axis of the covalent bond are called pi (π) molecular orbitals

Hybridisation

Hybridisation is the process of mixing atomic orbitals within an atom to generate a set of new atomic orbitals called hybrid orbitals, which are degenerate.

→ ALKANES.

In alkanes, the 2s orbital and the 3 2p orbitals of carbon hybridise to form 4 degenerate sp^3 orbitals. These adopt a tetrahedral arrangement. The sp^3 orbitals overlap end on to form σ bonds.

→ ALKENES.

In alkenes, the 2s and 2 2p orbitals hybridise to form 3 degenerate sp^2 orbitals. These adopt a trigonal planar arrangement. The hybrid sp^2 orbitals overlap end on to form σ bonds. The remaining 2p orbital on each carbon atom of the double bond is unhybridise and lies perpendicular to the axis of the σ bond. The unhybridis p orbitals overlap side on to form π bonds.

Colour in Organic Molecules.

→ ALKYNES:

The 2s orbital and one 2p orbital of carbon hybridise to form two degenerate sp orbitals, which adopt a linear arrangement. The hybrid sp orbitals overlap end on to form σ bonds. The remaining 2 2p orbitals on each carbon lie perpendicular to each other and the axis of the σ bond. The unhybridised p orbitals overlap side on to form π bonds.

→ BENZENE / OTHER AROMATIC SYSTEMS.

The 6 carbon atoms in benzene are arranged in a cyclic structure with σ bonds between the carbon atoms. The unhybridised p orbitals on each carbon atom overlap side on to form a π molecular system perpendicular to the plane of the σ bonds. The e^- in this system are delocalised.

Electrons fill bonding molecular orbitals, leaving higher energy antibonding orbitals unfilled.

The highest bonding molecular orbital containing electrons is called the highest occupied molecular orbital → HOMO

The lowest antibonding molecular orbital is called the lowest unoccupied molecular orbital → LUMO

↳ Absorption of E.M energy can cause e^- to be promoted from HOMO to LUMO.

Most organic molecules appear colourless because the energy difference between HOMO and LUMO is large, resulting in absorption of light from the ultraviolet region of the spectrum

↳ CHROMOPHORES.

· Chromophores exist in molecules containing a conjugated system – a system of unhybridised p orbitals that overlap side-on to form a molecular orbital across a number of carbon atoms. Electrons within this conjugated system are delocalised. Molecules with alternating single and double bonds and aromatic molecules have conjugate systems.

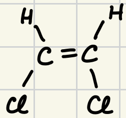
The more atoms in the conjugated system the smaller the energy gap between the HOMO and LUMO. A lower frequency of light (longer λ, lower E) is absorbed by the compound. When the λ of light absorbed in the visible region, the compound appears the complementary colour.

STEREOCHEMISTRY

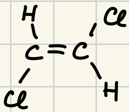
- Molecules that have the same molecular formula but different structural formulae are isomers
  - → Structural isomers occur when the atoms are bonded together in a different order in each isomers.
  - → Stereoisomers occur when the bonding in the atoms is the same but the spatial arrangement of the atoms is different in each isomer. There are 2 types of stereoisomers, geometric and optical.

Geometric Isomers.

- Can occur when there is restricted rotation around a carbon-carbon double bond or a carbon-carbon single bond in a cyclic compound.
- Must have 2 different groups attached to each of the carbon atoms that make up the bond w/ restricted rotation.
- Can be labelled cis or trans



cis,
same side



trans,
opposite sides.

- Different physical properties:
  - → Cis isomers have higher boiling points as they are usually more polar.
  - → Trans isomers have higher melting points and higher densities as their shapes allows tighter packing and thus stronger I.M.F.
- Can have different chemical properties.

Optical Isomers.

- Occur in compounds which contain a chiral carbon, a carbon which has 4 different groups arranged tetrahedrally around it.
- Optical isomers, or 'enantiomers' are non superimposable mirror images of eachother (like hands!).
- Easiest way to draw is by drawing original in tetrahedral form and then draw mirror image.
- Rotate plane polarised light by the same amount but in different directions, they are optically active. A 50:50 mixture of enantiomers is optically inactive as they cancel eachother out. This is called a racemic mixture.
- Have identical physical properties (except for effect on plane polarised light).
- Have identical chemical properties, except when in a chiral environment such as that found in biological systems (usually only one optical isomer is present.) eg. only one optical isomer fitting the active site of an enzyme.

DETERMINATION OF STRUCTURE

Empirical Formula.

Elemental microanalysis is used to determine the masses of C, H, O, S in a sample of an organic compound in order to determine its empirical formula. Elemental microanalyses can be determined from combustion product masses and percentage product by mass.

→ Empirical formula shows the simplest ratio of the elements in a molecule.

Infrared Spectroscopy.

Used to identify certain functional groups in an organic compound.

When infrared radiation is absorbed by organic compounds, bonds within the molecule vibrate (stretch and bend). The λ of infrared radiation that are absorbed depend on the type of atoms that make up the bond and the strength of the bond.

