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Updated to 2019-21 Syllabus

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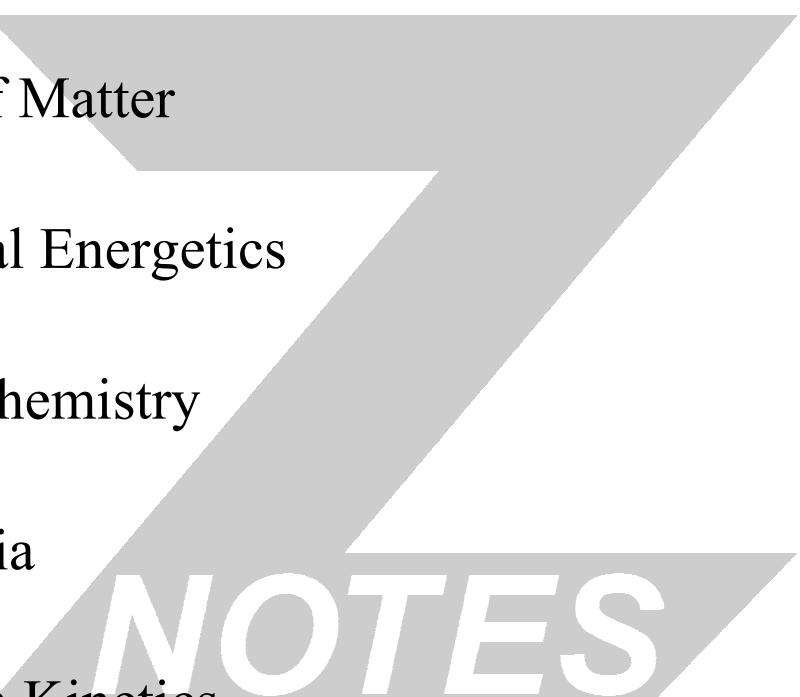
# CIE AS-LEVEL CHEMISTRY 9701

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SUMMARIZED NOTES ON THE SYLLABUS

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## Analytical Techniques

NOTES

## 1. ATOMS, MOLECULES AND STOICHIOMETRY

### 1.1 Relative Mass

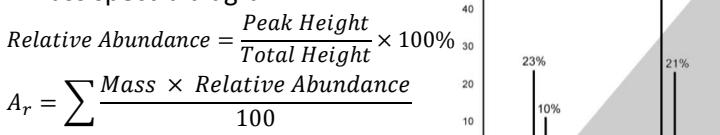
|                           |  |  |
|---------------------------|--|--|
| Atomic mass ( $A_r$ ):    | weighted average mass of an atom           | compared with $^{12}\text{C}$ where one atom of $^{12}\text{C}$ has mass of exactly 12 units |
| Molecular mass ( $M_r$ ): | mass of a molecule                         |  |
| Formula mass:             | mass of one formula unit of a compound     |  |
| Isotopic mass:            | mass of a particular isotope of an element |  |

### 1.2 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 =  $6.02 \times 10^{23}$

### 1.3 Mass Spectra

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



### 1.4 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 Mr of a compound and its empirical formula

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

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

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

### 1.5 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  $\text{dm}^3$  and  $1000\text{cm}^3 = 1\text{dm}^3$

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

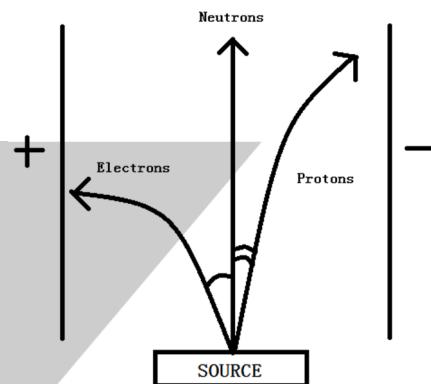
- Concentration unit =  $\text{mol dm}^{-3}$

## 2. ATOMIC STRUCTURE

### 2.1 Subatomic Particle

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

### 2.2 Behavior 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
- $e^-$  lighter than  $P^+$  ∴ deflected at greater angle

### 2.3 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  $e^-$ s
- Isotopes:** are atoms of the same element with the same proton number but different number of neutrons

### 2.4 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

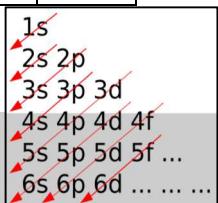


- When e<sup>-</sup>s are placed in a set of orbital of equal energy, they occupy them singly and then pairing takes place
- e<sup>-</sup>s placed in opposite direction: both -vely charge & if placed in same direction, they'd repel. In opposite direction they create a spin to reduce repulsion
- Completely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

## 2.5 Subshells

|                      | <i>s</i> | <i>p</i> | <i>d</i> | <i>f</i> |
|----------------------|----------|----------|----------|----------|
| Orbitals             | 1        | 3        | 5        | 7        |
| Max e <sup>-</sup> s | 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 ∴ an e<sup>-</sup> 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

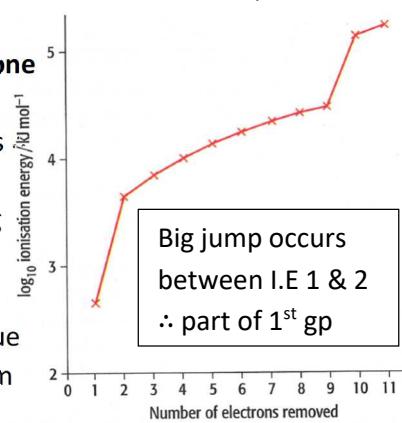


## 2.6 Shapes of Subshells

| <i>s</i> -Subshell   | <i>p</i> -Subshell   |
|--|--|
| <ul style="list-style-type: none"> <li>Spherical shape</li> <li>Increases in size as P.Q. no. increases</li> </ul> | <ul style="list-style-type: none"> <li>Dumbbell shape</li> </ul> |

## 2.7 Ionization Energies (I.E.)

- 1<sup>st</sup> I.E:** energy needed to remove 1 mole of e<sup>-</sup>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<sup>-</sup>s are removed, protons > e<sup>-</sup>s attraction between protons and remaining electrons increases
- Successive I.E.s have large jump in their value when e<sup>-</sup>s removed from lower energy shell
- Deduce group no. by checking when 1<sup>st</sup> big jump occurs



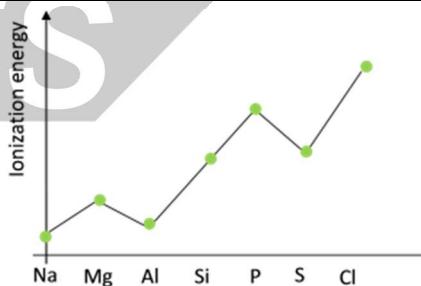
## 2.8 Factors affecting Ionization Energy

|                         |  |
|-------------------------|--|
| <b>Nuclear Charge</b>   | <ul style="list-style-type: none"> <li>+ve charge due to protons in nucleus</li> <li>Greater nuclear charge → greater ionization energy</li> </ul>   |
| <b>Shielding Effect</b> | <ul style="list-style-type: none"> <li>Inner shells of e<sup>-</sup>s repel outermost e<sup>-</sup>s, thus shielding them from +ve nucleus. The more e<sup>-</sup> shells, the greater is the shielding effect</li> <li>Greater effect → lower I.E because lesser attractive force between nucleus &amp; outer e<sup>-</sup>s</li> </ul> |
| <b>Atomic Radius</b>    | <ul style="list-style-type: none"> <li>Distance from the centre of the nucleus to the outermost orbit</li> <li>Greater radius → lower I.E; distance of outermost e<sup>-</sup> to nucleus is large ∴ less energy needed to remove e<sup>-</sup></li> </ul>   |
| <b>Stable Config.</b>   | <ul style="list-style-type: none"> <li>High I.E needed to remove e<sup>-</sup>s from completely or half-filled orbitals</li> </ul>   |

## 2.9 General 1<sup>st</sup> I.E Trends

| First Ionization Energy Trends   |  |
|--|--|
| Down a Group   | Across a Period  |
| <u>DECREASES</u> <ul style="list-style-type: none"> <li>New shells added</li> <li>Attraction of nucleus to valence e<sup>-</sup>s decreases</li> <li>Shielding effect increases</li> </ul> | <u>INCREASES</u> <ul style="list-style-type: none"> <li>Shell no. remains same</li> <li>Proton no. increases</li> <li>Effective nuclear charge increases</li> <li>Atomic radius decreases</li> </ul> |

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



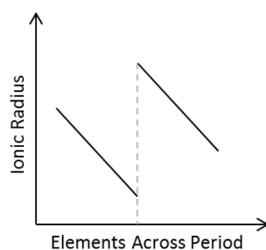
- I.E of Al lower than Mg:** e<sup>-</sup> removed in Al is from higher energy 3p orbital which is further away from nucleus than 3s e<sup>-</sup> being removed from Mg. Nuclear attraction is less for 3p than 3s ∴ I.E of Al is lower than Mg
- I.E of S lower than P:** e<sup>-</sup> being removed in P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

## 2.11 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<sup>-</sup>s added while nuclear charge remains same



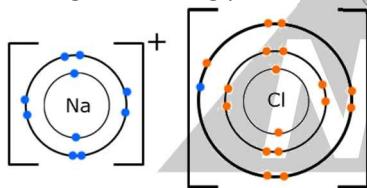
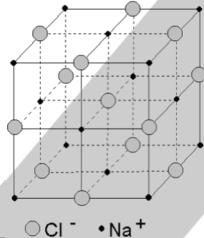
| Groups  | 1 to 3   | 5 to 7   |
|---|----------|----------|
| Ion   | Positive | Negative |
| No. of shells   | $n - 1$  | $n$      |
| →   |          |          |
| <ul style="list-style-type: none"> <li>Proton no. and effective nuclear charge increases</li> <li>Ionic radius decreases</li> </ul> |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

- Negative ions always larger than positive ions in the same period as they have one more shell

## 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

### 3.2 Covalent Bonding

- Covalent bond is the bond formed by the sharing of pairs of electrons between two atoms.
- Bonding electrons:** e<sup>-</sup>s involved in bond formation
- Non-bonding electrons or lone pair:** pair of valence e<sup>-</sup>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

### 3.3 Coordinate/Dative Bonding

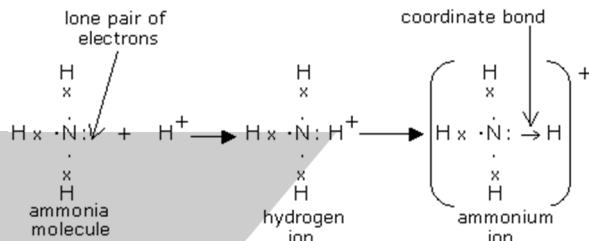
- Coordinate bond is a covalent bond where both electrons in the bond come from the same atom

#### Conditions:

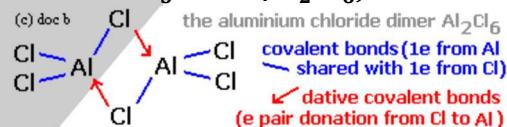
- An atom should have a lone pair of electrons
- An atom should be in need of a pair of electrons

