

# H2 Chemistry

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## Abstract

This set of notes follows the [Singapore GCE A-Level H2 Chemistry](#) syllabus.

## Values

<b>Standard temperature and pressure (s.t.p.)</b>	273 K, 1 bar ( $10^5$ Pa), molar volume $22.7 \text{ dm}^3 \text{ mol}^{-1}$
<b>Room temperature and pressure (r.t.p.)</b>	293 K, 1 atm (101325 Pa), molar volume $24.0 \text{ dm}^3 \text{ mol}^{-1}$
<b>Standard conditions</b>	298 K, 1 bar, $1 \text{ mol dm}^{-3}$
<b>Specific heat capacity of water</b>	$4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (or $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ )

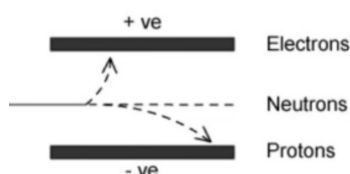
# §1 Atomic Structure

Term	Definition
<b>Isotope</b>	Atom of same element with same number of protons, different number of neutrons.
<b>Orbital</b>	Region in space where there is high probability of finding an electron.
<b>First ionisation energy</b>	Energy required to remove 1 mole of electrons from 1 mole of gaseous atoms of the element to form 1 mole of singly charged gaseous cations.
<b>Second ionisation energy</b>	Energy required to remove 1 mole of electrons from 1 mole of singly positively charged gaseous ions to form 1 mole of doubly charged gaseous cations.

## §1.1 Nucleus of atom

Particle	Charge	Mass	Angle of deflection
proton	+1	1	small
electron	-1	$\approx 0$	large
neutron	0	1	none

Deflection of subatomic particles in electric field:



$$\angle \propto \frac{q}{m}$$

**Remark.**  $\angle = k \left( \frac{q}{m} \right)$  where constant of proportionality  $k$  remains same under same experimental conditions.

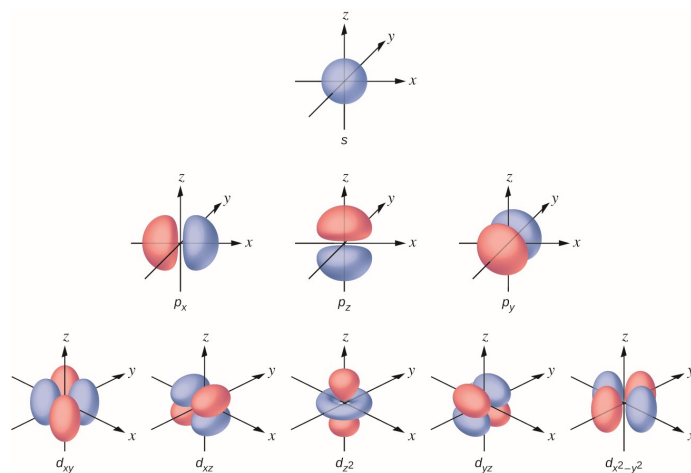
Distribution of mass and charges within an atom:

- Mass concentrated in nucleus, electrons are of negligible mass
- Nucleus positively charged due to protons, negatively charged electrons surround nucleus

**Isotopes:**

- Similar chemical properties: same no. of protons so same no. of electrons
- Different physical properties: different no. of neutrons so different masses

## §1.2 Electrons



$s$ -orbitals: spherical in shape

$p$ -orbitals: dumbbell in shape

$d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ : lobes between two axes

$d_{x^2-y^2}$ ,  $d_{z^2}$ : lobes along axes

(1)

### §1.2.1 Electronic configuration

Rules of orbital filling

1. **Aufbau principle:** electrons filled in the order of increasing orbital energy (4s filled before 3d, 4s removed before 3d)
2. **Hund's rule:** electrons added into orbitals singly first with parallel spins before pairing (electrons as far apart as possible to minimise repulsion)
3. **Pauli exclusion principle:** each orbital holds max 2 electrons in opposite spins

Exceptions:

- **Chromium:**  $[\text{Ar}] 3d^5 4s^1$  instead of  $[\text{Ar}] 3d^4 4s^2$   
partially filled 3d subshell is more stable due to less inter-electronic repulsion

- **Copper:**  $[\text{Ar}] 3d^{10} 4s^1$  instead of  $[\text{Ar}] 3d^9 4s^2$   
fully filled 3d subshell is more stable due to symmetrical charge distribution

### §1.2.2 Atomic trends

Explain atomic trends:

1. Explain factors affecting effective nuclear charge
  - Nuclear charge: no. of protons
  - Shielding effect: no. of inner shells
  - Distance of valence electrons from nucleus
  - Same no. of protons attract more/fewer electrons\*\*

(mention which factor outweighs another factor if both factors have opposing effects)
2. Change in effective nuclear charge
3. Link back to question

#### Atomic radius increases down the group:

- Each successive element in the group contains one additional PQS, valence electrons are further away from nucleus
- Increase in screening effect outweighs increase in nuclear charge
- Effective nuclear charge decreases

↪ **Electronegativity decreases down the group**

↪ **1st IE decreases down the group**

#### Atomic radius decreases across the period:

- Increase in nuclear charge due to increasing number of protons
- Screening effect remains relatively constant as electrons are added to same PQS
- Effective nuclear charge increases

↪ **Electronegativity increases across the period**

↪ **1st IE increases across the period**

#### Ionic radius of cations smaller than their respective atoms:

- One PQS fewer than atom
- Valence electrons are more strongly attracted by nucleus

#### Ionic radius of anions larger than their respective atoms:

- Same number of protons attract more electrons
- Outer electrons are less strongly attracted by the nucleus

#### Ionic radius increases down the group:

- Each successive element in the group contains one additional PQS, valence electrons are further away from nucleus
- Increase in screening effect outweighs increase in nuclear charge
- Effective nuclear charge decreases

#### Across the period, anions are bigger than cations:

- One more PQS than cations, outer electrons experience greater shielding effect, so less strongly attracted by nucleus

#### Successive IEs of an element increases

- More energy is required to remove an electron from an increasingly positive ion, stronger electrostatic force of attraction between nucleus and remaining electrons

#### Discontinuities in 1st IE:

- 1st IE of B is higher than Be

Electron in 2p orbital is at higher energy level (and further from nucleus) than one in 2s orbital of the same principal quantum shell. Hence 2p electron is easier to remove, requires less energy for ionisation.

- 1st IE of O is lower than that of N.

In O, inter-electron repulsion arising from 2 electrons occupying the same 2p orbital. Thus the paired 2p electron of O atom is more easily removed.

- Sudden drop in 1st IE from Ne to Na.

Outermost electron in Na is found in a different principal quantum shell at a higher energy level which is further away from the nucleus.

The increased effective shielding by the greater number of inner full quantum shells of electrons resulted in a weaker attractive force by the nucleus, and hence lower 1st IE.

## §2 Chemical Bonding

### §2.1 Types of Bonding

- **Ionic bond:** electrostatic forces of attraction b/w oppositely charged ions in giant ionic structure

$$LE \propto \left| \frac{q^+ \cdot q^-}{r^+ + r^-} \right|$$

- **Metallic bond:** electrostatic forces of attraction b/w lattice of cations & sea of delocalised electrons in giant metallic structure
  - No. of valence electrons available for delocalisation per atom
  - Size of metal cation (cationic radius)

- **Covalent bond:** electrostatic forces of attraction b/w positively charged nuclei of two atoms & shared pair of electrons

Bond dissociation energy, affected by:

- Bond order (no. of bonds)
- Effectiveness of orbital overlap: larger orbital is more diffused → orbital overlap less effective → shorter bond length → weaker bond strength
- Bond length:  $\sigma$  bond vs  $\pi$  bond
- Polar vs non-polar bond

**Dative bond:**

- **Donor:** lone pair of electrons available for donation (electron-rich)
- **Acceptor:** vacant low-lying orbital to accept electron pair (electron-deficient)

E.g. dimerisation of  $\text{AlCl}_3$  to form  $\text{Al}_2\text{Cl}_6$

**Hydrogen bonding (intramolecular):** e.g. boiling point of 2-nitrophenol is lower than 4-nitrophenol

- Formation of intramolecular hydrogen bonds in 2-nitrophenol (close proximity of  $-\text{OH}$  group and  $-\text{NO}_2$  group)
- Less extensive intermolecular hydrogen bonds in 4-nitrophenol

**Remark.** All chemical bonds are electrostatic in nature.

Know how to draw 'dot-and-cross' diagrams and Lewis structures.

### §2.2 Covalent Bonds

**Definition 2.1 (Bond energy)**

Energy required to break one mole of covalent bond in gaseous state.

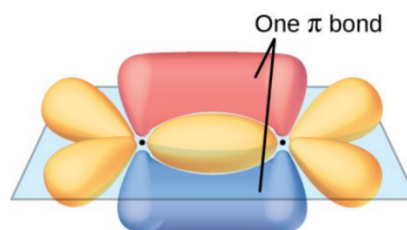
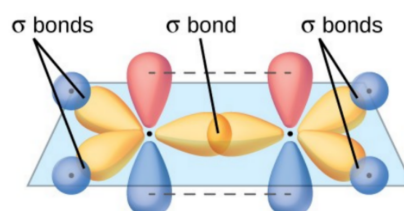
**Definition 2.2 (Bond length)**

Distance between nuclei of two bonding atoms.

#### §2.2.1 Overlap of orbitals

**sigma bond:** head-on overlap

**pi bond:** side-on overlap

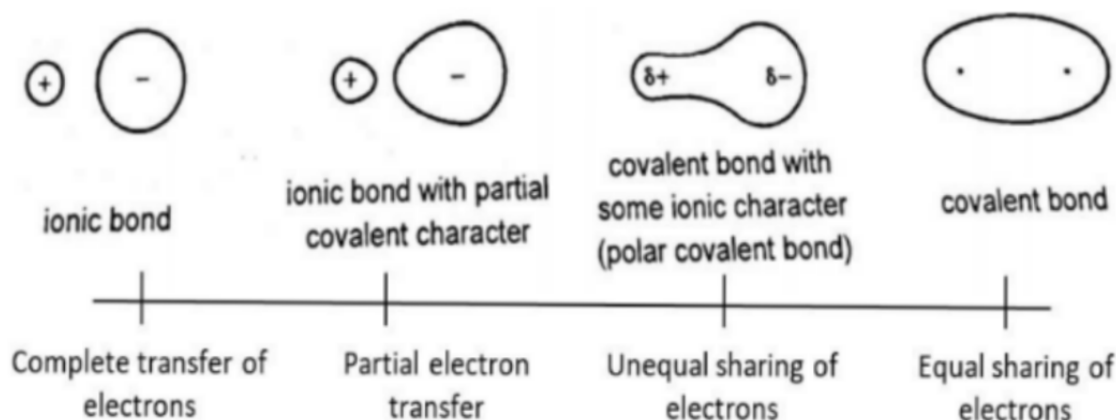


#### §2.2.2 Polarity

**Definition 2.3 (Electronegativity)**

Ability of atom to attract shared pair of electrons towards itself in a covalent bond.

Intermediate bond types:



Ionic bond with covalent character	Covalent bond with ionic character ( <b>polar</b> )
Cation polarise electron cloud of anion → partial electron sharing → induce covalent character	<b>Polar bond:</b> two atoms have significant $\Delta EN$ , attract shared electrons by different extent → unevenly distributed charge ( $\delta+$ and $\delta-$ ) <b>Polar molecule:</b> net dipole moment (dipole moments do not cancel out), depends on <ol style="list-style-type: none"> <li>1. bond polarity</li> <li>2. molecular shape</li> </ol>
Factors <ul style="list-style-type: none"> <li>• Polarising power of cation (charge density)</li> <li>• Polarisability of anion (electron cloud size)</li> </ul>	Factors <ul style="list-style-type: none"> <li>• Electronegativity difference</li> </ul>

Exceptions:

- $AlCl_3$ ,  $FeCl_3$ ,  $BeCl_2$  are covalent  
High charge density of cation + large anion which is easily polarised
- However,  $AlF_3$  is ionic  
Small anion which is not easily polarised

### §2.2.3 Octet rule

**Octet rule:** atoms gain / lose / share electrons until they have 8 valence electrons.

Exceptions:

- Central atom has odd no. of valence electrons (free radical) (Note that the single electron is NOT considered a lone pair) e.g.  $NO_2$
- Central atom has less than 8 valence electrons (electron deficient) e.g.  $BF_3$
- Central atom expand valence shells (Period 3 and beyond) due to vacant low-lying, energetically accessible 3d orbitals e.g.  $PCl_5$

### §2.2.4 VSEPR

#### Definition 2.4 (Valence Shell Electron Pair Repulsion theory)



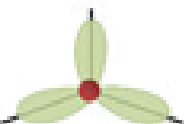
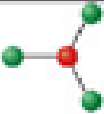
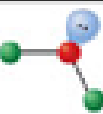
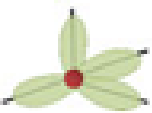
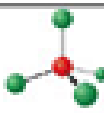


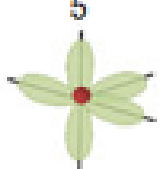
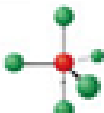
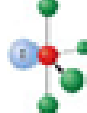
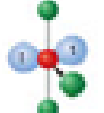
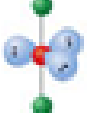
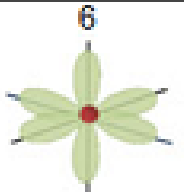
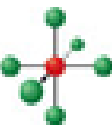
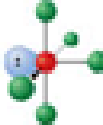
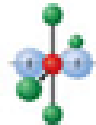
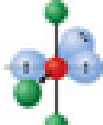

Regions of electron density arrange themselves as far apart as possible to minimise repulsion.

Repulsive force by l.p. > b.p.

- l.p. is only attracted central nucleus → closer to central atom
- b.p. is attracted by both central atom and bonding species → further away from central atom

To predict the shape of a covalent molecule:

1. Draw Lewis diagram
2. Determine basic geometry based on total no. of regions of electron density, then determine shape based on no. of bond pairs and lone pairs

Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2 	Linear	 Linear				
3 	Trigonal planar	 Trigonal planar	 Bent			
4 	Tetrahedral	 Tetrahedral	 Trigonal pyramidal	 Bent		
5 	Trigonal bipyramidal	 Trigonal bipyramidal	 Sawhorse	 T-shaped	 Linear	
6 	Octahedral	 Octahedral	 Square pyramidal	 Square planar	 T-shaped	 Linear

#### Factors affecting bond angle

1. Electron pair repulsion:

$$lp-lp > lp-bp > bp-bp > electron-bp$$

Lone pair closer to nucleus → exert greater repulsion → bond angle larger

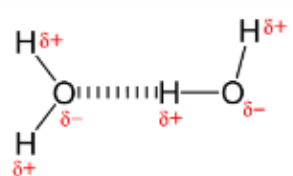
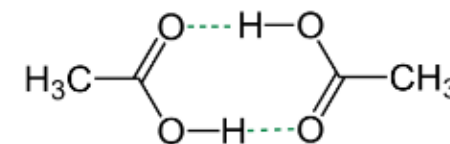
2. Electronegativity:

Central atom more electronegative → attract shared pair of electrons in bp closer to nucleus → bp closer to each other, exert stronger repulsive force → bond angle larger

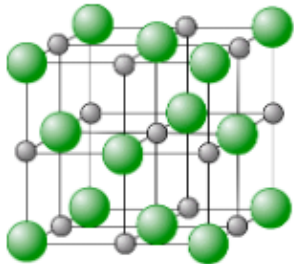
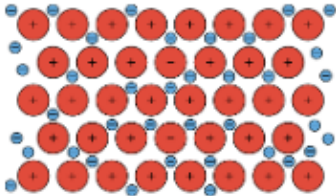

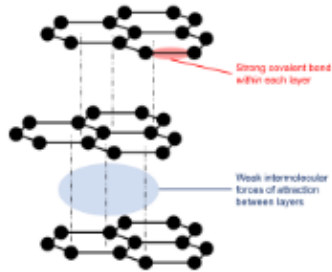
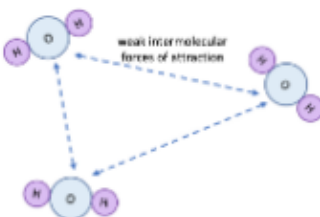
3. Size of surrounding atoms:

Larger surrounding atoms have larger electron clouds which exert repulsive force between one another, prevent surrounding atoms from coming close together → bond angle larger

## §2.3 Intermolecular Forces

hydrogen > pd-pd > id-id (molecules with similar electron cloud sizes)			
Forces	Instantaneous dipole-induced dipole interaction (id-id)	Permanent dipole-permanent dipole interaction (pd-pd)	Hydrogen bonding (intramolecular)
Figure	$\begin{array}{ccccc} \delta^+ & \delta^- & & \delta^+ & \delta^- \\ \text{Cl} - \text{Cl} & \text{-----} & \text{Cl} - \text{Cl} \end{array}$	$\begin{array}{ccccc} \delta^+ & \delta^- & & \delta^+ & \delta^- \\ \text{H} - \text{Cl} & \text{-----} & \text{H} - \text{Cl} \end{array}$	
Desc	<p><u>Momentary polarisation</u> of electron cloud at any instant when molecules are in continual random motion → temporarily generate <u>partial charge</u> on atom (<u>instantaneous dipole</u>) → <u>induce dipole</u> on neighbouring atom in molecule → attraction b/w partial charges of two molecules</p>	<p>Electronegativity difference (<math>\Delta\text{EN}</math>) b/w two elements → generate <u>partial charge</u> on atoms → attraction b/w partial charges of two molecules</p>	<p>1) H atom bonded to <u>F/O/N atom</u> 2) another F/O/N atom has <u>lone pair</u></p> <p><u>Dimerisation:</u></p> 
	All covalent molecules	Only polar molecules	Only polar molecules
Factors	<ul style="list-style-type: none"> <li>Size of molecule (<math>M_r</math>): larger electron cloud is more polarisable → stronger id-id</li> <li>Surface area of molecule: more branching → less surface area of contact (bcos shorter) → less extensive id-id (organic mol)</li> </ul>	<ul style="list-style-type: none"> <li>Electronegativity difference (<math>\Delta\text{EN}</math>): magnitude of dipole moment</li> </ul>	<ul style="list-style-type: none"> <li>No. of lone pairs of electrons on highly electronegative atom</li> <li>Number of H-bond formed per molecule</li> <li>Electronegativity difference (<math>\Delta\text{EN}</math>): magnitude of dipole moment</li> <li>Formation of intramolecular H-bond</li> </ul>

## §2.4 Physical Properties

Structure	Giant ionic lattice structure	Giant metallic lattice structure	Giant molecular lattice structure	Giant molecular layered lattice structure	Simple molecular structure
Figure					
Lattice forces	Strong ionic bonds b/w ions	Strong metallic bonds b/w metallic cations & sea of delocalised electrons	Strong covalent bonds b/w atoms	Strong covalent bonds b/w atoms in a layer Weak id-id b/w layers	Weak id-id / pd-pd / hydrogen bonding b/w molecules
Physical properties	High mp/bp	High mp/bp	High mp/bp	High mp/bp	Low mp/bp
	Non-conductor of electricity in solid state Good conductor of electricity in molten / aqueous state	Good conductors of electricity	Non-conductor of electricity	Non-conductor of electricity perpendicular to layers, good conductor of electricity parallel to layers	Non-conductors of electricity
	Soluble in water and polar solvents Insoluble in non-polar solvents	Insoluble in polar and non-polar solvents, some soluble in liquid ammonia	Insoluble in water and non-polar solvents	Insoluble in water and non-polar solvents	Soluble in non-polar solvents Insoluble in water
	Hard, brittle	Malleable, ductile	Hard	Soft, slippery	



**Answering format:**

- Melting/ boiling point  
Structure + large/ small amount of energy required to overcome strong/ weak bonds
- Electrical conductivity  
Mobile electrons/ ions are free to move to carry charges
- Solubility in polar/non-polar solvent  
Energy released during formation of (interactions, if any) is sufficient/ insufficient to overcome (bonds b/w solvent molecules & bonds b/w solute molecules)

**Remark.** In **graphite**, p orbitals of  $sp^2$  hybridised carbon atoms overlap, so electrons in p orbitals delocalise.

