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UPDATED TO 2022 SYLLABUS

CAIE AS LEVEL

# CHEMISTRY (9701)

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SUMMARIZED NOTES ON THE THEORY SYLLABUS

# 1. Atomic Structure

## 1.1. Subatomic Particle

Subatomic Particle	Relative Charge	Relative mass/ a.m.u
Protons (P)	+1	1
Neutrons (n)	0	1
Electrons (e <sup>-</sup> )	-1	1/1840

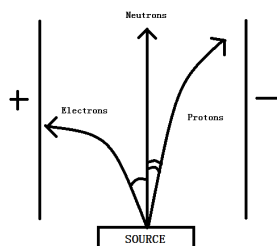
## 1.2. Protons, neutrons and electrons

- Mass concentrated within centre; **nucleus**
- An atom is electrically neutral;  $P^+ = e^-$
- Atomic no. or proton no. (Z) = no. of protons
- Atomic mass or nucleon no. (A) = no. of P + N

Nucleon number → 11 **B**  
 Proton number → 5

- **Isoelectronic ions:** ions having same no. of e<sup>-</sup>s
- **Isotopes:** are atoms of the same element with the same proton number but different number of neutrons
  - Isotopes have similar chemical properties since they have same number of protons and electrons (so chemical interactions are similar)
  - Isotopes have different physical properties since they have different number of neutrons, causing them to have different masses and therefore different physical interactions

## 1.3. Behaviour of a Beam of Subatomic Particles



- **Protons:** positively charged ∴ deflected to -ve pole
- **Neutrons:** no charge ∴ not deflected
- **Electrons:** negatively charged ∴ deflected to +ve pole

- e<sup>-</sup> lighter than P<sup>+</sup> ∴ deflected at greater angle

## 1.4. Electronic Configuration

- Electrons are arranged in energy levels called shells
- Each shell is described by a principle quantum no. (P.Q)
- As the P.Q. increases, energy of shell increases
- Inside the shell there are subshells: *s*, *p*, *d* and *f*
- **Orbital:** region in space where there is a maximum probability of finding an electron



- Each orbital can hold 2e<sup>-</sup>s in opposite directions
- When e<sup>-</sup>s are placed in a set of orbital of equal energy, they occupy them singly and then pairing takes place
- e<sup>-</sup>s placed in opposite direction: both -vely charge & if placed in same direction, they'd repel. In opposite direction they create a spin to reduce repulsion
- Completely filled or half filled (i.e. one e<sup>-</sup> in each orbital) are more stable (reduced repulsion)

Examples of this method are shown below:

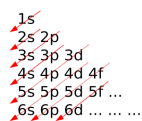
			1s	2s	2p
Lithium	Li	1s <sup>2</sup> 2s <sup>1</sup>	↑↓	↑	□ □ □
Beryllium	Be	1s <sup>2</sup> 2s <sup>2</sup>	↑↓	↑↓	□ □ □
Boron	B	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>	↑↓	↑↓	↑ □ □
Carbon	C	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>	↑↓	↑↓	↑ ↑ □
Nitrogen	N	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>	↑↓	↑↓	↑ ↑ ↑
Oxygen	O	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>	↑↓	↑↓	↑↓ ↑ ↑
Fluorine	F	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	↑↓	↑↓	↑↓ ↑↓ ↑
Neon	Ne	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>	↑↓	↑↓	↑↓ ↑↓ ↑↓

(e.g: period 3 elements), an electron would prefer the 4s orbital over 3d while filling up. For example, 2 electrons in Titanium would be filled into the 4s orbital before 2 electrons are filled in the 3d orbital. This is because the 4s orbital is a more stable (lower) energy level than the 3d orbital. However, while losing electrons, the electrons from the 4s orbital would be lost first and then those from 3d orbital will be lost. This is because the 4s orbital is outer than the 3d orbital.

## 1.5. Subshells

	s	p	d	f
<b>Orbitals</b>	1	3	5	7
<b>Max e<sup>-</sup>s</b>	2	6	10	14

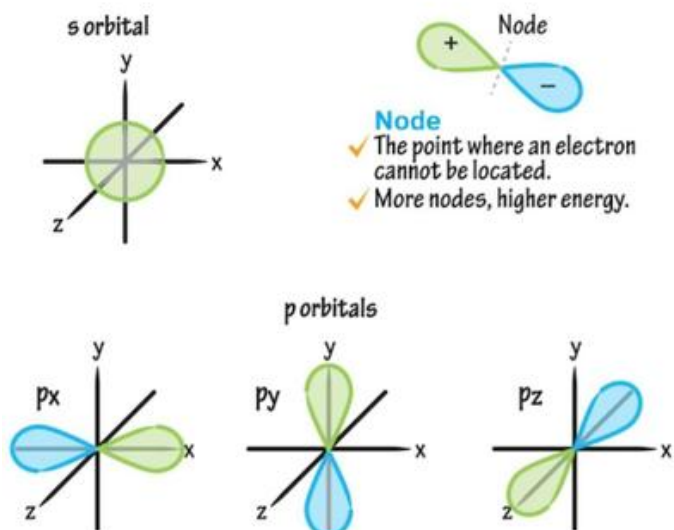
- **Aufbau's principle:** method of showing how atomic orbitals are filled in a definite order to give lowest energy arrangement possible



- Energy difference between  $4s$  &  $3d$  very small  $\therefore$  an  $e^-$  from  $4s$  can be promoted to half-fill or full-fill  $3d$  orbital, to make atom more stable
- When filling, fill  $4s$  before  $3d$  and when removing, also remove first from  $4s$

## Orbitals

$s$  orbitals are spherical with the nucleus at the centre  
 $p$  orbitals are dumbbell shaped

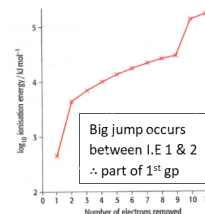


A free radical is a species with one or more unpaired electrons.

Note: ions and free radicals are different.

### 1.7. Ionization Energies (I.E)

- **1<sup>st</sup> I.E:** energy needed to remove 1 mole of  $e^-$ s from 1 mole of gaseous atom to form 1 mole of unipositive ions
- **Each successive I.E is higher than previous one** because as  $e^-$ s are removed, protons  $>$   $e^-$ s  $\therefore$  attraction between protons and remaining electrons increases
- Successive I.Es have large jump in their value when  $e^-$ s removed from lower energy shell
- Deduce group no. by checking when 1<sup>st</sup> big jump occurs



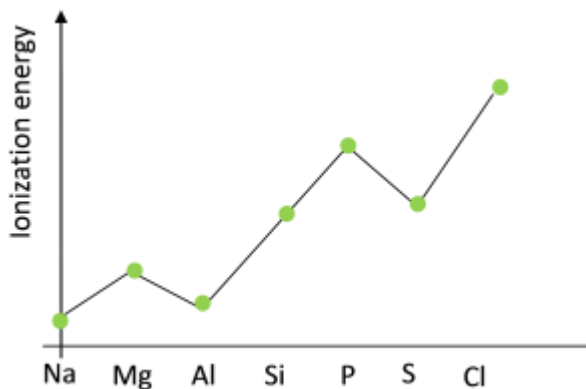
### 1.8. Factors affecting Ionization Energy

- Nuclear charge
  - +ve charge due to protons in nucleus
  - Greater nuclear charge greater ionization energy
- Shielding effect
  - Inner shells of  $e^-$ s repel outermost  $e^-$ s, thus shielding them from +ve nucleus. The more  $e^-$  shells, the greater is the shielding effect
  - Greater effect lower I.E because lesser attractive force between nucleus & outer  $e^-$ s
- Atomic radius
  - Distance from the centre of the nucleus to the outermost orbit
  - As number of electron shells increases, atomic radius increases
  - As number of electrons in outermost shell increases, atomic radius decreases as the electrostatic attraction between nucleus and outer electrons increases
  - Greater radius lower I.E; distance of outermost  $e^-$  to nucleus is large  $\therefore$  less energy needed to remove  $e^-$
- Stable config.
  - High I.E needed to remove  $e^-$ s from completely or half-filled orbitals

### 1.9. General 1<sup>st</sup> Ionization Energy Trends

- Down a group (**decreases**):
  - New shells added
  - Attraction of nucleus to valence  $e^-$ s decreases
  - Shielding effect increases
- Across a period (**increases**):
  - Shell no. remains same
  - Proton no. increases
  - Effective nuclear charge increases
  - Atomic radius decreases

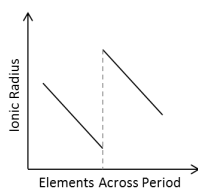
### 1.10. Trend in 1<sup>st</sup> I.E across 3<sup>rd</sup> Period



- **I.E of Al lower than Mg:**  $e^-$  removed in Al is from higher energy 3p orbital which is further away from nucleus than 3s  $e^-$  being removed from Mg. Nuclear attraction is less for 3p than 3s.  $\therefore$  I.E of Al is lower than Mg
- **I.E of S lower than P:**  $e^-$  being removed in P is in a half filled, more stable 3p orbital whereas in S, the pairing of electrons in 3p results in increased repulsion.  $\therefore$  less energy need to remove an  $e^-$

### 1.11. Ionic Radius

- **Ionic radius:** describes the size of an ion



- **Positive ion:** smaller radius than original neutral atom because shell no. decreases, screening effect decreases but the attraction of nucleus increases.
- **Negative ion:** larger ionic radius than neutral atom because  $e^-$ s added while nuclear charge remains same

Groups	1 to 3	5 to 7
Ion	Positive	Negative
No. of shells	$n - 1$	$n$
<b>Across the period:</b>		
<ul style="list-style-type: none"> <li>• Proton no. and effective nuclear charge increases</li> <li>• Ionic radius decreases</li> </ul>		

- Negative ions always larger than positive ions in the same period as they have one more shell
- Ionic radius increases down the group since number of electron shells increases
- As negative charge on anion increases, ionic radius increases since the number of electrons gained increases such that the number of electrons exceeds the number of protons

- As positive charge on cation increases, number of electrons lost increases, so electrostatic attraction between nucleus and outer electrons increases

## 2. Atoms, Molecules and Stoichiometry

### 2.1. Relative Mass

- **Atomic mass ( $A_r$ ):** weighted average mass of an atom
- **Molecular mass ( $M_r$ ):** mass of a molecule
- **Formula mass:** mass of one formula unit of a compound
- **Isotopic mass:** mass of a particular isotope of an element
- Compared with  $^{12}\text{C}$  where one atom of  $^{12}\text{C}$  has mass of exactly 12 units
- Unified atomic mass unit:  $u = 1.66 \times 10^{-27}\text{kg}$

### 2.2. The Mole

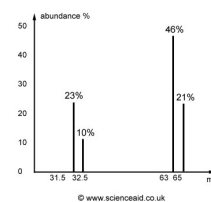
- **Mole:** amount of substance that has the same number of particles (atoms, ions, molecules or electrons) as there are atoms in exactly 12g of the carbon-12 isotope.
- **Avogadro's constant:** number of atoms, ions, molecules or electrons in a mole =  $6.02 \times 10^{23}$

### 2.3. Mass Spectra

- Abundance of isotopes can be represented on a mass spectra diagram

$$\text{Relative Abundance} = \frac{\text{Peak Height}}{\text{Total Height}} \times 100\%$$

$$A_r = \sum \frac{\text{Mass} \times \text{Relative Abundance}}{100}$$



### 2.4. Empirical and Molecular Formulae

- **Empirical formula:** gives simplest ratio of different atoms present in a molecule
- **Molecular formula:** gives actual numbers of each type of atom in a molecule
- Molecular formula can be calculated using the  $M_r$  of a compound and its empirical formula

$$\text{Molecular Formula} = (\text{Empirical Formula})_n$$

$$\text{Where } n = \frac{\text{Molecular Mass}}{\text{Mass of Empirical Formula}}$$



$$\% \text{ Composition} = \frac{\text{Atomic Mass} \times \text{No. of Moles}}{\text{Molar Mass of Compound}} \times 100\%$$

### Empirical vs Molecular Formula

Empirical	Molecular
Simplest whole number ratio of elements	Actual whole number ratio Multiple of Empirical
CO <sub>2</sub>	CO <sub>2</sub>
H <sub>2</sub> O	H <sub>2</sub> O
NO <sub>2</sub>	N <sub>2</sub> O <sub>4</sub>
P <sub>2</sub> O <sub>5</sub>	P <sub>4</sub> O <sub>10</sub>
C <sub>5</sub> H <sub>11</sub>	C <sub>10</sub> H <sub>22</sub>
C <sub>2</sub> H <sub>6</sub> O	C <sub>6</sub> H <sub>18</sub> O <sub>3</sub>

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## 2.5. Calculations involving Mole Concept

$$\text{Moles} = \frac{\text{Mass}}{\text{Molar Mass}}$$

$$\text{Volume of a Gas} = \text{Moles} \times 24$$

- Formula applies to gases at r.t.p.
- Unit of volume is  $dm^3$  and  $1000cm^3 = 1dm^3$

$$\text{Concentration} = \frac{\text{Moles}}{\text{Volume}}$$

- Concentration unit =  $mol\ dm^{-3}$

Anhydrous - a compound in which all water molecules are removed

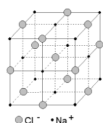
Hydrated - a compound which has a number of water molecules associated with its crystalline structure

Water of Crystallisation - these water molecules in a hydrated compound are called water of crystallisation

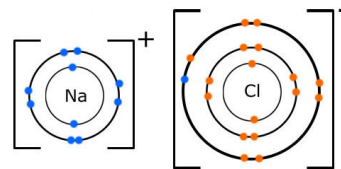
## 3. Chemical Bonding

### 3.1. Ionic (Electrovalent) Bonding

- Ionic bond is the electrostatic attraction between oppositely charged ions.
- Structure: giant ionic lattice, crystalline solids