Mass Spectrometry.

→ Used to determine accurate GFM and structural features of an organic compound.

- A small sample of an organic compound is bombarded by high energy e^-. This removes e^- from the organic molecule generating positively charged molecular ions known as parent ions. These molecular ions then break into smaller positively charged ion fragments. A mass spectrum is obtained showing the relative abundance of the ions detected against the mass to charge $\left(\frac{m}{z}\right)$ ratio.

→ The $\frac{m}{z}$ of the parent ion can be used to determine GFM.

→ Fragmentation data can be interpreted to obtain structural info.

FRAGMENTATION.

- Base peak → 100% abundance, very stable
- Molecular ion peak → highest m/z.

In infrared spectroscopy, infrared radiation is passed through a sample of the organic compound and then into a detector that measures the intensity of the transmitted radiation @ different λ. The absorbance of infrared radiation is measured in wavenumbers, $\frac{1}{\lambda}$, in cm^{-1}.

→ Characteristic absorptions by particular vibrations are given in the databooklet.

NMR.

NMR Spectroscopy

Proton nuclear magnetic resonance spectroscopy (proton NMR or ^1H NMR) can give info about the different environments of hydrogen atoms (protons or ^1H) in an organic molecule, and about how many ^1H there are in each environment.

→ ^1H nuclei behave like tiny magnets and in a strong magnetic field some align with it (lower energy), whilst others align against it (higher energy). Absorption of radio waves causes ^1H to 'flip' from lower to higher energy alignment. As they fall back down, the emitted energy is detected & plotted.

→ In a ^1H NMR spectrum, the chemical shift, δ, (peak position) is related to the environment of the ^1H atom and measured in parts per million (ppm)

→ Chemical shifts for different environments are given in the databook.

Height of peak is proportional to no. of ^1H atoms in an environment, so ratio of ^1H atoms in each environment can be determined by comparing peak height.

→ HIGH RESOLUTION NMR.

Uses higher radio frequencies (so higher energy) than those used in low-res, so provides more detailed spectra.

In a high-resolution ^1H NMR, an interaction with ^1H atoms of neighbouring carbon atoms can result in the splitting of peaks into "multiplets".

↳ The no. of ^1H atoms on adjacent carbon atoms will determine the no. of peaks in a multiplet. = n+1, where n is the no. of ^1H on neighbouring C atoms.

PHARMACEUTICALS

Drugs are substances that alter the biochemical processes in the body. Drugs with beneficial effects are used in medicines, which usually contain other ingredients such as fillers to add bulk or sweeteners to improve the taste.

They generally work by binding to specific protein molecules. These protein molecules can be found on the surface of the cell (receptor) or can be specific enzyme molecules within a cell.

Drugs that act on receptors can be:

- Agonists: mimics natural compound, to produce similar response.
- Antagonists: prevents natural compound from binding to receptor. Blocks natural response.

Many drugs that act on enzymes are enzyme inhibitors and act by binding to active site and blocking rxn.

Overall shape and size of a drug is such that it interacts with binding site of receptor/active site of enzyme. Types of interaction can include ionic bonds or Van der Waals forces.

The structural fragment of a drug molecule that allows it to form interactions with a receptor binding site or to an enzyme active site normally consists of different functional groups correctly oriented with respect to each other.

→ Called a pharmacophore.

UNIT 4: RESEARCHING CHEMISTRY.

RESEARCHING CHEMISTRY

Stochiometry

- Balanced equ can be used to calc. no of mols of reactants/products. → stochiometric equ.
- If substances react completely according to mole ratios, this is a quantitative rxn.

→ If this happens, one unknown can be determined, through:

① VOLUMETRIC ANALYSIS

② GRAVIMETRIC ANALYSIS.

① VOLUMETRIC ANALYSIS.

- Involves volume of solutions.

→ Uses sol. of known conc. & vol. to determine conc. of other reactant. → TITRATION

→ Usually involves STANDARD SOLUTIONS

→ TITRATIONS.

Three main types: acid/base (forward & back!), complexometric; redox (from higher).

Standard Solutions.

→ a standard sol is a sol. of accurately known conc.

A primary standard is a substance from which a standard sol. can be prepared directly.

Characteristics:

- High purity
- Stable as a solid and in solution.
- Soluble in water.
- Reasonably high formula mass

EXAMPLES:

Oxalic acid $H_2C_2O_4 \cdot 2H_2O$.

EDTA

Sodium carbonate Na_2CO_3

Silver nitrate $AgNO_3$

etc

→ Some substances, e.g NaOH, can't be used as they absorb H_2O and CO_2 from the air, affects conc.

PREPERATION → Common exam qu.

Calc. appropriate mass of primary standard req. Primary standard is accurately weighed on tared electronic balance using weighing boat. Dissolved in min. vol. of deionised water. Transferred to standard flask along w/ washings. Fill up to mark w/ deionised water. Stopper, invert, and label.