- Donor:** the atom that supplies the pair of electrons
- Acceptor:** the atom that accepts the pair of electrons
- Coordinate bond is represented by an "→" drawn from the atom donating to towards the atom accepting

#### Formation of Ammonium ion (NH<sub>4</sub><sup>+</sup>):



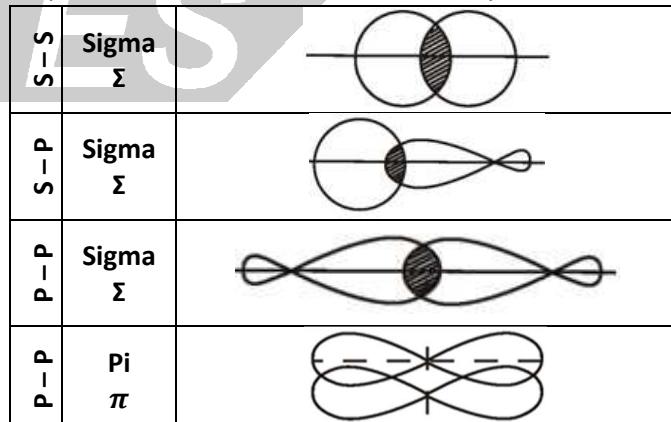
#### Formation of AlCl<sub>3</sub> dimer (Al<sub>2</sub>Cl<sub>6</sub>):



- 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°

### 3.4 Orbital Overlap

- For a covalent bond to form, atomic orbitals containing unpaired valence electrons must overlap each other

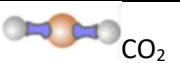
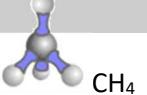
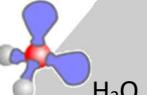
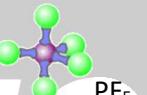
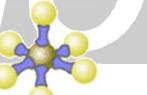


- Sigma bond has greater overlap  $\therefore \sigma > \pi$
- Pi bond cannot exist without a Sigma bond.

### 3.5 Shapes of Covalent Molecules

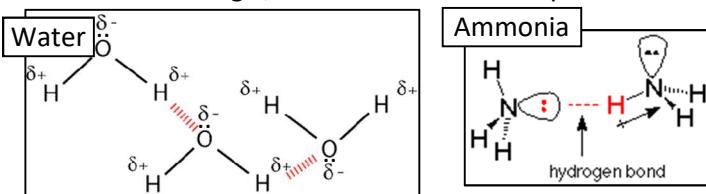
- Shape and bond angles of molecules depend on:
  - The number of pairs of electrons around central atom
  - Whether these pairs are lone pairs or bonded pairs
- Valence shell electrons are arranged in pairs to minimize repulsion between themselves
- Order of repulsion strength (VSEPR Theory):**

Lone -Lone      Lone - Bonded      Bonded - Bonded

| Type                             | Shape                | Angle  | Example  |
|----------------------------------|----------------------|--------|--|
| <b>2 Pairs of e<sup>-</sup>s</b> |                      |        |  |
| 2 bonded                         | Linear               | 180°   |  CO <sub>2</sub>    |
| <b>3 Pairs of e<sup>-</sup>s</b> |                      |        |  |
| 3 bonded                         | Trigonal Planar      | 120°   |  BF <sub>3</sub>    |
| <b>4 Pairs of e<sup>-</sup>s</b> |                      |        |  |
| 4 bonded                         | Tetrahedral          | 109.5° |  CH <sub>4</sub>    |
| 3 bonded<br>1 lone               | Pyramidal            | 107°   |  NH <sub>3</sub>   |
| 2 bonded<br>2 lone               | Angular              | 104.5° |  H <sub>2</sub> O |
| <b>5 Pairs of e<sup>-</sup>s</b> |                      |        |  |
| 5 bonded                         | Trigonal Bipyramidal | 90°    |  PF <sub>5</sub>  |
| <b>6 Pair of e<sup>-</sup>s</b>  |                      |        |  |
| 6 bonded                         | Octahedral           | 90°    |  SF <sub>6</sub>  |

### 3.6 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



### 3.7 Electronegativity

- Ability of a particular atom, covalently bonded, to attract the bonded pair of e<sup>-</sup>s towards itself
- Electronegativity depends on:
  - Radius of atom **inversely**  $\propto$  electronegativity
  - Nuclear attraction **directly**  $\propto$  electronegativity
- Electronegativity **increases across a period** because atomic radius  $\downarrow$  and nuclear attraction  $\uparrow$
- Electronegativity **decreases down a group** because atomic radius  $\uparrow$  and nuclear attraction  $\downarrow$
- Dipole moment:** slight charges on atoms in a covalent bond due to differences in electronegativity



Dipole Moment has a Magnitude and a Direction

### 3.8 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

Longer bond      Weaker bond      More reactive

### 3.9 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  $\therefore$  unequal sharing of electrons  $\therefore$  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

### 3.10 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

### 3.11 Metallic Bonding

- Strong electrostatic forces of attraction between metal cations and delocalized mobile electrons
- **Structure:** lattice of +ve ions surrounded by mobile e<sup>-</sup>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<sup>-</sup>s per atom**

### 3.12 Summary

|                         | Metal + Non-Metal   | Metals Only                | Non-Metals Only                               |                    |
|-------------------------|---------------------|----------------------------|---|--------------------|
| Bonding                 | Ionic               | Metallic                   | Covalent                                      |                    |
|                         |                     |                            | Molecular                                     |                    |
|                         |                     |                            | 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                                     |                    |
| 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 ∴ 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

$$PV = nRT \quad M_r = \frac{\text{Mass} \times RT}{PV}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

| Quantity    | Unit           | Conversion  |
|-------------|----------------|---|
| Pressure    | Pascal         | 1KPa = 1000Pa   |
| Volume      | m <sup>3</sup> | 1m <sup>3</sup> = 1000dm <sup>3</sup> = 1 × 10 <sup>6</sup> cm <sup>3</sup> |
| Temperature | °K             | °C + 273  |

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

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

Partial Pressure of a Gas = Mole Fraction × 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

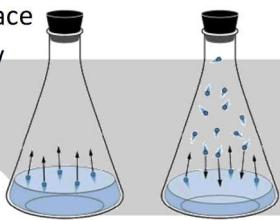
• **Enthalpy of vaporization:** heat energy required to change 1 mole of liquid into a gas at its boiling point

• **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

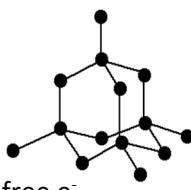
## 4.4 Solid State

| Ionic Lattice | Metallic Lattice | Simple Molecular |
|---------------|------------------|------------------|
|               |                  |                  |

**Macromolecular Lattice:**

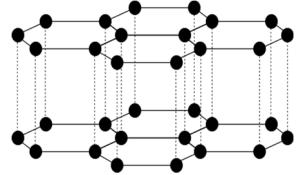
• **Diamond:**

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



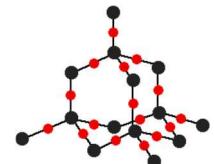
• **Graphite:**

- Three strong ( $sp^2$ ) covalent bonds
- Fourth  $e^-$  in p orbital  $\therefore$  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



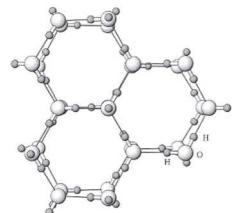
• **Silicon(IV) Oxide:**

- Each Si is bonded to 4 oxygen atoms, but each oxygen is bonded to 2 Si atoms
- Sand is largely  $SiO_2$
- Similar properties to diamond



**Hydrogen Bonded Lattice:**

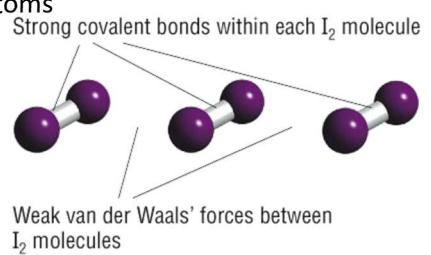
- In ice form, water molecules slow down and come closer together
- Due to polarity, molecules form hydrogen bonds between lone pairs of oxygen &  $\delta^+$  charge of hydrogens
- Each water molecule has 2 H-bonds
- They arrange themselves into an open crystalline, hexagonal structure
- Due to large 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



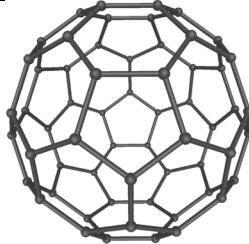
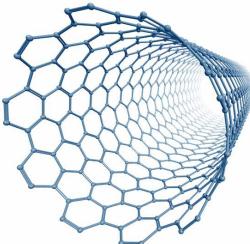
**Simple Molecular Lattice:**

• **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> )   | Nanotubes  |
|---|--|
|  <p>C atoms in pentagonal and hexagonal rings<br/>Spherical<br/>C<sub>60</sub> molecules held together by VDWs<br/>Conducts heat and electricity<br/>Very strong and tough<br/>Insoluble in water<br/>High m.p./b.p.</p> |  <p>C atoms in hexagonal rings only<br/>Cylindrical<br/>Structure is rod like due to continuing rings</p> |

## 4.5 Ceramics

- **Ceramic:** an inorganic non-metallic solid prepared by heating one or a mixture of substance(s) to a high temp.
- Most ceramic are giant molecular structures
- Properties of ceramics:
  - High m.p./b.p. and hard – strong covalent bonds
  - Don't conduct electricity/heat – no mobile ions or e<sup>-</sup>s
  - Chemically unreactive – e<sup>-</sup>s held in covalent bonds

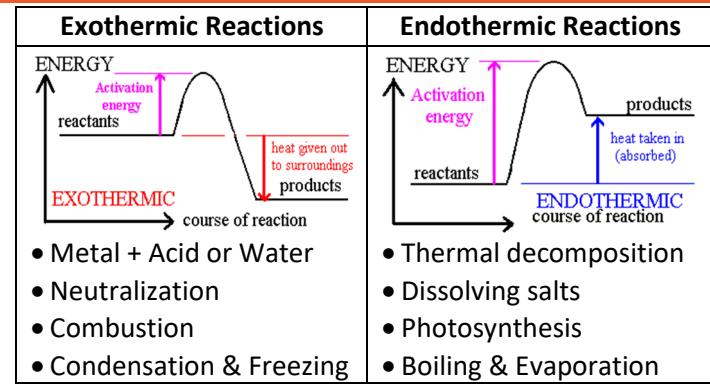
## 4.6 Recycling

- **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

## 5. CHEMICAL ENERGETICS

### 5.1 Energy Change in Reactions

| Exothermic Reactions  | Endothermic Reactions  |
|---|--|
| <ul style="list-style-type: none"> <li>• Energy given out</li> <li>• Surrounding warmer</li> <li>• Bond making</li> <li>• ΔH negative</li> </ul> $E_{Reactants} > E_{Products}$ | <ul style="list-style-type: none"> <li>• Energy taken in</li> <li>• Surrounding cooler</li> <li>• Bond breaking</li> <li>• ΔH positive</li> </ul> $E_{Reactants} < E_{Products}$ |