**Remark. Hydrogen bonding in ice and water**

- Ice: each water molecule is bonded to four other molecules in tetrahedral manner  
Water molecules orientate to maximise intermolecular hydrogen bonding → open structure, thus lower density
- Liquid water: some hydrogen bonds broken, lattice breaks up  
Water molecules packed more closely together thus higher density

## §3 Gaseous State

### §3.1 Gas laws

Gas laws:

- **Boyle's Law:**  $p \propto \frac{1}{V}$  at constant  $T$  and  $n$
- **Charles' Law:**  $V \propto T$  at constant  $p$  and  $n$
- **Gay-Lussac's Law:**  $p \propto T$  at constant  $V$  and  $n$
- **Avogadro's Law:**  $V \propto n$  at constant  $p$  and  $n$

**Remark.** Remember to take note which quantities are *variables* and *constants*!

**Remark.** SI units must be used for calculations:  $p$  (in Pa),  $T$  (in K),  $V$  (in  $\text{m}^3$ ),  $n$  (in mol)

#### §3.1.1 Ideal gas equation

Ideal gas equation:

$$pV = nRT \quad (2)$$

where  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$  is molar gas constant.

### §3.2 Kinetic theory of gases

Basic assumptions:

1. Small particles of negligible volumes, as compared to container
2. Negligible intermolecular forces of attraction
3. Perfectly elastic collisions between gas particles and walls of container

All gases are non-ideal; they are *real* gases.

Approach ideality	Deviate from ideality
High temperature: gas particles able to overcome most of the intermolecular forces of attraction	Low temperature: molecules move more slowly, intermolecular forces of attraction become less negligible
Low pressure: volume of gas particles becomes negligible as compared to volume occupied by gas	High pressure: intermolecular distances become less negligible
	Strong intermolecular forces of attraction e.g. $\text{NH}_3$ (hydrogen bonding)
	Large size of gas molecule e.g. $\text{N}_2$ (stronger id-id)

**Compressibility:** ratio of measured molar volume  $V_m$  to molar volume of ideal gas  $V_m^\circ$  at same temperature and pressure.

$$Z = \frac{V_m}{V_m^\circ} = \frac{pV_m}{RT} \quad (6)$$

From eq. (2) derive the expression for **molar mass** of gas:

$$M_r = \frac{mRT}{pV} \quad (3)$$

and expression for **density** of gas:

$$\rho = \frac{pM_r}{RT} \quad (4)$$

#### §3.1.2 Partial pressure

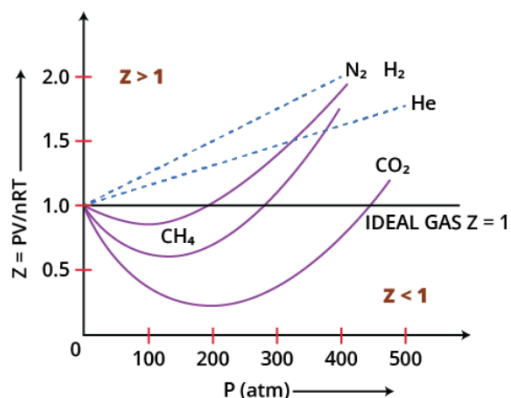
##### Definition 3.1 (Dalton's Law)

In a mixture of inert gases at constant volume and temperature, total pressure of mixture is the sum of partial pressures of constituent gases.

Partial pressure is dependent on molar fraction of gas:

$$p_{\text{gas}} = \frac{n_{\text{gas}}}{n_T} p_T \quad (5)$$

### §3.2.1 Compressibility against pressure

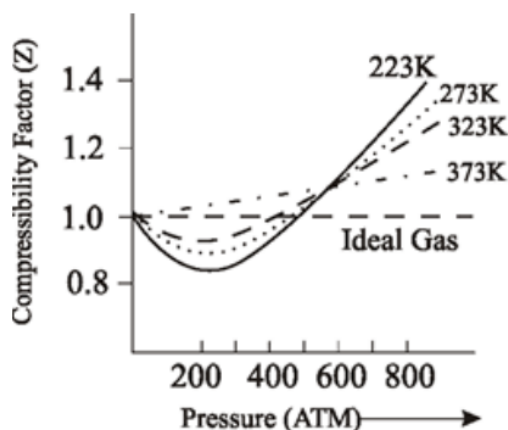


Gas has stronger intermolecular forces of attraction, deviates more significantly from ideal gas behaviour.

#### Remark.

- At low pressure,  $Z < 1$  because attractive forces between molecules, molar volume  $V_m$  is smaller than that of ideal gas  $V_m^\circ$ .
- At high pressure,  $Z > 1$  because repulsive forces between molecules, molar volume  $V_m$  is larger than that of ideal gas  $V_m^\circ$ .

### §3.2.2 Compressibility against temperature



Temperature decreases, average kinetic energy of gas particles decreases, gas particles closer together, intermolecular forces of attraction become significant, so deviates more significantly from ideal gas behaviour.

## §4 Periodic Table

### §4.1 Period 3 Elements

#### §4.1.1 Atomic and physical properties

- **Atomic radius** decreases across the period
- Ionic radius of isoelectronic ions decrease across period

Within the same period, ionic radii of anions are larger than cations

Ionic radius of cation is smaller than corresponding atomic radius, ionic radius of anion is larger than corresponding atomic radius

- **First ionisation energy** increases across the period  
Exception: 1st IE of Mg > Al, 1st IE of P > S
- **Electronegativity** increases across the period
- **Melting point:** increases from Na to Si, decreases from Si to S<sub>8</sub> to P<sub>4</sub> to Cl<sub>2</sub>
- **Electrical conductivity** increases from Na to Al, then decreases

#### §4.1.2 Variation in oxidation number

- Oxygen and chlorine are more electronegative than the other elements in Period 3

Oxygen has oxidation state of -2 in oxides; chlorine has oxidation state of -1 in chlorides.

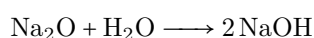
Elements Na and S usually have positive oxidation state that corresponds to number of bonding electrons.

- Max oxidation state of element corresponds to its group member  
This occurs when all valence electrons are used for bonding.
- Multiple oxidation states

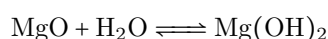
Phosphorus and sulfur have more than one oxidation state – able to use different numbers of electrons in bonding due to presence of vacant low-lying energetically accessible d orbitals.

#### §4.1.3 Reaction of oxides with water

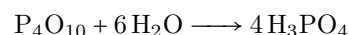
- Na<sub>2</sub>O dissolves in water in vigorous reaction, gives strongly basic solution (pH 13)



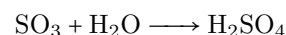
- MgO dissolves in water in less vigorous reaction, gives weakly alkaline solution (pH 9)



- Al<sub>2</sub>O<sub>3</sub> insoluble in water / does not react with water, due to high LE (pH 7)
- SiO<sub>2</sub> insoluble in water / does not react with water, due to giant molecular structure (pH 7)
- P<sub>4</sub>O<sub>10</sub> dissolves in water in violent reaction, gives strongly acidic solution (pH 2)

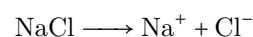


- SO<sub>3</sub> dissolves in water in violent reaction, gives strongly acidic solution (pH 2)

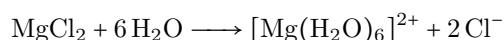


#### §4.1.4 Reaction of chlorides with water

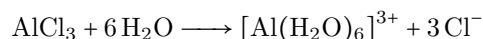
- NaCl dissolves readily in water, gives hydrated ions in a neutral solution (pH 7)



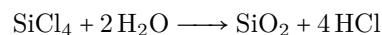
- MgCl<sub>2</sub> dissolves in water with partial hydrolysis, due to high polarising power of Mg<sup>2+</sup>, gives slightly acidic solution (pH 6.5)



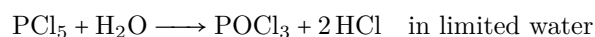
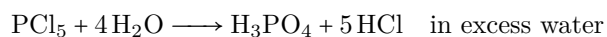
- AlCl<sub>3</sub> dissolves in water with partial hydrolysis, due to high polarising power of Al<sup>3+</sup>, gives acidic solution (pH 3)



- SiCl<sub>4</sub> dissolves in water due to complete hydrolysis, gives strongly acidic solution (pH 2)



- PCl<sub>5</sub> dissolves in water due to complete hydrolysis, gives strongly acidic solution (pH 2)

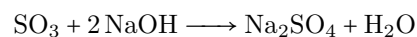


[HCl(g)] observed as white fumes]

**Acidic nature of Al<sup>3+</sup>(aq):** Al<sup>3+</sup> has high charge density, high polarising power, polarise electron clouds of surrounding water molecules, weaken O–H bonds in water molecule, release H<sup>+</sup>

**Remark.**  $\text{AlCl}_3$  is (purely) covalent!

- $\text{SO}_3$  is acidic, undergoes neutralisation with bases to give salt solution

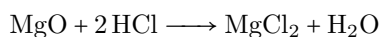


#### §4.1.5 Acid/base behaviour of oxides

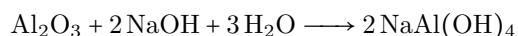
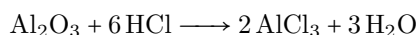
- $\text{Na}_2\text{O}$  is basic, undergoes neutralisation with acids to give salt solution



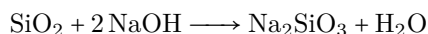
- $\text{MgO}$  is basic, undergoes neutralisation with acids to give salt solution



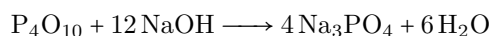
- $\text{Al}_2\text{O}_3$  is amphoteric, undergoes neutralisation with both acids and bases to give salt solution



- $\text{SiO}_2$  is acidic, undergoes neutralisation with bases to give salt solution [only reacts with hot conc  $\text{NaOH}$ ]

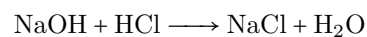


- $\text{P}_4\text{O}_{10}$  is acidic, undergoes neutralisation with bases to give salt solution

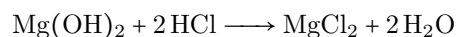


#### §4.1.6 Acid/base behaviour of hydroxides

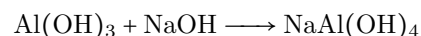
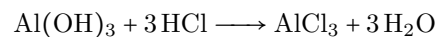
- $\text{NaOH}$  is basic, undergoes neutralisation with acids to give salt solution



- $\text{Mg(OH)}_2$  is basic, undergoes neutralisation with acids to give salt solution



- $\text{Al(OH)}_3$  is amphoteric, undergoes neutralisation with both acids and bases to give salt solution



## §4.2 Group 2 Elements

### §4.2.1 Atomic and physical properties

- **Atomic radius** increases down the group
- **Ionic radius** increases down the group
- **First ionisation energy** decreases down the group

### §4.2.2 Chemical properties

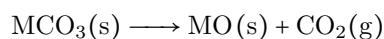
Reactivity as reducing agents increases down the group

- $E^\circ$  more negative, higher tendency to undergo oxidation
- Sum of 1st and 2nd IE decrease down the group. Increase ease of atom losing electrons to form cations during oxidation. Reducing power (and hence reactivity) of Group 2 metals increases.

Reactivity can be observed via

- **Reaction of metal with oxygen**
- **Reaction of metal with water**

**Thermal stability** of compounds (e.g. carbonates) increases down the group



- Cationic radius increases, charge same, so charge density of cation decreases, polarising power of cation decreases
- Polarise electron cloud of  $\text{CO}_3^{2-}$  to lower extent, weaken C–O bond in  $\text{CO}_3^{2-}$  to lower extent
- Thermal stability of carbonates increases, so decomposition temperature increases

**Remark.** Thermal stability depends on charge density of cation & polarisability of large anion.

**Remark.** For carbonates, C–O bond is broken; for nitrates, N–O bond is broken; for peroxides, O–O bond is broken.

## §4.3 Group 17 Elements

### §4.3.1 Physical properties

- **Electronegativity** decrease down the group
- **Melting point** increases, **volatility**<sup>1</sup> decreases

Mr increases, larger and more polarisable electron cloud, stronger id-id interactions which require more energy to overcome

### §4.3.2 Chemical properties

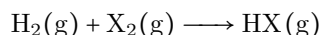
**Reactivity as oxidising agents** decreases down the group

- $E^\ominus$  less positive, lower tendency to undergo reduction
- Number of filled PQS increases down the group, each successive element has valence element has valence electrons located in shell with higher principal quantum number  
Valence electrons increasingly further away from nucleus, less strongly attracted to nucleus  
Less able to attract bonding electrons to undergo reduction
- Alternative explanation:  $E^\ominus$  values

**Displacement reactions of halogens**

- Halogens that are higher in Group 17 are stronger oxidising agents, oxidise aq halide ions lower in the group – displace halide ion from the solution

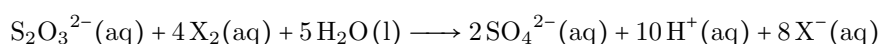
**Reaction with hydrogen**



- Down the group, reactivity as oxidising agent decreases, less vigorous reaction

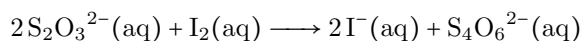
**Reaction with sodium thiosulfate**

- Stronger oxidising agent, gains electrons more readily, so greater magnitude of change in oxidation state of species oxidised
- Stronger oxidising agent:  $\text{Cl}_2$  and  $\text{Br}_2$  oxidise  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_4^{2-}$



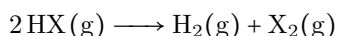
Change in oxidation state of S: +2 to +6

- Weaker oxidising agent:  $\text{I}_2$  oxidises  $\text{S}_2\text{O}_3^{2-}$  to  $\text{S}_4\text{O}_6^{2-}$



Change in oxidation state of S: +2 to +2.5

**Thermal stability** of hydrogen halides decreases down the group



- Halogen has larger electron cloud, orbital overlap less effective, bond length increases, bond energy decreases
- H–X bond weaker, which requires less energy to break, so thermal stability decreases

---

<sup>1</sup>volatility is inversely related to boiling point

## §5 Mole Concept and Stoichiometry

Term	Definition
<b>Relative isotopic mass</b> $A_r$	Mass of one atom of isotope of element relative to $\frac{1}{12}$ of mass of C-12 atom.
<b>Relative atomic mass</b> $A_r$	Average mass of atoms of element in isotopic mixture relative to $\frac{1}{12}$ of mass of C-12 atom.
<b>Relative molecular mass</b> $M_r$	Average mass of one molecule relative to $\frac{1}{12}$ of mass of C-12 atom.
<b>Relative formula mass</b> $M_r$	Average mass of one formula unit of substance relative to $\frac{1}{12}$ of mass of C-12 atom. [A formula unit is the smallest collection of atoms from which the formula of an ionic compound can be established. It is equal to the sum of the $A_r$ of the atoms shown in the formula unit.]
<b>Mole</b>	One mole contains as many particles as the number of atoms of carbon in 12 g of C-12.
<b>Avogadro constant</b> $L$	Number of carbon atoms in 12 g of C-12.
<b>Molar mass</b>	Mass of one mole of substance.
<b>Avogadro's law</b>	Equal volumes of all gases, under same conditions of temperature and pressure, contain same number of molecules/ atoms.
<b>Molar volume</b>	Volume occupied by one mole of gas.
<b>Empirical formula</b>	Shows ratio of atoms of different elements in the compound.
<b>Molecular formula</b>	Shows actual number of atoms of each element present in one molecule of the compound.

### §5.1 Relative masses

Given  $i$  isotopes,  $A_r$  is the weighted average of all isotopes:

$$A_r = \frac{\sum_i m_i \times \text{Abundance}_i}{\sum_i \text{Abundance}_i} \quad (7)$$

$M_r$  is sum of  $A_r$  of atoms in molecular formula:

$$M_r = \sum_i (A_r)_i \quad (8)$$

Number of moles of a molecule:

$$n = \frac{m}{M_r} \quad (9)$$

Number of moles in solution:

$$n = C \times V \quad (10)$$

Number of moles of gas:

$$n = \frac{V}{V_m} \quad (11)$$

where  $V_m$  is molar volume.

#### Exercise 1

Determine the  $A_r$  of chlorine given that there exist two isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , with percentage isotopic abundance 75% and 25%, respectively.

**Solution.** To calculate  $A_r$ , we need to consider the relative amount of each isotope. To calculate a weighted average,

$$A_r \text{ of chlorine} = \frac{75(35) + 25(37)}{75 + 25} = \boxed{35.5}$$

### §5.3 Empirical, molecular formulae

Determine empirical formula

1. Change percentage composition to mass.
2. Divide mass of each element by its relative atomic mass to get number of moles.
3. Divide number of moles of each element by the smallest number of moles to obtain mole ratio.