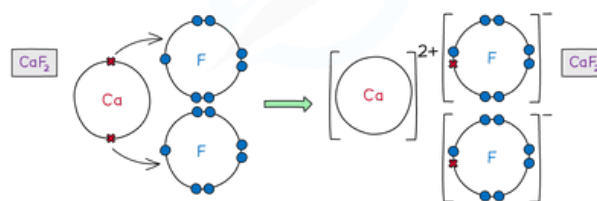
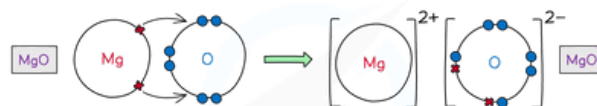
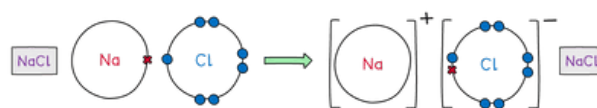
- Have high melting and boiling points



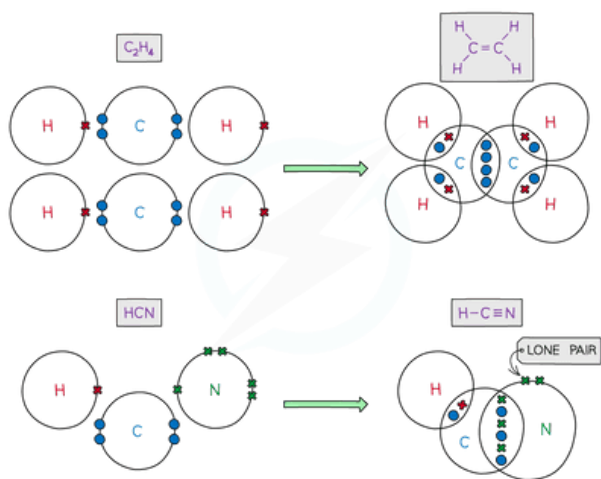
- Coordination number:** number of oppositely charged ions that surround a particular ion in an ionic solid
- E.g: NaCl, MgCl<sub>2</sub>

## Dot and Cross Diagrams

- For anions, electrons are added to the atom (e.g. Chlorine forms Chloride Cl<sup>-</sup> ions)
- For cations, electrons are removed from the atom (e.g. Sodium forms Na<sup>+</sup> ions)
- Atoms form the same number of bonds as the number of electrons required to be added/removed for maximum stability. (e.g: Chlorine will form 1 bond, Sodium will form 1 bond, but Calcium Ca<sup>2+</sup> will form 2 bonds)
- The central atom may expand its octet to form more bonds if necessary (e.g: S<sub>8</sub>)
- In ionic compounds, electrons are shown to be completely transferred to each of the ions in the compound.



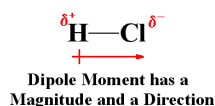
- In covalent compounds, electrons are shown to be shared between the atoms in the molecule



7. Use a legend of different shapes (e.g solid circle, unfilled circle, triangle, cross etc) to show which electrons come from which atom in the same way as colours have been used in the above diagrams

### 3.3. Electronegativity

- Ability of a particular atom, covalently bonded, to attract the bonded pair of  $e^-$ s towards itself
- Electronegativity depends on:
  - Radius of atom (atomic size) **inversely**  $\propto$  electronegativity
  - Nuclear attraction **directly**  $\propto$  electronegativity
- Electronegativity **increases across a period** because atomic radius  $\downarrow$  and nuclear attraction  $\uparrow$ , so polarity  $\uparrow$
- Electronegativity **decreases down a group** because atomic radius  $\uparrow$  and nuclear attraction  $\downarrow$ , so polarity  $\downarrow$
- **Dipole moment:** slight charges on atoms in a covalent bond due to differences in electronegativity
- The difference between the electronegativity of two atoms in a compound determines the overall dipole moment and overall polarity of the compound.
- A large difference in electronegativity will make the bond more polar (more ionic in nature) but a small difference in electronegativity will make the bond less polar (more covalent in nature)

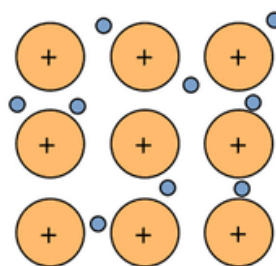


### 3.4. Metallic Bonding

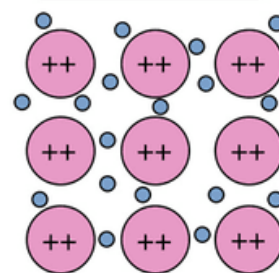
- Strong electrostatic forces of attraction between metal cations and delocalized mobile electrons
- **Structure:** lattice of +ve ions surrounded by mobile  $e^-$ s
- **Strength of metallic bond increases with:**
  - Increasing **positive charge** on the ions in the lattice
  - Decreasing **size of metal ions** in the lattice
  - Increasing **number of mobile  $e^-$ s** per atom

## Metallic Bond Examples

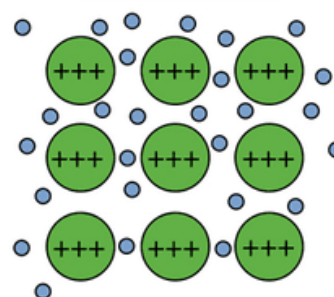
### Sodium



### Magnesium



### Aluminum



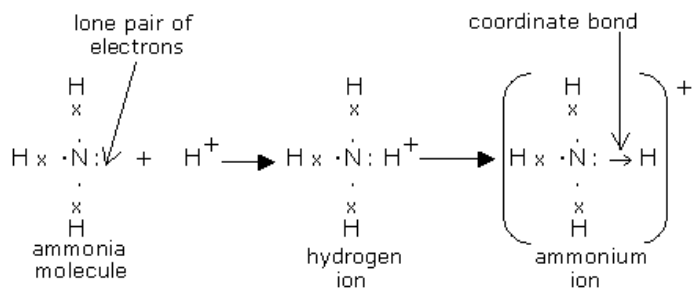
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### 3.5. Covalent Bonding

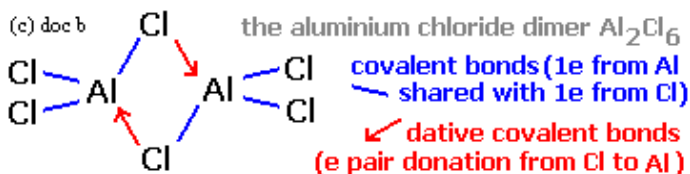
- Covalent bond is the bond formed by the sharing of pairs of electrons between the nuclei of two atoms.
- **Bonding electrons:**  $e^-$ s involved in bond formation
- **Non-bonding electrons** or **lone pair:** pair of valence  $e^-$ s that are not involved in bond formation
- Covalent compounds are made of molecules which are held together by weak intermolecular forces
- They have low melting and boiling points

### 3.6. Coordinate/Dative Bonding

- Coordinate bond is a covalent bond where both electrons in the bond come from the same atom
- **Conditions:**
  - An atom should have a lone pair of electrons
  - An atom should be in need of a pair of electrons
- **Donor:** the atom that supplies the pair of electrons
- **Acceptor:** the atom that accepts the pair of electrons
- Coordinate bond is represented by an " $\rightarrow$ " drawn from the atom donating to towards the atom accepting
- **Formation of Ammonium ion  $NH_4^+$ :**



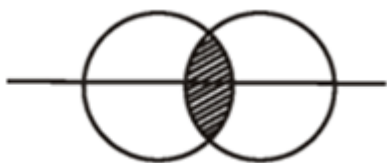
• Formation of AlCl<sub>3</sub> dimer (Al<sub>2</sub>Cl<sub>6</sub>):



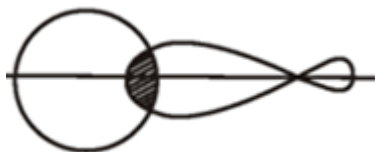
- Above 750°C, exists as vapor & covalent molecule AlCl<sub>3</sub>
- As vapor cools, exists as dimer Al<sub>2</sub>Cl<sub>6</sub>
- Bond angle as AlCl<sub>3</sub> = 120°
- Bond angle as Al<sub>2</sub>Cl<sub>6</sub> = 109.5°

### 3.7. Orbital Overlap

- For a covalent bond to form, atomic orbitals containing unpaired valence electrons must overlap each other
- S - S (Sigma  $\Sigma$ )



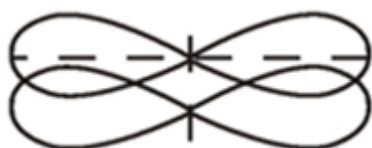
- S - P (Sigma  $\Sigma$ )



- P - P (Sigma  $\Sigma$ )



- P - P (Pi  $\pi$ )



- Sigma bond has greater overlap, ∴  $\sigma > \pi$
- Pi bond cannot exist without a Sigma bond.

**Note:** Elements in Period 3 can expand their octet by making use of the energetically accessible but lower lying d-subshell for bonding. This means that some elements of period 3 can bond with more than 4 electrons at once. (e.g: Sulfur, Phosphorus etc)

### 3.8. Shapes of Covalent Molecules

- Shape and bond angles of molecules depend on:
  - The number of pairs of electrons around central atom
  - Whether these pairs are lone pairs or bonded pairs
- Valence shell electrons are arranged in pairs to minimize repulsion between themselves
- Order of repulsion strength (VSEPR Theory):



- 2 pairs of e's
  - 2 bonded
  - Linear
  - 180°
  - E.g. CO<sub>2</sub>



- 3 pairs of e's
  - 3 bonded
  - Trigonal planar
  - 120°
  - E.g. BF<sub>3</sub>



- 4 pairs of e's
  - 4 bonded
  - Tetrahedral
  - 109.5°
  - E.g. CH<sub>4</sub>



- 3 bonded, 1 lone
  - Pyramidal
  - 107°
  - E.g. NH<sub>3</sub>



- 2 bonded, 2 lone
  - Angular
  - 104.5°
  - E.g. H<sub>2</sub>O



- 5 pairs of e<sup>-</sup>s
  - 5 bonded
    - Trigonal Bipyramid
    - 90°
    - E.g. PF<sub>5</sub>



- 6 pairs of e<sup>-</sup>s
  - 6 bonded
    - Octahedral
    - 90°
    - E.g. SF<sub>6</sub>



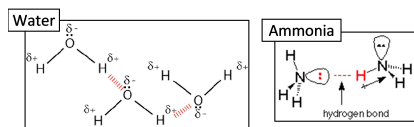
### 3.9. Bonds

- **Bond energy:** energy needed to break one mole of a given bond in one mole of gaseous molecules
- **Bond length:** distance between the centers of two nuclei of two adjacent atoms
- Double bonds are shorter than single bonds because double bonds have a greater negative charge density between the two atomic nuclei hence greater attraction
- Bond length depends on radii of the two bonded atoms; larger the radius, longer the bond length
- Strength of the bond depends on the length of the bond



### 3.10. Hydrogen Bonding

- Strongest type of intermolecular force in covalent bonds
- For hydrogen bonding to occur, we need:
  - Molecule having a H atom bonded to F, O or N
  - Molecule having F, O or N atom with lone pair of e<sup>-</sup>s



**Note:** Important properties of water (high melting/boiling points, high surface tension) are due to the strong hydrogen bonds present between water molecules.

### 3.11. Polar and Non-Polar

#### Polar Covalent Bonds

- Bonds with slight ionic character
- Bond formed with **atoms of different electronegativity**
- Bonding e<sup>-</sup>s attracted more towards atom with greater electronegativity ∴ unequal sharing of electrons ∴ molecule develops slight charges = **Polar Molecule**

- Polar molecules have dipoles; electric charges of equal magnitude and opposite sign
- The greater the difference in electronegativity of the two bonded atoms, the greater is the ionic character

#### Non-Polar Covalent Bonds

- Bond formed between:
  - **Identical atoms:** the electronegativity of both atoms is the same so pair of electron shared equally
  - **Symmetrical polyatomic molecules:** dipoles of bond exert equal & opposite effects hence cancel charge
- Non-polar molecules have no overall charge

### 3.12. Intermolecular Forces

- **Intermolecular forces:** weak forces present between two covalent molecules

#### Induced Dipole (Van Der Waals' Forces)

- Very weak forces present between **non-polar molecules**
- Due to constant motion of e<sup>-</sup>s, at an instant, a non-polar molecule develops poles due to distortion of electron density giving rise to instantaneous dipole, which is able to induce a dipole in the adjacent molecules
- Van der Waals forces **increase with:**
  - increasing **number of contact points** between molecules; point where molecules come close together
  - increasing **number of electrons** (+ protons) in molecule



#### Permanent Dipole-Dipole Forces

- Weak forces present between polar molecules
- Molecules always attracted to charged rod, whether +ve or -ve because molecules have +ve and -ve charges

### 3.13. Summary

	Metal + Non-Metal	Metals Only	Non-Metals Only		
Bonding	Ionic	Metallic	Covalent		
			Molecular		Macromolecule
			Polar	Non-Polar	
Structure	Giant ionic lattice	Giant metallic lattice	Molecular Structure	Giant Covalent	
Particles Present	+ve and -ve ions	+ve ions and -ve electrons	Molecular	Atoms	
Forces	Electrostatic		Weak intermolecular and Strong intramolecular	Strong covalent	
M.P. / B.P.	High		Low	Highest	
Solubility in Water	Yes	No	No except hydrogen-bonded	No	
Physical State at R.T.P	Solid (hard)		Soft solid, liquid or gas	Very Hard Solid	
Electrical Conductivity	Molten/aqueous	Good	No	No except graphite	

## 4. States of Matter

### 4.1. Basic Assumptions of Kinetic Theory

- **Ideal gas:** a gas whose volume varies in proportion to temperature and in inverse proportion to pressure.
- Noble gases such as helium and neon approach ideal behavior because of their low intermolecular forces.