- **Standard Enthalpy Conditions:**

- Temperature: 298K or 25°C
- Pressure: 101KPa or 1atm
- Solution Conc.: 1mol dm<sup>-3</sup>

### 5.2 Enthalpy Change Definitions

| Standard molar enthalpy change of                     |  |  |  |  |   |
|---|--|--|--|--|---|
| Combustion<br>ΔH <sub>c</sub>                         | Formation<br>ΔH <sub>f</sub>                   | Solution<br>ΔH <sub>sol</sub>  | Hydration<br>ΔH <sub>hyd</sub>                         | Atomisation<br>ΔH <sub>at</sub>                | Neutralisation<br>ΔH <sub>n</sub>   |
| Enthalpy change when                                  |  |  |  |  |   |
| 1 mole of element or compound is completely combusted | 1 mole of compound is formed from its elements | 1 mole of a solute is dissolved in a solvent to form an infinitely dilute solution | 1 mole of ions in the gas phase are dissolved in water | 1 mole of gaseous atom formed from its element | 1 mole of H <sup>+</sup> and OH <sup>-</sup> combine to form 1 mole of H <sub>2</sub> O |
| 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

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

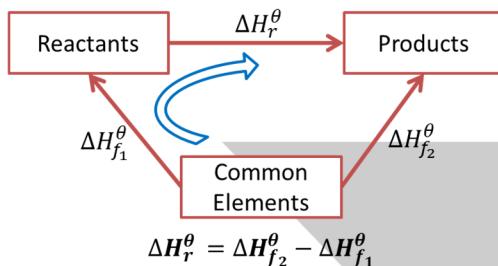
- When substance dissolved in water use c & m of water
- ΔT is change in temp.: add -ve or +ve to show rise/fall

## 5.5 Hess's Law

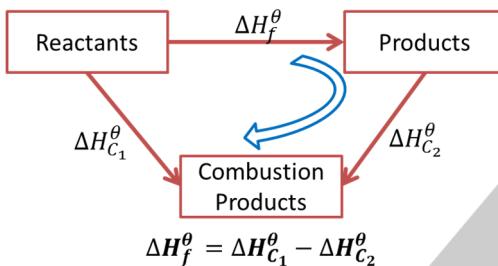
- The total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same.
- Reason to use Hess's Law:**
  - Std. conditions hard to maintain (e.g. exo/endo)
  - Elements don't always react directly

## 5.6 Calculating Enthalpy Change of...

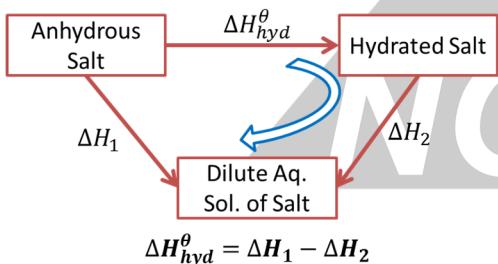
### ...Reaction from Formation



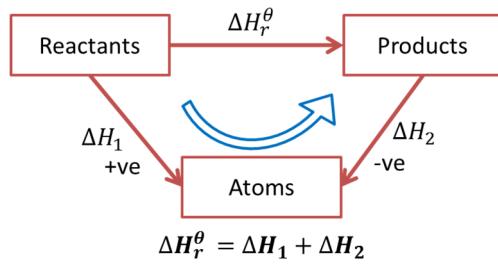
### ...Formation from Combustion



### ...Hydration from Anhydrous Salt



### ...Reaction from Bond Energies



## 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.  $Ca_2Si + 6H_2O \rightarrow 2Ca(OH)_2 + SiO_2 + 4H_2$ 
  - $Ca = +4 \rightarrow +2 \Rightarrow$  gain of negative charge  $\therefore$  reduction
  - $Si = -4 \rightarrow +4 \Rightarrow$  loss of negative charge  $\therefore$  oxidation

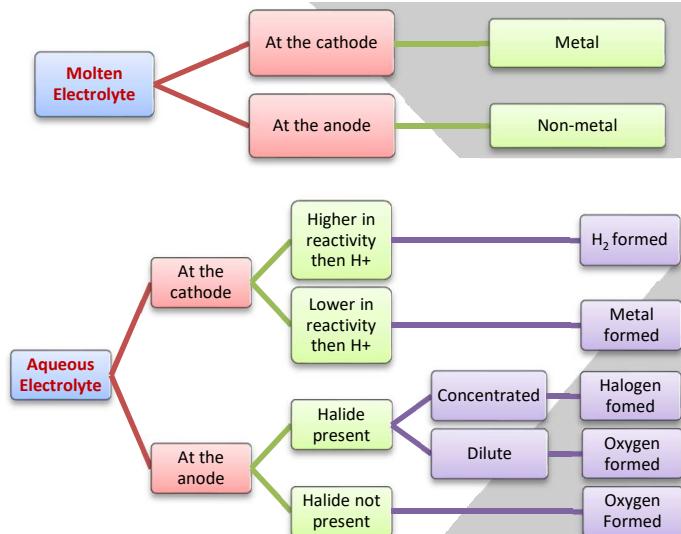
### 6.3 Balancing Equations

- 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:**  $4HI + 2HNO_3 \rightarrow 2I_2 + N_2O_3 + 3H_2O$

## 6.4 Electrolysis

- **Electrolysis:** decomposition of an electrolyte by an electric current. Electrical energy is used to bring about a chemical reaction; endothermic
- **Electrolyte:** an aqueous solution of an ionic substance or a molten ionic salt that conducts electricity due to mobile ions
- **Electrodes:**
  - Rods which help current enter the electrolyte
  - **Inert electrodes:** do not take part in the reaction e.g. graphite or platinum. Steel/titanium used in industry.
  - **Reactive electrodes:** take part in the reaction

## 6.5 Products of Electrolysis



## 7.2 Equilibrium Constants

### Equilibrium Constant

Expressed in terms of concentration

$$K_C = \frac{[\text{Product}]^{\text{mols}}}{[\text{Reactant}]^{\text{mols}}}$$

Only liquids and gases

Expressed in terms of partial pressure

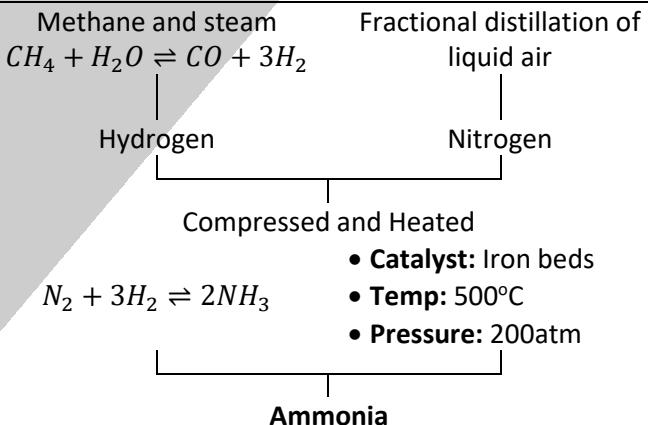
$$K_P = \frac{p(\text{Product})^{\text{mols}}}{p(\text{Reactant})^{\text{mols}}}$$

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

## 7.3 Manufacture of Ammonia

### HABER PROCESS FLOWCHART



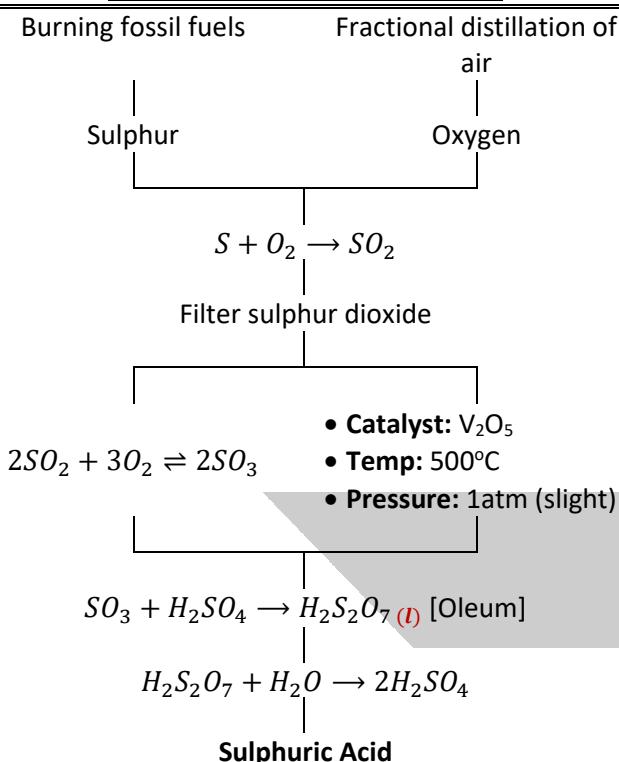
## 7. EQUILIBRIA

- **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

## 7.1 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         |

**7.4 Manufacture of Sulphuric Acid****CONTACT PROCESS FLOWCHART**

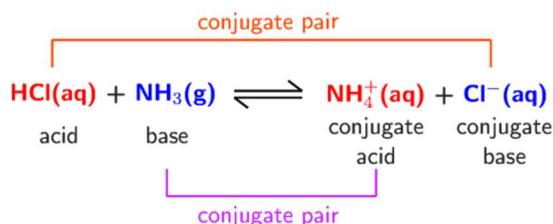
- $SO_3$  not dissolved directly into water because reaction explosive and causes  $H_2SO_4$  to vaporize
- Forward reaction exothermic  $\therefore$  temp. not too high so rate of backward reaction doesn't increase & not too low so particles have  $E_K$  for collision and catalyst works
- Since reaction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

**7.5 Acid-Base Equilibria**

- **Brønsted-Lowry Theory:**
  - An acid is a proton ( $H^+$ ) donor
  - A base is a proton ( $H^+$ ) acceptor
- **Amphoteric:** substances that can act like bases or acids

**7.6 Conjugate Pairs**

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



- $HCl$  is a conjugate acid of base  $Cl^-$  & vice versa
- $HCl$  is acid-I and  $Cl^-$  is base-I
- $NH_4^+$  is a conjugate acid of base  $NH_3$  & vice versa
- $NH_4^+$  is acid-II and  $NH_3$  is base-II

**7.7 Strong and Weak Acids and Bases**

- **Strong acids/bases:** acids/bases which dissociate almost completely in solutions
- **Weak acids/bases:** acids/bases which are only partially dissociated in solutions
- Strong and weak acids and bases can be distinguished by the pH value of their aqueous solutions
- **Monoprotic acids:** donate one  $H^+$  proton per molecule
- **Diprotic acids:** donate two  $H^+$  protons per molecule