□ Determine molecular formula

4. Molecular formula =  $n(\text{empirical formula})$  where  $n$  is positive integer

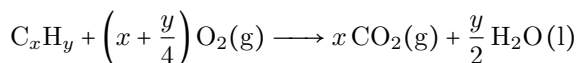
### §5.2 Mole

One mole of any substance contains  $6.02 \times 10^{23}$  particles.

$$n = \frac{\text{relative molecular mass}}{\text{relative mass in empirical formula}}$$



**Combustion analysis:** determine molecular formula of hydrocarbons by complete combustion in oxygen



An alkali is used to remove  $\text{CO}_2$ . Number of moles of  $\text{CO}_2$  formed is equal to number of moles of C in the hydrocarbon.

$\text{H}_2\text{O}$  exists as liquid at r.t.p. Number of moles of  $\text{H}_2\text{O}$  formed is equal to half of number of moles of H in the hydrocarbon.

2. ON of H in compound = +1 (except in metal hydrides)
3. ON of O in compound = -2 (except in peroxides)
4. ON of more electronegative atom is negative
5. ON of less electronegative atom is positive
6. ON of uncharged compound = sum of individual ON = 0

**Remark.** Remember to consider bond order.

## §5.4 Reacting masses and volumes

**Limiting reagent:** completely used up at the end of reaction – determines yield of reaction

$$\% \text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \quad (12)$$

$$\% \text{purity} = \frac{\text{mass of pure substance}}{\text{mass of sample}} \times 100\% \quad (13)$$

**Standard solution:** has a known concentration

**Dilution:**

$$C_0 V_0 = C_d V_d \quad (14)$$

**Back titration:**

1. Sample X is reacted with known excess of reagent Y.
2. Excess unreacted reagent Y titrated against reagent Z to determine amount of unreacted Y.
3. Amount of X can be determined using stoichiometry.

$$n_Y(\text{reacted}) = n_Y(\text{added}) - n_Y(\text{unreacted})$$

## §5.5 Oxidation number

Rules to assign oxidation number

1. ON of element = 0

## §5.6 Redox reactions

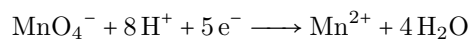
To construct redox equation in acidic medium,

1. Construct unbalanced oxidation and reduction half-equations
2. Balance all elements except H and O
3. Balance O atoms by adding  $\text{H}_2\text{O}$
4. Balance H atoms by adding  $\text{H}^+$  ions
5. Balance charges by adding electrons
6. Add both half-equations

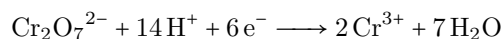
To construct a redox equation in alkaline medium,

7. Neutralise  $\text{H}^+$  ions by adding  $\text{OH}^-$  ions, combine  $\text{H}^+$  and  $\text{OH}^-$  to form  $\text{H}_2\text{O}$

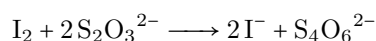
**Manganate(VII)** as oxidising agent



**Dichromate(VI)** as oxidising agent



**Thiosulfate** as reducing agent



## §6 Chemical Energetics

### §6.1 Thermochemistry

#### §6.1.1 Enthalpy changes

Term	Definition
<b>Standard enthalpy change of reaction <math>\Delta H^\circ</math></b>	Energy change when molar quantities of reactants as specified by the chemical equation react to form products at <u>standard conditions</u> .
<b>Standard enthalpy change of formation <math>\Delta H_f^\circ</math></b>	Energy change when one mole of the substance is formed from its constituent elements under standard conditions.
<b>Standard enthalpy change of combustion <math>\Delta H_c^\circ</math></b>	Energy <i>released</i> when one mole of the substance is completely burnt in oxygen under standard conditions.
<b>Standard enthalpy change of hydration <math>\Delta H_{\text{hyd}}^\circ</math></b>	Energy <u>released</u> when one mole of gaseous ions is hydrated under standard conditions.
<b>Standard enthalpy change of solution <math>\Delta H_{\text{sol}}^\circ</math></b>	Energy change when one mole of substance is completely dissolved in a solvent to form an infinitely dilute solution under standard conditions.
<b>Standard enthalpy change of neutralisation <math>\Delta H_n^\circ</math></b>	Energy <i>released</i> when one mole of water is formed from the neutralisation between acid and base under standard conditions.
<b>Standard enthalpy change of atomisation <math>\Delta H_{\text{atom}}^\circ</math></b>	Energy absorbed when one mole of gaseous atoms is formed from the element under standard conditions.
<b>Bond dissociation energy</b>	Energy required to break one mole of covalent bond in a specific molecule in the gaseous state to form gaseous atoms.
<b>Bond energy</b>	Average energy absorbed to break one mole of covalent bond in the gaseous state to form gaseous atoms under standard conditions.
<b>First ionisation energy</b>	Energy absorbed when one mole of gaseous atoms loses one mole of electrons to form one mole of singly charged gaseous cations.
<b>Second ionisation energy</b>	Energy absorbed when one mole of singly charged gaseous cations loses one mole of electrons to form one mole of doubly charged gaseous cations.
<b>First electron affinity</b>	Energy <i>released</i> when one mole of gaseous atoms acquires one mole of electrons to form one mole of singly charged gaseous anions.
<b>Second electron affinity</b>	Energy absorbed when one mole of singly charged gaseous anions acquires one mole of electrons to form one mole of doubly charged gaseous anions.
<b>Lattice energy</b>	Energy <i>released</i> when one mole of the solid ionic compound is formed from its constituent gaseous ions under standard conditions.

Short cuts: (use Hess' Law to derive)

$$\Delta H^\circ = \sum H_f^\circ (\text{products}) - \sum H_f^\circ (\text{reactants}) \quad (15)$$

$$\Delta H^\circ = \sum H_c^\circ (\text{reactants}) - \sum H_c^\circ (\text{products}) \quad (16)$$

$$\Delta H^\circ = \sum \text{BE (bonds broken)} - \sum \text{BE (bonds formed)} \quad (17)$$

$$\text{BE (A}_2) = 2\Delta H_{\text{atom}}^\circ (\text{A}_2) \quad (18)$$

$$\Delta H_{\text{sol}}^\circ = -\text{LE} + \sum \Delta H_{\text{hyd}}^\circ \quad (19)$$

Formulae:

$$\Delta H_{\text{hyd}}^\circ \propto \left| \frac{q^+}{r^+} \right| \quad (20)$$

$$\text{LE} \propto \left| \frac{q^+ \cdot q^-}{r^+ + r^-} \right| \quad (21)$$

Solubility of ionic salt:

- Soluble:  $\Delta H_{\text{soln}}^{\circ} < 0 \implies |\Delta H_{\text{hyd}}^{\circ}| > |\text{LE}|$

Hydration energy evolved is enough to compensate for lattice energy required to break down crystal lattice

- Insoluble:  $\Delta H_{\text{soln}}^{\circ} > 0 \implies |\Delta H_{\text{hyd}}^{\circ}| < \text{LE}$

Hydration energy evolved is not enough to compensate for lattice energy required to break down crystal lattice

**Remark.** Take note of the following when writing equations:

1. State symbols
2. Stoichiometric coefficients
3. Sign for  $\Delta H$

### §6.1.2 Calorimetry

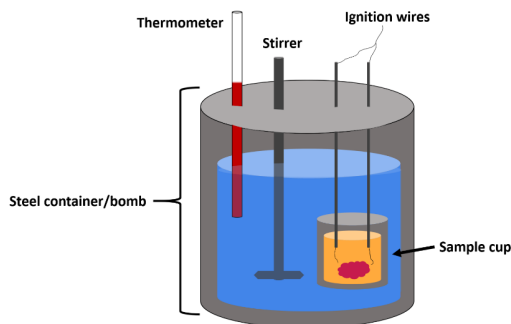
Heat change:

$$Q = mc\Delta T \quad (22)$$

$$\Delta H = \pm \frac{Q}{n} \quad (23)$$

where  $n$  is number of moles of limiting reagent / depends on type of  $\Delta H$ .

**Calorimeter:**



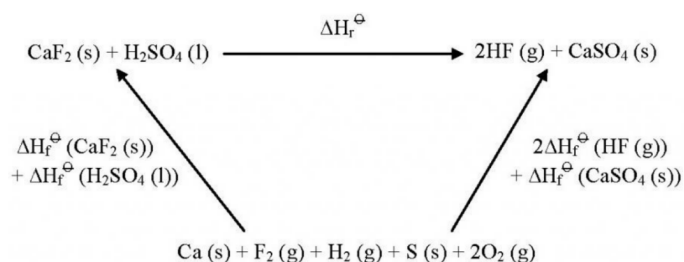
Water jacket ensures temperature of surrounding water is at the same temperature as those in the water jacket, to minimise heat loss.

### §6.1.3 Hess' Law

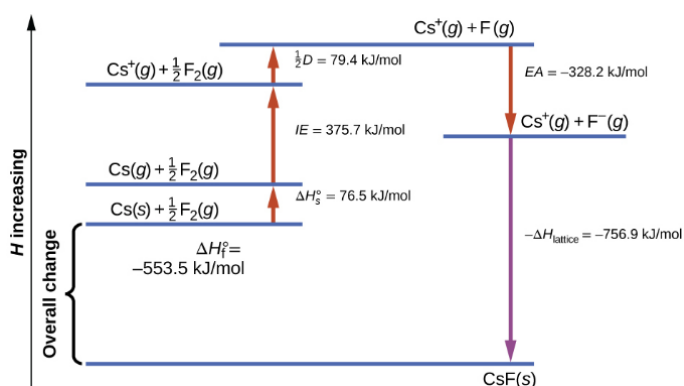
#### Definition 6.1 (Hess' Law)

Enthalpy change accompanying a chemical reaction is same regardless of route by which chemical change occurs, provided initial and final states are same.

**Energy cycle:**



**Energy level diagram:**



**Remark.** Refer to Data Booklet for bond energies, ionisation energies.

## §6.2 Thermodynamics

### §6.2.1 Entropy

#### Definition 6.2 (Entropy $S$ )

Degree of disorder or randomness in a system.

Factors affecting entropy change  $\Delta S$ :

- **Temperature**

At higher temperature, average kinetic energy of particles increases. More ways to distribute greater amount of energy among particles. Entropy increases.

- **Change of phase** (same species)

Particles move about more freely and with greater speeds. More ways to distribute particles and energy. Entropy increases,  $\Delta S > 0$ .

- **Number of gaseous particles**

More particles moving randomly. More ways to distribute particles and energy. Entropy increases,  $\Delta S > 0$ .

- **Mixing of particles**

When gases are mixed, each gas expands to occupy the whole container. More ways to distribute particles and energy in a larger volume. Entropy increases,  $\Delta S > 0$ .

### §6.2.2 Spontaneity

At standard conditions, **Gibbs free energy change**  $\Delta G$  is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (24)$$

**Remark.** Note that since the units of  $\Delta S$  is usually given in  $\text{J mol}^{-1} \text{K}^{-1}$ , so it has to be converted to  $\text{kJ mol}^{-1} \text{K}^{-1}$  for calculations of  $\Delta G$ .

Spontaneity of a reaction:

- $\Delta G < 0$ : reaction is spontaneous
- $\Delta G > 0$ : reaction is non-spontaneous
- $\Delta G = 0$ : reaction is at equilibrium (reversible reaction or phase change)

To determine the change in spontaneity of reaction with temperature, use the **signs** of  $\Delta H$  and  $-T\Delta S$  to determine change in  $\Delta G$ .<sup>2</sup>

$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G$	Spontaneity
-	+	-	always negative	Spontaneous at ALL temperatures
+	-	+	always positive	Non-spontaneous at ALL temperatures
+	+	-	negative if $ T\Delta S  >  \Delta H $	Spontaneous at HIGH temperatures
-	-	+	negative if $ \Delta H  >  T\Delta S $	Spontaneous at LOW temperatures

Limitations in the use of  $\Delta G^\circ$  to predict spontaneity:

- Kinetic feasibility

Some reactions are energetically feasible (also known as thermodynamically feasible) since  $\Delta G$  is negative, but kinetically not feasible since it occurs very slowly due to high activation energy. Such reactions are spontaneous but very slow.

- Non-standard conditions

$\Delta G^\circ$  can only be used to predict the spontaneity of a reaction under standard conditions. Under non-standard conditions,  $\Delta G$  must be calculated.

<sup>2</sup>sketch out graph of  $\Delta G$  against  $T$  to visualise better.

## §7 Kinetics

Term	Definition
<b>Rate of reaction</b>	Rate of change in concentration of reactant or product.
<b>Rate equation</b>	Mathematical equation that relates rate of reaction to concentration of reactants raised to appropriate powers.
<b>Order of reaction</b>	Power to which concentration of reactant is raised to in the rate equation (determined experimentally).
<b>Rate constant</b>	Constant of proportionality in the rate equation.
<b>Half-life</b>	Time taken for concentration of reactant to decrease to half of its original value.
<b>Rate-determining step</b>	Slowest step in the sequence of steps leading to formation of product.
<b>Activation energy</b>	Minimum amount of energy that reactant particles must possess for effective collisions to result in chemical reaction.
<b>Catalyst</b>	Substance that increases rate of reaction by providing alternative pathway with lower activation energy, while remaining chemically unchanged.

### Rate of reaction:

$$\text{rate of reaction} = \frac{d[\text{product}]}{dt} = -\frac{d[\text{reactant}]}{dt} \quad (25)$$

### §7.1 Theories

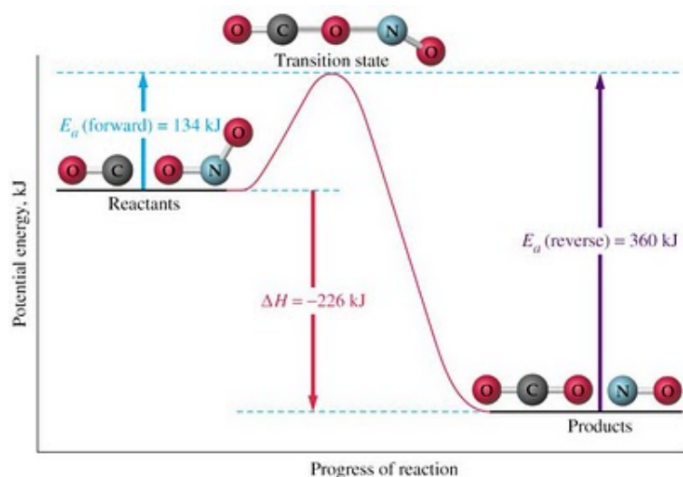
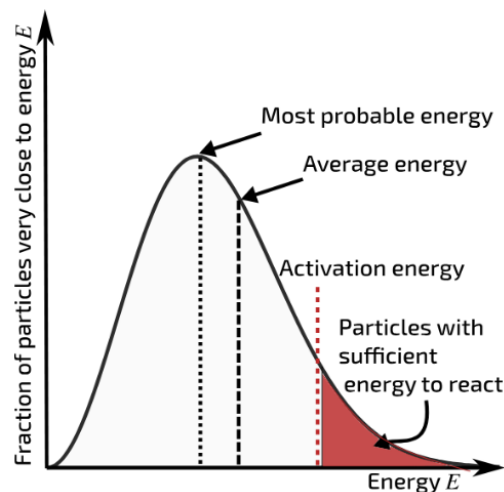
**Collision Theory:** chemical reactions occur only if reactant particles undergo **effective collisions**, where reactant particles collide

1. with energy greater than or equal to activation energy
2. in correct orientation

**Transition state theory:** when reactant molecules collide, **transition state** is formed where old bonds *partially* broken + new bonds *partially* formed.

Transition state has maximum energy in reaction pathway (peak of curve), very unstable, so cannot be isolated as a compound.

**Maxwell-Boltzmann distribution curve:** represents amount of energy possessed by a particular fraction of particles.



## §7.2 Rate of reaction

Factors affecting rate of reaction:

- **Temperature**

Average kinetic energy of reactant particles increases.  
Number of reactant particles with energy  $\geq E_a$  increases ...

Distribution curve: displaced towards the right, peak is lowered

- **Catalyst**

Lower activation energy by providing alternative reaction pathway. Number of reactant particles with energy  $\geq E_a$  increases ...

Distribution curve:  $E'_a$  (catalysed) is to the left of  $E_a$  (uncatalysed)

- **Concentration of reactant**

Number of reactant particles per unit volume increases ...

- **Physical state of reactant**

Larger surface area over which solid comes into contact with liquid / gaseous reactants ...

- **Light**

Upon absorbing light energy, average kinetic energy of reactant particles increases. Number of reactant particles with energy  $\geq E_a$  increases ...

... Frequency of effective collisions increases. Since rate of reaction is proportional to frequency of effective collisions, rate of reaction increases.

### §7.2.1 Order of reaction

**Rate equation:**

$$\text{rate} = k[A]^m[B]^n \quad (26)$$

**Remark.**  $m+n$  is the overall order of reaction. Overall order of 3 and above is rare as probability of many reactant particles colliding together to form products is low.

**Remark.** Rate constant can be determined by **Arrhenius equation:**

$$k = Ae^{-\frac{E_a}{RT}} \quad (27)$$

Hence rate constant is only affected by temperature and activation energy.

Half life and rate constant are related by

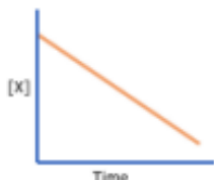
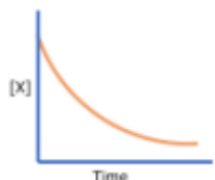
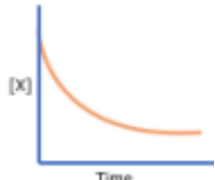
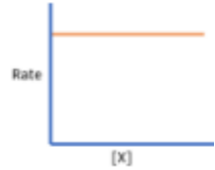
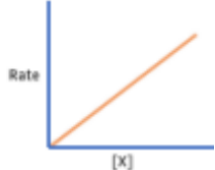
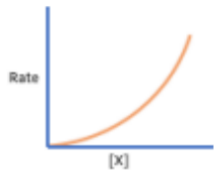
$$t_{1/2} = \frac{\ln 2}{k}. \quad (28)$$

A useful formula is, for reactant X,

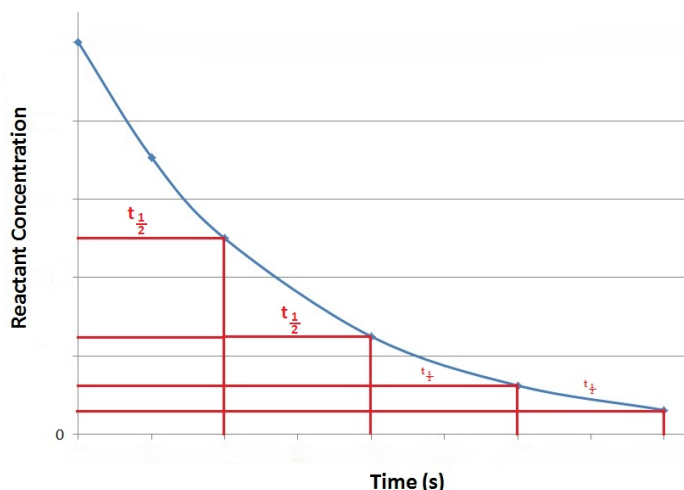
$$[X] = [X]_0 \left(\frac{1}{2}\right)^n. \quad (29)$$

where  $n = \frac{t}{t_{1/2}}$  is number of half-lives.