#### Ideal Gas Laws:

- Gas molecules move rapidly and randomly
- Distance between gas molecules is greater than diameter of molecules  $\therefore$  volume is negligible
- No forces of attraction/repulsion between molecules
- All collisions between particles are elastic  $E_K$  conserved
- Temperature of gas related to average  $E_K$  of molecules
- **Conditions at which gases behave ideally:**
  - High temperature
  - Low pressure

#### Limitations of Ideal Gas Laws:

- Real gases do not obey kinetic theory in two ways:
  - There is **not** zero attraction between molecules
  - We **cannot** ignore volume of molecules themselves

#### Deviations visible at low temp. and high pressure

- Molecules are close to each other
- Volume of molecules not negligible relative to container
- VDW forces present, pulling molecules to each other
- Pressure is lower than expected from ideal gas
- Effective volume is less than expected from ideal gas

### 4.2. General Gas Equations

$$PV = nRT$$

$$M_r = \frac{Mass \times RT}{PV}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Quantity	Unit	Conversion
Pressure	Pascal	1KPa = 1000Pa
Volume	m <sup>3</sup>	1m <sup>3</sup> = 1000dm <sup>3</sup> = 1x10 <sup>6</sup> cm <sup>3</sup>
Temperature	°K	°C + 273

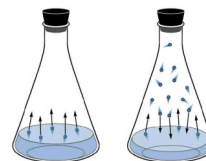
- **Standard Conditions:** 101KPa and 273°K

$$\text{Mole Fraction} = \frac{\text{Mols of One Gas}}{\text{Total Mols of Gases}}$$

$$\text{Partial Pressure of a Gas} = \text{Mole Fraction} \times \text{Total Pressure}$$

### 4.3. Liquid State

- Particles touching but may have gaps
- Have  $E_K$  to slide past each other in random motion
- **Enthalpy of fusion:** heat energy required to change 1 mole of solid into a liquid at its melting point
- **Heating a solid (melting):**
  - Energy transferred makes solid particles vibrate faster
  - Forces of attraction weaken & solid changes to liquid
- **Enthalpy of vaporization:** heat energy required to change 1 mole of liquid into a gas at its boiling point
- **Heating a liquid (vaporization):**
  - Energy transferred makes liquid particles move faster
  - Forces of attraction weaken
  - Highest energy particles escape first
  - Liquid starts to evaporate – temp. below b.p.
  - Forces weaken further – particles move faster & spread
  - Liquid boils – temp. at b.p.
- **The evaporation of a liquid in a closed container**



- Constant evaporation from surface
- Particles continue to break away from surface but are trapped in space above the liquid
- As gaseous particles collide, some of them hit the surface of the liquid again, and become trapped there
- An equilibrium is set up in which number of particles leaving surface is balanced by number rejoining it.
- Liquid water molecules  $\rightleftharpoons$  Vapor water molecules
- In this equilibrium, there will be a fixed number of the gaseous particles in the space above liquid.
- **Vapor pressure:** pressure exerted by a vapor in equilibrium with a liquid.
- Vapor pressure **increases** as:

Temp. ↑ Ek ↑ Forces weaken More vapor

## 4.4. Recycling

- **Finite resource:** resource which doesn't get replaced at the same rate that it is used up.
- **Examples of finite resources:** copper, aluminium, glass
- **Advantage of Recycling:**
  - Saves energy
  - Reduces environmental issues
  - Conserves ore supplies
  - Less wastage
  - Cheaper than extracting

## States of Matter & Properties

### 4.5. Solubility

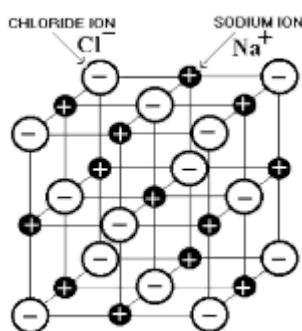
- For solids, generally solubility increases with increasing temperature as the increase in temperature facilitates the overcoming of intermolecular bonds, making it easier for the solid to dissolve
- For gases, generally solubility decreases with increasing temperature as the pressure of the gas increases (pressure only affects solubility of gases)

### Conductivity

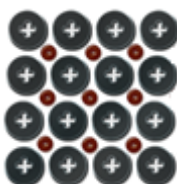
- Solids (metals) are generally the best conductors of electricity while gases are the worst conductors
- Solids (metals) are generally better conductors of heat than liquids, while liquids are better thermal conductors than gases. This is because of the proximity of molecules in solids allowing heat to be transferred rapidly through vibrations of neighbouring molecules

### 4.6. Solid State

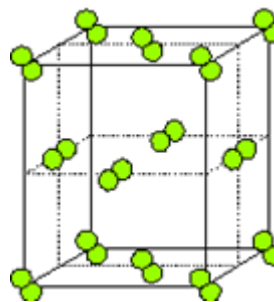
- Ionic lattice



- Metallic lattice

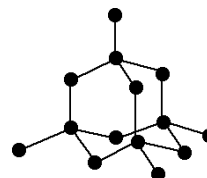


- Simple molecular

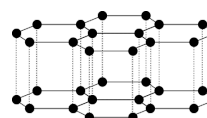


#### Macromolecular Lattice:

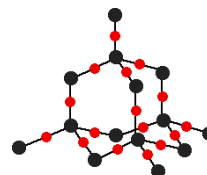
- **Diamond:**
  - High m.p./b.p. - each carbon forms four covalent bonds
  - Hard - tetrahedral structure
  - Doesn't conduct heat or electricity - no free e<sup>-</sup>
  - Used for cutting as is strongest known substance and has sharp edges



- **Graphite:**
  - Three strong (sp<sup>2</sup>) covalent bonds
  - Fourth e<sup>-</sup> in p orbital ∴ forms a pi bond, forming a cloud of delocalised electron above and below the planes
  - Layers kept together by weak Van der Waal's forces
  - High m.p./b.p. - strong covalent bonds throughout
  - Soft - forces between layers are weak
  - Conducts electricity - has delocalized electrons



- **Silicon(IV) Oxide:**
  - Each Si is bonded to 4 oxygen atoms, but each oxygen is bonded to 2 Si atoms
  - Sand is largely SiO<sub>2</sub>
  - Similar properties to diamond

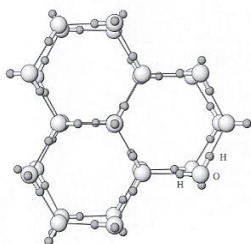


#### Hydrogen Bonded Lattice:

- In ice form, water molecules slow down and come closer together
- Due to polarity, molecules form hydrogen bonds between lone pairs of oxygen & δ<sup>+</sup> charge of hydrogens
- Each water molecule has 2 H-bonds



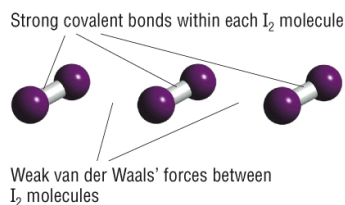
- They arrange themselves into an open crystalline, hexagonal structure
- Due to large spaces, ice is less dense than water



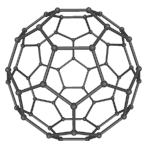
- **Effect of Hydrogen Bonding on Physical Properties:**
  - **Relatively high m.p./b.p.:** many strong H-bonds
  - **High viscosity:** hydrogen bonding reduces ability of water molecules to slide over each other
  - **High surface tension:** hydrogen bonds in water exert a downward force on surface of liquid
  - **Ice less dense than water:** larger spaces between molecules in hexagonal structure

#### Simple Molecular Lattice:

- **Iodine:**
  - Dark grey crystalline solid; vaporizes into purple gas
  - m.p./b.p. are slightly higher than room temp
  - Slightly soluble in water; dissolves in organic solvents
  - Diatomic molecule formed due to covalent bond between individual atoms
  - Molecules have weak Van der Waals forces of attraction between them

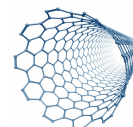


- **Fullerenes:**
  - **Buckminsterfullerenes(C<sub>60</sub>)**
    - C atoms in pentagonal and hexagonal rings
    - Spherical
    - C<sub>60</sub> molecules held together by VDWs
    - Conducts heat and electricity
    - Very strong and tough
    - Insoluble in water
    - High m.p./b.p.



- **Nanotubes**
  - C atoms in hexagonal rings only
  - Cylindrical
  - Structure is rod like due to continuing rings

- Conducts heat and electricity
- Very strong and tough
- Insoluble in water
- High m.p./b.p.



## 5. Chemical Energetics

### 5.1. Energy Change in Reactions

Exothermic Reactions	Endothermic Reactions
Energy given out	Energy taken in
Surrounding warmer	Surrounding cooler
Bond making	Bond breaking
$\Delta H$ negative	$\Delta H$ positive
$E_{\text{Reactants}} > E_{\text{Products}}$	$E_{\text{Reactants}} < E_{\text{Products}}$

$1 \text{ mol dm}^{-3}$

### 5.2. Enthalpy Change Definitions

Standard molar enthalpy change of:

1. **Combustion  $\Delta H_C$** 
  1. Enthalpy change when 1 mole of element or compound is completely combusted under standard conditions in their standard states
2. **Formation  $\Delta H_f$** 
  1. Enthalpy change when 1 mole of compound is formed from its elements under standard conditions in their standard state
3. **Solution  $\Delta H_{sol}$** 
  1. Enthalpy change when 1 mole of a solute is dissolved in a solvent to form an infinitely dilute solution under standard conditions in their standard states
4. **Hydration  $\Delta H_{hyd}$** 
  1. Enthalpy change when 1 mole of ions in the gas phase are dissolved in water under standard conditions in their standard states
5. **Atomisation  $\Delta H_{at}$** 
  1. Enthalpy change when 1 mole of gaseous atom formed from its element under standard conditions in their standard states
6. **Neutralization  $\Delta H_n$** 
  1. Enthalpy change when 1 mole of  $H^+$  and  $OH^-$  combine to form 1 mole of  $H_2O$  under standard conditions in their standard states

### 5.3. Bond Energy

- Energy needed to break a specific covalent bond
- Also how much energy is released when a bond forms

### 5.4. Calculating Enthalpy Changes

$$\Delta H = -mc\Delta T$$

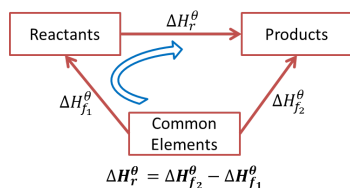
- When substance dissolved in water use *c* & *m* of water
- $\Delta T$  is change in temp.: add -ve or +ve to show rise/fall

### 5.5. Hess's Law

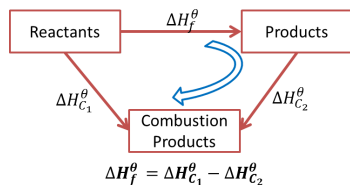
- The total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same.
- Reason to use Hess's Law:
  - Std. conditions hard to maintain (e.g. exo/endo)
  - Elements don't always react directly

### 5.6. Calculating Enthalpy Change of...

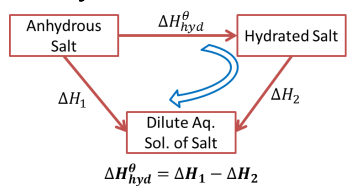
...Reaction from Formation



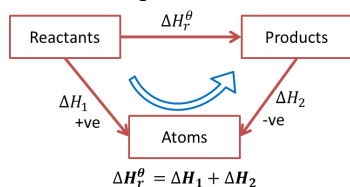
...Formation from Combustion



...Hydration from Anhydrous Salt



...Reaction from Bond Energies



## Worked examples - Hess Cycle

5 Alkanes such as methane, CH<sub>4</sub>, undergo few chemical reactions. Methane will, however, react with chlorine but not with iodine.

Relevant standard enthalpy changes of formation for the reaction of methane with chlorine to form chloromethane, CH<sub>3</sub>Cl, are given below.

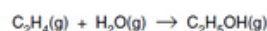
	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
CH <sub>4</sub>	-75
CH <sub>3</sub> Cl	-82
HCl	-92

(a) (i) Use the data to calculate  $\Delta H^\circ_{\text{reaction}}$  for the formation of CH<sub>3</sub>Cl.



Ethanol, C<sub>2</sub>H<sub>5</sub>OH, is a most important industrial chemical and is used as a solvent, a fuel and an intermediate in large scale organic synthesis.

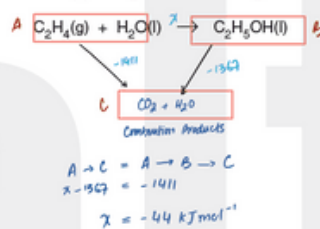
Ethanol is prepared industrially by the reaction of ethene and steam in the presence of a catalyst.



The standard enthalpy change of the reaction can be determined by using the standard enthalpy changes of combustion,  $\Delta H_c^\circ$ , at 298 K.

	$\Delta H_c^\circ / \text{kJ mol}^{-1}$
C <sub>2</sub> H <sub>4</sub> (g)	-1411
C <sub>2</sub> H <sub>5</sub> OH(l)	-1367

(a) Calculate the standard enthalpy change for the following reaction.