**8. REACTION KINETICS**

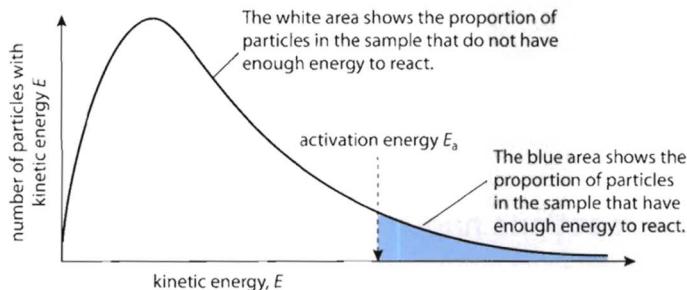
- **Rate of a reaction:** change in concentration of reactants or products per unit time
- **Activation energy:** minimum energy colliding particles must possess for a successful collision to take place
- **Catalysis:** acceleration of a chemical reaction by catalyst

**8.1 Effect of Concentration Changes**

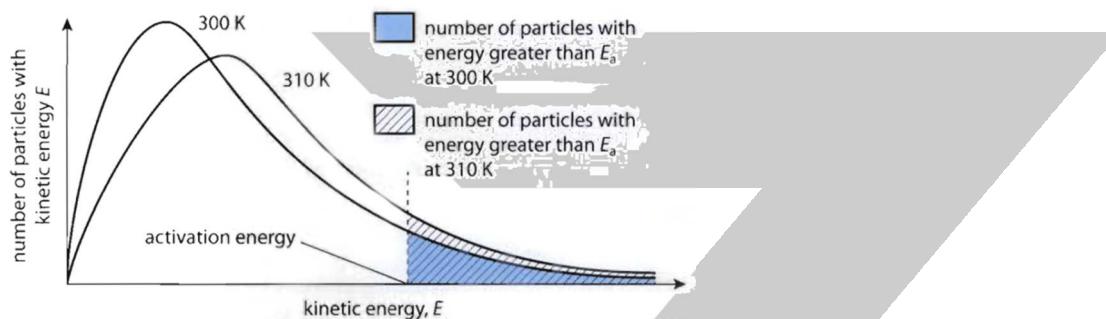
- **Increasing conc. of reactants increases rate of reaction:** more particles per unit volume, collision rate between reacting particles increases,  $\therefore$  rate of successful collision increases, resulting in increased rate of reaction.

## 8.2 Maxwell-Boltzmann Theory

- Explains effect of temp. & catalyst on rate of reaction
- Based on distribution of energy among reacting molecules under different conditions



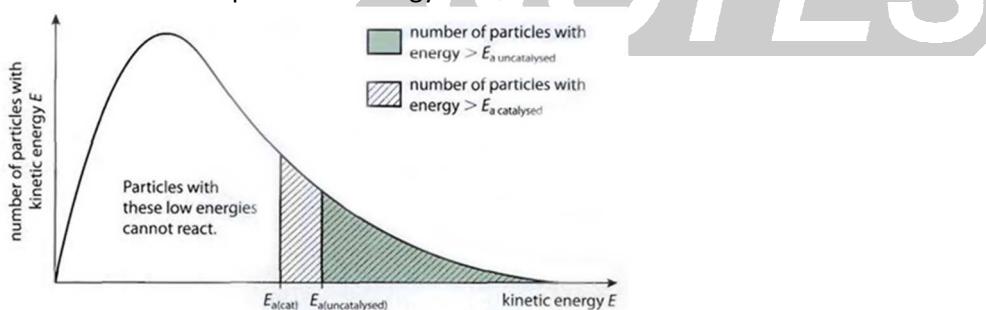
## 8.3 Effect of Temperature



- Number of collisions and chance of success will increase

## 8.4 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

## IIT JEE LEVEL CHEMISTRY // 970

### 9. CHEMICAL PERIODICITY

| Group     | 1  | 2         | 3         | 4       | 5           | 6       | 7        | 0     |
|-----------|--|-----------|-----------|---------|-------------|---------|----------|-------|
| Element   | Sodium   | Magnesium | Aluminium | Silicon | Phosphorous | Sulphur | Chlorine | Argon |
| Character | Metal  |           |           |         |             |         |          |       |
| Structure | Giant metallic lattice                                       |           |           |         |             |         |          |       |
| Bonding   | Metallic bond between cations and delocalized e <sup>-</sup> |           |           |         |             |         |          |       |
| Diagram   |  |           |           |         |             |         |          |       |

### 9.1 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                    | Amphoteric                      |              |
| Si       | SiO <sub>2(s)</sub>               | Coating                    |                                 |              |
| P        | P <sub>2</sub> O <sub>3(s)</sub>  | Burns yellow flame         | Giant covalent Simple molecular | +4 W. acidic |
| S        | SO <sub>2(g)</sub>                | Burns blue flame           |                                 | +5 S. acidic |
|          | SO <sub>3(g)</sub>                |                            | +4                              | S. acidic    |
|          |                                   |                            | +6                              | S. acidic    |

### 9.2 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> |  |       |             |
|  | SiO <sub>2(s)</sub>               |  |       |             |

### NO REACTION

|  |                                  | Reaction  | Oxid. | Nature    |
|--|----------------------------------|---|-------|-----------|
|  | 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    | S. Acidic |
|  | 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    | S. Acidic |

### 9.4 Acid-Base Reactions

- Aluminium oxide is amphoteric :: reacts with acid and base  
 $\text{Al}_2\text{O}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$      $\text{Al}_2\text{O}_3 + \text{NaOH} \rightarrow \text{NaAlO}_2 + \text{H}_2\text{O}$
- Silicon dioxide is acidic:  $\text{SiO}_2 + \text{NaOH}$  (hot & conc.) →  $\text{Na}_2\text{SiO}_3$
- 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 |

### 9.3 Reaction of Na & Mg with Water

|            |  |   |
|------------|--|---|
| Na & Water | 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 |
| Mg & Water | 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                                 |
| Mg & Steam | Mg <sub>(s)</sub> + H <sub>2</sub> O <sub>(g)</sub> → MgO <sub>(s)</sub> + H <sub>2(g)</sub>       | Very fast                                 |

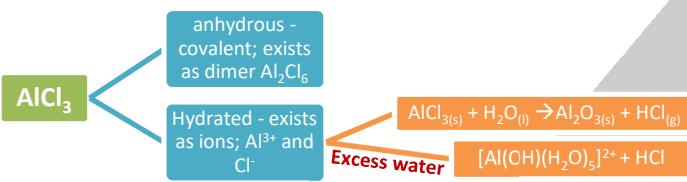
## 9.5 Reactions of Elements with Chlorine

|    | Formula                                    | Structure        | Oxid.    | Nature    |
|----|--|------------------|----------|-----------|
| Na | $\text{NaCl}_{(s)}$                        | Giant ionic      | +1       | Neutral   |
| Mg | $\text{MgCl}_{2(s)}$                       |                  | +2       | Neutral   |
| Al | $\text{AlCl}_{3(s)}$                       |                  | +3       | Acidic    |
| Si | $\text{SiCl}_{4(l)}$                       | Simple molecular | +4       | S. Acidic |
| P  | $\text{PCl}_{3(l)}$<br>$\text{PCl}_{5(l)}$ |                  | +3<br>+5 | S. Acidic |

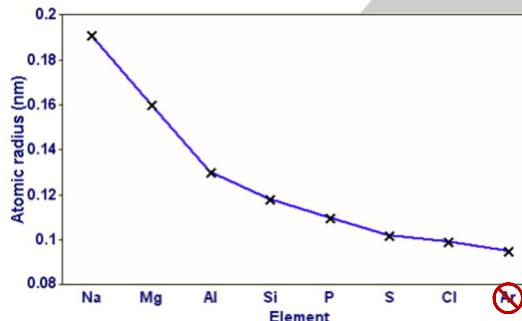
## 9.6 Reactions of Chloride with Water

|  | Reaction   | Nature    |
|--|--|-----------|
| $\text{NaCl}_{(s)}$                        | $\text{NaCl}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{NaCl}_{(aq)}$  | Neutral   |
| $\text{MgCl}_{2(s)}$                       | $\text{MgCl}_{2(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{MgCl}_{2(aq)}$  | W. Acidic |
| $\text{AlCl}_{3(s)}$                       | $\text{AlCl}_{3(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{Al}_2\text{O}_{3(s)} + \text{HCl}_{(g)}$  | Acidic    |
| $\text{SiCl}_{4(l)}$                       | $\text{SiCl}_{4(l)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{SiO}_{2(s)} + \text{HCl}_{(g)}$   | S. Acidic |
| $\text{PCl}_{3(l)}$<br>$\text{PCl}_{5(l)}$ | $\text{PCl}_{3(l)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{PO}_{3(aq)} + \text{HCl}_{(g)}$<br>$\text{PCl}_{5(l)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{PO}_{4(aq)} + \text{HCl}_{(g)}$ | S. Acidic |

- Sodium chloride simply dissolves in water. Water is polar  $\therefore$  positive  $\text{Na}^+$  attracted to  $\text{OH}^-$  while  $\text{Cl}^-$  attracted to  $\text{H}^+$
- $\text{MgCl}_2$  slightly acidic because Mg ion has smaller radius & higher charge  $\therefore$  attraction to water is so strong that  $\text{H}_2\text{O}$  loses a proton and solution becomes slightly acidic

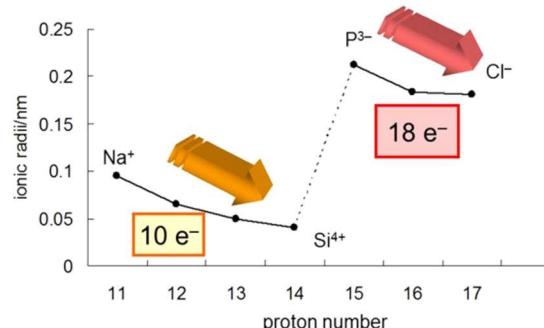


## 9.7 Atomic Radius



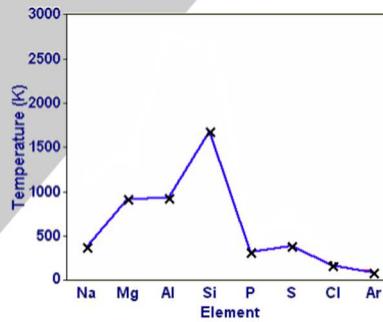
- $\text{P}^+$  in nucleus increases so nuclear charge increases
- There are more  $e^-$ , but increase in shielding is negligible because each extra  $e^-$  enters same principal energy level
- $\therefore$  force of attraction between nucleus &  $e^-$  increases ...
- So atomic radius decreases.