Order of reaction:

	Zero-order reaction	First-order reaction	Second-order reaction
Rate equation	$\text{rate} = k$	$\text{rate} = k[A]$	$\text{rate} = k[A]^2$
Unit of $k$	$\text{mol dm}^{-3} \text{s}^{-1}$	$\text{s}^{-1}$	$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
Half life	decreases with time	constant	increases with time
Conc-time graph			
Rate-conc graph			

Determine graphically half life for 1st order reaction:



**Pseudo first order reaction:**

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

If B is in large excess or catalyst, [B] is effectively constant, so

$$\text{rate} = k[A][B] = k'[A], \quad \text{where } k' = k[B]$$

thus reaction is pseudo 1st order wrt A. Hence  $t_{1/2} = \frac{\ln 2}{k'}$   
 $\frac{\ln 2}{k[B]}$  so change in [B] will affect half life.

## §7.2.2 Experimental techniques

### Sampling and titration

- Sampling: withdraw samples from reaction mixture at regular time intervals  
 Quenching: add large volume of ice cold water to reaction sample (slow down rate of reaction by lowering temp and conc)  
 Titration: titrate reaction sample against reagent of known concentration to determine concentration of unreacted reactant
- Example:  $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$   
 $[\text{I}_2] \text{ remaining} \propto V_{\text{S}_2\text{O}_3^{2-}}$ . Plot  $V_{\text{S}_2\text{O}_3^{2-}}$  against  $t$ , obtain straight line graph, hence zero order wrt  $\text{I}_2$  (since gradient represents rate, rate is constant when  $[\text{I}_2]$  changes)

### Clock experiment

- Prominent visual changes (formation of solid) when a fixed amount of product is formed
- Example:  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{SO}_2(\text{g}) + \text{S}(\text{s}) + \text{H}_2\text{O}(\text{l})$   
 Record time taken for sufficient sulfur to be produced such that "X" mark can no longer be seen through reaction mixture

Determine orders of reaction from experiment → compare one, keep others constant

- Direct comparison:

Comparing Experiments 1 and 2, when  $[\text{CH}_3\text{COCH}_3]$  and  $[\text{I}_2]$  are kept constant, when  $[\text{H}^+]$  doubles, rate doubles. Hence, reaction is first order wrt  $\text{H}^+$ .

- Mathematical method:

Let rate equation be  $\text{rate} = k[\text{H}^+]^x[\text{CH}_3\text{COCH}_3]^y[\text{I}_2]^z$ .

Comparing Experiments 1 and 2,

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k(1.0)^x(0.8)^y(0.05)^z}{k(0.5)^x(0.8)^y(0.05)^z} \implies x = 1.$$

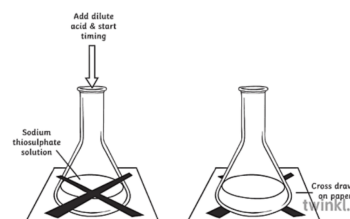
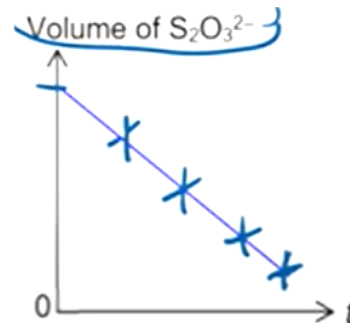
Hence order of reaction wrt  $\text{H}^+ = 1$ .

- Graphical data:

Graph given is [A] against  $t$ , 2 lines with varying initial [B]

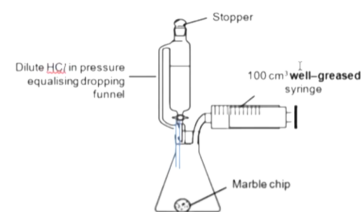
Wrt A: use one of the graphs, find half life. Constant half life → 1st order

Wrt B: draw tangent at  $t = 0$  for both graphs, compare gradients



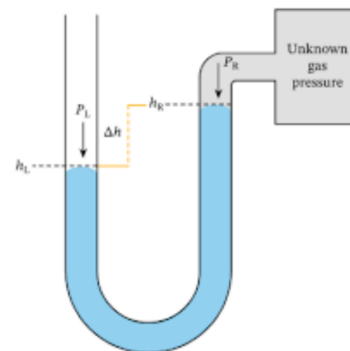
### Change in gas volume

- Gas produced from reaction b/w solids and liquids
- Gas syringe (well-lubricated): collect gas, measure volume of gas at regular time intervals
- Plot volume of gas against time
- Example:  $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \longrightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$



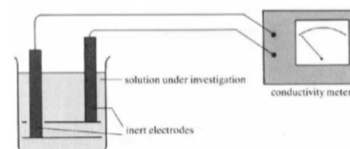
### Change in gas pressure

- Number of moles of gaseous reactants differs from that of gaseous products
- Manometer: measure gas pressure
- Example:  $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$



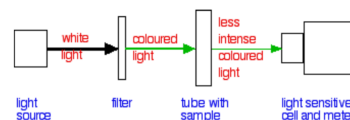
### Change in electrical conductivity

- Change in number of ions in mixture
- Conductivity meter: measure electrical conductivity
- Example:  $\text{H}_2\text{O}_2(\text{aq}) + 2\text{I}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{I}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$   
As  $\text{H}^+$  and  $\text{I}^-$  are consumed, electrical conductivity of mixture decreases.



### Change in colour intensity (colorimetry)

- Colorimeter: measure amount of light absorbed as it passes through solution, recorded as absorbance of solution
- Plot curve of absorbance against concentration
- Example:  $\text{CH}_3\text{COCH}_3 + \text{I}_2 \longrightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{H}^+ + \text{I}^-$   
Brown solution fades through orange to yellow to colourless as iodine is consumed.



## §7.3 Reaction mechanism

A reaction consist of **one slow step** and **many fast steps**.

Slow step has high activation energy (e.g. strong bonds to break), is rate-determining step

Rate equation for overall equation is obtained from stoichiometry of rate-determining step (stoichiometric coefficient of reactant = order of reaction wrt reactant)

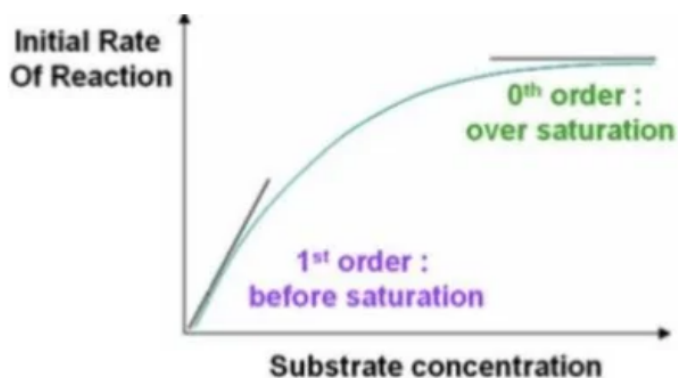
**Remark.** If slow step contains intermediates, look at fast step for reactants.



## §7.4 Catalysis

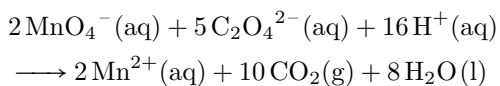
Homogeneous catalyst	Heterogeneous catalyst	Enzyme
<p>Acts in <u>same phase</u> as reactants</p> <p>Able to exist in various oxidation states</p> <p>Provides alternative pathway with lower activation energy by first forming an intermediate which is later consumed</p>	<p>Acts in <u>different phase</u> from reactants</p> <p>Transition metal has vacant / partially filled low-lying, energetically accessible 3d orbitals</p> <p>Provides alternative pathway with lower activation energy through adsorption</p> <ol style="list-style-type: none"><li>1. <b>Adsorption:</b> reactant molecules diffuse towards catalyst surface, adsorb on active sites</li><li>2. <b>Reaction:</b> weaken covalent bonds within reactant molecules, lower activation energy + increase surface concentration of reactant molecules on catalyst surface</li><li>3. <b>Desorption:</b> product molecule desorb, diffuse away, free up active site for adsorption with new reactant molecules</li></ol>	<p>Biological catalysts that speed up rate of reaction in living systems while remaining chemically unchanged at the end of reaction</p> <p>Provide alternative pathway with lower activation energy through formation of enzyme-substrate complex</p> <ol style="list-style-type: none"><li>1. Substrate arrives at active site of enzyme</li><li>2. Substrate fits into active site (correct orientation), rearrangement of molecules occurs to form products</li><li>3. Products leave active site, active site free to receive new substrate molecules</li></ol>
<ul style="list-style-type: none"><li>• <math>\text{Fe}^{2+}</math> catalyses <math>\text{I}^-/\text{S}_2\text{O}_8^{2-}</math> reaction</li></ul> $2\text{I}^-(\text{aq}) + \text{S}_2\text{O}_8^{2-}(\text{aq}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$ <p>High <math>E_a</math> as energy required to overcome electrostatic forces of repulsion between anions.</p> <p>Intermediate <math>\text{Fe}^{3+}</math> ions are formed</p> $2\text{Fe}^{2+}(\text{aq}) + \text{S}_2\text{O}_8^{2-}(\text{aq}) \longrightarrow 2\text{Fe}^{3+}(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq})$ $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \longrightarrow \text{I}_2(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$ <ul style="list-style-type: none"><li>• Nitrogen oxides catalyses oxidation of sulfur dioxide in atmosphere</li></ul> $\text{NO}_2(\text{g}) + \text{SO}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g}) + \text{NO}(\text{g})$ $\text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{NO}_2(\text{g})$	<ul style="list-style-type: none"><li>• Haber process</li></ul> $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightleftharpoons{\text{Fe}} 2\text{NH}_3(\text{g})$ <ul style="list-style-type: none"><li>• Catalytic removal of nitrogen oxides in car exhaust gases</li></ul> $2\text{NO}(\text{g}) + 2\text{CO}(\text{g}) \xrightarrow{\text{Rh}} 2\text{CO}_2(\text{g}) + \text{N}_2(\text{g})$ $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{\text{Pd/Rt}} 2\text{CO}_2(\text{g})$ $\text{C}_x\text{H}_y + \left(x + \frac{y}{4}\right)\text{O}_2(\text{g}) \xrightarrow{\text{Pd/Rt}} x\text{CO}_2(\text{g}) + \frac{y}{2}\text{H}_2\text{O}(\text{g})$	

Enzyme graph:



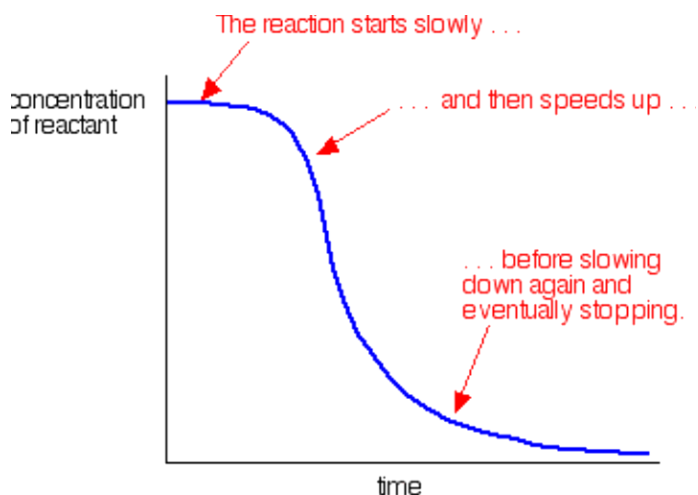
- Low [substrate]: active sites not fully filled, enzyme not saturated, more enzyme-substrate complex can be formed by increasing [substrate] → rate directly proportional to [substrate] → reaction is first order wrt [substrate]
- High [substrate]: active sites fully filled, increase in substrate conc has no effect on rate → reaction is zero order wrt [substrate]

**Autocatalysis:** product catalyses reaction



The product  $\text{Mn}^{2+}$  is an autocatalyst

- Start: no  $\text{Mn}^{2+}$  produced yet → low rate
- Progress:  $\text{Mn}^{2+}$  formed → rate increase
- End: concentration of reactants decrease → rate decrease



## §8 Chemical Equilibria

### §8.1 Dynamic equilibrium

#### Definition 8.1 (Dynamic equilibrium)

State of reversible process at which rates of forward and backward reactions are equal, but not equal to zero.

No net change in concentrations of reactants and products.

### §8.2 Equilibrium law, equilibrium constants

For reaction  $aA + bB \rightleftharpoons cC + dD$ , **equilibrium constant** in concentrations is

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (30)$$

where all concentrations are at equilibrium.

In pressures, equilibrium constant is

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \quad (31)$$

where all partial pressures are at equilibrium. Use Dalton's law  $p_A = \frac{n_A}{n_T} p_T$  to find partial pressure.

Note that

$$K_c = \frac{k_f}{k_b}. \quad (32)$$

What to include and what not to include:

- $\text{Ag}^+(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightleftharpoons \text{Fe}^{3+}(\text{aq}) + \text{Ag}(\text{s})$ :  $[\text{Ag}]$  is not included in  $K_c$  expression since concentration of solid (density) is constant.

$$K_c = \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^+]}$$

- $\text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq})$ : water is a solvent and thus in excess, its concentration is approximately constant, so  $[\text{H}_2\text{O}]$  is not included in  $K_c$  expression.

$$K_c = \frac{[\text{F}^-][\text{H}_3\text{O}^+]}{[\text{HF}]}$$

- $\text{CH}_3\text{COOH}(\text{l}) + \text{CH}_3\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOCH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$ :  $[\text{H}_2\text{O}]$  is included in  $K_c$  expression since it is not a solvent; it is treated as a product.

$$K_c = \frac{[\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{OH}]}$$

**Remark.**  $K_c$  and  $K_p$  are constants for a given temperature, and only affected by temperature.

Degree of dissociation of A

$$\alpha = \frac{n_{A,\text{dissociated}}}{n_{A,\text{initial}}} \quad (33)$$

Position of equilibrium is related to  $K_c$ :

- $K_c > 1$ : More products at equilibrium, reaction proceeds in forward direction to larger extent, POE lies to the right.
- $K_c < 1$ : More reactants at equilibrium, reaction proceeds in backward direction to larger extent, POE lies to the left.

Use **ICE table** to do calculations:

	A	B	C	D
Initial moles / mol				
Change in moles / mol				
Equilibrium moles / mol				

**Remark.** Note when to use moles, concentration, or partial pressure; use moles when total pressure is not constant.

Gibbs free energy change

- $\Delta G < 0$ : Forward reaction is spontaneous,  $K > 1$ , POE lies to right
- $\Delta G = 0$ : Equilibrium,  $K = 1$
- $\Delta G > 0$ : Backward reaction is spontaneous,  $K < 1$ , POE lies to left

## §8.3 Le Chatelier's Principle

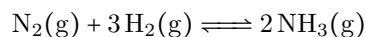
### Definition 8.2 (Le Chatelier's Principle)

If system at dynamic equilibrium is subjected to change which disturbs equilibrium, system responds in such a way so as to counteract the effect of change to re-establish equilibrium.

Change	By LCP	[reactants]	[products]	$K_C$ or $K_p$
Add reactant	[reactant] increase. By LCP, POE shift right to reduce [reactant] partially.	decrease, except for added reactant	increase	constant
Add product	[product] increase. By LCP, POE shift left to reduce [product] partially.	increase	decrease, except for added product	constant
Increase pressure (decrease container volume)	$p_T$ and partial pressures increase. By LCP, POE shift to favour reaction that forms fewer moles of gaseous molecules to reduce pressure	depends	depends	constant
Add inert gas at constant pressure	$p_T$ increase, partial pressures unchanged. No change in eqm hence POE does not shift	no change	no change	constant
Increase temperature	By LCP, POE shift to favour endothermic reaction to absorb excess heat to decrease temperature partially	depends	depends	change
Decrease temperature	By LCP, POE shift to favour exothermic reaction to release heat to increase temperature partially	depends	depends	change
Add catalyst	Increase rates of forward and backward reactions to same extent. POE does not shift.	no change	no change	constant

Change in concentration Change in pressure Change in temperature Addition of catalyst  
graph: sharp increase / gradual increase in conc

## §8.4 Haber process



	Temperature	Pressure
Expectation	Reaction is favoured by low temperature	Reaction is favoured by high pressure
Reality	High temperature used for higher rate of reaction, economical production	Low pressure used, as high cost of maintaining equipment for high pressure

## §9 Chemistry of Aqueous Solutions

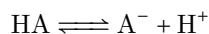
### §9.1 Theories of Acids and Bases

Theory	Acid	Base
Arrhenius	hydrogen-containing substance, ionises and releases $\text{H}^+$ ions in aq solution	hydroxide-containing substance, ionises and releases $\text{OH}^-$ ions in aq solution
Brønsted–Lowry	proton donor	proton acceptor
Lewis	electron pair acceptor (electrophile)	electron pair donor (nucleophile)

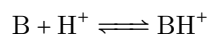
#### §9.1.1 Conjugate acid-base pair

**Conjugate acid-base pair:** a pair of compounds or ions which *differ by one proton*

- When acid HA donates proton to base, conjugate base  $\text{A}^-$  is formed.



- When base B receives proton from acid, conjugate acid  $\text{BH}^+$  is formed.



Conjugate acid-base pairs: HA and  $\text{A}^-$ , B and  $\text{BH}^+$

#### §9.1.2 Lewis acids

Types of species which can act as Lewis acids

- Electron-deficient molecules  
Less than an octet of electrons around one atom. Dative bond formed in adduct<sup>3</sup>.
- Molecules with central atom that can expand octet  
Low-lying vacant orbitals to accept lone pairs of electrons.
- Molecules with multiple bonds that has atom with partial positive charge  
Lewis base donates lone pair of electrons to form bond with central atom, one pair of electrons displaced from multiple bond to become lone pair on terminal atom.
- Metal cations  
Accept lone pair of electrons via dative bond to form complex ions.