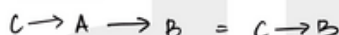
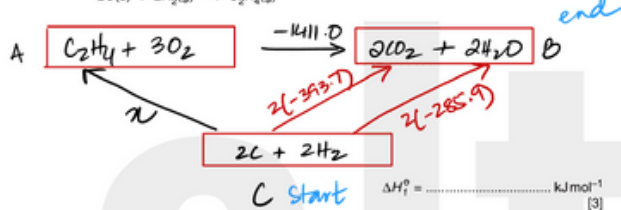




9 Carbon, hydrogen and ethene each burn exothermically in an excess of air.



Use the data to calculate the standard enthalpy change of formation,  $\Delta H_f^\circ$ , in  $\text{kJ mol}^{-1}$ , of ethene at 298 K.



$$x + (-1411) = 2(-393.7) + 2(-285.9)$$

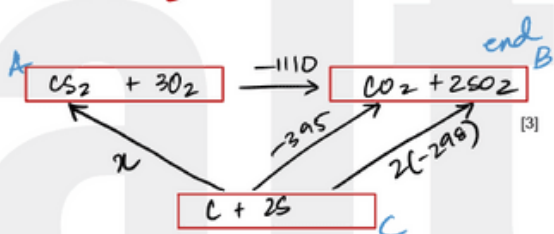
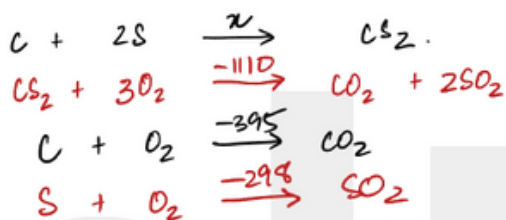
$$x = +51.8 \text{ kJ mol}^{-1}$$

Calculate the standard enthalpy change of formation of  $CS_2$  from the following data. Include a sign in your answer.

standard enthalpy change of combustion of  $CS_2 = -1110 \text{ kJ mol}^{-1}$

standard enthalpy change of formation of  $CO_2 = -395 \text{ kJ mol}^{-1}$

standard enthalpy change of formation of  $SO_2 = -298 \text{ kJ mol}^{-1}$



$$x + (-1110) = (-395) + 2(-298)$$

$$x = +119 \text{ kJ mol}^{-1}$$

Source: Alt Academy

## 6. Electrochemistry

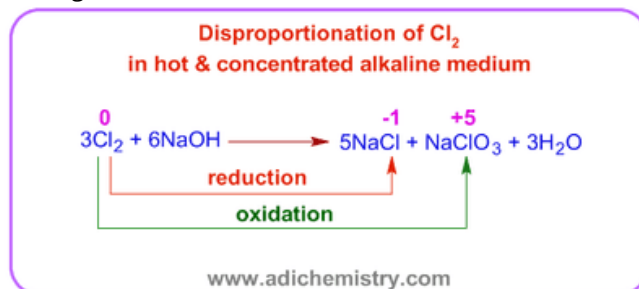
### 6.1. Calculating Oxidation Numbers

- Ionic Molecules: group number = valence electrons
- Covalent molecules:
  - Rules:
    - Atoms in a diatomic molecule; oxidation number = 0
    - Oxygen in a compound; oxidation number = -2

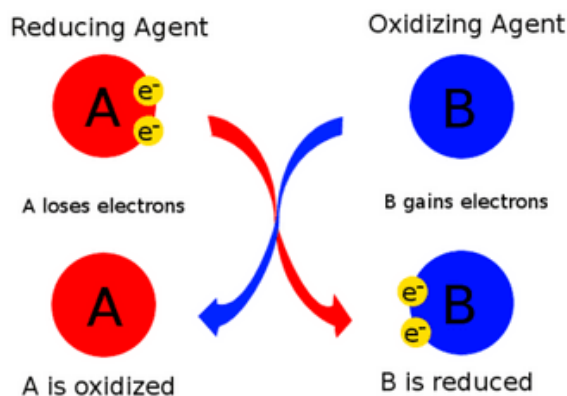
- Oxygen as peroxide; oxidation number = -1
- 1<sup>st</sup> group elements & hydrogen; oxidation number = +1
- H with highly reactive metal; oxidation number = -1
- Following these rules, all other atoms in a covalent bond must balance out the charge

### 6.2. Redox Reactions

- Reaction where both oxidation and reduction occur
- Can be shown with changes in oxidation numbers of elements from the product side to the reactant side
- E.g.  $Ca_2Si + 6H_2O \rightarrow 2Ca(OH)_2 + SiO_2 + 4H_2$ 
  - $Ca = +4 \rightarrow +2 \implies$  gain of negative charge  $\therefore$  reduction
  - $Si = -4 \rightarrow +4 \implies$  loss of negative charge  $\therefore$  oxidation
- Disproportionation Reaction: When the same species undergoes both oxidation and reduction in a reaction.



- Oxidising Agent: A substance which helps to oxidise another species by accepting electrons from it and itself gets reduced in the process
- Reducing Agent: A substance which helps to reduce another species by donating electrons to it and itself gets oxidised in the process



### 6.3. Balancing Equations

- Equation:  $HI + HNO_3 \rightarrow I_2 + N_2O_3 + H_2O$
- Half ionic:  $2I^- - 2e^- \rightarrow I_2$     $N^{+5} + 2e^- \rightarrow N^{+3}$

- For every 2 iodines, there will be 1 nitrogen
- Thus first put in correct ratio for iodine and nitrogen then balance hydrogens and oxygens
- **Balanced:**  $4HI + 2HNO_3 \rightarrow 2I_2 + N_2O_3 + 3H_2O$

## 7. Equilibria

- **Reversible reaction:** a reaction in which products can be changed back to reactants by reversing the conditions
- **Dynamic Equilibrium:** the state of a reversible reaction carried out in a closed container where the rates of forward and backward reactions are equal and constant

### 7.2. Le Chatelier's Principle

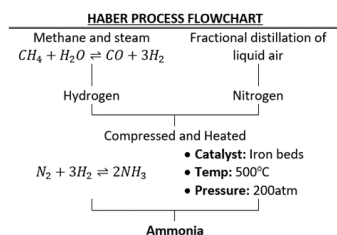
- When a chemical system in dynamic equilibrium is disturbed (conditions changed) it tends to respond in such a way so as to oppose the change and a new equilibrium is set up

By Le Chatelier's principle, when the	temperature	is increased, the system opposes the change by favouring	the endothermic side
	pressure		the side with fewer gas mols
	reactant conc.		the forward reaction

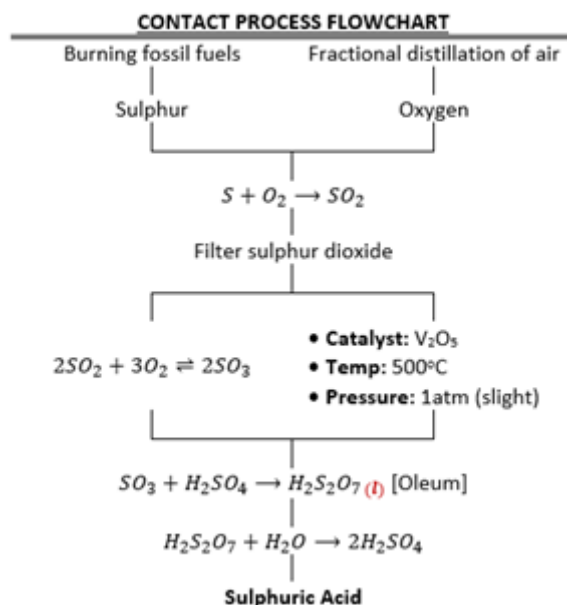
### 7.3. Equilibrium Constants

- Equilibrium constant expressed in terms of **concentration**
  - $K_C = \frac{[\text{Product}]^{\text{mols}}}{[\text{Reactant}]^{\text{mols}}}$
  - Only liquids and gases
- Equilibrium constant expressed in terms of **partial pressure**
  - $K_P = \frac{p(\text{Product})^{\text{mols}}}{p(\text{Reactant})^{\text{mols}}}$
  - Only gases
- Large value of  $K_C/K_P \Rightarrow$  equi. towards products side
- Smaller value of  $K_C/K_P \Rightarrow$  equi. towards reactants side
- $K_C/K_P$  changes only with changes in temperature
- The amount of reactants that disappear will always appear in the products in the same ratio as present in a balanced equation

### 7.4. Manufacture of Ammonia



### 7.5. Manufacture of Sulphuric Acid



- $SO_3$  not dissolved directly into water because reaction explosive and causes  $H_2SO_4$  to vaporize
- Forward reaction exothermic  $\therefore$  temp. not too high so rate of backward reaction doesn't increase & not too low so particles have  $E_K$  for collision and catalyst works
- Since reaction highly exothermic, gases must be cooled
- No impurities otherwise catalyst will be poisoned
- Atmospheric pressure enough because equilibrium already favours product side

### 7.6. Acid-Base Equilibria

- **Brønsted-Lowry Theory:**
  - An acid is a proton ( $H^+$ ) donor
  - A bases is a proton ( $H^+$ ) acceptor
- **Amphoteric:** substances that can act like bases or acids
- **Strong acid:** an acid that dissociates completely in solution (e.g: HCl)
- **Weak acid:** an acid that dissociates partially in solution (e.g: ethanoic acid)
- **Strong base:** a base that dissociates completely in solution (e.g: NaOH)
- **Weak base:** a base that dissociates partially in solution (e.g: ammonia)

Strong acids/bases react more vigorously than weak acids/bases.

Strong acids have lower pH values than weak acids.

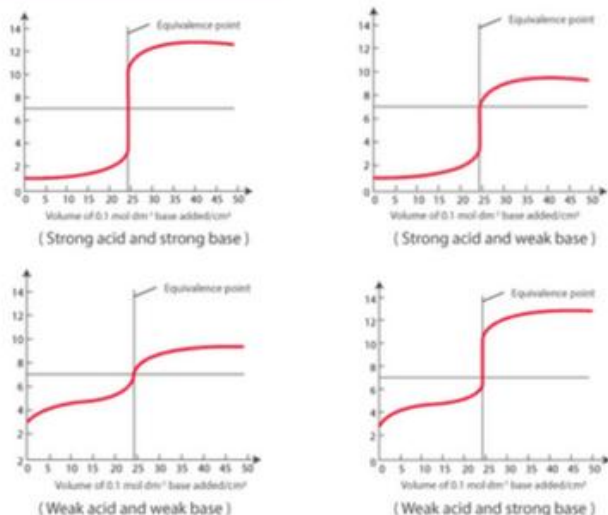
Strong bases have higher pH values than weak bases.

When an acid reacts with a base, salt & water are formed.

The pH changes in this neutralisation reaction can be graphed as shown in the image below:

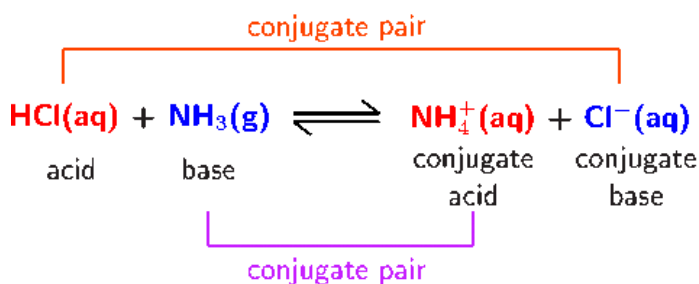
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TITRATION CURVES



7.7. Conjugate Pairs

- When acid-base reacts, an equilibrium mixture is formed



- HCl is a conjugate acid of base  $\text{Cl}^-$  & vice versa
- HCl is acid-I and  $\text{Cl}^-$  is base-I
- $\text{NH}_4^+$  is a conjugate acid of base  $\text{NH}_3$  & vice versa
- $\text{NH}_4^+$  is acid-II and  $\text{NH}_3$  is base-II

8. Reaction Kinetics

- Rate of a reaction:** change in concentration of reactants or products per unit time
- Activation energy:** minimum energy colliding particles must possess for a successful collision to take place
- Catalysis:** acceleration of a chemical reaction by catalyst

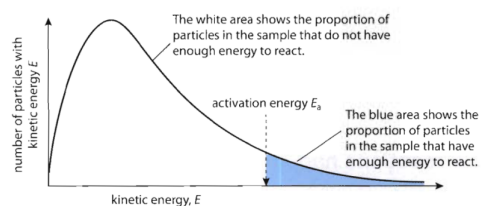
8.2. Effect of Concentration Changes

- Increasing conc. of reactants increases rate of reaction: more particles per unit volume, collision rate between reacting particles increases,  $\therefore$  rate of successful collision increases, resulting in increased rate of reaction.

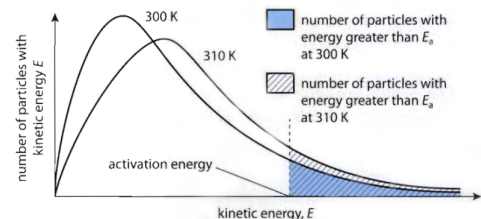
8.3. Maxwell-Boltzmann Theory

- Explains effect of temp. & catalyst on rate of reaction

- Based on distribution of energy among reacting molecules under different conditions



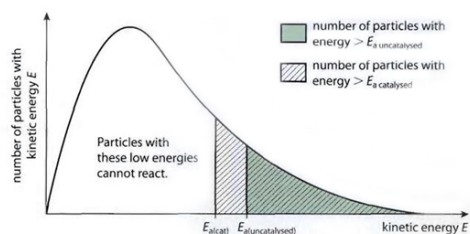
8.4. Effect of Temperature



- Number of collisions and chance of success will increase

8.5. Effect of Catalyst

- Catalyst:** a substance that increases rate of reaction but remains chemically unchanged itself at the end
- Does not alter the chemical composition of substances and only lowers the activation energy
- It provides a new route or mechanism to follow for reactants that requires less energy



- Curve unchanged, only activation energy changes
- Homogeneous catalysts:** reactant and catalyst are in the same physical state
- Heterogeneous catalysts:** reactant and catalyst are in different physical states
- Enzymes:** a protein molecule that is a biological catalyst. Most are specific to a substrate & function as lock-key

9. Chemical Periodicity

Group	1	2	3	4
Element	Sodium	Magnesium	Aluminium	Silicon
Character	Metal			Metalloid
Structure	Giant metallic lattice			Macromolecular
Bonding	Metallic bond between cations and delocalized e <sup>-</sup>			Covalent bonds between atoms

Group	1	2	3	4
Diagram				

### 9.2. Reaction of Elements with Oxygen

	Formulae	Reaction	Structure	Oxid.	Nature
Na	Na <sub>2</sub> O <sub>(s)</sub>	Burns yellow flame	Giant ionic lattice	+1	Basic
Mg	MgO <sub>(s)</sub>	Burns blinding white flame		+2	Basic
Al	Al <sub>2</sub> O <sub>3(s)</sub>	Coating		+3	Amphoteric
Si	SiO <sub>2(s)</sub>	Coating	Giant covalent	+4	W. acidic
P	P <sub>2</sub> O <sub>3(s)</sub> P <sub>2</sub> O <sub>5(s)</sub>	Burns yellow flame	Simple molecular	+3 +5	S. Acidic
S	SO <sub>2(g)</sub> SO <sub>3(g)</sub>	Burns blue flame		+4 +6	S. acidic

### 9.3. Reaction of Na & Mg with Water

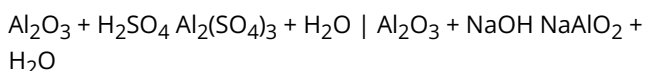
<b>Na &amp; Water</b>	2Na <sub>(s)</sub> + 2H <sub>2</sub> O <sub>(l)</sub> → 2NaOH <sub>(aq)</sub> + H <sub>2(g)</sub>	Very fast, floats, forms ball & dissolves
<b>Mg &amp; Water</b>	Mg <sub>(s)</sub> + 2H <sub>2</sub> O <sub>(l)</sub> → Mg(OH) <sub>2(aq)</sub> + H <sub>2(g)</sub>	Very slow
<b>Mg &amp; Steam</b>	Mg <sub>(s)</sub> + H <sub>2</sub> O <sub>(g)</sub> → MgO <sub>(s)</sub> + H <sub>2(g)</sub>	Very fast