## 9.8 Ionic Radius



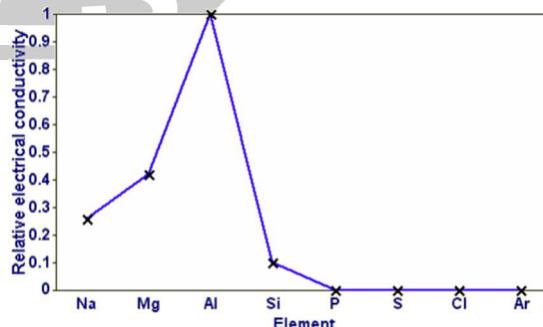
- Ionic radius decreases across a period however, since non-metals gain electrons, they have one more shell than metals therefore they always have a larger radius than metal ions

## 9.9 Melting Point



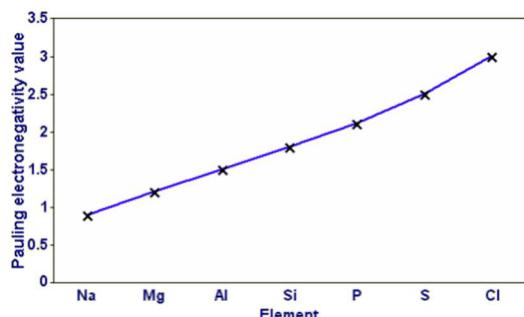
- $\text{Na} \rightarrow \text{Al}$  m.p. increases because delocalized  $e^-$  per atom increases making metallic bond stronger
- Si has highest m.p. due to giant covalent structure
- The larger the molecule size, the stronger the VDW forces  $\therefore \text{S}_8 > \text{P}_4 > \text{Cl}_2 > \text{Ar}$

## 9.10 Electrical Conductivity



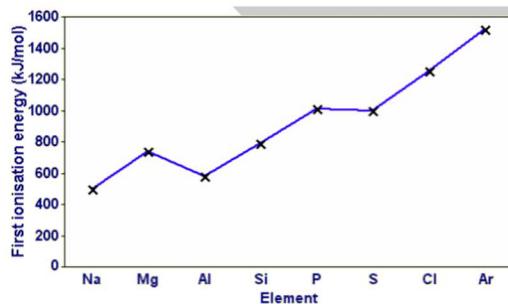
- $\text{Na} < \text{Mg} < \text{Al}$  because no. of delocalized electrons which can carry charge increases
- Silicon is a semi-conductor
- Non-metals – covalent  $\therefore$  no charge

## 9.11 Electronegativity



- Increases across period because the bonded  $e^-$  are in the same energy level but are attracted more strongly as no. of protons increases

## 9.12 First Ionization Energy



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

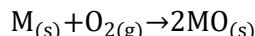
## 10. GROUP II – ALKALINE EARTH METALS

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

## 10.1 Reactivity of Alkaline Earth Metals

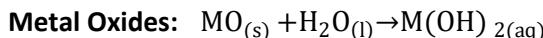
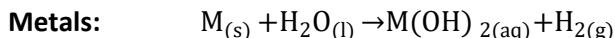
- Atomic radius increases down group
- Ionisation energy (I.E) decreases down the group
- The lower the I.E, easier to remove electrons
- Hence metals more reactive down the group
- Gp. 2 less reactive than gp. 1 since they need to lose two e<sup>-</sup>s  $\therefore$  total I.E = 1<sup>st</sup> I.E. and 2<sup>nd</sup> I.E.
- Gp. 2 metals form ionic compounds

## 10.2 Reaction of Gp. 2 Metals with Oxygen



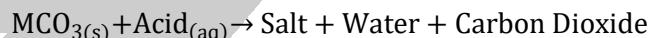
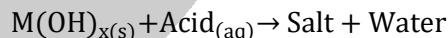
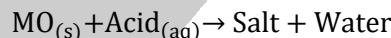
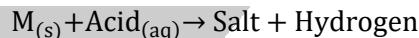
- All gp. 2 metals tarnish in air forming oxide coatings
- Burn vigorously in oxygen forming white solids

## 10.3 Reactions with Water

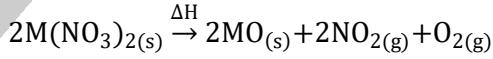
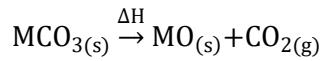


- Solubility of M, MO and  $M(OH)_2$  increases down group
- Alkalinity of solution increases down the group
- Solubility of M and MO increases down the group
- Solubility of  $M(OH)_2$  and  $MSO_4$  decreases down group

## 10.4 Reaction with Acid



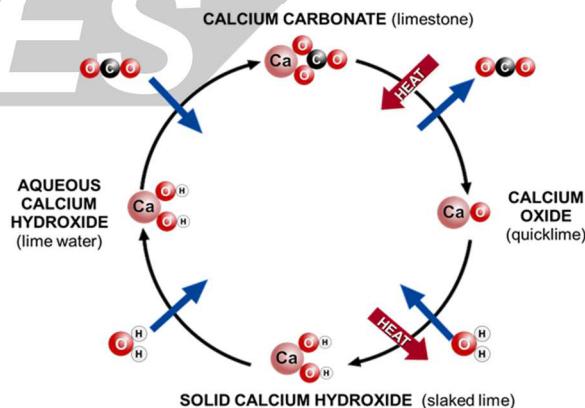
## 10.5 Thermal Decomposition of Gp. 2 Metals



- $NO_2$ : thick brown, acidic and soluble gas
- Thermal stability increases down the group  $\therefore$  decomposition becomes more difficult.

## 10.6 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

## 11. GROUP 17 – HALOGENS

### 11.1 Trends in Colour and Volatility

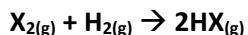
|          |              |        |                               |                              |
|----------|--------------|--------|-------------------------------|------------------------------|
| Fluorine | Yellow       | Gas    | m.p. & b.p.<br>increases<br>↓ | Volatility<br>decreases<br>↓ |
|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

- As atomic number increases, the number of electrons increases, this increases VDW forces so stronger bonds thus m.p./b.p. increases and volatility decreases

### 11.2 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.

### 11.3 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

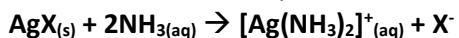
### (Sub) Halide ions and aq. Silver Ions



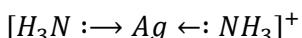
| Halide Ion      | With Silver Nitrate | With dilute aq. ammonia | With conc. aq. ammonia |
|-----------------|---------------------|-------------------------|------------------------|
| Cl <sup>-</sup> | White ppt.          | ppt. dissolves          |                        |
| Br <sup>-</sup> | Cream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

- The solubility of these ppts. are tested with dilute and conc. aq. ammonia to confirm presence of ion.

- If ppt. dissolves, it forms a complex ion:



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



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



- Conc.  $H_2SO_4_{(aq)}$  is an oxidising agent

- This reaction is used for preparation of hydrogen halides

|          |   |
|----------|---|
| Chlorine | $NaCl_{(s)} + H_2SO_4_{(aq)} \rightarrow HCl_{(g)} + NaHSO_4_{(aq)}$          |
| Bromine  | $NaBr_{(s)} + H_2SO_4_{(aq)} \rightarrow HBr_{(g)} + NaHSO_4_{(aq)}$          |
|          | $HBr_{(g)} + H_2SO_4_{(aq)} \rightarrow Br_2_{(g)} + SO_2_{(g)} + H_2O_{(l)}$ |
| Iodine   | $NaI_{(s)} + H_2SO_4_{(aq)} \rightarrow HI_{(g)} + NaHSO_4_{(aq)}$            |
|          | $HI_{(g)} + H_2SO_4_{(aq)} \rightarrow I_2_{(g)} + SO_2_{(g)} + H_2O_{(l)}$   |
|          | $HI_{(g)} + H_2SO_4_{(aq)} \rightarrow I_2_{(g)} + H_2S_{(g)} + H_2O_{(l)}$   |

### 11.4 The reactions of chlorine with aqueous sodium hydroxide

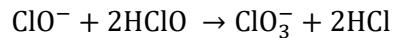
- Disproportionation:** a reaction in which the same substance is oxidized and reduced simultaneously producing two different products
- When chlorine reacts with a solution of cold aqueous sodium hydroxide, the disproportionation goes to lower oxidation states



- 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

### 11.5 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

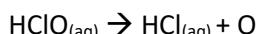
#### • Bromine and Iodine: manufacture of photographic films

#### • 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

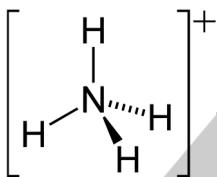
## 12. NITROGEN AND SULPHUR

### 12.1 Lack of Reactivity of Nitrogen

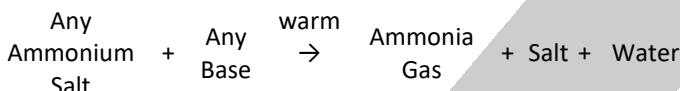
- Nitrogen molecule has three strong covalent bonds
- Bond is very strong and requires high energy for splitting the two nitrogen atoms of a molecule.
- It reacts only under extreme temperature or pressure or in presence of catalyst.

### 12.2 Ammonium

- Lone pair of e<sup>-</sup>s of nitrogen forms a coordinate bond with the H<sup>+</sup> ion
- Formation:** NH<sub>3(g)</sub> + H<sup>+</sup> → NH<sub>4</sub><sup>+</sup>
- Shape: tetrahedral
- Bond angle: 109.5°
- Bond length: equal lengths



#### Displacement of ammonia from its salts:



### 12.3 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

### 12.4 Eutrophication

- Nitrate fertilisers leach into rivers and lakes after rain
- Water plants grow more than usual
- They block sunlight and kill plants underneath
- Bacteria/fungi decompose remains using the O<sub>2</sub>
- Fish and other creatures die from oxygen starvation

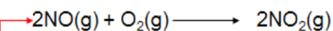
### 12.5 Oxides of Nitrogen



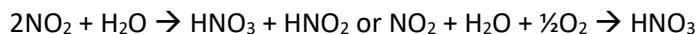
- Naturally:** during lightning, E<sub>A</sub> provided for N<sub>2</sub> to react
- Man-made:** in car engine, high temp. and pressure

- Catalytic converters:** exhaust gases passed through catalytic converters containing a catalyst (platinum/palladium/nickel) helping to reduce oxides to nitrogen.

- Catalytic role in oxidation of sulphur dioxide:**



### 12.6 Pollution



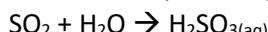
- Damages trees & plants, kills fish and other river life, buildings, statues and metal structures

#### 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
- Carbon monoxide (CO):** source: incomplete combustion of hydrocarbon fuel, toxic effect on haemoglobin

### 12.7 Food Preservation

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



- SO<sub>2</sub> & 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.

## 13. 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 CH<sub>2</sub>
  - similar chemical properties
  - gradual change in physical properties as M<sub>r</sub> 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

### 13.1 Hybridization

- **Hybridisation:** mixing up of different atomic orbitals resulting in new orbitals of equal energy.