→ Permanent colour change → end point. This is when completion is observed. The point where the reaction is just finished, equivalence point, cannot always be observed. Ideally end point = equivalence point, but this isn't always true.

→ If not self indicating (i.e permanganate going purple) indicator required.

CONTROLS.

A control validates a technique and may involve carrying out a determination on a solution of known concentration.

→ Redox titrations, Gravimetric analysis.

BACK TITRATIONS

Substances which are insoluble in water cannot be measured in a normal titration → must use 'back' titration.

→ Involves reacting a known amount of insoluble substance with an excess of a reactant of known conc. The amount remaining, the excess is determined by titrating it against a standard solution → the "back" titration.

The difference between the initial and excess amount of reactant is the amount reacted w/ the insoluble substance.

∴ Can calculate amount of insoluble substance.

REDOX TITRATION

→ Higher revision.

KEY POINTS:

- Oxidising + reducing agent.

→ Oxidising agent is reduced. Reducing agent is oxidised.

- OILRIG.
- Ion electron eqn → equal charge / no. of e^-.

COMPLEXOMETRIC TITRATIONS.

These titrations are based on the formation of a complex between a metal ion and a chelating agent (explained in later topic).

→ Usually EDTA, which forms a 1-to-1 complex with metal ions.

End point of titrations w/ EDTA uses murexide or eriochrome black indicator.

② GRAVIMETRIC ANALYSIS.

→ Quantitative analysis technique in which the substance being determined is converted to a solid which can be isolated completely + weighed accurately.

This is done by:

- forming precipitates, removed by filtration, dried and weighed.
- heat, allow to cool down in dessicator (provides dry environment to prevent reabsorption of water from air.) and reweigh.
- repeat until constant mass.

→ Gives more accurate results than volumetric, but more time!

ERRORS + UNCERTAINTIES.

Accurate → Close agreement w/ true or accepted value.

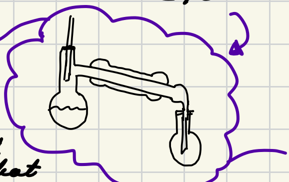
Precise → Measurements in close agreement w/ eachother.

A quantitive measurement is incomplete without error. The uncertainty of equipment is on data sheet.

Purification and Seperation

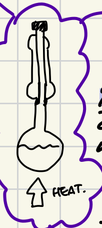
DISTILLATION.

Used for identification AND purification. B. P can be found by distillation and used w/ other info to identify it. Also used to separate a compound from a more/less volatile material.



REFLUXING.

Boiling a rxn mix. and condensing vapours back into rxn flask. To prevent boiling over, anti bumping granules are added. Allows substances to be heated without loss of volatile/ flammable reactants.



VACUUM FILTRATION.

Buchner, hirsch or sintered glass funnel. Filtration under reduced pressure to speed it up.

RECRYSTALISATION.

Purify solids based on solubility. Solvent must be selected so that the impure compound is insoluble at low temps but soluble at high temps.

Impure compound dissolved in min vol. of hot solvent then filtered to remove insoluble impurities. Filtrate is cooled slowly to force crystallisation. More soluble impurities left behind in solvent.

SEPERATING FUNNEL.

Two solvents form 2 seperate layers in the funnel and the lower layer is run off into one container and the upper another.

Solvents must be: immiscable w/ eachother, unreactive w/ solute, and solute must be more soluble in one solvent than the other.

Melting Point & Mixed M.P.

If a product is solid, its M.P can be determined and compared w/ the accepted/literature value to identify it.

A crystalline substance has a sharp M.P, with a range of about 1°C.

Impurities lower M.P and extends range.

Mixed melting point involves mixing a pure sample and the product. If melting point is sharp and close to literature/accepted value then compounds are identical and product is pure.

Impurities have same effect as above.

If product is a liquid, use distillation to measure B.P to help w/ identification.

Identification

THIN LAYER CHROMATOGRAPHY. → HIGHER!

Assess purity of a product.

Distribution of a substance between a mobile phase and stationary phase.

A pure substance will only show one spot on developed chromatogram.

Impure will have many. Compare pure to product.

$$\boxed{R_f = \frac{\text{dist. travelled by substance.}}{\text{dist. travelled by solvent front.}}}$$

COLORIMETRY + CALIBRATION CURVES.

Uses relationship between how coloured a substance is and its concentration.

↳ More coloured → higher conc.

The colour intensity can be measured by checking the light absorption of a sol using a colorimeter. Solutions that are coloured absorb the opposite/complementary colour of light (use colour wheel) so the opposite filter must be used.

Between measurements, a cuvette must be filled w/ water and measured as a blank as reference in order to zero the machine.

→ CALIBRATION CURVE.

Produced using the absorbance (A) of a range of different known concs of the solution being measured (standard solutions). From this graph can be plotted and unknown conc. can be determined from its absorbance.