### 9.4. Reaction of Oxides with Water

	Reaction	Oxid.	Nature
Na <sub>2</sub> O <sub>(s)</sub>	Na <sub>2</sub> O <sub>(s)</sub> + H <sub>2</sub> O <sub>(l)</sub> → 2NaOH <sub>(aq)</sub>	+1	S. Alkaline
MgO <sub>(s)</sub>	MgO <sub>(s)</sub> + H <sub>2</sub> O <sub>(l)</sub> → Mg(OH) <sub>2(aq)</sub>	+2	W. Alkaline
Al <sub>2</sub> O <sub>3(s)</sub>	<b>NO REACTION</b>		
SiO <sub>2(s)</sub>	<b>NO REACTION</b>		
P <sub>2</sub> O <sub>3(s)</sub>	P <sub>2</sub> O <sub>3(s)</sub> + 3H <sub>2</sub> O <sub>(l)</sub> → 2H <sub>3</sub> PO <sub>3(aq)</sub>	+3	S. Acidic
P <sub>2</sub> O <sub>5(s)</sub>	P <sub>2</sub> O <sub>5(s)</sub> + 3H <sub>2</sub> O <sub>(l)</sub> → 2H <sub>3</sub> PO <sub>4(aq)</sub>	+5	
SO <sub>2(g)</sub>	SO <sub>2(g)</sub> + H <sub>2</sub> O <sub>(l)</sub> → H <sub>2</sub> SO <sub>3(aq)</sub>	+4	S. Acidic
SO <sub>3(g)</sub>	SO <sub>3(g)</sub> + H <sub>2</sub> O <sub>(l)</sub> → H <sub>2</sub> SO <sub>4(aq)</sub>	+6	

### 9.5. Acid-Base Reactions

- Aluminium oxide is amphoteric ∴ reacts with acid and base



- Silicon dioxide is acidic: SiO<sub>2</sub> + NaOH (hot & conc.) → Na<sub>2</sub>SiO<sub>3</sub>
- Sulphur dioxide and trioxide are strongly acidic

	With	Produces
SO <sub>2(g)</sub>	NaOH	NaHSO <sub>3(aq)</sub>
SO <sub>2(g)</sub>	Excess NaOH	Na <sub>2</sub> SO <sub>3(aq)</sub> + H <sub>2</sub> O
SO <sub>3(g)</sub>	NaOH	NaHSO <sub>4(aq)</sub>
SO <sub>3(g)</sub>	Excess NaOH	Na <sub>2</sub> SO <sub>4(aq)</sub> + H <sub>2</sub> O

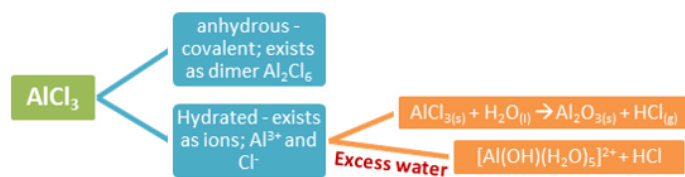
### 9.6. Reactions of Elements with Chlorine

	Formula	Structure	Oxid.	Nature
Na	NaCl <sub>(s)</sub>	Giant ionic	+1	Neutral
Mg	MgCl <sub>2(s)</sub>		+2	Neutral
Al	AlCl <sub>3(s)</sub>	Simple molecular	+3	Acidic
Si	SiCl <sub>4(l)</sub>		+4	S. Acidic
P	PCl <sub>3(l)</sub> PCl <sub>5(l)</sub>		+3 +5	S. Acidic

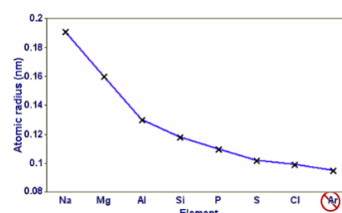
### 9.7. Reactions of Chloride with Water

	Reaction	Nature
NaCl <sub>(s)</sub>	NaCl <sub>(s)</sub> + H <sub>2</sub> O <sub>(l)</sub> → NaCl <sub>(aq)</sub>	Neutral
MgCl <sub>2(s)</sub>	MgCl <sub>2(s)</sub> + H <sub>2</sub> O <sub>(l)</sub> → MgCl <sub>2(aq)</sub>	W. Acidic
AlCl <sub>3(s)</sub>	AlCl <sub>3(s)</sub> + H <sub>2</sub> O <sub>(l)</sub> → Al <sub>2</sub> O <sub>3(s)</sub> + HCl <sub>(aq)</sub>	Acidic
SiCl <sub>4(l)</sub>	SiCl <sub>4(l)</sub> + H <sub>2</sub> O <sub>(l)</sub> → SiO <sub>2(s)</sub> + HCl <sub>(aq)</sub>	S. Acidic
PCl <sub>3(l)</sub> PCl <sub>5(l)</sub>	PCl <sub>3(l)</sub> + H <sub>2</sub> O <sub>(l)</sub> → H <sub>3</sub> PO <sub>3(aq)</sub> + HCl <sub>(g)</sub> PCl <sub>5(l)</sub> + H <sub>2</sub> O <sub>(l)</sub> → H <sub>3</sub> PO <sub>4(aq)</sub> + HCl <sub>(g)</sub>	S. Acidic

- Sodium chloride simply dissolves in water. Water is polar ∴ positive Na<sup>+</sup> attracted to OH<sup>-</sup> while Cl<sup>-</sup> attracted to H<sup>+</sup>
- MgCl<sub>2</sub> slightly acidic because Mg ion has smaller radius & higher charge ∴ attraction to water is so strong that H<sub>2</sub>O loses a proton and solution becomes slightly acidic



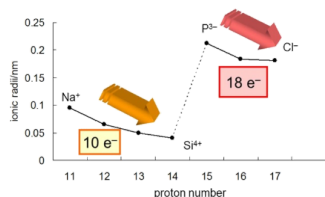
### 9.8. Atomic Radius



- P<sup>+</sup> in nucleus increases so nuclear charge increases
- There are more e<sup>-</sup>, but increase in shielding is negligible because each extra e<sup>-</sup> enters same principal energy level

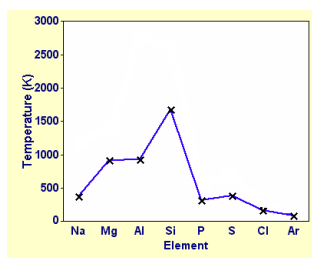
- ∴ force of attraction between nucleus & e<sup>-</sup> increases ...
- So atomic radius decreases.

### 9.9. Ionic Radius



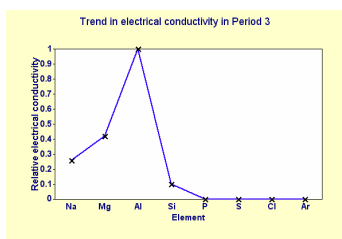
- Ionic radius decreases across a period however, since non-metals gain electrons, they have one more shell than metals therefore they always have a larger radius than metal ions

### 9.10. Melting Point



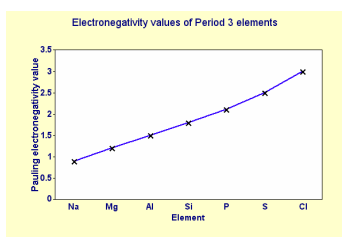
- Na Al m.p. increases because delocalized e<sup>-</sup> per atom increases making metallic bond stronger
- Si has highest m.p. due to giant covalent structure
- The larger the molecule size, the stronger the VDW forces ∴ S<sub>8</sub> > P<sub>4</sub> > Cl<sub>2</sub> > Ar

### 9.11. Electrical Conductivity



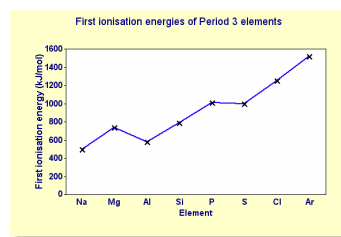
- Na < Mg < Al because no. of delocalized electrons which can carry charge increases
- Silicon is a semi-conductor
- Non-metals – covalent ∴ no charge

### 9.12. Electronegativity



- Increases across period because the bonded e<sup>-</sup> are in the same energy level but are attracted more strongly as no. of protons increases

### 9.13. First Ionization Energy

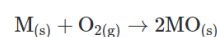


- Generally, increases as no. of protons increases
- Decrease Mg → Al: more distant and less effective nuclear charge on 3p orbital
- Decrease P → S: in S, one electron paired ∴ causing repulsion and easier to lose electron

### 9.14. Group II – Alkaline Earth Metals

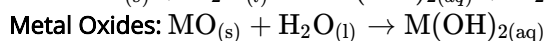
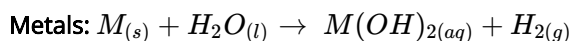
- m.p./b.p. decreases down group: atoms/ions get larger, distance between nuclei & e<sup>-</sup>s increases ∴ bonds weaker
- m.p./b.p. higher in gp. 2 than 1: 2e<sup>-</sup>s per atom donated into delocalized system ∴ metallic bonding stronger
- density increases down group: mass of atoms increases faster than their size (volume) as atomic no. increases

### 9.15. Reaction of Gp. 2 Metals with Oxygen



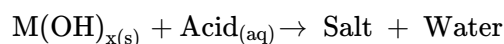
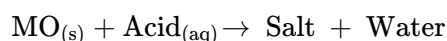
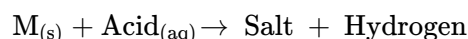
- All gp. 2 metals tarnish in air forming oxide coatings
- Burn vigorously in oxygen forming white solids

### 9.16. Reactions with Water

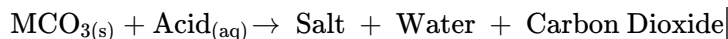


- Solubility of M, MO and M(OH)<sub>2</sub> increases down group
- Alkalinity of solution increases down the group
- Solubility of M and MO increases down the group
- Solubility of M(OH)<sub>2</sub> increases and MSO<sub>4</sub> decreases down group

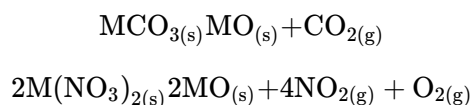
### 9.17. Reaction with Acid







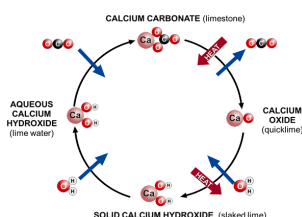
### 9.18. Thermal Decomposition of Gp. 2 Metals



- **NO<sub>2</sub>**: thick brown, acidic and soluble gas
- Thermal stability increases down the group ∴ decomposition becomes more difficult.

### 9.19. Uses of Group II Metals

- Calcium compounds:



- **Calcium oxide (lime)**: basic oxide used to neutralize acidic soil and used as a drying agent for drying ammonia
- **Calcium carbonate (limestone)**: used as building material (cement, concrete) etc., for extraction of iron, glass industry, neutralize soil or chemical waste

## 10. Group 17 – Halogens

### 10.1. Trends in Colour and Volatility

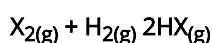
Fluorine	Yellow	Gas	m.p. & b.p. increases ↓	Volatility decreases ↓
Chlorine	Yellow-Green			
Bromine	Orange-Brown	Liquid		
Iodine	Grey-Blue	Solid		
Astatine	Black			

increases and volatility decreases

### 10.2. Oxidising Ability

- Halogens have high electron affinity (they gain electrons easily) hence they are good oxidising agents
- Oxidising ability decreases down the group because electron affinity decreases as atomic size increases.

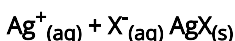
### 10.3. Some reactions of the halide ions



Product	Reaction Description
HF	Reacts explosively in all conditions
HCl	Reacts explosively in sunlight
HBr	Reacts slowly on heating
HI	Forms an equilibrium mixture on heating

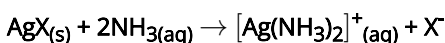
- **Thermal stability of halogen hydrides decreases down the group because:**
  - Size of halogen atom increases
  - ∴ nuclear attraction decreases
  - The H – X bond becomes longer and weaker
  - Thus, less energy needed to break the bond
- Bond energies decrease down the group

### 10.4. (Sub) Halide ions and aq. Silver Ions

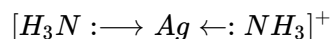


Halide Ion	With Silver Nitrate	With dilute aq. ammonia	With conc. aq. ammonia
Cl <sup>-</sup>	White ppt.	ppt. dissolves	
Br <sup>-</sup>	Cream ppt.	X	ppt. dissolves
I <sup>-</sup>	Yellow ppt.	X	X

dissolves, it forms a complex ion:



- The complex ion formed is called Diamine Silver(I) ion



### 10.5. (Sub) Halide ions and aq. Sulphuric Acid

Metal Halide + Conc. H<sub>2</sub>SO<sub>4(aq)</sub> → Hydrogen Halide

- Conc. H<sub>2</sub>SO<sub>4(aq)</sub> is an oxidising agent
- This reaction is used for preparation of hydrogen halides

Chlorine	NaCl <sub>(s)</sub> + H <sub>2</sub> SO <sub>4(aq)</sub> → HCl <sub>(g)</sub> + NaHSO <sub>4(aq)</sub>
Bromine	NaBr <sub>(s)</sub> + H <sub>2</sub> SO <sub>4(aq)</sub> → HBr <sub>(g)</sub> + NaHSO <sub>4(aq)</sub>
	HBr <sub>(g)</sub> + H <sub>2</sub> SO <sub>4(aq)</sub> → Br <sub>2(g)</sub> + SO <sub>2(g)</sub> + H <sub>2</sub> O <sub>(l)</sub>
Iodine	NaI <sub>(s)</sub> + H <sub>2</sub> SO <sub>4(aq)</sub> → HI <sub>(g)</sub> + NaHSO <sub>4(aq)</sub>
	HI <sub>(g)</sub> + H <sub>2</sub> SO <sub>4(aq)</sub> → I <sub>2(g)</sub> + SO <sub>2(g)</sub> + H <sub>2</sub> O <sub>(l)</sub>
	HI <sub>(g)</sub> + H <sub>2</sub> SO <sub>4(aq)</sub> → I <sub>2(g)</sub> + H <sub>2</sub> S <sub>(g)</sub> + H <sub>2</sub> O <sub>(l)</sub>

### 10.6. The reactions of chlorine with aqueous sodium hydroxide

- **Disproportionation**: a reaction in which the same substance is oxidized and reduced simultaneously producing two different products

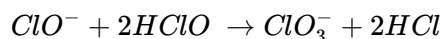
- When chlorine reacts with a solution of cold aqueous sodium hydroxide, the disproportionation goes to lower oxidation states



- With a hot solution, the oxidation state of chlorine goes up to +V



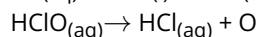
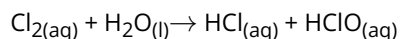
- This happens as the chlorate is formed by disproportionation of hypochlorite and hypochlorous acid



Higher temperatures promotes the formation of hypochlorous acid through hydrolysis of hypochlorite and therefore speeds up the reaction

## 10.7. Some important uses of halogens and of halogen compounds

- Fluorine:**
  - To make chlorofluorocarbon (CFCs)
  - As fluoride in toothpaste
  - To make polytetrafluoroethylene (PTFE) – non sticking coating in pots and pans
- Bromine and Iodine:** manufacture of photographic films
- Chlorine:**
  - In bleaches
  - To make PVC and chlorofluorocarbon (CFCs)
  - As solvents
- Use of chlorine in water purification:**
  - The oxidising power of chlorine is used in treatment of water to kill bacteria



- This disproportionation reaction produces reactive oxygen atoms which kill bacteria

## 11. Nitrogen and Sulphur

### 11.1. Lack of Reactivity of Nitrogen

- Nitrogen molecule has three strong covalent bonds
- Bond is very strong and requires high energy for splitting the two nitrogen atoms of a molecule.
- It reacts only under extreme temperature or pressure or in presence of catalyst.