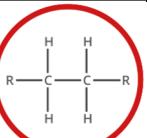
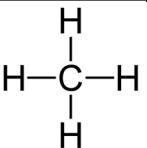
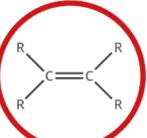
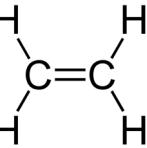
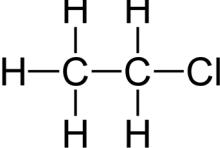
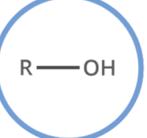
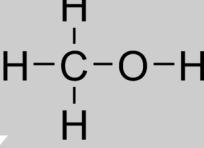
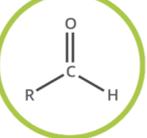
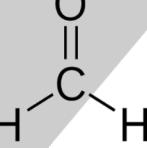
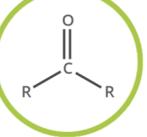
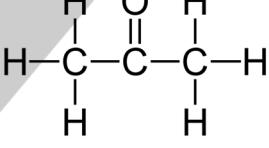
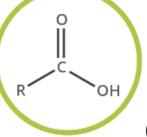
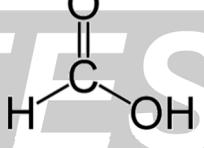
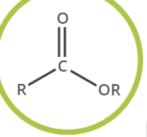
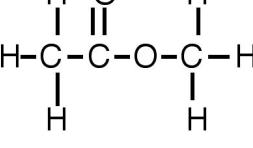
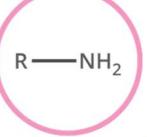
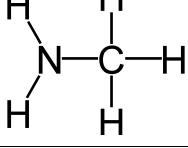
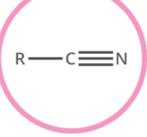
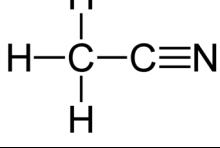
- **Carbon's electron configuration:**

| Ground State |    |   | Excited State |    |   |
|--------------|----|---|---------------|----|---|
| 2s           | 2p |   | 2s            | 2p |   |
|              | x  | y | z             |    | x |
| 1↓           | ↑  | ↑ |               | ↑  | ↑ |

| $sp^3$                                | $sp^2$   | $sp$  |
|---------------------------------------|--|---|
| All orbitals mix<br>4 $sp^3$ orbitals | 2s, $2p_x$ , $2p_y$ mix<br>3 $sp^2$ orbitals<br>1 pure p orbital | 2s and $2p^x$ mix<br>2 sp orbitals<br>2 pure p orbitals |
| <b>Ratio of characteristics s : p</b> |  |   |
| 1 : 3                                 | 1 : 2  | 1 : 1   |



13.2 Classes of Compound

| 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 |
|  Amines          | -amine         |  | Methylamine      |
|  Nitriles        | -nitrile       |  | Ethyl nitrile    |

### 13.3 Types of Formulae

| Hexane   |   |
|--|---|
| Displayed Formula  | Structural Formula  |
| <pre>       H   H   H   H   H   H                         H—C—C—C—C—C—C—H                           H   H   H   H     </pre> | $\text{CH}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-CH}_3$<br>or<br>$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ |
| Skeletal Formula   | Molecular Formula   |
|   | $\text{C}_6\text{H}_{14}$   |

### 13.4 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

### 13.5 Breaking of Covalent Bonds

#### Homolytic Fission:

- Two atoms sharing  $e^-$  pair of similar electronegativity
- 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  $\rightarrow$  very reactive
- Free radical reaction catalysed by heat or light

#### Heterolytic Fission:

- Two atoms sharing  $e^-$  pair are of different electronegativity
- 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

### 13.6 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:  $\text{CH}_3^-, \text{Cl}^-, \text{NH}_3, \text{H}_2\text{O}, \text{CN}^-$

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

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

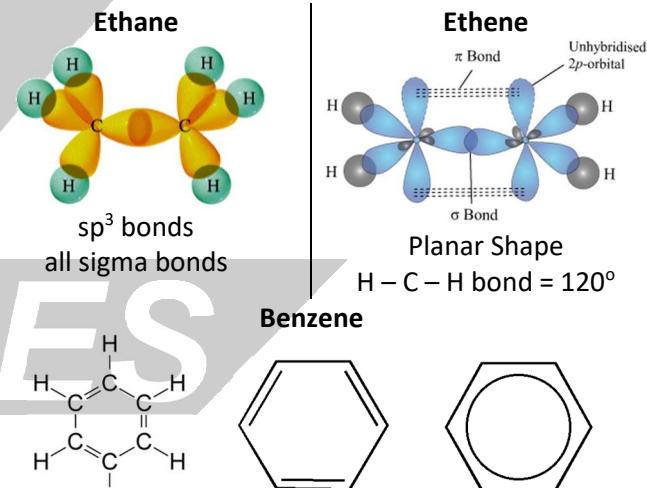
### 13.7 Types of Reaction

- 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)

### 13.8 Oxidation and Reduction

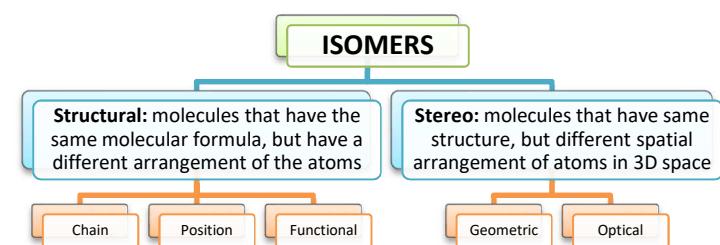
- Oxidation:** addition of oxygen or removal of hydrogen
- Reduction:** addition of hydrogen or removal of oxygen

### 13.9 Shapes of Ethane and Ethene



### 13.10 Isomerism

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

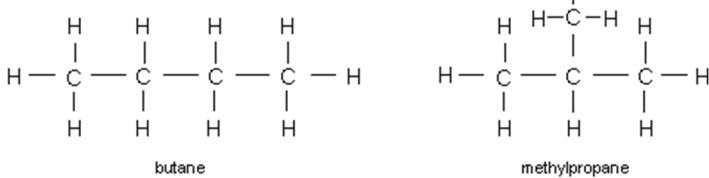


**Note:**

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

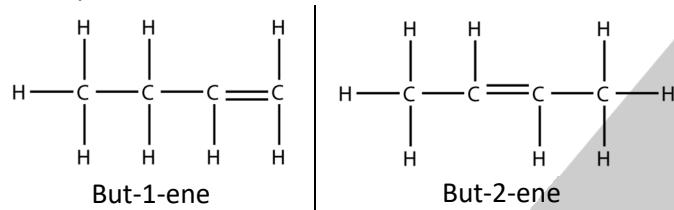
### 13.11 Chain Isomers

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



### 13.12 Position Isomers

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



### 13.13 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<br>Must have O <sub>2</sub> | Carboxylic acid & Ester | C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> |

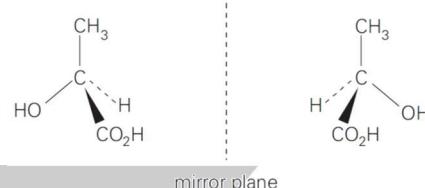
### 13.14 Geometric (cis/trans) Isomers

- 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**



### 13.15 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 =  $2^n$



### 14. HYDROCARBONS

#### 14.1 Properties

##### Generally unreactive:

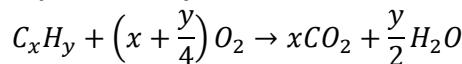
- All C–C bonds single; alkanes = saturated hydrocarbons
- Non-polar ∴ no center of charge to act as either nucleophile or electrophile ∴ cannot attract polar reagents like acids, bases, metals or oxidizing agents

##### 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

#### 14.2 Combustion

- Used as fuel because they burn in oxygen to give out large amounts of energy
- Alkanes kinetically stable in presence of O<sub>2</sub>; combustion occurs when necessary amount of E<sub>a</sub> supplied
- Reaction occurs **only in gas phase**
- **Complete:** carbon dioxide + water
- **Incomplete:** carbon monoxide + carbon (soot) + water
- **General Equation of Hydrocarbon Combustion:**



### 14.3 Substitution

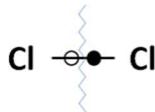
- Alkanes react with halogens:  $Cl_2$  and  $Br_2$

#### Example: Chlorination of Methane

| Reagent     | Condition | Type         | Mechanism    |
|-------------|-----------|--------------|--------------|
| $Cl_{2(g)}$ | UV light  | Substitution | Free Radical |

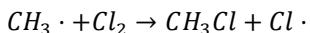
#### Initiation:

- Energy of a photon of light absorbed
- $Cl - Cl$  bond breaks homolytically



#### Propagation:

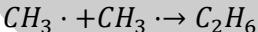
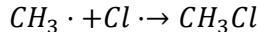
- Highly reactive  $Cl\cdot$  collides with a  $CH_4$  molecule forming a new free radical;  $CH_3\cdot$



- This can then react with another  $Cl_2$  and process repeats if sufficient  $Cl_2$  present until all H are replaced

#### Termination:

- Reaction ends when 2 free radicals collide & combine



#### Products:

forms large amounts of  $CH_3Cl$  and  $HCl$  and small amount  $C_2H_6$ ; separated by fractional distillation

#### Products and free radicals differ due to:

- Halogen used: bromine requires more light
- Alkane used: ↑ no. of C = ↑ variety of products

### 14.4 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

### 14.5 Hydrocarbons as Fuels

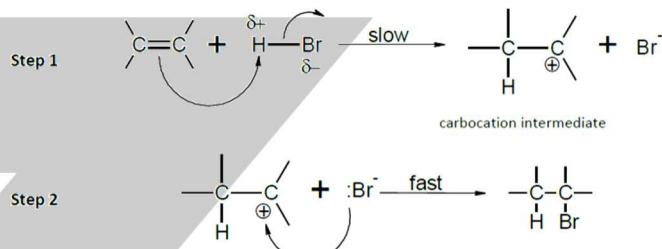
- Source of alkanes: crude oil
- Steady change in b.p. of alkanes allows crude oil to be separated by fractional distillation
- Catalytic conversion of CO and  $NO_x$ :

  - $2NO_2 + 4CO \rightarrow N_2 + 4CO_2$
  - $2NO + 2CO \rightarrow N_2 + 2CO_2$

### 14.6 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

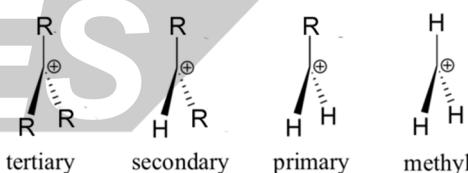
### 14.7 Electrophilic Addition Mechanism



- 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

### 14.8 Carbocations

most stable → 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  $e^-$  to the ring
  - Producing a positive inductive effect
  - A larger alkyl group has a weaker inductive effect