<sup>3</sup>compound that contains a dative bond between the Lewis acid and the Lewis base

## §9.2 Acid–Base Equilibria

### §9.2.1 Strength of acids and bases

**Strength** is a measure of extent of dissociation to give ions in solution. (independent of concentration)

	Strong	Weak
Definition	Complete dissociation in aq solution	Partial dissociation in aq solution
Extent of dissociation	100% For acid, $[\text{H}^+] = [\text{acid}]$ For base, $[\text{OH}^-] = [\text{base}]$	$\ll 100\%$ For acid, $[\text{H}^+] < [\text{acid}]$ For base, $[\text{OH}^-] < [\text{base}]$
Arrow	$\longrightarrow$	$\rightleftharpoons$
Equilibrium constant	–	$K_a, K_b$

$$\text{Acidity / basicity of solutions} \quad pK_b = -\lg K_b \quad (40)$$

- **acidic:**  $[\text{H}^+] > [\text{OH}^-]$
- **basic:**  $[\text{H}^+] < [\text{OH}^-]$
- **neutral:**  $[\text{H}^+] = [\text{OH}^-]$

For a monoacidic weak base,  $\text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{BH}^+(\text{aq}) + \text{OH}^-(\text{aq})$

$$[\text{OH}^-] = \sqrt{K_b \times [\text{B}]_{\text{initial}}} \quad (41)$$

**Power of hydrogen:**

$$\text{pH} = -\lg[\text{H}^+] \quad (34)$$

since B is weak base with small  $K_b$ , assume extent of dissociation of B is negligible, so  $[\text{OH}^-]$  is so small such that  $[\text{B}] = [\text{B}]_{\text{initial}}$ .

**Power of hydroxide:**

$$\text{pOH} = -\lg[\text{OH}^-] \quad (35)$$

**Remark.** This formula CANNOT be used to calculate  $K_b$  or  $[\text{B}]_{\text{initial}}$ ! Instead use ICE table.

For a strong acid,  $\text{H}_n\text{A}(\text{aq}) \longrightarrow n\text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$

$$[\text{H}^+] = n \times [\text{H}_n\text{A}]$$

For a strong base,  $\text{M}(\text{OH})_n(\text{aq}) \longrightarrow \text{M}^{n+}(\text{aq}) + n\text{OH}^-(\text{aq})$

$$[\text{OH}^-] = n \times [\text{M}(\text{OH})_n]$$

### §9.2.2 Ionic product of water

Self-ionisation of water:  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

**Ionic product of water:**

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 298 \text{ K} \quad (42)$$

**Acid dissociation constant:**

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (36)$$

In pure water,

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol dm}^{-3}$$

$$pK_a = -\lg K_a \quad (37)$$

Taking -log on both sides,

For a monobasic weak acid,  $\text{HA}(\text{aq}) \rightleftharpoons \text{A}^-(\text{aq}) + \text{H}^+(\text{aq})$

$$\text{pH} + \text{pOH} = pK_w = 14 \text{ at } 298 \text{ K}. \quad (43)$$

$$[\text{H}^+] = \sqrt{K_a \times [\text{HA}]_{\text{initial}}} \quad (38)$$

since HA is weak acid with small  $K_a$ , assume extent of dissociation of HA is negligible, so  $[\text{H}^+]$  is so small such that  $[\text{HA}] \approx [\text{HA}]_{\text{initial}}$ .

For a conjugate acid-base pair:

$$K_w = K_a K_b. \quad (44)$$

**Remark.** This formula CANNOT be used to calculate  $K_a$  or  $[\text{HA}]_{\text{initial}}$ ! Instead use ICE table.

Taking -log on both sides,

$$pK_a + pK_b = pK_w = 14 \text{ (298 K)}. \quad (45)$$

**Base dissociation constant:**

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \quad (39)$$

This suggests a reciprocal strength relationship: the stronger the acid, the weaker its conjugate base (and vice versa).

### §9.2.3 Salt solutions

Salts undergo hydration to form solutions. Then cations / anions undergo hydrolysis to form acidic / alkaline solutions.

**Acidic salt solution:** conjugate acid of WB hydrolyses partially in water to give  $\text{H}_3\text{O}^+$

$$[\text{H}^+] = \sqrt{K_a \times [\text{HA}]_{\text{initial}}} \quad (46)$$

**Alkaline salt solution:** conjugate base of WA hydrolyses partially in water to give  $\text{OH}^-$

$$[\text{OH}^-] = \sqrt{K_b \times [\text{B}]_{\text{initial}}} \quad (47)$$

**Remark.** When solutions are mixed, remember to calculate the new concentrations.

### §9.2.4 Buffer solutions

#### Definition 9.1 (Buffer solution)

Solution capable of maintaining a fairly constant pH (by resisting pH change) when small amounts of acid or base are added to it.

**Acidic buffer solution:** weak acid + salt of conjugate base ( $\text{HA}$  and  $\text{A}^-$ )

$$\text{pH} = \text{p}K_a + \lg \frac{[\text{A}^-]}{[\text{HA}]} \quad (48)$$

- Large reservoir of  $\text{HA}$  and  $\text{A}^-$  present is able to cope with small amount of  $\text{H}^+$  and  $\text{OH}^-$  added.
- On addition of acid:  $\text{A}^-(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow \text{HA}(\text{aq})$   
On addition of base:  $\text{HA}(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{A}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- Maximum buffer capacity:  $[\text{HA}] = [\text{A}^-] \implies \text{pH} = \text{p}K_a$

**Basic buffer solution:** weak base + salt of conjugate acid ( $\text{B}$  and  $\text{BH}^+$ )

$$\text{pOH} = \text{p}K_b + \lg \frac{[\text{BH}^+]}{[\text{B}]} \quad (49)$$

- Large reservoir of  $\text{B}$  and  $\text{BH}^+$  present is able to cope with small amount of  $\text{H}^+$  and  $\text{OH}^-$  added.
- On addition of acid:  $\text{B}(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow \text{BH}^+(\text{aq})$   
On addition of base:  $\text{BH}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

- Maximum buffer capacity:  $[\text{B}] = [\text{BH}^+] \implies \text{pOH} = \text{p}K_b$

**$\text{H}_2\text{CO}_3/\text{HCO}_3^-$  buffer pair** used to control pH of blood:



- On addition of acid:  $\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow \text{H}_2\text{CO}_3(\text{aq})$
- On addition of base:  $\text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$

### §9.2.5 Acid-base titration

Titrate titrant against analyte / Analyte titrated against titrant

**Equivalence point:** stoichiometric amounts of acid & base react together

**End-point:** when indicator first changes colour permanently

Indicator	Acidic	Basic	pH range
<b>methyl orange</b>	red	yellow	3.1 – 4.4
<b>phenolphthallein</b>	colourless	pink	8.3 – 10.0

Choice of pH indicator is **appropriate** if its pH transition range lies within range of rapid pH change over equivalence point (pH at equivalence point is close to  $\text{p}K_a$  of indicator).

pH graph sketching

1. initial, equivalence, final pH
2. initial, equivalence, final volume
3. pH, volume at MBC

Types of titration

- strong acid–strong base
- strong acid–weak base
- weak acid–strong base
- weak acid–weak base

pH change is gradual, no sharp increase/decrease in pH at equivalence point, so no suitable indicator.

## §9.3 Solubility Equilibria

Term	Definition
<b>Solubility</b>	<i>Maximum</i> mass / amount of solute that can be dissolved per $\text{dm}^3$ of solvent to produce a <i>saturated solution</i> at a given temperature.
<b>Solubility product</b> $K_{sp}$	<i>Equilibrium constant</i> which is the product of molar concentrations of dissolved / dissociated ions (each raised to its appropriate power) in a <i>saturated solution</i> of salt at a given temperature.
<b>Ionic product</b> $IP$	Product of molar concentrations of constituent ions in solution <i>at that instant</i> (each raised to its appropriate power) at a given temperature.

For a sparingly soluble salt  $MX$ ,  $MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$ . **Solubility product:**

$$K_{sp} = [M^+]_{\text{satn}}[X^-]_{\text{satn}} \quad (50)$$

**Example.**

$$K_{sp}(\text{Ca}_3(\text{PO}_4)_2) = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

Factors affecting solubility of salt

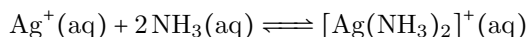
- **Common ion effect** (addition of cation/anion)

Saturated sparingly soluble salt solution  $MX$  added to soluble salt solution  $\text{NaX}(aq)$  (containing common ion  $X^-$ ).

$[X^-]$  increases. By LCP, POE shift left to decrease  $[X^-]$ , so dissociation of  $MX$  suppressed, solubility decreases.

$IP$  increase above  $K_{sp}$ , so  $MX$  precipitated.

- **Formation of complex ions** (removal of cation)



$[\text{Ag}^+]$  decreases. By LCP, POE shift right to increase  $[\text{Ag}^+]$ , so dissociation of salt favoured, solubility increases.

$[\text{Ag}^+]$  decreases,  $IP$  fall below  $K_{sp}$ , so salt dissolves.

- **pH of solution** (removal of anion)

$\text{H}^+$  added to saturated sparingly soluble salt solution  $\text{MOH}$ .

$[\text{OH}^-]$  decreases. By LCP, POE shift right to increase  $[\text{OH}^-]$ . Hence solubility increases.

**Ionic product:**

$$IP = [M^+][X^-] \quad (51)$$

Condition for precipitation:

Condition	Saturation	Precipitation
$IP < K_{sp}$	Below saturation point	No
$IP = K_{sp}$	At saturation point	No
$IP > K_{sp}$	Beyond saturation point	Yes

### Exercise 2

Given that  $K_{sp}$  of  $\text{CaSO}_4$  is  $2.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$  at  $25^\circ\text{C}$ , predict if  $\text{CaSO}_4$  precipitate will be formed when  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$   $\text{Ca}(\text{NO}_3)_2$  solution and  $3.0 \times 10^{-2} \text{ mol dm}^{-3}$   $\text{Na}_2\text{SO}_4$  solution are mixed in equal volumes.

**Remark.** Concentration will change after mixing solutions.

*Solution.*

$$\begin{aligned} IP &= [\text{Ca}^{2+}][\text{SO}_4^{2-}] = \frac{2.0 \times 10^{-2}}{2} \frac{3.0 \times 10^{-2}}{2} \\ &= 1.50 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

Since  $IP > K_{sp}$ ,  $\text{CaSO}_4$  precipitate will be formed.  $\square$

### Exercise 3

A solution contains  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$   $\text{AgNO}_3$  and  $1.5 \times 10^{-3} \text{ mol dm}^{-3}$   $\text{Pb}(\text{NO}_3)_2$ . If solid sodium iodide is added, show that  $\text{AgI}$  precipitates before  $\text{PbI}_2$  precipitates out.

Given  $K_{sp}$  of  $\text{AgI}$  is  $8.3 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$ ,  $K_{sp}$  of  $\text{PbI}_2$  is  $7.1 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$ .

*Solution.* To precipitate out  $\text{AgI}$ ,  $IP > K_{sp} \implies [\text{I}^-] > 4.15 \times 10^{-13} \text{ mol dm}^{-3}$ .

To precipitate out  $\text{PbI}_2$ ,  $IP > K_{sp} \implies [\text{I}^-] > 2.176 \times 10^{-3} \text{ mol dm}^{-3}$ .

Since the minimum  $[\text{I}^-]$  required to precipitate out  $\text{AgI}$  is less than that to precipitate out  $\text{PbI}_2$ ,  $\text{AgI}$  will precipitate out first.  $\square$



## §10 Electrochemistry

**Electrochemical cell:** convert chemical from spontaneous redox reaction to electrical energy

**Electrolytic cell:** use electrical energy from external power source to drive non-spontaneous redox reaction

When recharging an electrochemical cell, it becomes electrolytic cell, reaction goes in backward direction (electricity drives non-spontaneous reaction).

### §10.1 Electrochemical cells

Electrodes (mnemonic: **CROAK**)

- Anode: oxidation half-cell [negative charge (electrons generated during oxidation)]
- Cathode: reduction half-cell [positive charge (electrons consumed during reduction)]

Electrons flow from anode to cathode in external circuit (wire)

Functions of **salt bridge**:

1. Complete the circuit

Electrons move from anode to cathode through wire

Anions in salt bridge move into anode compartment, cations in salt bridge move into cathode compartment

2. Maintain electrical neutrality in each half-cell

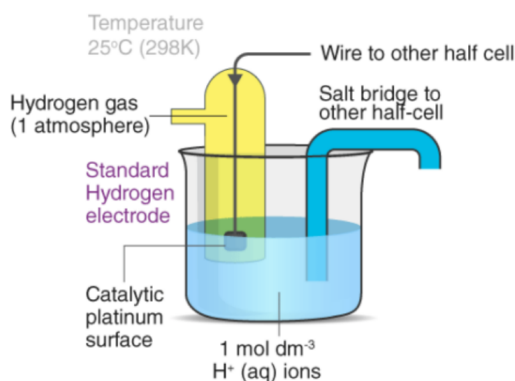
Excess of cations/anions in anode/cathode, so ions move from salt bridge into anode/cathode compartment

**Remark.** Sometimes, a porous membrane may be used in place of salt bridge.

#### §10.1.1 Electrode potentials

**Standard hydrogen electrode (SHE):** assigned  $E^\ominus = 0$  V

- Platinised Pt electrode
- $1 \text{ mol dm}^{-3}$  of  $\text{H}^+$
- $\text{H}_2(\text{g})$  at 1 bar, 298 K



#### Definition 10.1 (Standard electrode potential $E^\ominus$ )

Potential of half-cell relative to that of SHE, measured at standard conditions.

#### Definition 10.2 (Standard cell potential $E^\ominus_{\text{cell}}$ )

Maximum potential difference between two half-cells under standard conditions.

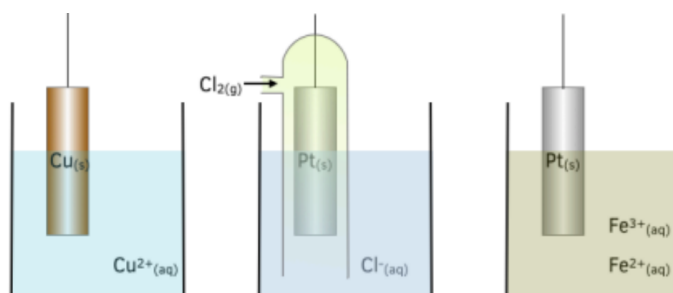
$E^\ominus$  measures tendency of reduction

- $E^\ominus$  more positive, higher tendency to undergo reduction (itself), stronger **oxidising agent**
- $E^\ominus$  more negative, higher tendency to undergo oxidation (itself), stronger **reducing agent**

Methods used to measure the standard electrode potentials of:

- metal-ion half cell
- gas-ion half cell
- ion-ion half cell

If no reactive metal electrode, use Pt as inert electrode.



#### §10.1.2 Spontaneity

Gibb's free energy:

$$\Delta G^\ominus_{\text{cell}} = -nFE^\ominus_{\text{cell}} \quad (52)$$

where  $n$  is number of moles of electrons transferred (take LCM of electrons in two half-equations),  $F = 96500 \text{ C mol}^{-1}$  is Faraday constant (charge of 1 mol of electrons)

**Remark.** Remember to convert units of  $\Delta G^\ominus_{\text{cell}}$  from  $\text{J mol}^{-1}$  to  $\text{kJ mol}^{-1}$ .

**Remark.**  $\Delta G_{\text{cell}}^{\circ}$  can be used for all chemical reactions;  $E_{\text{cell}}^{\circ}$  is only used for redox reactions.

Spontaneity	$\Delta G_{\text{cell}}^{\circ}$	$E_{\text{cell}}^{\circ}$
spontaneous	$< 0$	$> 0$
non-spontaneous	$> 0$	$< 0$
at equilibrium	0	0

### Given reactants, predict spontaneity

1. Write down ALL half-equations involving given reactants
2. Identify possible pair(s) of oxidation and reduction half-equations (the two reactants should be on opposite sides of half-equation so that one acts as reducing agent, one acts as oxidising agent)
3. Calculate  $E_{\text{cell}}^{\circ}$ , determine spontaneity

### §10.1.3 Limitations

Limitation of using  $E_{\text{cell}}^{\circ}$  to predict spontaneity of reaction

- Non-standard conditions: (use LCP to explain)
  1. concentration
  2. temperature
  3. pressure

Write equations in reversible arrows.

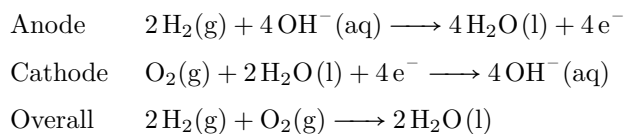
When  $[\text{H}^+]$  increase, by LCP, POE shifts right to partially decrease  $[\text{H}^+]$ , favouring reduction.  $E_{\text{red}}$  more positive,  $E_{\text{cell}}$  more positive.

- thermodynamically feasible but kinetically unfavourable ( $E_a$  is too high, reaction rate is too slow)
- side reactions may occur (in the half-cell)

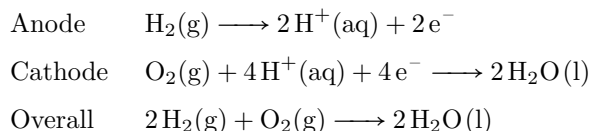
### §10.1.4 Battery and fuel cells

#### Hydrogen fuel cell

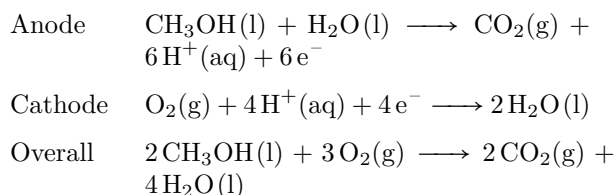
Alkaline electrolyte: hot KOH(aq)



Acidic electrolyte: hot HCl(aq)



#### Methanol fuel cell (acidic medium)

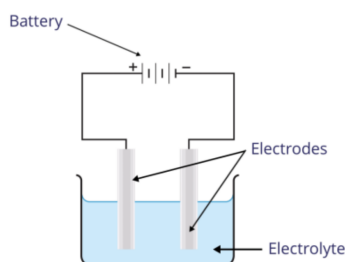


Considerations in development of batteries and fuel cells

- smaller size, lower mass for portability
- higher voltage for larger power supply
- lower cost
- longer shelf life

## §10.2 Electrolytic cells

### §10.2.1 Predict products



Steps

1. Identify species in electrolyte, reactive electrode
2. Migration of species to electrode
3. Compare  $E^\circ$  values, identify which species preferentially oxidised/reduced

Compare electrode potential  $E^\circ$ :

- **Anode:**  $E^\circ$  more negative, preferentially oxidised
- **Cathode:**  $E^\circ$  more positive, preferentially reduced

**Remark.** Consider  $\text{H}_2\text{O}$  if electrolyte is aqueous.

**Relative concentration of ions in electrolyte** e.g. conc NaCl

- **Anode:**  $E_{\text{ox}(\text{Cl}^-/\text{Cl}_2)}^\circ$  and  $E_{\text{ox}(\text{H}_2\text{O}/\text{O}_2)}^\circ$  have same sign, small difference in magnitude.