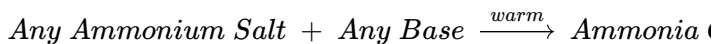
### 11.2. Ammonium

- Lone pair of e<sup>-</sup>s of nitrogen forms a coordinate bond with the H<sup>+</sup> ion

- Formation:**  $\text{NH}_3(\text{g}) + \text{H}^+ \rightarrow \text{NH}_4^+$
- Shape: tetrahedral
- Bond angle: 109.5°
- Bond length: equal lengths



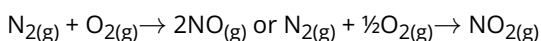
Displacement of ammonia from its salts:



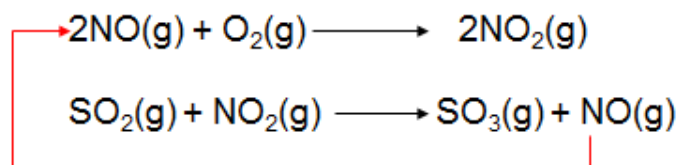
### 11.3. Uses of Ammonia & its Compounds

- Used in the production of nitric acid
- Used in the production of inorganic fertilizers
- Used in the production of nylon
- Used in the production of explosives

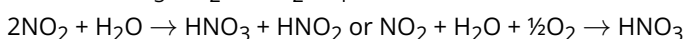
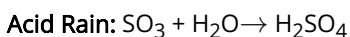
### 11.4. Oxides of Nitrogen



- Naturally:** during lightning, E<sub>A</sub> provided for N<sub>2</sub> to react
- Man-made:** in car engine, high temp. and pressure
- Catalytic convertors:** exhaust gases passed through catalytic convertors containing a catalyst (platinum/palladium/nickel) helping to reduce oxides to nitrogen.
- Catalytic role in oxidation of sulphur dioxide:**



### 11.5. Pollution



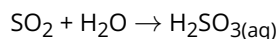
- Damages trees & plants, kills fish and other river life, buildings, statues and metal structures

Combustion Pollutants:

- Nitrogen oxide (NO):** formed by reaction of N<sub>2</sub> and O<sub>2</sub> in the engine, forms acid rain and respiratory problems
- Atmospheric oxides of nitrogen (NO & NO<sub>2</sub>) can react with unburned hydrocarbons to form peroxyacetyl nitrate (PAN) which is a component of photochemical smog
- Carbon monoxide (CO):** source: incomplete combustion of hydrocarbon fuel, toxic effect on haemoglobin

### 11.6. Food Preservation

- SO<sub>2</sub> is used by itself or as a sulphite to preserve food





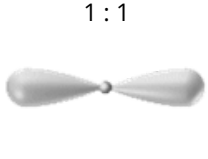
- $\text{SO}_2$  & sulphites inhibit growth of bacteria, yeasts, etc. & are reducing agents, so reduce rate of oxidation of food.
- Used to prevent spoilage of dried fruit, dehydrated vegetables and fruit juices.

## 12. Introduction to Organic Chemistry

- **Organic chemistry:** study of hydrocarbons and their derivatives
- Carbon can form a variety of compounds because:
  - Carbon is tetravalent
  - Carbon-carbon bonds can be single, double or triple
  - Atoms can be arranged in chains, branches and rings
- **Homologous series:** a series of compounds of similar structures in which:
  - contain the same functional group
  - all share same general formula
  - formula of homologue differs from neighbour by  $\text{CH}_2$
  - similar chemical properties
  - gradual change in physical properties as  $M_r$  increases
- **Functional group:** an atom or group of atoms in an organic molecule that determine the characteristic reactions of a homologous series.
- **Alkyl group:** a reactive group which is alkane minus 1 H

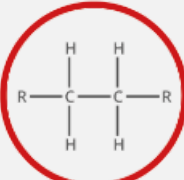
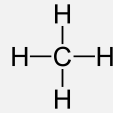
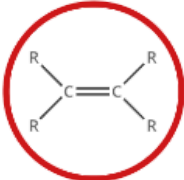
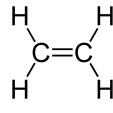
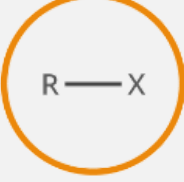
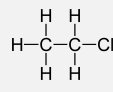
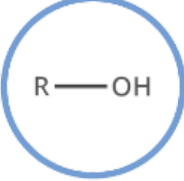
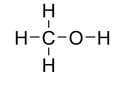
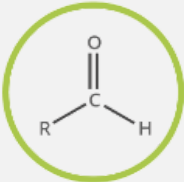
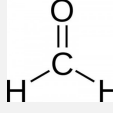
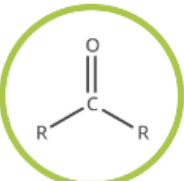
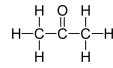
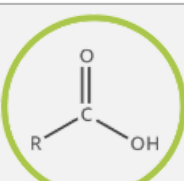
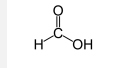
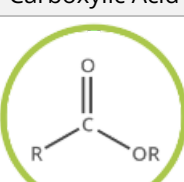
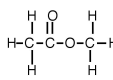
### 12.2. Hybridization

- **Hybridisation:** mixing up of different atomic orbitals resulting in new orbitals of equal energy.
- **Carbon's electron configuration:**

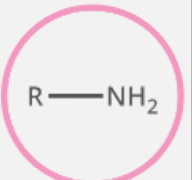
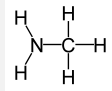

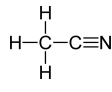
Ground State		Excited State		
2s	2p	2s	2p	
	x y z		x	y z
$1\downarrow$	$\uparrow \uparrow$	$\uparrow$	$\uparrow$	$\uparrow \uparrow$
$sp^3$	$sp^2$	$sp$		
All orbitals mix	$2s, 2p_x, 2p_y$ mix	$2s$ and $2p^x$ mix		
4 $sp^3$ orbitals	3 $sp^2$ orbitals 1 pure p orbital	2 $sp$ orbitals 2 pure p orbitals		
Ratio of characteristics s : p				
1 : 3	1 : 2	1 : 1		
				

### 12.3. Classes of Compound

Organic Family	Suffix	Example
----------------	--------	---------

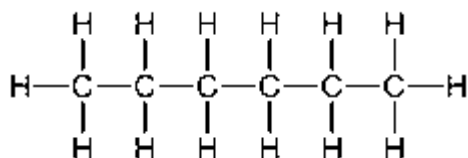
Organic Family	Suffix	Example
 Alkanes	-ane	 Methane
 Alkenes	-ene	 Ethene
 Halogenoalkanes	halo- ... -ane	 Chloroethane
 Alcohols	-ol	 Methanol
 Aldehydes	-al	 Methanal
 Ketones	-one	 Propanone
 Carboxylic Acid	-oic	 Methanoic acid
 Esters	-oate	 Methyl ethanoate



Organic Family	Suffix	Example	
 Amines	-amine	 Methylamine	
 Nitriles	-nitrile	 Ethyl nitrile	

## 12.4. Types of Formulae

- Displayed formula (Hexane)



- Structural formula (Hexane)
  - $\text{CH}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-CH}_3$  or  $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$
- Skeletal formula (Hexane)



- Molecular formula (Hexane)
  - $\text{C}_6\text{H}_{14}$

## 12.5. Nomenclature

- Select longest chain as the main chain
- Other carbon chains as substituent alkyl groups
- Give lowest number C in main chain to substituent
- If different alkyl groups present on identical position, give simpler alkyl smaller number
- Two or more alkyl groups present, order alphabetically
- If same substituent repeated use di, tri, tetra prefix
- If ring of carbon present, use prefix cyclo
- Write position of double bond in alkene e.g. but-1-ene

## 12.6. Breaking of Covalent Bonds

Homolytic Fission:

- Two atoms sharing  $e^-$  pair of similar electro-tivity
- When bond breaks, each atom takes one  $e^-$  from pair of electrons forming free radicals
- Free radicals:** electrically neutral atoms or group of atoms with unpaired electrons very reactive
- Free radical reaction catalysed by heat or light

Heterolytic Fission:

- Two atoms sharing  $e^-$  pair are of different electro-tivity
- When bond breaks, one of the bonded atoms takes both bonding  $e^-$ s
- Results in formation of +ve and -ve ions
- If +ve charge on C, its called carbocation or carbonium
- If -ve charge on C, its called carbanion

*Note: homolytic fission require less energy than heterolytic*

## 12.7. Types of Reagents

**Nucleophilic reagent (nucleophile):** donator of pair of  $e^-$

- Must have lone pair of  $e^-$ s
- Attack centre of +ve charge (positive pole)
- Reaction with nucleophile called nucleophilic reactions
- Examples:  $\text{CH}^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CN}^-$

**Electrophilic reagent (electrophile):** acceptor of pair of  $e^-$

- +ve ions or  $e^-$  deficient molecules
- Attack regions of high  $e^-$  density
- Examples:  $\text{Br}^+$ ,  $\text{CH}_3^+$ ,  $\text{AlCl}_3$

## 12.8. Types of Reaction

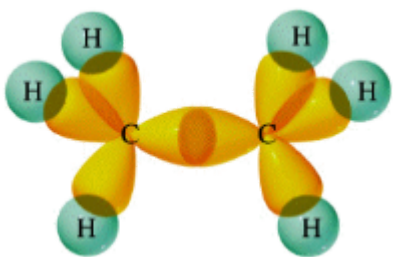
- Addition reaction:** single product formed
  - Electrophilic addition (alkenes)
  - Nucleophilic addition (carbonyl compounds)
- Substitution reaction:** two products formed
  - Nucleophilic substitution (halogenoalkanes)
  - Free radical substitution (alkanes)
- Elimination reaction:** more than one product formed, small molecule removed from reactant (alcohols and halogenoalkanes)
- Hydrolysis reaction:** breaking down of molecule by water, sped up by acid or alkali (esters and alkenes)

## 12.9. Oxidation and Reduction

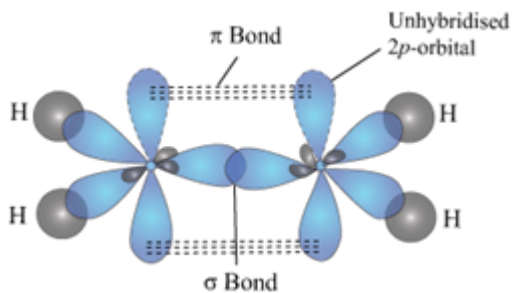
- Oxidation:** addition of oxygen or removal of hydrogen
- Reduction:** addition of hydrogen or removal of oxygen

## 12.10. Shapes of Ethane and Ethene

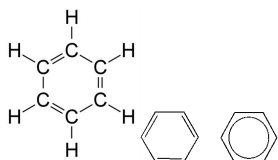
- Ethane:**  $sp^3$  bonds, all sigma bonds



- **Ethene:** Planar Shape, H - C - H bond =  $120^\circ$

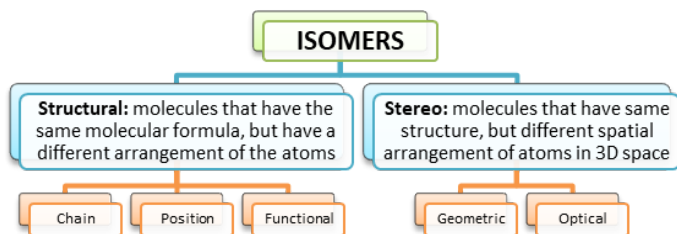


- **Benzene**



## 12.11. Isomerism

- Existence of two or more compounds with the same molecular formula but different structural formula

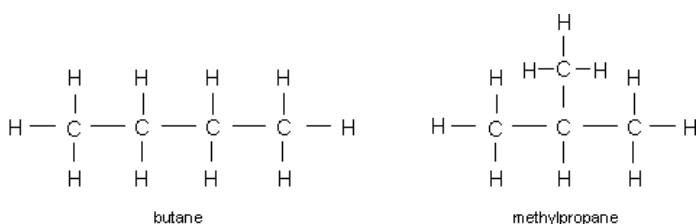


Note:

- **Straight** chain alkanes have **higher b.p.** than branched
- Branching makes molecule more spherical reduces contact points VDW forces decreases

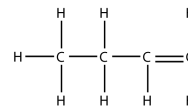
## 12.12. Chain Isomers

- Isomers have different carbon chain length
- **Same chemical** properties but slightly **different physical**
- Example:

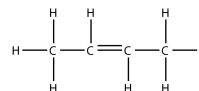


## 12.13. Position Isomers

- Isomers differ in position of substituent atoms or group or the functional group
- **Same chemical** properties but slightly **different physical**
- Example: But-1-ene



- Example: But-2-ene



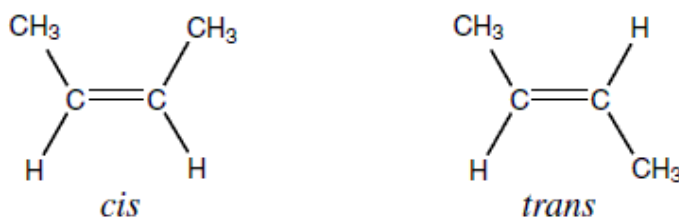
## 12.14. Functional Isomers

- Isomers have different functional groups, belong to different homologous series
- Have **different physical and chemical** properties

Ratio of C : H	Functional Gps.	Example
1 : 3	Alcohol & Ether	C <sub>2</sub> H <sub>6</sub> O
1 : 2	Aldehyde & Ketone	C <sub>3</sub> H <sub>6</sub> O
1 : 2 Must have O <sub>2</sub>	Carboxylic acid & Ester	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>

## 12.15. Geometric (cis/trans) Isomers

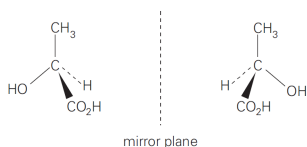
- Shown only by alkenes
- Arises due to restriction of double bond
- Only possible when each carbon has 2 different groups
- cis-trans isomers have different b.p.
- **cis** isomers have **higher dipole**
- **trans** isomer of **symmetrical** alkene has **zero dipole**



## 12.16. Optical Isomers

- Arises from different arrangement of atoms or groups in 3D space resulting in two isomers
- Have effect on polarised light
- **Chiral carbon:** a carbon having 4 single bonds and 4 different atoms or groups
- Isomers non-super-imposable images of each other
- Have **same physical and chemical** properties

- No. of optical isomers in a molecule containing  $n$  chiral carbons =  $2^n$



## 13. Hydrocarbons

### 13.1. Properties

Generally unreactive:

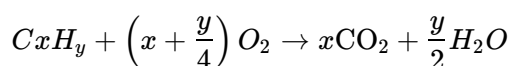
- All C-C bonds single; alkanes = saturated hydrocarbons
- Non-polar  $\therefore$  no center of charge to act as either nucleophile or electrophile  $\therefore$  cannot attract polar reagents like acids, bases, metals or oxidizing agents

Physical properties:

- The volatility of the alkanes decreases and m.p/b.p increases as number of carbon atoms increases
- Reason: increasing Van der Waals forces

### 13.2. Combustion

- Used as fuel because they burn in oxygen to give out large amounts of energy
- Alkanes kinetically stable in presence of  $O_2$ ; combustion occurs when necessary amount of  $E_a$  supplied
- Reaction occurs **only in gas phase**
- Complete:** carbon dioxide + water
- Incomplete:** carbon monoxide + carbon (soot) + water
- General Equation of Hydrocarbon Combustion:**



### 13.3. Substitution

- Alkanes react with halogens:  $Cl_2$  and  $Br_2$

Example: Chlorination of Methane

Reagent	Condition	Reaction	
		Type	Mechanism
$Cl_2(g)$	UV light	Substitution	Free Radical

### 13.4. Cracking

- Breaking of large less useful alkanes into useful, more energy value smaller products using heat & catalyst
- Products:**
  - smaller alkanes and **alkenes** or
  - smaller **alkenes** and hydrogen gas
- Thermal cracking:** high temp. & pressure

- Catalytic cracking:** high temp. & catalyst

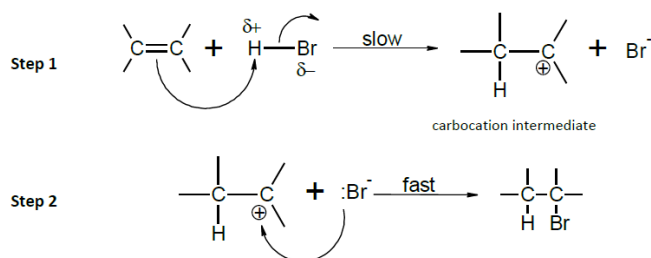
## 13.5. Hydrocarbons as Fuels

- Source of alkanes: crude oil
- Steady change in b.p. of alkanes allows crude oil to be separated by fractional distillation
- Catalytic conversion of CO and  $NO_x$ :
  - $2NO_2 + 4CO \rightarrow N_2 + 4CO_2$
  - $2NO + 2CO \rightarrow N_2 + 2CO_2$

### 13.6. Alkenes

- Unsaturated hydrocarbons
- Contain at least one C=C double bond
- General formula:  $C_nH_{2n}$  (like cycloalkanes)
- Source of alkenes:
  - Cracking alkanes
  - Dehydration of alcohols
- More reactive than alkanes due to presence of double bond; pi electrons loosely and more susceptible to attacks by  $e^-$  deficient groups like electrophiles
- Alkenes combust completely carbon dioxide + water
- Give energy but not used as fuels; have other uses

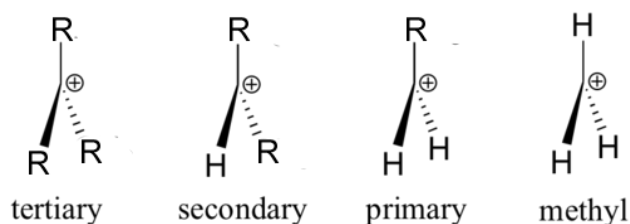
### 13.7. Electrophilic Addition Mechanism



- Electrophile forms by heterolytic fission
- Electrophile attacks double bond
- Pair of  $e^-$ s from double bond migrate to electrophile and  $\pi$  bond breaks
- Carbocation formed which attacks the nucleophile

### 13.8. Carbocations

most stable  $\rightleftharpoons$  least stable



- Markovnikov's principle:** an electrophile adds to an unsymmetrical alkene so that the most stable carbocation is formed as an intermediate

- Hydrogen binds to carbon with more hydrogens
- Inductive effect of alkyl groups:
  - Alkyl groups donate e<sup>-</sup> to the ring
  - Producing a positive inductive effect
  - A larger alkyl group has a weaker inductive effect

### 13.9. Addition Reactions

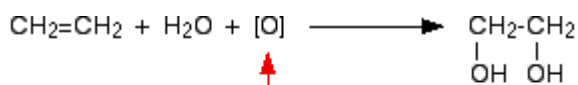
- Hydrogenation (**Alkene + H<sub>2</sub> Alkane**)
  - Reagent: H<sub>2(g)</sub>
  - Condition:
    - Catalyst: Nickel
    - Temp.: 100°C
    - Press.: 2 atm.
  - Use: convert liquid oils to saturated solid fats
- Halogenation (**Alkene + X<sub>2</sub> Dihaloalkane**)
  - Reagent: Halogen<sub>(aq)</sub>
  - Condition: r.t.p./dark
- Halogenation (**Alkene + Hydrohalogen Halogenoalkane**)
  - Reagent: Hydrohalogen<sub>(g)</sub>
  - Condition: r.t.p.
- Hydration (**Alkene + H<sub>2</sub>O<sub>(g)</sub> Alcohol**)
  - Reagent: steam
  - Condition:
    - Catalyst: H<sub>3</sub>PO<sub>4</sub> – phosphoric acid
    - Temp.: 300°C
    - Press.: 70atm

### 13.10. Oxidation of Alkenes

- Both oxidation and addition to double bond involved
- KMnO<sub>4</sub> changes from pink to colourless

With Cold Dil. Acidified KMnO<sub>4</sub>/H<sup>+</sup>

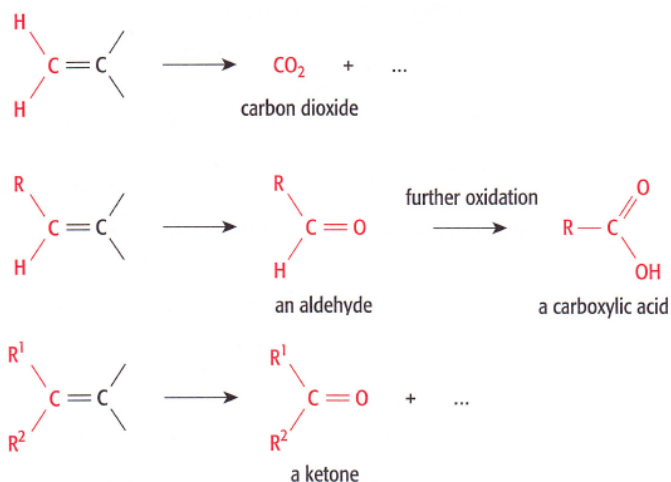
- Diol is formed



↑  
oxygen from the oxidising agent

With Hot Conc. Acidified KMnO<sub>4</sub>/H<sup>+</sup>

- Leads to the rupture of the double bond
- Two compounds are formed
- Products formed depend on alkene



### 13.11. Polymerization

- Repeated addition of 1000s of alkene molecules (monomer) to each other forming a macromolecule
- Polyethene:**
  - LDPE: cling wrap
  - HDPE: water pipes, wire insulation



- Polychloroethene (PVC):**
  - Water pipes
  - Insulation of wires

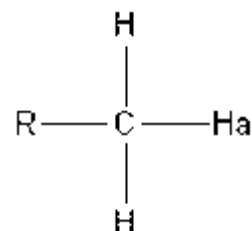


- General conditions:** high pressure, high temperature and catalyst
- Disadvantages:**
  - Non-biodegradable: does not break down so increases amount of volume needed for landfill sites
  - Combustion produces harmful gases which contribute to global warming e.g. SO<sub>2</sub>, CO<sub>2</sub> and HCl from PVCs
- Disposal of Polymers:**
  - Recycle existing plastic
  - Make polymers biodegradable by adding starch units

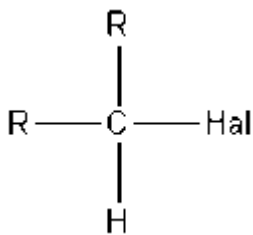
## 14. Halogen Derivatives

### 14.1. Types of Halogenoalkanes

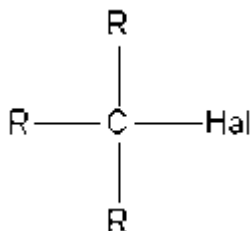
- Primary 1<sup>o</sup> (S<sub>N</sub>2)



- Secondary 2° (S<sub>N</sub>2)



- Tertiary 3° (S<sub>N</sub>1)



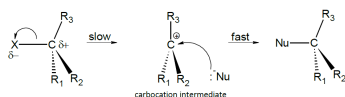
## 14.2. Strength of C – Hal Bond

	Polar Nature	Bond Energy	Reactivity
Fluoro	Decrease	Decrease	Increases
Chloro			
Bromo			
Iodo			
	Electro-tivity decreases down group	Bond length increases, bond energy decreases, lower E <sub>A</sub> so more reactive	

## 14.3. Nucleophilic Substitution Mechanism

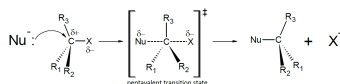
- The C – X bond is a polar bond, has partial charges due to high electro-tivity of halogen.
- The δ<sup>+</sup> carbocation is easily susceptible to attack by a nucleophile

S<sub>N</sub>1 Mechanism:



- Unimolecular – only one molecule involved in 1<sup>st</sup> step
- Tertiary halogenoalkanes

S<sub>N</sub>2 Mechanism:



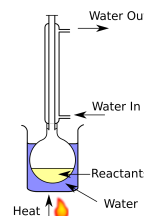
- Bimolecular – two molecules involved in 1<sup>st</sup> step
- Primary and secondary halogenoalkanes

## 14.4. Nucleophilic Substitution Reaction

- Hydrolysis (R – X + OH<sup>-</sup> → R – OH + X<sup>-</sup>)
  - Reagent: strong alkali; NaOH<sub>(aq)</sub> or KOH<sub>(aq)</sub>
  - Condition: heat/reflux
  - Fluoroalkanes are not hydrolysed because the C – F bond is too strong
  - Ease of hydrolysis increases: Primary < Secondary < Tertiary
  - Tertiary halogenoalkanes can be hydrolysed without alkali
  - Note: if any Cl<sup>-</sup> or Br<sup>-</sup> ions present in NaOH<sub>(aq)</sub>, these ions will interfere with reaction
- Nitrile (cyanide) (R – X + CN<sup>-</sup> → RCN + X<sup>-</sup>)
  - Reagent: KCN or NaCN in ethanol
  - Condition:
    - Solvent: Ethanol
    - Heat/Reflux
  - Reaction forms a C – C bond therefore no. of C increases; name has one more carbon
- Primary Amines (R – X + NH<sub>3</sub> → RNH<sub>2</sub>(l) + HX<sub>(g)</sub>)
  - Reagent: Ammonia (NH<sub>3</sub>)
  - Condition: ammonia in alcohol under pressure in sealed container
  - Note:** if excess conc. ammonia used, HX reacts with it forming NH<sub>4</sub>X

## 14.5. Reflux

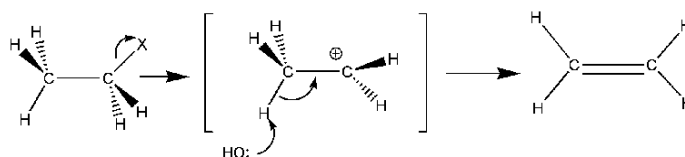
- Many organic reactions proceed slowly
- Heating done under reflux to prevent volatile organic solvents to evaporate
- Mechanism similar to simple distillation



## 14.6. Elimination Reaction



Mechanism:



- Reagent: ethanolic NaOH or KOH
- Conditions: temp. 60°C, reflux
- OH<sup>-</sup> acts as a proton acceptor; it accepts the H<sup>+</sup> loss from the halogenoalkanes during elimination
- Elimination become progressively easier

Primary < Secondary < Tertiary

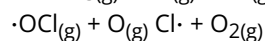
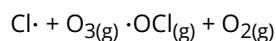
- Note: the carbon atom adjacent to carbon with halide must have at least one hydrogen attached to it.