## 14.9 Addition Reactions

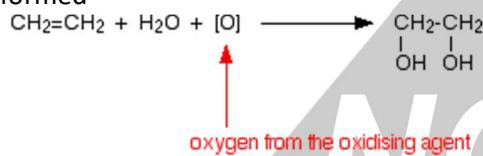
|               |   |
|---------------|---|
|               | <b>Alkene + H<sub>2</sub> → Alkane</b>  |
| Hydrogenation | <ul style="list-style-type: none"> <li>Reagent: H<sub>2(g)</sub></li> <li>Condition: <ul style="list-style-type: none"> <li>Catalyst: Nickel</li> <li>Temp.: 100°C</li> <li>Press.: 2 atm.</li> </ul> </li> <li>Use: convert liquid oils to saturated solid fats</li> </ul> |
| Halogenation  | <b>Alkene + X<sub>2</sub> → Dihaloalkane</b>  |
|               | <ul style="list-style-type: none"> <li>Reagent: Halogen<sub>(aq)</sub></li> <li>Condition: r.t.p./dark</li> </ul>   |
|               | <b>Alkene + Hydrohalogen → Halogenoalkane</b>   |
|               | <ul style="list-style-type: none"> <li>Reagent: Hydrohalogen<sub>(g)</sub></li> <li>Condition: r.t.p.</li> </ul>  |
| Hydration     | <b>Alkene + H<sub>2</sub>O<sub>(g)</sub> → Alcohol</b>  |
|               | <ul style="list-style-type: none"> <li>Reagent: steam</li> <li>Condition: <ul style="list-style-type: none"> <li>Catalyst: H<sub>3</sub>PO<sub>4</sub> – phosphoric acid</li> <li>Temp.: 300°C</li> <li>Press.: 70atm</li> </ul> </li> </ul>                                |

## 14.10 Oxidation of Alkenes

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

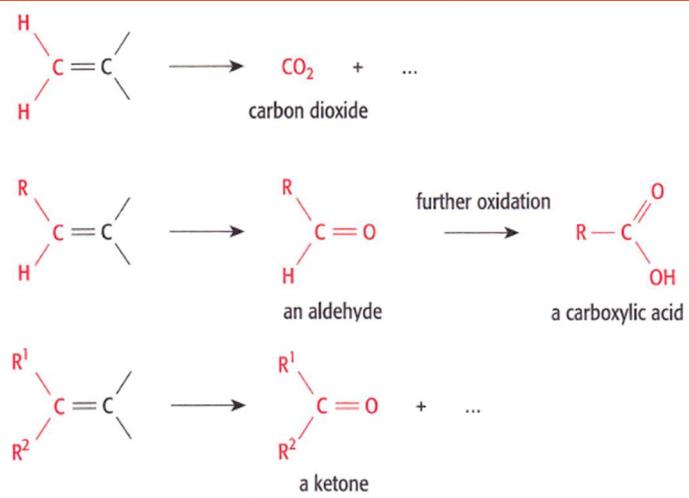
### With Cold Dil. Acidified KMnO<sub>4</sub>/H<sup>+</sup>

- Diol is formed



### 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

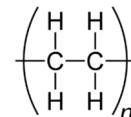


## 14.11 Polymerization

- Repeated addition of 1000s of alkene molecules (monomer) to each other forming a macromolecule

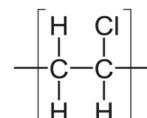
### Polyethene:

- LDPE: cling wrap
- HDPE: water pipes, wire insulation



### Polychloroethene (PVC):

- Water pipes
- Insulation of wires



- General conditions: high pressure, high temperature and catalyst

### Disadvantages:

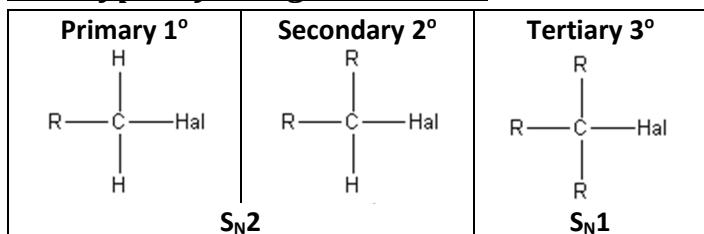
- Non-biodegradable: does not break down so increases amount of volume needed for landfill sites
- Combustion produces harmful gases which contribute to global warming e.g. SO<sub>2</sub>, CO<sub>2</sub> and HCl from PVCs

### Disposal of Polymers:

- Recycle existing plastic
- Make polymers biodegradable by adding starch units

## 15. HALOGEN DERIVATIVES

### 15.1 Types of Halogenoalkanes



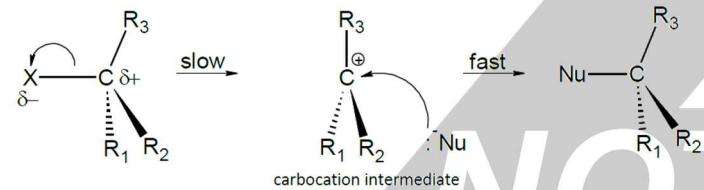
### 15.2 Strength of C – Hal Bond

|        | Polar Nature                        | Bond Energy  | Reactivity  |
|--------|-------------------------------------|--|-------------|
| Fluoro | Decrease ↓                          | Decrease ↓   | Increases ↓ |
| Chloro |                                     |  |             |
| Bromo  |                                     |  |             |
| Iodo   |                                     |  |             |
|        | Electro-tivity decreases down group | Bond length increases, bond energy decreases, lower $E_A$ so more reactive |             |

### 15.3 Nucleophilic Substitution Mechanism

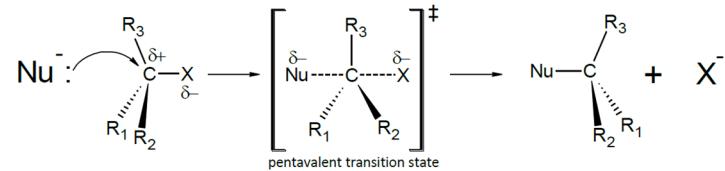
- The C – X bond is a polar bond, has partial charges due to high electro-tivity of halogen.
- The  $\delta +$  carbocation is easily susceptible to attack by a nucleophile

#### $\text{S}_{\text{N}}1$ Mechanism:



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

#### $\text{S}_{\text{N}}2$ Mechanism:



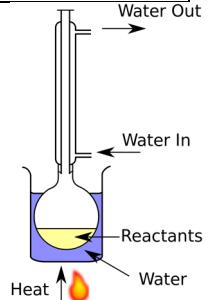
- Bimolecular – two molecules involved in 1<sup>st</sup> step
- Primary and secondary halogenoalkanes

### 15.4 Nucleophilic Substitution Reaction

|                   |  |
|-------------------|--|
| Hydrolysis        | $\text{R}-\text{X} + \text{OH}^- \rightarrow \text{R}-\text{OH} + \text{X}^-$ <ul style="list-style-type: none"> <li>Reagent: strong alkali; <math>\text{NaOH}_{(\text{aq})}</math> or <math>\text{KOH}_{(\text{aq})}</math></li> <li>Condition: heat/reflux</li> <li>Fluoroalkanes are not hydrolysed because the C – F bond is too strong</li> <li>Ease of hydrolysis increases: Primary &lt; Secondary &lt; Tertiary</li> <li>Tertiary halogenoalkanes can be hydrolysed without alkali</li> <li>Note: if any <math>\text{Cl}^-</math> or <math>\text{Br}^-</math> ions present in <math>\text{NaOH}_{(\text{aq})}</math>, these ions will interfere with reaction</li> </ul> |
| Nitrile (cyanide) | $\text{R}-\text{X} + \text{CN}^- \rightarrow \text{RCN} + \text{X}^-$ <ul style="list-style-type: none"> <li>Reagent: <math>\text{KCN}</math> or <math>\text{NaCN}</math> in ethanol</li> <li>Condition: <ul style="list-style-type: none"> <li>Solvent: Ethanol</li> <li>Heat/Reflux</li> </ul> </li> <li>Reaction forms a C – C bond therefore no. of C increases; name has one more carbon</li> </ul>   |
| Primary Amines    | $\text{R}-\text{X} + \text{NH}_3 \rightarrow \text{RNH}_{2(\text{l})} + \text{HX}_{(\text{g})}$ <ul style="list-style-type: none"> <li>Reagent: Ammonia (<math>\text{NH}_3</math>)</li> <li>Condition: ammonia in alcohol under pressure in sealed container</li> <li>Note: if excess conc. ammonia used, <math>\text{HX}</math> reacts with it forming <math>\text{NH}_4\text{X}</math></li> </ul>  |

### 15.5 Reflux

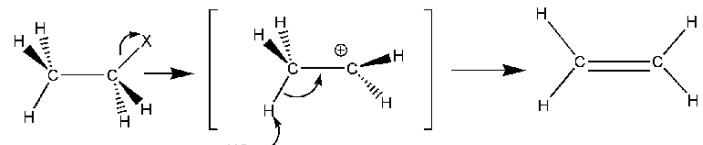
- Many organic reactions proceed slowly
- Heating done under reflux to prevent volatile organic solvents to evaporate
- Mechanism similar to simple distillation



### 15.6 Elimination Reaction



#### Mechanism:



- Reagent: ethanolic  $\text{NaOH}$  or  $\text{KOH}$
- Conditions: temp.  $60^\circ\text{C}$ , reflux
- $\text{OH}^-$  acts as a proton acceptor; it accepts the  $\text{H}^+$  loss from the halogenoalkanes during elimination
- Elimination become progressively more easier  
Primary < Secondary < Tertiary
- Note: the carbon atom adjacent to carbon with halide must have at least one hydrogen attached to it.

### 15.7 Uses of Halogenoalkanes

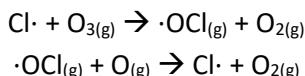
- CFCs are inert and can be liquefied easily: Strength of C – X bond is very high, hence do not decompose easily and are not flammable.

#### • Uses:

- As propellants → in aerosol cans
- As solvents → in dry-cleaning
- As refrigerant → for freezers and fridges
- Fire extinguishers, insecticides and pesticides

### 15.8 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

## 16. HYDROXY COMPOUNDS

### 16.1 Types of Alcohols

| Primary 1°   | Secondary 2°  | Tertiary 3°  |
|--|---|--|
| $\begin{array}{c} \text{OH} \\   \\ \text{H}_3\text{C}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$ | $\begin{array}{c} \text{OH} \\   \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\   \\ \text{H} \end{array}$ | $\begin{array}{c} \text{OH} \\   \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$ |

#### • Source of Alcohols:

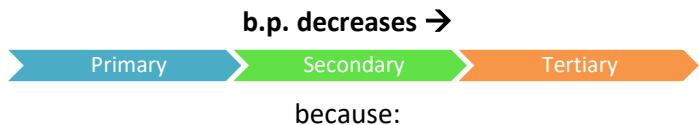
- Hydration of alkenes
- Fermentation

### 16.2 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. of alcohols > alkenes as they have hydrogen bonds

#### Solubility of Alcohols in Water:

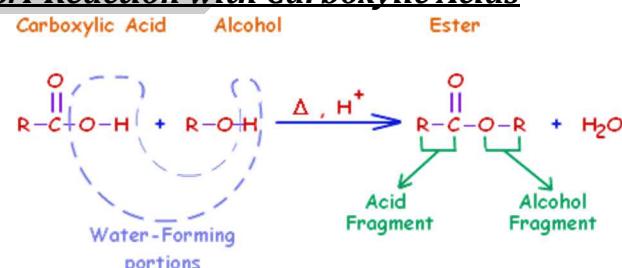
- Smaller alcohols mix completely with water since strong hydrogen bonds occur between alcohols and water
- As hydrocarbon nature increase (i.e. more C-C... bonds), the non-polar character outweighs the ability of the OH to form hydrogen bonds and ∴ solubility decreases
- Small alcohols (e.g. ethanol)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