$[\text{Cl}^-]$  is high, by LCP, POE shift right (use oxidation eqn) to decrease  $[\text{Cl}^-]$  partially, favour oxidation.

$E_{\text{ox}(\text{Cl}^-/\text{Cl}_2)}^\circ$  less positive than  $E_{\text{ox}(\text{H}_2\text{O}/\text{O}_2)}^\circ$ , so  $\text{Cl}^-$  preferentially oxidised to  $\text{Cl}_2(\text{g})$ .

- **Cathode:**  $E_{\text{red}(\text{Na}^+/\text{Na})}^\circ$  and  $E_{\text{red}(\text{H}_2\text{O}/\text{H}_2)}^\circ$  have same sign, large difference in magnitude.

When  $[\text{Na}^+]$  is high, by LCP, POE shift right to decrease  $[\text{Na}^+]$  partially, favour reduction.

$E_{\text{red}(\text{Na}^+/\text{Na})}^\circ$  becomes more positive but is still less positive than  $E_{\text{red}(\text{H}_2\text{O}/\text{H}_2)}^\circ$ . Hence  $\text{H}_2\text{O}$  preferentially reduced to  $\text{H}_2(\text{g})$ .

**Nature of electrode:** if reactive electrode, reactive metal can only be oxidised, so only need to consider at anode

### §10.2.2 Calculations

Quantity of charge passed during electrolysis:

$$Q = I \times t \quad (53)$$

Faraday's constant  $F$  is charge per mole of electrons:

$$n_e = \frac{Q}{F} \quad (54)$$

Combining,

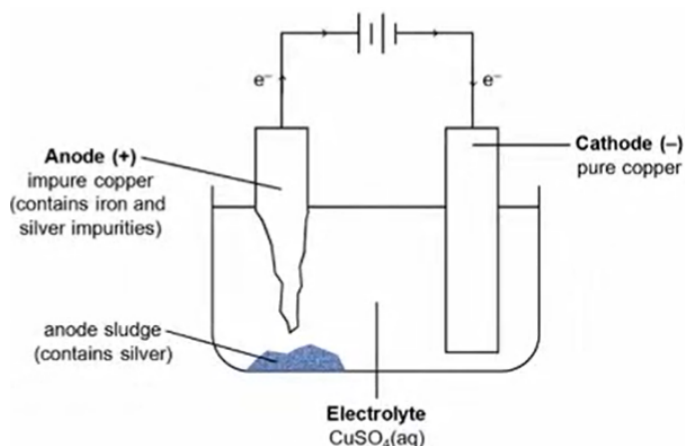
$$F = L \times e \quad (55)$$

where Avogadro's constant  $L = 6.02 \times 10^{23} \text{ mol}^{-1}$ , electro charge  $e = 1.6 \times 10^{-19} \text{ C}$ .

After calculating  $n_e$ , use mole ratio from half equation to find moles of product.

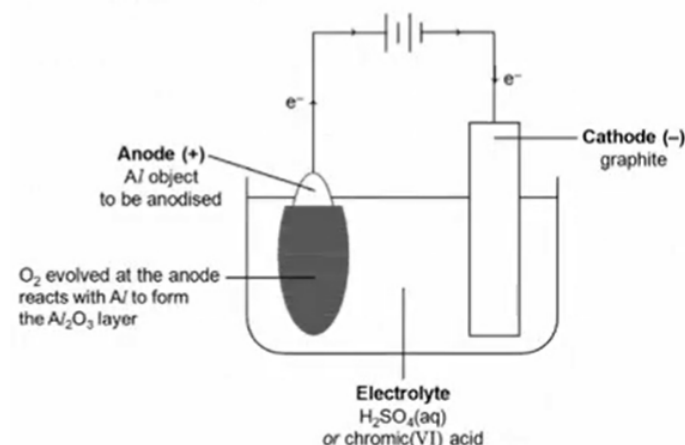
### §10.2.3 Industrial uses

**Purification of copper:**



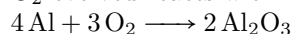
- Anode: Fe and Cu preferentially oxidised, Ag falls to bottom as sludge
- Cathode: Cu preferentially reduced so deposited on cathode, Fe remains in electrolyte

**Anodising of aluminium:** (thicken protective  $\text{Al}_2\text{O}_3$  oxide layer)



- Cathode:  $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$
- Anode:  $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

$\text{O}_2$  evolved reacts with Al to form  $\text{Al}_2\text{O}_3$ :



Overall reaction:  $2\text{Al} + 3\text{H}_2\text{O} \longrightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2$

## §11 Transition Elements

### Definition 11.1 (Transition element)

d block element that forms one or more stable ions with partially filled d subshells.

Sc and Zn are not transition elements

- $\text{Sc}^{3+}$  has vacant d subshell
- $\text{Zn}^{2+}$  has a fully filled d subshell

### §11.1 Electronic configuration

**First in, first out:** 4s subshell fills first but also empties first when forming ions

- Empty 4s subshell is lower in energy than empty 3d subshell
- Filled 4s subshell is higher in energy than filled 3d subshell (energy levels are very close in the first place, addition of electrons changes the energy levels slightly so they swap over)

Exceptions: **chromium** and **copper** (half-filled or full d subshell offers more stability than a full s subshell)

- Chromium:  $[\text{Ar}] 3d^5 4s^1$  (half-filled 3d subshell) is more stable than  $[\text{Ar}] 3d^4 4s^2$
- Copper:  $[\text{Ar}] 3d^{10} 4s^1$  (fully filled 3d subshell) is more stable than  $[\text{Ar}] 3d^9 4s^2$

[Small difference in energy between 3d and 4s subshells makes it possible for the electrons to move freely from one subshell to another.]

To find electronic configuration of ions: write configuration for atom first, then remove electrons (do not skip steps)

### §11.2 Physical properties

- **Atomic radii** is relatively invariant  
Nuclear charge increases. Electrons added to *inner* 3d subshell, shielding effect increases, cancels out increase in nuclear charge. Effective nuclear charge remains relatively invariant.
- **1st IE** is relatively invariant  
1st IE involves removal of outermost 4s electron. Electrons added to inner 3d subshell, shielding effect increases, cancel out increase in nuclear charge. Effective nuclear charge remains relatively invariant. Energy required to remove outermost electrons remains relatively invariant.

- **Density** is higher than s block element

Higher atomic mass, smaller atomic radius. Close-packed structure results in more heavy atoms per unit volume.

- **Melting point** is higher than s block element

Both have giant metallic structure. Valance electrons from 4s and 3d are delocalised due to similar energy level. More energy required to overcome stronger metallic bonding (strength proportional to # delocalised electrons).

- **High electrical and heat conductivities**

Both 3d and 4s electrons available for donation into sea of delocalised electrons.

### §11.3 Chemical properties

- **Variable oxidation states**

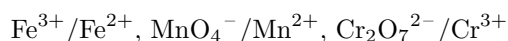
4s and 3d electrons are similar in energy. Once 4s electrons are removed, 3d electrons (outer subshell) can also be removed without requiring much more energy.

In general, max oxidation state = #4s electrons + #unpaired 3d electrons.

Number of available ox states increases from Sc to Mn, decreases from Mn to Zn (pairing of 3d electrons occurs, number of unpaired 3d electrons available for covalent bond formation decreases)

Ions of transition elements in higher oxidation states exist only as covalent compounds (e.g.  $\text{V}_2\text{O}_5$ ,  $\text{CrO}_3$ ,  $\text{TiCl}_4$ ) and oxo-anions (e.g.  $\text{MnO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ), because cation has high charge density, high polarising power, distort electron cloud of neighbouring anion to large extent, leading to overlap of electron cloud, thus great degree of covalent character.

- **Redox systems**



Reactions

1. **Precipitation**
2. **Acid-base**
3. **Ligand exchange**
4. **Redox**

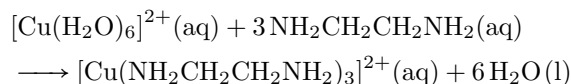
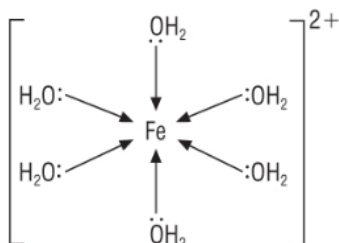
## §11.4 Complexes

### Definition 11.2 (Ligand)

Neutral molecule/anion containing at least one atom with lone pair of electrons that can be donated to form dative bond with metal atom/ion.

### Definition 11.3 (Complex)

Central atom/ion surrounded by ligands bonded to it by dative bonds.



When monodentate ligands are replaced with multidentate ligands, entropy increases. Since enthalpy change is minimal, feasibility of reaction is down to entropy. By  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G$  becomes more negative, reaction is feasible, hence stability of multidentate complex ion is high.

Why do transition elements form complexes

- high charge density, high polarising power, attract ligands rich in electrons
- vacant low-lying orbitals to accept lone pairs of electrons from ligands to form dative bonds with them

**Coordination number:** number of dative bonds<sup>4</sup> to the central metal atom/ion

**Net charge on complex:** sum of charge on metal atom/ion and ligands<sup>5</sup>

Types of ligands

- **Monodentate:** 1 dative bond per ligand e.g.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$
- **Bidentate:** 2 dative bond per ligand e.g.  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , ethanedioate
- **Tridentate:** 3 dative bond per ligand e.g. diethylenetriamine (DETA)
- **Hexadentate:** 6 dative bond per ligand

**Chelate effect:** multidentate ligands form stable complexes

### §11.4.3 Ligand exchange reaction

Stronger ligand can replace weaker ligand from a complex ion. (Weaker ligand can replace stronger ligand, only if high concentration)

**Example 11.4** (Ligand exchange between  $\text{H}_2\text{O}$  /  $\text{NH}_3$  ligands in  $\text{Cu}(\text{II})$  complexes).

- $\text{CuSO}_4$  dissolves in water, form blue  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ .



<sup>4</sup>NOT ligands, as some ligands can form more than 1 dative bond with central atom/ion

<sup>5</sup>can be deduced by looking at charge of counterion

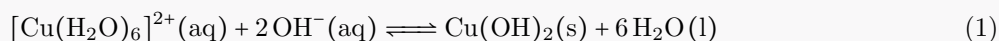
### §11.4.1 Shapes

Coordination number	Geometry
2	linear
4	tetrahedral
4	square planar
6	octahedral

### §11.4.2 Isomerism

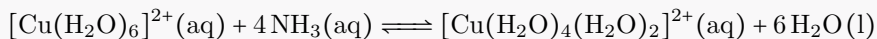
- **Ionisation isomerism:** exchange of ions inside and outside the coordination sphere
- **Conformational isomerism:** complex ions with different geometries e.g. square planar vs tetrahedral
- **Cis-trans isomerism:** ligands occupy positions adjacent to each other (cis), or on opposite sides of central ion (trans)
- **Enantiomerism:** non-superimposable mirror images of each other

- On addition of  $\text{NH}_3(\text{aq})$ , weak base dissociates in water to produce  $\text{OH}^-$ , precipitation reaction occurs.



Blue ppt  $\text{Cu}(\text{OH})_2$  forms when  $\text{IP} > K_{sp}$ .

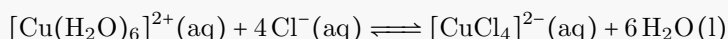
- On addition of excess  $\text{NH}_3(\text{aq})$ , ligand exchange reaction:  $\text{NH}_3$  ligand replaces  $\text{H}_2\text{O}$  ligand in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$



$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  decrease. By LCP, POE of (1) shift left to increase  $[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}]$ , IP fall below  $K_{sp}$ , blue ppt  $\text{Cu}(\text{OH})_2(\text{s})$  dissolves.

**Example 11.5** (Ligand exchange between  $\text{Cl}^-$  /  $\text{H}_2\text{O}$  ligands in  $\text{Cu}(\text{II})$  complexes).

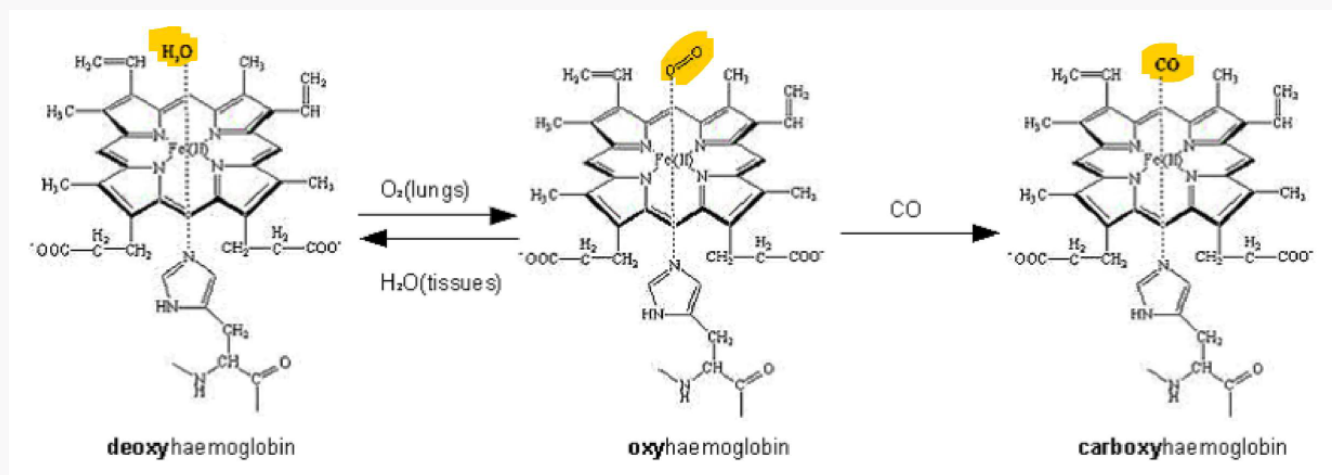
- Due to high conc of  $\text{HCl}$ ,  $\text{Cl}^-$  ligand replace  $\text{H}_2\text{O}$  ligand in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$



Intermediate green colour is due to presence of both blue  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and yellow  $[\text{CuCl}_4]^{2-}$ .

- On addition of more conc  $\text{HCl}$ ,  $[\text{Cl}^-]$  increases. By LCP, POE shift right to decrease  $[\text{Cl}^-]$ . More  $[\text{CuCl}_4]^{2-}$  formed, solution turns yellow.
- On diluting mixture, adding  $\text{H}_2\text{O}$  shifts POE to left,  $\text{H}_2\text{O}$  ligand displace  $\text{Cl}^-$  ligand, green solution turns blue.

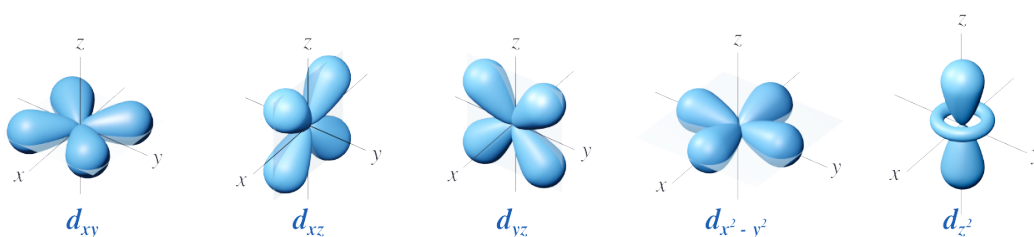
**Example 11.6** (Ligand exchange in haemoglobin).



- $\text{O}_2$  ligand replaces  $\text{H}_2\text{O}$  ligand reversibly, to transport oxygen to cells in body.
- Stronger  $\text{CO}$  ligand replaces  $\text{H}_2\text{O}$  ligand irreversibly, prevent oxygen molecules from binding to  $\text{Fe}^{2+}$  in haemoglobin, less haemoglobin to transport  $\text{O}_2$ , so cells in body become deprived of oxygen.

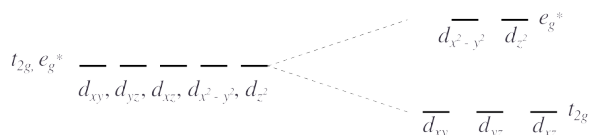
**Remark.** If addition of ligand results in colour change, new complex formed, so ligand exchange reaction occurred.