## 14.7. Uses of Halogenoalkanes

- CFCs are inert and can be liquefied easily: Strength of C - X bond is very high, hence do not decompose easily and are not flammable.
- Uses:
  - As propellants in aerosol cans
  - As solvents in dry-cleaning
  - As refrigerant for freezers and fridges
  - Fire extinguishers, insecticides and pesticides

## 14.8. CFCs Effect on Ozone Layer

- Causes the destruction of the ozone layer
- CFCs escape in atmosphere and because of their inertness, remain without further reaction until they reach the stratosphere and ozone layer.
- In stratosphere, high energy U.V causes Cl atom to split of CFC molecule forming Cl· which reacts with ozone
- This is a catalytic cycle where one Cl· can react with many O<sub>3</sub> thus causing destruction of ozone layer:



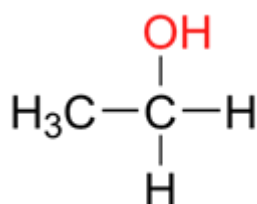
Can react and breakdown another O<sub>3</sub> molecule

- Note: alternative is using HCFCs (replace Cl with H or more F atoms) as they break down more easily and do not release Cl → less effect on ozone layer

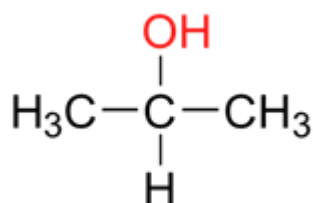
## 15. Hydroxy Compounds

### 15.1. Types of Alcohols

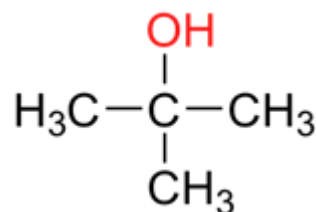
- Primary 1°



- Secondary 2°



- Tertiary 3°



- Source of Alcohols:
  - Hydration of alkenes
  - Fermentation

### 15.2. Properties

Physical Properties:

- Colourless liquids at r.t.p
- b.p. and density increases with increasing C atoms and also with increasing OH groups

Boiling Point:

b.p. decreases →



because:



- b.p. of alcohols > alkenes as they have hydrogen bonds

Solubility of Alcohols in Water:

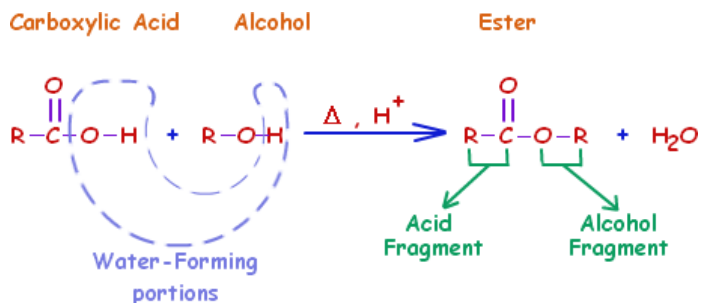
- Smaller alcohols mix completely with water since strong hydrogen bonds occur between alcohols and water
- As hydrocarbon nature increase (i.e. more C-C... bonds), the non-polar character outweighs the ability of the OH to form hydrogen bonds and ∴ solubility decreases
- Small alcohols (e.g. ethanol) are good solvents for both polar and non-polar compounds as they have polar and non-polar components

### 15.3. Reaction with Sodium



- Type of reaction: acid-base
- Reagent used: liquid sodium metal
- Reactivity of alcohols decreases with increasing chain lengths of hydrocarbon
- Reaction less vigorous than that of Na and water which shows water is a stronger acid than alcohol

### 15.4. Reaction with Carboxylic Acids

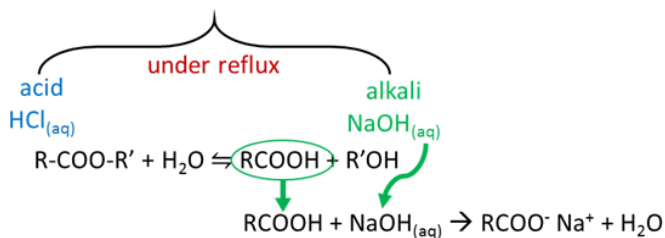


Reagent	Condition	Type of Reaction
R-COOH	Heat-reflux Conc. H <sub>2</sub> SO <sub>4</sub>	Esterification

as fats, oils & flavours in fruits

- Used in food flavourings and perfumes and as solvents

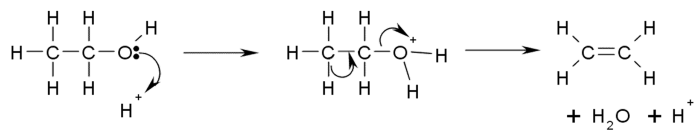
### 15.5. Hydrolysis of Esters



### 15.6. Dehydration of Alcohols

- Alcohol(l) → Alkene + H<sub>2</sub>O(l)
  - Condition:
    - Conc. H<sub>2</sub>SO<sub>4</sub> OR
    - H<sub>3</sub>PO<sub>4</sub> at 180°C OR
    - Al<sub>2</sub>O<sub>3</sub> at 300°C
  - Type of reaction: Elimination

Mechanism:



- Adjacent carbon to carbon with OH must have at least one hydrogen (tertiary cannot undergo dehydration)

### 15.7. Halogenation

- Type of Reaction: Nucleophilic Substitution

R-OH		R-X	
Forming Reagent	Producing:	R-OH+	Reactions      Condition
	Alkyl Chlorides		Conc. HCl RCl(l) + H <sub>2</sub> O      Zn + Heat/Reflux

		R-OH	R-X	
			SOCl <sub>2</sub> RCl(l) + SO <sub>2</sub> (g) + HCl(g)	r.t.p
			PCl <sub>5</sub> RCl(l) + POCl <sub>3</sub> (aq) + HCl(g)	
			PCl <sub>3</sub> RCl(l) + H <sub>3</sub> PO <sub>3</sub> (aq) + HCl(g)	Heat/Reflu
NaBr + H <sub>2</sub> SO <sub>4</sub> (aq)	HBr	Alkyl Bromides	HBr(g) RBr(l) + H <sub>2</sub> O	r.t.p
P + Br <sub>2</sub> - warm	PBr <sub>3</sub>		PBr <sub>3</sub> (g) RBr(l) + H <sub>3</sub> PO <sub>3</sub> (aq)	
P + I <sub>2</sub> - warm	PI <sub>3</sub>	Alkyl Iodide	PI <sub>3</sub> (g) RI(l) + H <sub>3</sub> PO <sub>3</sub> (aq)	r.t.p

### 15.8. Oxidation of Alcohols

- Reagent: Oxidising agents

Reagent	Type of Reaction	
Acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>4</sub> Orange to Green	Acidified KMnO <sub>4</sub> Pink to Colourless	Oxidation

png)

- Tertiary alcohols not oxidised because no hydrogens attached to carbon with OH group so oxidising agent colour does not change

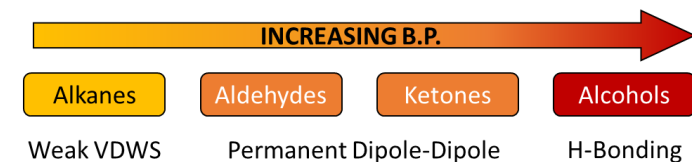
### 15.9. Tests for Alcohols

Reagent	Result with:		
	Primary	Secondary	Tertiary
Na metal	Bubble of H <sub>2</sub> Gas		
K <sub>2</sub> Cr <sub>2</sub> O <sub>4</sub> /H <sup>+</sup>	Green		X
KMnO <sub>4</sub> /H <sup>+</sup>	Colourless		X

## 16. Carbonyl Compounds

Boiling Point:





### Solubility:

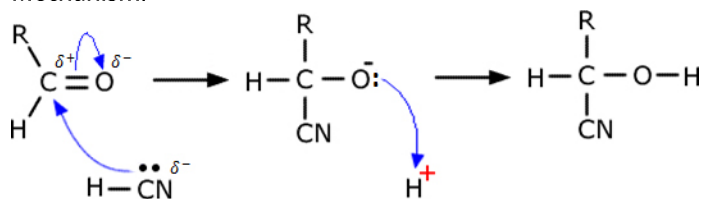
- **Smaller carbonyl compounds:** completely soluble as they form hydrogen bonds with water molecules; are good solvents for polar & non-polar solutes
- **Larger carbonyl compounds:** polar nature decreases, and non-polar nature increases; ability to form hydrogen bonds decreases

## 16.2. Nucleophilic Addition with HCN

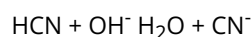
Reagent	Condition	Type of Reaction
HCN	HCN w/alkali or HCN w/KCN	Nucleophilic Addition

- Since HCN added, carbon chain increases
- Product formed is hydroxynitrile or cyanohydrin
- Aldehydes are more susceptible to nucleophilic attacks than ketones
- Smaller carbonyl compounds more reactive
- Product has a chiral carbon ∴ exhibits optical isomerism

### Mechanism:



- **Note:** HCN is a poor nucleophile and with few CN<sup>-</sup> ions, the reaction is slow. To increase CN<sup>-</sup> conc.:
- Make HCN react in presence of alkali



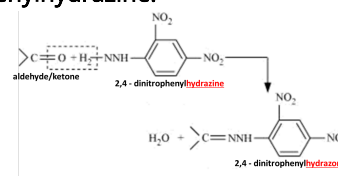
- Addition of KCN and dilute H<sub>2</sub>SO<sub>4</sub> can provide HCN and more CN<sup>-</sup> ions

## 16.3. Reduction of Carbonyl Compounds

- **Type of Reaction:** nucleophilic addition (H<sup>-</sup> ions)
- **Reducing agents:**
  - NaBH<sub>4</sub> – sodium tetrahydriborate
  - LiAlH<sub>4</sub> – lithium aluminium hydride
  - H<sub>2</sub>/Pt or Ni
- **Aldehydes** ⇒ 1<sup>o</sup> Alcohols
  - R-CHO + 2 [H] RCH<sub>2</sub>OH
- **Ketones** ⇒ 2<sup>o</sup> Alcohols
  - R-CO-R + 2 [H] R-CH(OH)-R

## 16.4. Testing Carbonyl Compounds

### 2,4,- dinitrophenylhydrazine:



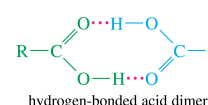
- It is a nucleophilic addition & condensation/elimination
- Forms: **red/orange ppt.**
- The m.p. of the ppt. can be used to identify individual aldehydes and ketones

### Tests Given only by Aldehydes:

- **Tollen's Reagent**
  - Solution of AgNO<sub>3</sub> + aq. NH<sub>3</sub> excess
$$\text{Ag}(\text{NH}_3)_2^+ + \text{RCHO} + 2\text{OH}^- \rightarrow \text{Ag} + \text{RCOO}^- + \text{H}_2\text{O} + \text{NH}_3$$
- **Aldehyde + Tollen's Reagent Silver Mirror**
  - Ag<sup>+</sup> reduced to Silver and -CHO oxidised to acid
- $2\text{Ag}^+ + \text{RCHO} \rightarrow 2\text{Ag} + \text{RCOOH} + \text{H}^+$
- **Fehling's Solution**
  - CuSO<sub>4</sub> in ammonia solution
- **Aldehyde + Fehling's Solution Red ppt.**
  - Cu<sup>2+</sup> reduced to Cu(I) oxide and -CHO oxidised to acid
- $2\text{Cu}^{2+} + \text{RCHO} \rightarrow 2\text{Cu}^+ + \text{RCOOH} + \text{H}^+$

## 17. Carboxylic Acids and Derivatives

- Weak acids; don't dissociate completely
- Forms hydrogen bonds:
  - High m.p./b.p.
  - High solubility of smaller carboxylic acids
- Forms hydrogen bonded dimers when pure vapour, liquid or solid & when dissolved in non-polar organic solvents

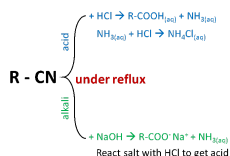


### 17.2. Formation of Carboxylic Acids

- **From alcohols:** complete oxidation of primary alcohols
- **From aldehydes:** oxidation of aldehydes

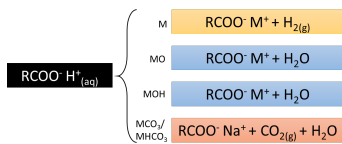


- From nitriles: acid/base hydrolysis of a nitrile



### 17.3. Formation of Salts

- Heterolytic fission of the hydroxyl bond (-OH)
- Salts called carboxylates

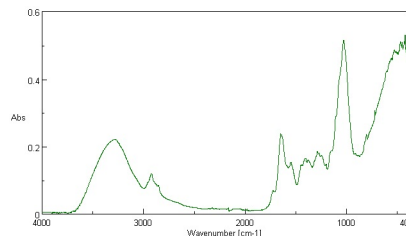


## 18. Analytical Techniques

### 18.1. Infra-red Spectroscopy

- This is when a sample being analysed is irradiated with electromagnetic waves in the infra-red region of the electromagnetic spectrum.
- Machine used is spectrophotometer and it detects intensity of wavelengths of infra-red that pass through the sample

- The energy absorbed corresponds to changes in vibration of bonds leading to the bond being to stretch, bend and twist
- At a specific frequency, the **resonance frequency**, the largest vibrations are obtained
- Each type of vibration will absorb characteristic wavelengths of infra-red radiation
- We can hence identify the presence (or absence) of different functional groups from the absorbance pattern on an infra-red spectrum



### 18.2. Monitoring Air Pollution

- IR spectroscopy identifies particular bonds in a molecule, and so each pollutant will show a different pattern of absorptions – this allows the identification of the pollution
- It is also possible to measure the concentration of each pollutant with the different amounts of absorption

# CAIE AS LEVEL Chemistry (9701)

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