### 16.3 Reaction with Sodium

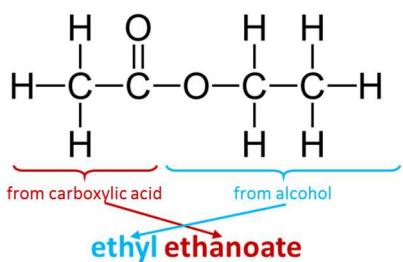


- Type of reaction: acid-base
- Reagent used: liquid sodium metal
- Reactivity of alcohols decreases with increasing chain lengths of hydrocarbon
- Reaction less vigorous than that of Na and water which shows water is a stronger acid than alcohol

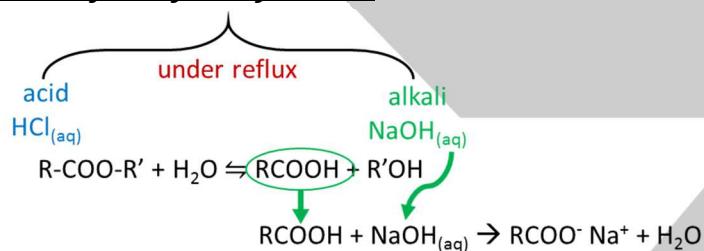
### 16.4 Reaction with Carboxylic Acids



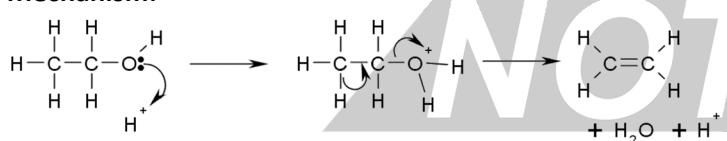
| Reagent | Condition   | Type of Reaction |
|---------|---|------------------|
| R-COOH  | Heat-reflux<br>Conc. H <sub>2</sub> SO <sub>4</sub> | Esterification   |

**Naming esters:****Properties of Esters:**

- Esters are volatile compounds – no H-bonds so low m.p.
- Polar molecules – soluble in organic solvents
- Sweet, fruity smelling liquids
- Many occur naturally e.g. as fats, oils & flavours in fruits
- Used in food flavourings and perfumes and as solvents

**16.5 Hydrolysis of Esters****16.6 Dehydration of Alcohols**

| Condition                                      | Type of Reaction |
|--|------------------|
| Conc. $\text{H}_2\text{SO}_4$                  | or               |
| $\text{H}_3\text{PO}_4$ at $180^\circ\text{C}$ | or               |
| $\text{Al}_2\text{O}_3$ at $300^\circ\text{C}$ | Elimination      |

**Mechanism:**

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

## 16.7 Halogenation

- Type of Reaction: Nucleophilic Substitution

| R - OH → R - X  |                 |          |   |                  |  |
|---|-----------------|----------|---|------------------|--|
| Forming Reagent   | Producing:      | R - OH + | Reactions   | Condition        |  |
| NaBr + H <sub>2</sub> SO <sub>4(aq)</sub> → HBr<br>P + Br <sub>2</sub> –warm→ PBr <sub>3</sub><br>P + I <sub>2</sub> –warm→ PI <sub>3</sub> | Alkyl Chlorides | R - OH + | Conc. HCl → RCl <sub>(l)</sub> + H <sub>2</sub> O   | Zn + Heat/Reflux |  |
|   |                 |          | SOCl <sub>2</sub> → RCl <sub>(l)</sub> + SO <sub>2(g)</sub> + HCl <sub>(g)</sub>                | r.t.p            |  |
|   | Alkyl Bromides  |          | PCl <sub>5</sub> → RCl <sub>(l)</sub> + POCl <sub>3(aq)</sub> + HCl <sub>(g)</sub>              |                  |  |
|   |                 |          | PCl <sub>3</sub> → RCl <sub>(l)</sub> + H <sub>3</sub> PO <sub>3(aq)</sub> + HCl <sub>(g)</sub> | Heat/Reflux      |  |
| HBr <sub>(g)</sub> → RBr <sub>(l)</sub> + H <sub>2</sub> O  | Alkyl Iodide    |          | PBr <sub>3(g)</sub> → RBr <sub>(l)</sub> + H <sub>3</sub> PO <sub>3(aq)</sub>                   | r.t.p            |  |
|   |                 |          | PI <sub>3(g)</sub> → RI <sub>(l)</sub> + H <sub>3</sub> PO <sub>3(aq)</sub>                     | r.t.p            |  |

## 16.8 Oxidation of Alcohols

- Reagent: Oxidising agents

| Reagent  | Type of Reaction                                  |
|--|---|
| Acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub><br>Orange to Green | Acidified KMnO <sub>4</sub><br>Pink to Colourless |

| Primary Alcohol<br>R-CH <sub>2</sub> -OH                                    | Secondary Alcohol<br>R-CH(OH)-R |
|---|---------------------------------|
| Heat / Reflux<br><br>R - CHO<br>aldehyde<br><br>R - COOH<br>carboxylic acid | <br>ketone                      |

If aldehyde needed, must distil as soon as it forms

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

## 16.9 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>7</sub> /H <sup>+</sup> | Green                        | X         | X        |
| KMnO <sub>4</sub> /H <sup>+</sup>                             | Colourless                   | X         | X        |

## 17. CARBONYL COMPOUNDS

### Boiling Point:



Weak VDWS      Permanent Dipole-Dipole      H-Bonding

### Solubility:

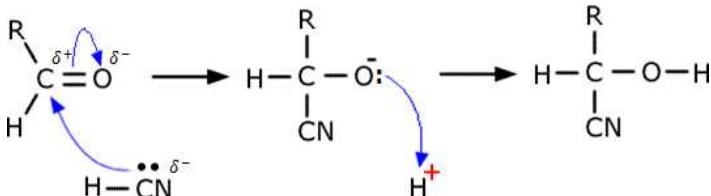
- Smaller carbonyl compounds: completely soluble as they form hydrogen bonds with water molecules; are good solvents for polar & non-polar solutes
- Larger carbonyl compounds: polar nature decreases and non-polar nature increases; ability to form hydrogen bonds decreases

## 17.1 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 cyanohydrine
- 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  $\text{CN}^-$  ions, the reaction is slow. To increase  $\text{CN}^-$  conc.:
 
$$\text{HCN} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CN}^-$$
- Make HCN react in presence of alkali
- Addition of KCN and dilute  $\text{H}_2\text{SO}_4$  can provide HCN and more  $\text{CN}^-$  ions

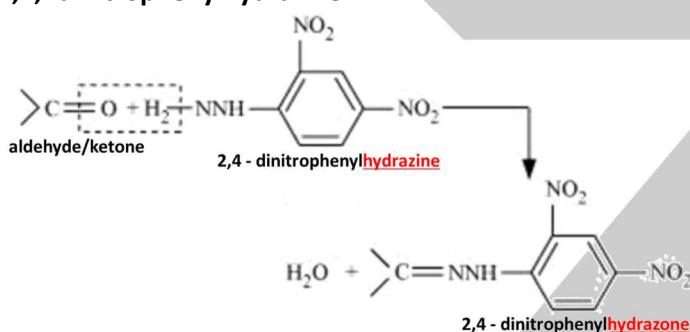
## 17.2 Reduction of Carbonyl Compounds

- Type of Reaction:** nucleophilic addition ( $\text{H}^-$  ions)
- Reducing agents:**
  - $\text{NaBH}_4$  – sodium tetrahydrioborate
  - $\text{LiAlH}_4$  – lithium aluminium hydride
  - $\text{H}_2/\text{Pt}$  or Ni

| Aldehydes $\Rightarrow 1^\circ$ Alcohols                       | Ketones $\Rightarrow 2^\circ$ Alcohols                      |
|--|---|
| $\text{R-CHO} + 2[\text{H}] \rightarrow \text{RCH}_2\text{OH}$ | $\text{R-CO-R} + 2[\text{H}] \rightarrow \text{R-CH(OH)-R}$ |

## 17.3 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  $\text{AgNO}_3$  + aq.  $\text{NH}_3 \rightarrow$  excess  $[\text{Ag}(\text{NH}_3)_2]^+$

**Aldehyde + Tollen's Reagent  $\rightarrow$  Silver Mirror**

$\text{Ag}^+$  reduced to Silver and  $-\text{CHO}$  oxidised to acid



### Fehling's Solution

$\text{CuSO}_4$  in ammonia solution

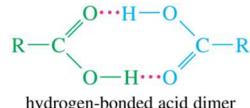
**Aldehyde + Fehling's Solution  $\rightarrow$  Red ppt.**

$\text{Cu}^{2+}$  reduced to  $\text{Cu(I)}$  oxide and  $-\text{CHO}$  oxidised to acid



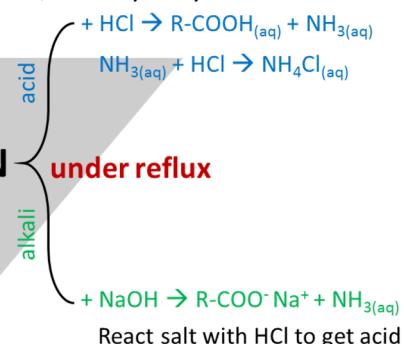
## 18. CARBOXYLIC ACIDS AND DERIVATIVES

- 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



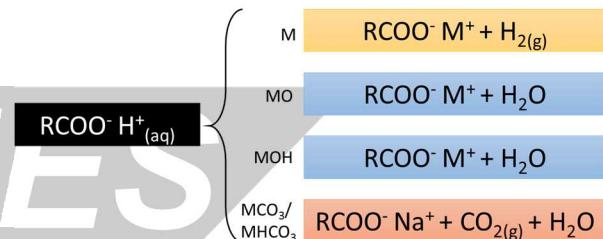
## 18.1 Formation of Carboxylic Acids

- From alcohols:** complete oxidation of primary alcohols
- From aldehydes:** oxidation of aldehydes
- From nitriles:** acid/base hydrolysis of a nitrile



## 18.2 Formation of Salts

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

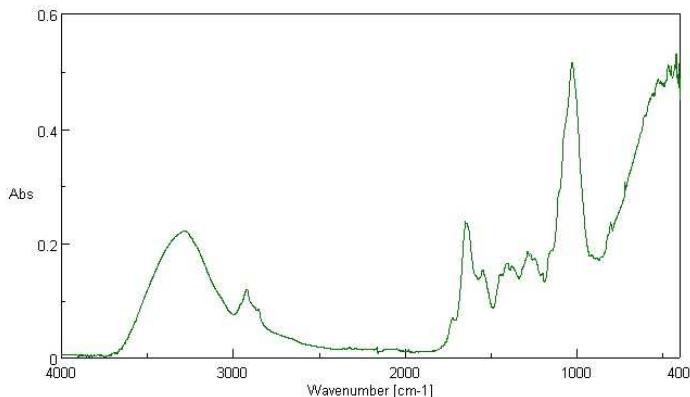


## 19. ANALYTICAL TECHNIQUES

### 19.1 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



## 19.2 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

# NOTES

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