#### §11.4.4 Colour



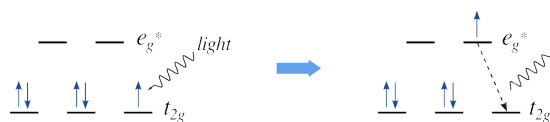
## d orbital splitting (octahedral complex)

1. Ligands approach metal ion along  $x$ -,  $y$ -,  $z$ -axes, all d orbitals experience repulsion, destabilised, higher energy levels
2.  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals have lobes along axes, direct head-on repulsion with lone pair on ligands, larger extent of repulsion, orbitals more destabilised, higher energy level
3.  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals have lobes in between axes, no direct head-on repulsion with lone pair on ligands, smaller extent of repulsion, orbitals less destabilised, lower energy level

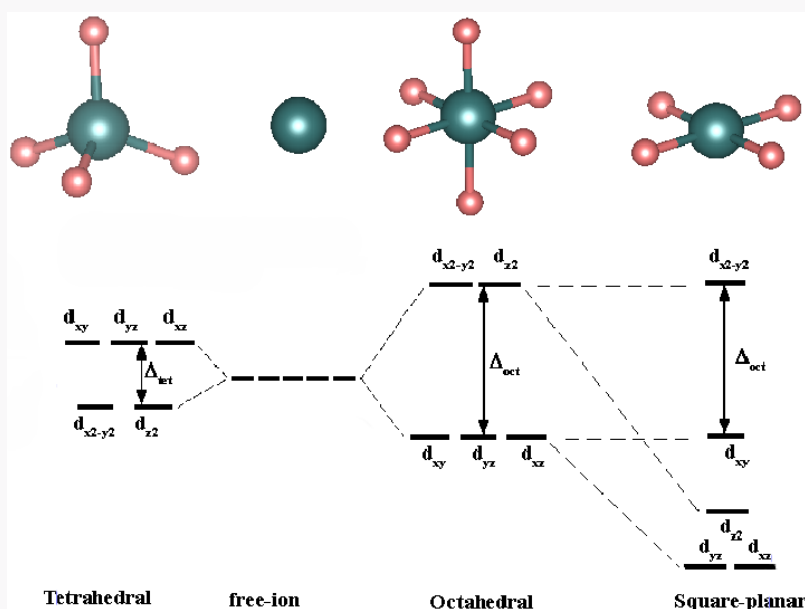


## d-d transition

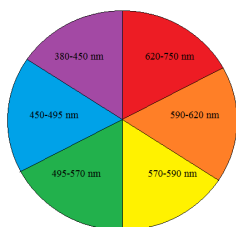
1. When white light shines on complex, d electron absorbs photon of wavelength of light from visible spectrum, matching energy gap  $\Delta E$ , promoted to vacant / partially-filled d orbital at higher energy level
2. Transmitted light, which is complementary to wavelength of light absorbed, gives transition metal complex its colour



**Remark.** d-orbital splitting in different complexes:



## Colour wheel:



## Factors affecting colour of complexes

### • Nature of ligand:

different ligand, different extent of repulsion, split d orbitals to different extent, different energy gap ...

### • Identity of metal and oxidation state:

- Sc(III), Zn(II), Cu(I) compounds appear white, as they contain empty / fully-filled d subshell, so d-d transition not possible
- Higher oxidation state, higher charge density, ligand attracted closer, greater extent of repulsion, split d orbitals to larger extent, larger energy gap  $\Delta E$ , smaller  $\lambda$  of light absorbed during d-d transition

### • Shape of complex ion:

different splitting pattern, so different energy gap  $\Delta E$ , different wavelength of light absorbed during d-d transition

## List of colours

Element	Oxidation state	Formula	Colour
copper	+2	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	blue
	+2	$\text{Cu}(\text{OH})_2$	blue ppt*
	+2	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	dark blue*
	+2	$[\text{CuCl}_4]^{2-}$	yellow
	0	Cu	reddish-brown solid
	+2	CuO	black solid
chromium	+2	$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	blue
	+3	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	green
	+3	$\text{Cr}(\text{OH})_3$	grey green ppt*
	+3	$[\text{Cr}(\text{OH})_6]^{3-}$	dark green*
	+6	$\text{CrO}_4^{2-}$	yellow
	+6	$\text{Cr}_2\text{O}_7^{2-}$	orange
iron	+2	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	(pale) green
	+3	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	yellow
	+2	$\text{Fe}(\text{OH})_2$	dirty green ppt*
	+3	$\text{Fe}(\text{OH})_3$	reddish brown ppt*
	+2	$[\text{Fe}(\text{CN})_6]^{4-}$	yellow
	+3	$[\text{Fe}(\text{CN})_6]^{3-}$	orange brown
	+3	$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	blood red
	+3		
cobalt	+2	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	pink
	+2	$[\text{Co}(\text{NH}_3)_6]^{2+}$	yellow / brown
manganese	+2	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	colourless / pale pink
	+4	$\text{MnO}_2$	dark brown ppt
	+6	$\text{MnO}_4^{2-}$	green
	+7	$\text{MnO}_4^-$	purple
vanadium	+2	$\text{V}^{2+}$	violet
	+3	$\text{V}^{3+}$	green
	+4	$\text{VO}^{2+}$	blue
	+5	$\text{VO}_2^+$	yellow
nickel	+2	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	green
	+2	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	blue
	+2	$[\text{Ni}(\text{CN})_4]^{2-}$	yellow
zinc**	+2	$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$	colourless
	+2	$[\text{Zn}(\text{OH})_4]^{2-}$	colourless*
	+2	$[\text{Zn}(\text{NH}_3)_4]^{2+}$	colourless*
aluminium**	+3	$[\text{Al}(\text{OH})_4]^-$	colourless*

\* Found in qualitative analysis notes

\*\* Non transition metal



**Remark.** “soluble in excess” indicates formation of complex.

### §11.4.5 Catalysis

- **Heterogeneous catalyst**

Transition elements and compounds can form temporary weak bonds with reactants at solid surface

- use low-lying vacant d orbitals to accept lone pairs from reactant molecules
- use electrons in d orbitals to form temporary bonds with reactant molecules

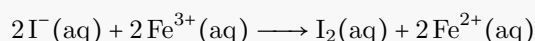
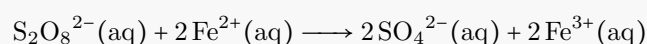
- **Homogeneous catalyst**

Variable oxidation states, so can form intermediates via alternative reaction pathways that have lower  $E_a$

- transition metal ion undergoes redox reaction, converted to intermediate
- intermediate undergoes another redox reaction, regenerate catalyst

**Example 11.7.** The reaction  $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^-(\text{aq}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$  is thermodynamically feasible but kinetically unfeasible. Low rate of reaction as two anions repel one another, so high activation energy - energy required to overcome electrostatic forces of repulsion.

Catalyst:  $\text{Fe}^{2+}$  (or  $\text{Fe}^{3+}$ )



$\text{Fe}^{2+}$  is catalyst,  $\text{Fe}^{3+}$  is intermediate.

Alternative pathway has lower activation energy as each step involves reaction between two oppositely charged species, so higher rate of reaction.

Suggest a redox couple that can catalyse  $\text{S}_2\text{O}_8^{2-} / \text{I}^-$  reaction: find  $E^\ominus_{\text{couple}}$  in between the two  $E^\ominus$  values.

## §12 Organic Chemistry

### Question Types

#### 1. Mechanism question

Remember to include lone pair, partial charges, curly arrows.

#### 2. Synthesis question

- Change in carbon chain length
- Change in type of functional group
- Change in number of functional groups
- Change in position of functional group (may or may not be the same as starting reagent)

#### 3. Structure elucidation question

- molecular formula: determine benzene ring (C:H ratio close to 1:1), Degrees of Unsaturation

$$\text{DoU} = \frac{2C + 2 - H - X + N}{2}$$

where each  $\pi$  bond or ring reduces hydrogen count by 2, contributes to 1 degree of unsaturation.

- type of reaction
- functional group(s) present / absent

#### 4. Distinguishing test

- reagents and conditions
- observations (positive and negative)

#### 5. Explanation question

##### (a) Stereochemical outcome

Chiral molecule: (1) chiral centre (2) no internal plane of symmetry

Impact of mechanism on chirality of product: nucleophile attack  $sp^2$  hybridised trigonal planar carbon from top and bottom of the plane with equal probability. Racemic mixture formed, equal proportion of each enantiomer rotates plane-polarised light by same magnitude in opposite directions, optical activity cancelled out, thus optically inactive.

##### (b) **Acidity**: stability of conjugate base

Alcohols are neutral: electron-donating alkyl groups increase intensity of negative charge on  $O^-$  of alkoxide ion, alkoxide ion less stable, acid dissociation of alcohol not favoured

Phenols are acidic: lone pair of electrons on  $O^-$  of phenoxide delocalise into benzene ring, decrease intensity of negative charge on  $O^-$ , ...

Carboxylic acids are acidic: lone pair of electrons on  $O^-$  of carboxylate are delocalised over two electronegative O atoms, ...

##### (c) **Basicity**: availability of lone pair of electrons on N for donation to $H^+$

Amines are basic: lone pair of electrons on N available for donation to  $H^+$  (act as Lewis base)

[can be affected by steric hindrance]

Amides are neutral: lone pair of electrons on N delocalise into  $C=O$  bond, not available for donation to  $H^+$

##### (d) Reactivity

- electronegativity
- electron-donating / electron-withdrawing effect
- delocalisation effect
- steric effect

## §12.1 Introduction

Types of chemical formulae

- **Empirical formula:** simplest ratio of number of atoms of the elements
- **Molecular formula:** actual number of atoms of the elements present
- **Structural formula:** atoms sequentially arranged, using conventional groups for an unambiguous structure
- **Displayed formula** (full structural formula): show all atoms and bonds, with relative placing of atoms
- **Skeletal formula:** only show bonds and functional groups
- **Stereochemical formula:** show 3D spatial arrangement

Nomenclature: **prefix – stem – suffix**

**Prefix: substituents**

prefix	name	prefix	name
$-\text{C}_n\text{H}_{2n+1}$	(alkyl)	-F	fluoro
$-\text{NH}_2$	amino	-OH	hydroxy
-Br	bromo	-I	iodo
-Cl	chloro	$-\text{NO}_2$	nitro
-CN	cyano	$-\text{C}_6\text{H}_5$	phenyl

- Numbers to indicate position (distance from principal functional group) → lowest possible numbering
- Number prefixes if more than one (use commas to separate numbers)
- Order different prefixes alphabetically (use hyphens to separate words)

**Stem: number of carbon atoms in longest continuous carbon chain**

no. of C atoms	stem	no. of C atoms	stem
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-

For alicyclic compounds, “cyclo-” is added to the front of stem.

**Suffix: principal functional group of highest priority**

Order of priority (highest to lowest)

1. Carboxylic acid (-oic acid)
2. Carboxylic acid derivatives
  - Ester ((alkyl) -oate)
  - Acid/acyl chloride (-oyl halide)
  - Amide (-amide)
3. Nitrile (-nitrile)
4. Carbonyl compounds
  - Aldehyde (-al)
  - Ketone (-one)
5. NH, OH
  - Phenol (phenol)
  - Alcohol (-ol)
  - Amine (-amine)
6. Hydrocarbons
  - Arene (benzene)
  - Alkyne (-yne)
  - Alkene (-ene)
  - Alkane (-ane)

### §12.1.1 Terminology for reactions

Types of organic species

- **Free radical**: species with unpaired electron(s)
- **Nucleophile** (Lewis base): electron pair donor
- **Electrophile** (Lewis acid): electron pair acceptor

Types of bond fission

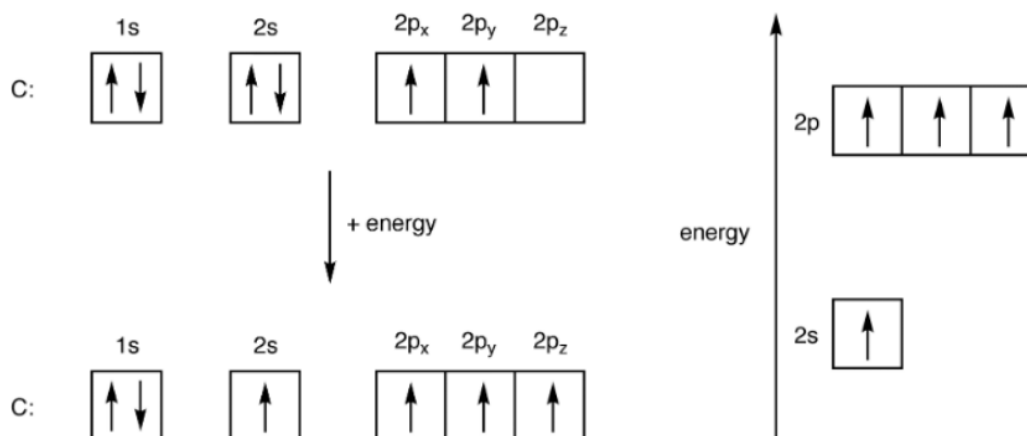
- **Homolytic fission**: breaking of covalent bond such that shared pair of electrons are split equally between the two atoms, which forms free radicals  
[single arrow for movement of single electron]
- **Heterolytic fission**: breaking of covalent bond such that shared pair of electrons are split unequally between the two atoms after bond broken, which forms ions  
[full arrow for movement of electron pair]

Types of reactions<sup>6</sup>


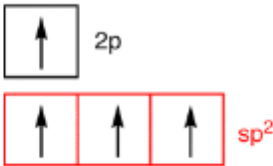
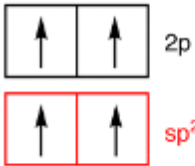



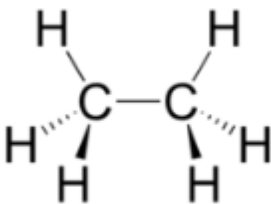
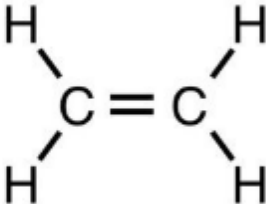
- **Addition**: two reactants added together to form one single product (one  $\pi$  bond broken, two  $\sigma$  bonds formed)
- **Substitution**: an atom / group of atoms replaces another atom / group of atoms (one  $\sigma$  bond broken, one  $\sigma$  bond formed)
- **Elimination**: two atoms / groups of atoms from adjacent atoms removed from one molecule (two  $\sigma$  bonds broken, one  $\pi$  bond formed)
- **Condensation**: two molecules react to form a larger molecule + simple molecule eliminated
- **Hydrolysis**: reaction with water /  $\text{H}^+$  /  $\text{OH}^-$
- **Oxidation**: increase in oxidation state, oxidised by  $[\text{O}]$
- **Reduction**: decrease in oxidation state, reduced by  $[\text{H}]$

### §12.1.2 Hybridisation

One of 2s electron is promoted to empty 2p orbital (from ground state to excited state)  $\rightarrow$  4 singly occupied orbitals for forming 4 covalent bonds



<sup>6</sup>Do not use these terms when asked for the type of reaction! Give answers such as free radical substitution, electrophilic addition etc.

Hybrid orbital	$sp^3$	$sp^2$	$sp$
Orbitals involved	one s, three p → 4 degenerate $2sp^3$ hybrid orbitals 	one s, two p → 3 degenerate $2sp^2$ hybrid orbitals 	one s, one p → 2 degenerate $2sp$ hybrid orbitals 
Orientation	<u>Tetrahedral</u> about hybridised C atom	<u>Trigonal planar</u> about hybridised C atom	<u>Linear</u> about hybridised C atom
	bond angle = 109.5	bond angle = 120	bond angle = 180
		Unhybridised p orbital perpendicular to plane of hybrid orbitals	Unhybridised p orbitals perpendicular to plane of hybrid orbitals
			
Bonding	4 $\sigma$ bonds	3 $\sigma$ bonds, 1 $\pi$ bond	2 $\sigma$ bonds, 2 $\pi$ bonds
Example	ethane 	ethene 	ethyne $H-C\equiv C-H$

Effect of hybridisation on bond strength: electrons in s orbital closer to nucleus compared to p orbitals, higher percentage of s character in hybrid orbital → shorter bond length → stronger bond strength

#### Hybridisation of nitrogen / oxygen:

- Count total number of lone pairs + bond pairs

4:  $sp^3$ , 3:  $sp^2$ , 2:  $sp$

- Exception: rehybridisation

O and N atom with 4 electron regions adjacent to  $\pi$  electron system, lone pair located in unhybridised 2p orbital, able to delocalise

E.g. oxygen in phenol is  $sp^2$  hybridised, nitrogen in phenylamine is  $sp^2$  hybridised, nitrogen in amide is  $sp^2$  hybridised

### §12.1.3 Isomerism

**Isomers:** compounds having same molecular formula but different arrangement of atoms.

1. Structural isomerism: same molecular formula but different arrangements of atoms

- **Chain isomerism:** different arrangement of carbon chain (straight or branched)
- **Positional isomerism:** different position of functional group
- **Functional group isomerism:** different functional group

2. Stereoisomerism: same molecular formula and structural formula but different spatial arrangement of atoms

- **Cis-trans isomerism**

- (a) Restricted rotation of bond due to  $\pi$  bond OR rigid ring structure ( $\pi$  bond has to break for bond to rotate, then  $\pi$  bond reforms)
- (b) Two different atoms / substituents attached to each carbon atom

**Cis-isomer:** same groups on same side

**Trans-isomer:** same groups on opposite sides

Properties:

- Chemical: Similar chemical properties
- Physical: Bp: cis-isomer > trans-isomer (stronger pd-pd than weaker id-id)  
Mp: trans-isomer > cis-isomer (higher symmetry, pack more closely in lattice structure, more extensive id-id)

- **Enantiomerism**

- (a) Non-superimposable mirror image
- (b) No internal plane of symmetry
- (c) **Chiral centre:** a carbon atom with four different atoms or substituents attached to it

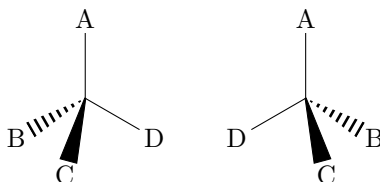
**Chiral:** non-superimposable with mirror image

**Racemic mixture:** equal proportions of each enantiomer

Each enantiomer rotates plane-polarised light by the same magnitude in opposite directions. Since they cancel each other out, there is no overall effect on plane-polarised light, hence no optical activity.

**Meso compound:** multiple chiral centres + internal plane of symmetry

Each chiral carbon rotates plane-polarised light by the same magnitude in opposite directions. Since they cancel each other out, there is no overall effect on plane-polarised light, hence no optical activity.



Properties:

- Physical: identical physical properties, different optical activity
- Chemical: identical chemical properties, different interactions with another chiral molecule
- Biological: different biological properties in drug action  
Protein molecules are chiral: different reactions with the two enantiomers of a chiral drug → can accept only one of the two enantiomers due to difference in 3-dimensional structure

## §12.2 Reactions

Be familiar with *all* reactions.

## §12.3 Chemical properties

### Alkane

Alkanes: generally unreactive

- Fully saturated: all carbon atoms are  $sp^3$  hybridised and C–C, C–H bonds are strong and difficult to break, so alkanes *do not undergo addition*.
- C–H bonds are non-polar: lack electron-rich ( $\delta^-$ ) and electron-deficient ( $\delta^+$ ) sites, so *unreactive towards polar reagents*.

Small cycloalkanes (e.g. cyclopropane, cyclobutane) are unstable due to **ring strain**, as molecules are forced into smaller bond angles.

### Alkene

Alkenes: generally reactive

- Electron rich C=C bond is easily accessible to approaching reactants ( $\pi$  electrons are located above and below the plane of bond)  $\rightarrow$  act as nucleophiles, attract electrophiles OR induce dipoles in approaching molecules to form electrophiles
- Carbon atoms in C=C bond are unsaturated:  $sp^2$  hybridised, can bond with one more atom  $\rightarrow$  undergo electrophilic addition

### Benzene

Benzene: resonance stabilised

- Due to overlapping p-orbitals, delocalised  $\pi$  electron cloud above and below plane of ring. Benzene is resonance stabilised, thus is weaker nucleophile than alkene, less reactive towards electrophiles.
- Do not undergo reactions that destroy resonance stability e.g. electrophilic addition, thus only undergoes electrophilic substitution, remain resonance stabilised.

Effect of substituents:

- Activating group:** Electron-donating, increase electron density of benzene ring  $\rightarrow$  increase reactivity of benzene ring (stronger nucleophile)  
Reaction requires milder conditions e.g. lower temp, dilute reagents, catalyst not needed
- Deactivating group:** Electron-withdrawing, decrease electron density of benzene ring  $\rightarrow$  decrease reactivity of benzene ring (weaker nucleophile)  
Reaction requires harsher conditions e.g. higher temp, conc reagents, catalyst needed

Resonance effect and inductive effect:

	<b>Resonance effect:</b> Overlap of p orbital on substituent & p orbital on carbon atom of benzene ring	<b>Inductive effect:</b> Sigma bond, electronegativity difference
Electron-donating	Lone pair of electrons donated from substituent to benzene ring	Substituent inductively donates electrons through sigma bond
Electron-withdrawing	$\pi$ electrons of benzene ring pulled towards substituent	Substituent inductively withdraws electrons through sigma bond

Positions of substitution: (position of incoming group determined by nature of existing group)

- **2,4-directing group:** incoming electrophile E added to 2nd or 4th positions (relative to G)
- **3-directing group:** incoming electrophile E added to 3rd position (relative to G)

Alkylbenzene - Effect of substituents: electron-donating alkyl group is ring-activating, increases electron density of benzene ring, making it more susceptible to electrophilic substitution

## Halogenoalkane

Down the group, atomic orbital of halogen atom becomes more diffused, effectiveness of orbital overlap decreases, strength of C–X bond decreases, less energy required to break C–X bond increases, R–X more reactive towards nucleophilic substitution

**Remark.** Do not use bond polarity to explain.

Halogenoarene: unreactive towards nucleophilic substitution

- **Electronic:** p-orbital of halogen atom overlaps with p-orbitals of carbon atoms on benzene ring. Lone pair of electrons in p-orbital of halogen atom delocalises into benzene ring to form delocalised  $\pi$  electron cloud.  
Partial double bond character in C–X bond, more energy required to break stronger C–X bond to displace halogen atom.
- **Steric:** Bulky benzene ring sterically hinders approach of nucleophile towards electrophilic carbon from opposite side of halogen.

## Phenol

–OH group is strongly activating

- Delocalisation of lone pair of electrons on oxygen into benzene ring increases electron density in ring, makes phenol more susceptible than benzene towards electrophilic attack, thus phenol undergoes electrophilic substitution more readily.
- Hence milder conditions are required & multi-substitution at 2,4 positions with respect to –OH group is favoured.

## Carbonyl compounds

Aldehyde is more reactive than ketone towards nucleophilic substitution:

- **Electronic:** Carbonyl carbon of aldehyde bonded to one less electron-donating alkyl group, more electron deficient, attacked more readily by nucleophile.
- **Steric:** Carbonyl carbon of aldehyde bonded to one less bulky alkyl group than ketone, less steric hindrance about carbonyl carbon in aldehydes to hinder approach of attacking nucleophile.

Benzaldehyde:  $\pi$  electrons delocalise from benzene ring to carbonyl carbon, so least electron-deficient.

Reactivity between carbonyl compounds and alkenes towards nucleophilic reagents

- Polar C=O bond has electron-deficient carbon susceptible to attack by nucleophiles, non-polar C=C bond lacks electron-deficient sites
- Electron-rich C=C bond repels electron-rich nucleophile



## Carboxylic acid and derivatives

Redox and acid-base reactions:

Reagents & conditions	Na(s)	NaOH(aq)	NaHCO <sub>3</sub> (aq) / Na <sub>2</sub> CO <sub>3</sub> (aq)
alcohol (neutral)	✓		
phenol (slightly acidic)	✓	✓	
carboxylic acid (acidic)	✓	✓	✓

Reducing agents:

	LiAlH <sub>4</sub> in dry ether	NaBH <sub>4</sub> in ethanol	H <sub>2</sub> with Ni catalyst, heat <b>OR</b> H <sub>2</sub> with Pt catalyst
alkene			✓
cyanide	✓		✓
aldehyde	✓	✓	✓
ketone	✓	✓	✓
carboxylic acid	✓		

Ease of hydrolysis: depends on strength of C–X bond

- **Delocalisation:** In aryl chlorides, delocalisation of lone pair of electrons on halogen into benzene ring, partial double bond character in C–Cl bond, stronger bond requires more energy to break.
- **Electron-withdrawing effect:** In acyl chlorides, carbon in COCl group bonded to two electronegative O and Cl atoms, greater electron-withdrawing effect than carbon bonded to only one electronegative Cl atom in alkyl chlorides. Larger  $\delta^+$  charge, more susceptible to attack by nucleophiles in hydrolysis reaction.

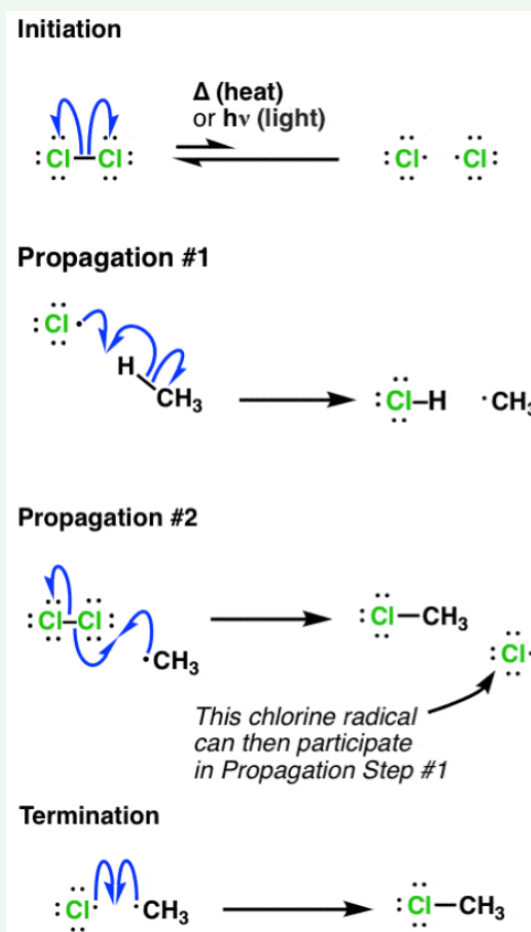
**Remark.** Do NOT explain using polarity of C–X bonds using difference in electronegativity of atoms.

Experimentally, add AgNO<sub>3</sub>(aq) to halogen compounds, AgCl ppt formed

- rate of formation of ppt: acyl chloride > alkyl chloride > aryl chloride
- white ppt observed immediately, white ppt observed on heating, no ppt even with heating

## §12.4 Mechanisms

### Mechanism 1 (Alkane: free radical substitution)



**Step 1:** Initiation

**Step 2:** Propagation

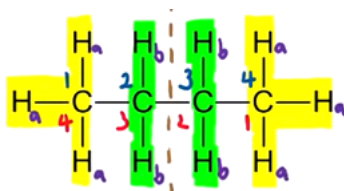
**Step 3:** Termination

Stability of carbon radical intermediates

- **Electron-donating (inductive) effect:** Electron-donating alkyl groups increase electron density on C atom with unpaired electron, stabilising carbon radical
- **Delocalisation:** Delocalisation of unpaired electron into adjacent  $\pi$  electron clouds leads to resonance stabilisation of radical

**Theoretical product ratio:**

Count the number of equivalent H atoms that give rise to each product



**Actual product ratio:**

#### Exercise 4

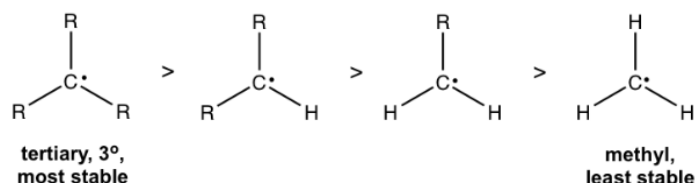
In the mono-substitution of butane, we predict the ratio of 1-bromobutane to 2-bromobutane is 3:2. However, the actual product ratio is 1:4.

Why does the actual product ratio differ from the theoretical ratio?

*Solution.* Secondary carbon radical forms 2-bromobutane, primary carbon radical forms 1-bromobutane.

Due to presence of more adjacent electron-donating alkyl groups around secondary carbon radical which donate electron density, secondary carbon radical is less electron-deficient, hence it is more stable.

Formation of more stable secondary carbon radical increases rate of reaction, hence 2-bromobutane is formed at a greater proportion.

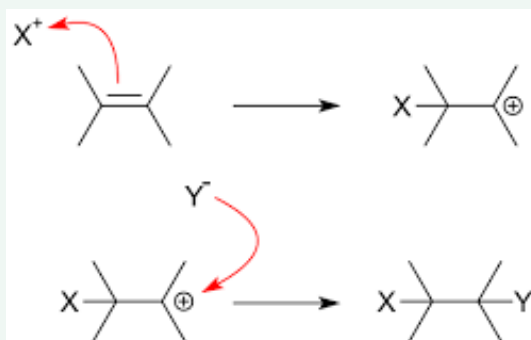


□

Mono-substitution: limited halogen

Multiple substitutions: excess halogen

#### Mechanism 2 (Alkenes: electrophilic addition)



**Step 1:** Addition of electrophile: formation of carbocation (Markovnikov's rule)

**Step 2:** Ions combine

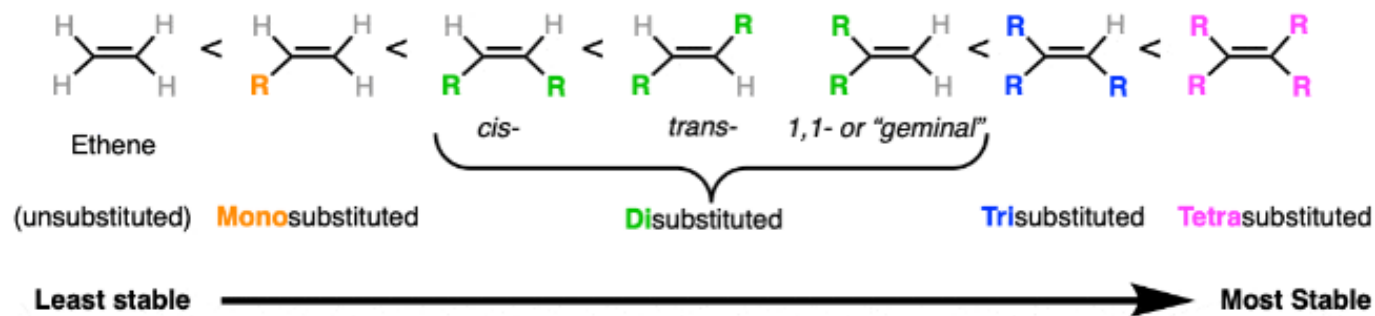
**Markovnikov's rule:** X component added to carbon with fewest hydrogens; hydrogen atom added to carbon with most hydrogens.

- Explanation: More electron-donating alkyl groups disperse positive charge of carbon atom by a larger extent → carbocation more stable, forms at a faster rate → major product of larger yield

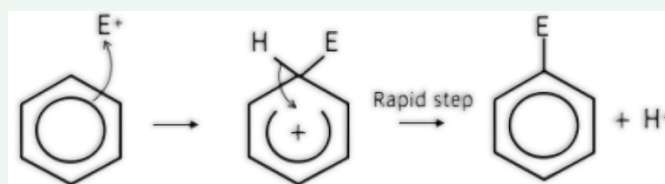
Stability of carbonation intermediates

- **Electron-donating effect:** Electron-donating alkyl groups disperse positive charge on C atom, stabilising carbocation
- **Delocalisation:** Delocalisation of  $\pi$  electrons (from adjacent  $\pi$  electron cloud) over positively charged C atom

**Zaitsev's rule:** major product of elimination reaction → more stable alkene with more highly substituted double bond



### Mechanism 3 (Benzene: electrophilic substitution)

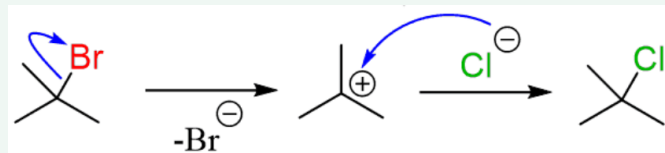


**Step 1:** Generation of strong electrophile

**Step 2:** Addition into benzene ring (position dependent on group which is already present)

**Step 3:** Deprotonation

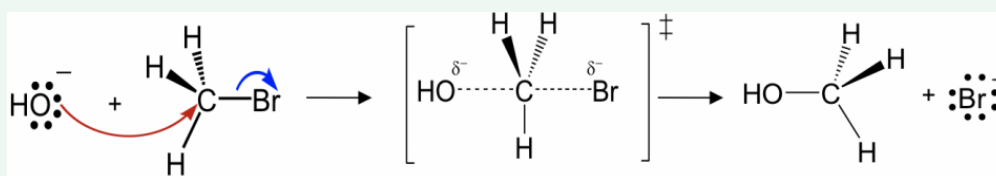
### Mechanism 4 (Halogenoalkane: unimolecular nucleophilic substitution $S_N1$ )



**Step 1:** Formation of carbocation intermediate

**Step 2:** Attack of carbocation by nucleophile

### Mechanism 5 (Halogenoalkane: bimolecular nucleophilic substitution $S_N2$ )



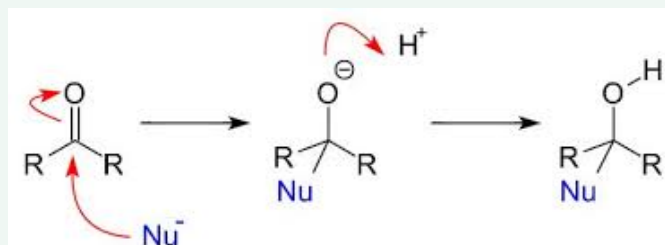
**Step 1:** Nucleophile attacks from opposite side of halogen atom

Pentavalent transition state formed, where both nucleophile and halogen are partially bonded to carbon atom, both bond breaking and bond forming process take place simultaneously.

	S <sub>N</sub> 1	S <sub>N</sub> 2
1st step	one molecule in first step	two molecules in first step
# steps	two steps	one step
Electronic	tertiary halogenoalkane gives stable tertiary carbocation intermediate	methyl and primary halogenoalkane give less stable methyl carbocation and primary carbocation intermediate
Steric	tertiary halogenoalkane has three bulky groups which hinder approach of nucleophile to electron-deficient carbon atom, more steric hindrance	methyl and primary halogenoalkane have no or only one alkyl group which allows easy approach of nucleophile to electron-deficient carbon atom, less steric hindrance
Stereochemistry	inversion of stereochemical configuration (for chiral reactants)	racemic mixture (for chiral reactants)

Exceptions due to other electronic and steric considerations

#### Mechanism 6 (Aldehyde/ketone: nucleophilic addition)



**Step 1:** Nucleophile attack electron-deficient carbonyl carbon, C–O pi bond breaks

**Step 2:** Alkoxide protonated to form alcohol derivative

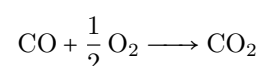
## §12.5 “General knowledge” stuff

Usage as fuels

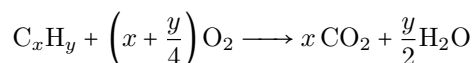
Pollutant	Cause of emission	Effects
CO	Incomplete combustion of hydrocarbon	Carbon monoxide poisoning: CO competes with oxygen to bond datively to haemoglobin in red blood cells. As CO is a stronger ligand, it bonds irreversibly with $\text{Fe}^{2+}$ ion in haemoglobin and decreases its ability to carry oxygen to other parts of the body, causing headaches, breathing difficulties and even death.
$\text{NO}_x$	$\text{N}_2$ react with $\text{O}_2$ at high temperature of car engine	Form acid rain: reacts with water in atmosphere to form nitric acid $\rightarrow$ corrode buildings, destroy crops, harm aquatic life $\text{NO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g})$ $2 \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{HNO}_3(\text{aq}) + \text{HNO}_2(\text{aq})$ Form photochemical smog, cause lung damage Respiratory problems in humans
unburnt $\text{C}_x\text{H}_y$	Incomplete combustion of hydrocarbon	Form photochemical smog in strong sunlight, cause lung damage
$\text{SO}_2$		Form acid rain: oxidised by nitrogen dioxide to give $\text{SO}_3$ , which reacts with rainwater to form sulfuric acid $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{SO}_4(\text{aq})$ $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g}) + \text{NO}(\text{g})$ $\text{NO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{NO}_2(\text{g})$ Note: $\text{NO}_2$ acts as homogeneous catalyst
CFC		Thinning of ozone layer
$\text{CO}_2$		Greenhouse gas $\rightarrow$ enhanced greenhouse effect
$\text{CH}_4$		Greenhouse gas $\rightarrow$ enhanced greenhouse effect

**Catalytic converter** in diesel engine: removes pollutants from exhaust gas

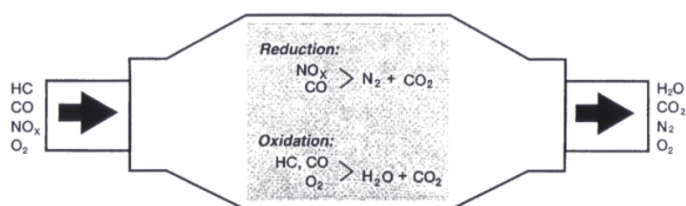
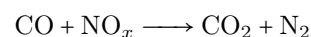
- Carbon monoxide oxidised to carbon dioxide



- Hydrocarbons oxidised into carbon dioxide and water



- Nitrogen oxides reduced into elemental nitrogen and oxygen



Fluoroalkanes and fluorohalogenoalkanes are generally stable and unreactive (chemically inert) due to strong C–F bond (high bond energy), used as **inert materials** in fire extinguisher, refrigerant, aerosol propellant etc.

**Chlorofluorocarbons (CFCs)** lead to ozone depletion, by free radical substitution:

