

HIGHER CHEMISTRY

CONTENT STATEMENTS

Unit 1: Energy Matters

a) Reaction rates

(i) Following the course of a reaction

Reactions can be followed by measuring changes in concentration, mass and volume of reactants and products.

The average rate of a reaction, or stage in a reaction, can be calculated from initial and final quantities and the time interval.

The rate of a reaction, or stage in a reaction, is proportional to the reciprocal of the time taken.

(ii) Factors affecting rate

The rates of reactions are affected by changes in concentration, particle size and temperature.

The collision theory can be used to explain the effects of concentration and surface area on reaction rates.

Temperature is a measure of the average kinetic energy of the particles of a substance.

The activation energy is the minimum kinetic energy required by colliding particles before reaction will occur.

Energy distribution diagrams can be used to explain the effect of changing temperature on the kinetic energy of particles.

The effect of temperature on reaction rate can be explained in terms of an increase in the number of particles with energy greater than the activation energy.

With some chemical reactions, light can be used to increase the number of particles with energy greater than the activation energy.

(iii) The idea of excess

The reactant that is in excess can be calculated.

(iv) Catalysts

Catalysts can be classified as either heterogeneous or homogeneous.

Catalysts are used in many industrial processes.

Heterogeneous catalysts work by the adsorption of reactant molecules.

The surface activity of a catalyst can be reduced by poisoning.

Impurities in the reactants result in the industrial catalysts having to be regenerated or renewed.

Catalytic converters are fitted to cars to catalyse the conversion of poisonous carbon monoxide and oxides of nitrogen to carbon dioxide and nitrogen.

Cars with catalytic converters only use 'lead-free' petrol to prevent poisoning of the catalyst.

Enzymes catalyse the chemical reactions which take place in the living cells of plants and animals.

Enzymes are used in many industrial processes.

b) Enthalpy

(i) Potential energy diagrams

Exothermic changes cause heat to be released to the surroundings; endothermic changes cause absorption of heat from the surroundings.

A potential energy diagram can be used to show the energy pathway for a reaction.

The enthalpy change is the energy difference between products and reactants.

The enthalpy change can be calculated from a potential energy diagram.

The enthalpy change has a negative value for exothermic reactions and a positive value for endothermic reactions.

The activated complex is an unstable arrangement of atoms formed at the maximum of the potential energy barrier, during a reaction.

The activation energy is the energy required by colliding molecules to form an activated complex.

The activation energy can be calculated from potential energy diagrams.

The effect of a catalyst can be explained in terms of alternative reaction pathways with lower activation energy.

A potential energy diagram can be used to show the effect of a catalyst on activation energy.

(ii) Enthalpy changes

The enthalpy of combustion of a substance is the enthalpy change when one mole of the substance burns completely in oxygen.

The enthalpy of solution of a substance is the enthalpy change when one mole of the substance dissolves in water.

The enthalpy of neutralisation of an acid is the enthalpy change when the acid is neutralised to form one mole of water.

The enthalpy changes can be calculated using $c \cdot m \cdot \Delta T$.

c) Patterns in the Periodic Table

The modern Periodic Table is based on the work of Mendeleev who arranged the known elements in order of increasing atomic masses in conjunction with similar chemical properties, leaving gaps for yet to be discovered elements.

There are variations in the densities, melting points and boiling points of the elements across a period and down a group.

The atomic size decreases across a period and increases down a group.

The first ionisation energy is the energy required to remove one mole of electrons from one mole of gaseous atoms.

The second and subsequent ionisation energies refer to the energies required to remove further moles of electrons.

The trends in the first ionisation energy across periods and down groups can be explained in terms of the atomic size, nuclear charge and the screening effect due to inner shell electrons.

Atoms of different elements have different attractions for bonding electrons.

Electronegativity is a measure of the attraction an atom involved in a bond has for the electrons of the bond.

Electronegativity values increase across a period and decrease down a group.

d) Bonding, structure and properties

(i) Types of bonding

Metallic bonding is the electrostatic force of attraction between positively charged ions and delocalised outer electrons.

Atoms in a covalent bond are held together by electrostatic forces of attraction between positively charged nuclei and negatively charged shared electrons.

The polarity of a covalent bond depends on the difference in electronegativity between the bonded atoms.

Ionic bonding is the electrostatic force of attraction between positively and negatively charged ions.

The type of bonding in a compound is related to the positions of its constituent elements in the Periodic Table.

(ii) Intermolecular forces of attraction

Van der Waals' forces are forces of attraction which can operate between all atoms and molecules.

Van der Waals' forces are much weaker than all other types of bonding.

Van der Waals' forces are a result of electrostatic attraction between temporary dipoles and induced dipoles caused by movement of electrons in atoms and molecules.

The strength of van der Waals' forces is related to the size of the atoms or molecules.

A molecule is described as polar if it has a permanent dipole.

Permanent dipole-permanent dipole interactions are additional electrostatic forces of attraction between polar molecules.

Permanent dipole-permanent dipole interactions are stronger than van der Waals' forces for molecules of equivalent size.

The spatial arrangement of polar covalent bonds can result in a molecule being polar.

Bonds consisting of a hydrogen atom bonded to an atom of a strongly electronegative element such as fluorine, oxygen or nitrogen are highly polar.

Hydrogen bonds are electrostatic forces of attraction between molecules which contain these highly polar bonds.

A hydrogen bond is stronger than other forms of permanent dipole-permanent dipole interaction but weaker than a covalent bond.

(iii) Structure

A metallic structure consists of a giant lattice of positively charged ions and delocalised outer electrons.

A covalent molecular structure consists of discrete molecules held together by weak intermolecular forces.

A covalent network structure consists of a giant lattice of covalently bonded atoms.

An ionic structure consists of a giant lattice of oppositely charged ions.

A monatomic structure consists of discrete atoms held together by van der Waals' forces.

The first 20 elements in the Periodic Table can be categorised according to bonding and structure:

- metallic (Li, Be, Na, Mg, Al, K, Ca)
- covalent molecular (H₂, N₂, O₂, F₂, Cl₂, P₄, S₈ and C (fullerenes))
- covalent network (B, C (diamond, graphite), Si)
- monatomic (noble gases)

Compounds each adopt one of three structures in the solid state:

1. covalent molecular
2. covalent network, including silicon dioxide and silicon carbide
3. ionic

(iv) Properties

The melting points, boiling points and hardness/softness of elements and compounds are related to their bonding and structures.

The melting and boiling points of polar substances are higher than the melting and boiling points of non-polar substances with similar molecular sizes.

Ionic compounds and polar molecular compounds tend to be soluble in polar solvents such as water and insoluble in non-polar solvents.

Non-polar molecular substances tend to be soluble in non-polar solvents and insoluble in polar solvents.

The anomalous boiling points of ammonia, water and hydrogen fluoride are a result of hydrogen bonding.

Boiling points, melting points, viscosity and miscibility in water are properties of substances which are affected by hydrogen bonding.

Hydrogen bonding between molecules in ice results in an expanded structure which causes the density of ice to be less than that of water at low temperatures.

The uses of diamond, graphite and silicon carbide are related to their structures and properties.

Fullerenes are the subject of current research and applications are being sought.

e) The mole

(i) The Avogadro Constant

One mole of any substance contains $6.02 \cdot 10^{23}$ formula units.

Equimolar amounts of substances contain equal numbers of formula units.

(ii) Molar volume

The molar volume (in units of mol l^{-1}) is the same for all gases at the same temperature and pressure.

The volume of a gas can be calculated from the number of moles and vice versa.

(iii) Reacting volumes

The volumes of reactant and product gases can be calculated from the number of moles of each reactant and product.

Carry out experiments to calculate the molar volume for several gases.

Unit 2: The World of Carbon

a) Fuels

(i) Petrol

Petrol can be produced by the reforming of naphtha.

Reforming alters the arrangement of atoms in molecules without necessarily changing the number of carbon atoms per molecule.

As a result of the reforming process, petrol contains branched-chain alkanes, cycloalkanes and aromatic hydrocarbons as well as straight-chain alkanes.

Any petrol is a blend of hydrocarbons of different volatilities which takes account of prevailing temperatures.

In a petrol engine, the petrol-air mixture is ignited by a spark.

'Knocking' is caused by auto-ignition.

The tendency of alkanes to auto-ignite is reduced by the addition of lead compounds.

Unleaded petrol uses components which have a high degree of molecular branching and/or aromatics and/or cycloalkanes to improve the efficiency of burning.

(ii) Alternative fuels

Sugar cane is a renewable source of ethanol for mixing with petrol.

There are both advantages and disadvantages associated with the use of methanol as an alternative fuel to petrol.

Some biological materials, under anaerobic conditions, ferment to produce methane.

In the future a 'hydrogen economy' could see the use of hydrogen as a means of storing and distributing energy.

Hydrogen could be produced by the electrolysis of water using solar energy, a renewable source of energy.

The use of hydrogen in the internal combustion engine instead of petrol would reduce the build up of carbon dioxide in the atmosphere.

b) Nomenclature and structural formulae

(i) Hydrocarbons

Systematic names, full and shortened structural formulae can be used for straight and branched-chain alkanes, alkenes and alkynes (only to C8).

The functional group in an alkene is the carbon to carbon double bond.

The functional group in an alkyne is the carbon to carbon triple bond.

(ii) Substituted alkanes

An alcohol can be identified from the hydroxyl functional group and the '-ol' name ending.

Alkanols are a homologous series of alcohols based on the corresponding parent alkanes.

Systematic names, full and shortened structural formulae can be used for straight- and branched-chain alkanols (only C1 to C8).

An aldehyde and ketone can be identified from the carbonyl functional group.

Alkanals are a homologous series of aldehydes based on the corresponding parent alkanes.

Alkanones are a homologous series of ketones based on the corresponding parent alkanes.

Alkanals and alkanones can be identified from the '-al' and '-one' name endings.

Systematic names, full and shortened structural formulae can be used for straight- and branched-chain alkanals and alkanones (only C1 to C8).

A carboxylic acid can be identified from the carboxyl functional group and the '-oic' name ending.

Alkanoic acids are a homologous series of carboxylic acids based on the corresponding parent alkanes.

Systematic names, full and shortened structural formulae can be used for straight and branched-chain alkanolic acids (only C1 to C8).

(iii) Esters

An ester can be identified from the functional group and the '-oate' ending.

An ester can be named given the names of the parent alkanol and alkanolic acid, or from shortened and full structural formulae.

Shortened and full structural formulae for esters can be drawn given the names of the parent alkanol and alkanolic acid, or the names of esters.

The products of the breakdown of an ester can be named or shortened, and full structural formulae can be drawn, given the name of the ester or the shortened or full structural formula of the ester.

(iv) Aromatic hydrocarbons

Benzene is the simplest member of the class of aromatic hydrocarbons.

The benzene ring has a distinctive structural formula.

The stability of the benzene ring is due to the delocalisation of electrons.

A benzene ring in which one hydrogen atom has been substituted by another group is known as the phenyl group.

The phenyl group has the formula $-C_6H_5$.

c) Reactions of carbon compounds

(i) Addition

The characteristic reaction of an alkene is the addition reaction.

Alkenes can undergo the addition of hydrogen, hydrogen halides, halogens and water to form saturated products.

Ethyne can also undergo the addition of hydrogen, hydrogen halides and halogens to form saturated products in two stages.

To meet market demand ethanol is made by means other than fermentation.

Direct catalytic hydration of alkenes is another way of making alkanols.

Alkanols can be converted to alkenes by dehydration.

The benzene ring resists addition reactions.

(ii) Oxidation

Alcohols burn in oxygen and air to produce carbon dioxide and water.

Alcohols can be classified as primary, secondary or tertiary.

Primary and secondary alcohols can be oxidised by a number of oxidising agents, including copper(II) oxide and acidified potassium dichromate solution.

Primary alcohols are oxidised, first to aldehydes and then to carboxylic acids.

Secondary alcohols are oxidised to ketones.

Aldehydes, but not ketones, can be oxidised by a number of oxidising agents, including Fehling's solution, to carboxylic acids.

When applied to carbon compounds, oxidation results in an increase in the oxygen to hydrogen ratio.

When applied to carbon compounds, reduction results in a decrease in the oxygen to hydrogen ratio.

(iii) Making and breaking down esters

Esters are formed by the condensation reaction between a carboxylic acid and an alcohol.

The ester link is formed by the reaction of a hydroxyl group with a carboxyl group.

The parent carboxylic acid and the parent alcohol can be obtained by hydrolysis of an ester.

The formation and hydrolysis of an ester is a reversible reaction.

(iv) Percentage yields

Percentage yields can be calculated from mass of reactant(s) and product(s) using balanced equations.

d) Uses of carbon compounds

There are competing demands for the use of crude oil for fuels and the manufacture of petroleum-based consumer products.

Many consumer products are compounds of carbon.

Uses of esters include flavourings, perfumes and solvents.

Carboxylic acids are used in a variety of ways.

Halogenoalkanes have properties which make them useful in a variety of consumer products.

In the atmosphere, ozone, O₃, forms a protective layer which absorbs ultraviolet radiation from the sun.

The depletion of the ozone layer is believed to have been caused by the extensive use of certain CFCs.

Benzene and its related compounds are important as feedstocks.

One or more hydrogen atoms of a benzene molecule can be substituted to form a range of consumer products.

e) Polymers

(i) Early plastics and fibres

Ethene is a starting material of major importance in the petrochemical industry especially for the manufacture of plastics.

Ethene can be formed by cracking the ethane from the gas fraction or the naphtha fraction from oil.

Propene can be formed by cracking the propane from the gas fraction or the naphtha fraction from oil.

Condensation polymers are made from monomers with two functional groups per molecule.

The repeating unit or the structure of a condensation polymer can be drawn given the monomer structures and vice-versa.

Polyesters are examples of condensation polymers.

Polyesters are manufactured for use as textile fibres and resins.

Polyesters used for textile fibres have a linear structure whereas cured polyester resins have a three-dimensional structure.

An amine can be identified from the functional group.

Polyamides are examples of condensation polymers.

The amide link is formed by the reaction of an amine group with a carboxyl group.

An example of a polyamide is nylon which is a very important engineering plastic.

The strength of nylon is related to the hydrogen bonding between polymer chains.

Methanal is an important feedstock in the manufacture of thermosetting plastics.

Methanol, a feedstock for methanal, is made industrially from synthesis gas, a mixture of carbon monoxide and hydrogen.

Synthesis gas can be obtained by steam reforming of methane from natural gas, or by steam reforming of coal.

(ii) Recent developments

Kevlar is an aromatic polyamide which is extremely strong because of the way in which the rigid, linear molecules are packed together.

Kevlar has many important uses.

Poly(ethenol) is a plastic which readily dissolves in water.

Poly(ethenol) is made from another plastic by a process known as ester exchange.

The percentage of acid groups which have been removed in the production process influences the strengths of the intermolecular forces upon which the solubility depends.

Poly(ethenol) has many important uses.

Poly(ethyne) can be treated to make a polymer which conducts electricity.

The conductivity depends on delocalised electrons along the polymer chain.

Poly(vinyl carbazole) is a polymer which exhibits photoconductivity and is used in photocopiers.
Biopol is an example of a biodegradable polymer.
The structure of low density polythene can be modified during manufacture to produce a photodegradable polymer.

f) Natural products

(i) Fats and oils

Natural fats and oils can be classified according to their origin as animal, vegetable or marine.
The lower melting points of oils compared to those of fats is related to the higher unsaturation of oil molecules.
The low melting points of oils is a result of the effect that the shapes of the molecules have on close packing, hence on the strength of van der Waals' forces of attraction.
The conversion of oils into hardened fats involves the partial removal of unsaturation by addition of hydrogen.
Fats and oils in the diet supply the body with energy and are a more concentrated source of energy than carbohydrates.
Fats and oils are esters.
The hydrolysis of fats and oils produces fatty acids and glycerol in the ratio of three moles of fatty acid to one mole of glycerol.
Glycerol (propane-1,2,3-triol) is a trihydric alcohol.
Fatty acids are saturated or unsaturated straight-chain carboxylic acids containing even numbers of carbon atoms ranging from C₄ to C₂₄, primarily C₁₆ and C₁₈.
Fats and oils consist largely of mixtures of triglycerides in which the three fatty acid molecules which are combined with each molecule of glycerol may or may not be identical.
Soaps are produced by the hydrolysis of fats and oils.

(ii) Proteins

Nitrogen is essential for protein formation by plants and animals.
Proteins are condensation polymers made up of many amino acid molecules linked together.
The structure of a section of protein is based on the constituent amino acids.
Condensation of amino acids produces the peptide (amide) link.
The peptide link is formed by the reaction of an amine group with a carboxyl group.
Proteins specific to the body's needs are built up within the body.
The body cannot make all the amino acids required for body proteins and is dependent on dietary protein for supply of certain amino acids known as essential amino acids.
During digestion, the hydrolysis of proteins produces amino acids.
The structural formulae of amino acids obtained from the hydrolysis of proteins can be identified from the structure of a section of the protein.
Proteins can be classified as fibrous or globular.
Fibrous proteins are long and thin and are the major structural materials of animal tissue.
Globular proteins have the spiral chains folded into compact units.
Globular proteins are involved in the maintenance and regulation of life processes and include enzymes and many hormones, eg insulin and haemoglobin.
Enzyme function is related to the molecular shapes of proteins.
Denaturing of a protein involves physical alteration of the molecules as a result of temperature change or pH change.
The ease with which a protein is denatured is related to the susceptibility of enzymes to changes in temperature and pH.
Enzymes are most efficient within a narrow range of temperature and pH.

Unit 3: Chemical Reactions

a) The chemical industry

The UK chemical industry is a major contributor to both the quality of our life and our national economy. Stages in the manufacture of a new product can include research, pilot study, scaling-up, production and review.

A chemical manufacturing process usually involves a sequence of steps.

A feedstock is a reactant from which other chemicals can be extracted or synthesised.

The major raw materials in the chemical industry are fossil fuels, metallic ores and minerals, air and water.

Chemical manufacturing may be organised as a batch or as a continuous process.

Process conditions are chosen to maximise economic efficiency.

Manufacturing costs include capital costs, fixed costs and variable costs.

The UK chemical industry is, by and large, capital rather than labour intensive.

Safety and environmental issues are of major importance to the chemical industry.

Both historical and practical factors affect the location of chemical industries.

The efficient use of energy is significant in most chemical processes.

Factors influencing the choice of a particular route include cost, availability and suitability of feedstock(s), yield of product(s), opportunities for the recycling of reactants and marketability of by-products.

b) Hess's law

Hess's law states that the enthalpy change for a chemical reaction is independent of the route taken.

Enthalpy changes can be calculated by application of Hess's law.

c) Equilibrium

(i) The concept of dynamic equilibrium

Reversible reactions attain a state of dynamic equilibrium when the rates of forward and reverse reactions are equal.

At equilibrium, the concentrations of reactants and products remain constant, although not necessarily equal.

(ii) Shifting the equilibrium position

Changes in concentration, pressure and temperature can alter the position of equilibrium.

A catalyst speeds up the rate of attainment of equilibrium but does not affect the position of equilibrium.

The effects of pressure, temperature, the use of a catalyst, recycling of unreacted gases and the removal of product can be considered in relation to the Haber Process.

d) Acids and bases

(i) The pH scale

The pH scale is a continuous range from below 0 to above 14.

Integral values of pH from 0 to 14 can be related to concentrations of $\text{H}^+(\text{aq})$ in mol l^{-1} .

In water and aqueous solutions with a pH value of 7 the concentrations of $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ are both $10^{-7} \text{ mol l}^{-1}$ at 25 °C.

The concentration of $\text{H}^+(\text{aq})$ or $\text{OH}^-(\text{aq})$ in a solution can be calculated from the concentration of the other by using $[\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]=10^{-14} \text{ mol}^2 \text{ l}^{-2}$.

In water and aqueous solutions there is an equilibrium between $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ ions and water molecules.

(ii) The concept of strong and weak

In aqueous solution, strong acids are completely dissociated but weak acids are only partially dissociated. Equimolar solutions of weak and strong acids differ in pH, conductivity, and reaction rates, but not in stoichiometry of reactions.

The weakly acidic nature of solutions of ethanoic acid, sulphur dioxide and carbon dioxide can be explained by reference to equations showing the equilibrium.

In aqueous solution, strong bases are completely ionised but weak bases are only partially ionised. Equimolar solutions of weak and strong bases differ in pH and conductivity, but not in stoichiometry of reactions.

The weakly alkaline nature of a solution of ammonia can be explained by reference to an equation showing the equilibrium.

(iii) The pH of salt solutions

A soluble salt of a strong acid and a strong base dissolves in water to produce a neutral solution.

A soluble salt of a weak acid and a strong base dissolves in water to produce an alkaline solution.

A soluble salt of a strong acid and a weak base dissolves in water to produce an acidic solution.

Soaps are salts of weak acids and strong bases.

The acidity, alkalinity or neutrality of the above kinds of salt solution can be explained by reference to the appropriate equilibria.

e) Redox reactions

(i) Oxidising and reducing agents

An oxidising agent is a substance which accepts electrons; a reducing agent is a substance which donates electrons.

Oxidising and reducing agents can be identified in redox reactions.

Ion-electron equations can be written for oxidation and reduction reactions.

Ion-electron equations can be combined to produce redox equations.

Given reactant and product species, ion-electron equations which include $\text{H}^+(\text{aq})$ and $\text{H}_2\text{O}(\text{l})$ can be written.

(ii) Redox titrations

The concentration of a reactant can be calculated from the results of redox titrations.

(iii) Electrolysis

The production of one mole of an element from its ion, by electrolysis, always requires n times 96,500 C where n is the number of electrons in the relevant ion-electron equation.

96,500 C is the charge associated with one mole of electrons.

The mass or volume of an element discharged can be calculated from the quantity of electricity passed and vice-versa.

f) Nuclear chemistry

(i) Types of radiation

Radioactive decay involves changes in the nuclei of atoms.

Unstable nuclei (radioisotopes) are transformed into more stable nuclei by releasing energy.

The stability of nuclei depends on the proton/neutron ratio.

The natures and properties of alpha, beta and gamma radiation can be described.

Balanced nuclear equations, involving neutrons, protons, alpha particles and beta particles, can be written.

(ii) Half-lives

The half-life is the time taken for the activity or mass of a radioisotope to halve.

The decay of individual nuclei within a sample is random and is independent of chemical or physical state.

The quantity of radioisotope, half-life or time elapsed can be calculated given the value of the other two variables.

(iii) Radioisotopes

Radioisotopes are used in medicine, in industry, for scientific research including carbon dating, and to produce energy by uranium fission and nuclear fusion.

Nuclear fuels and fossil fuels can be compared in terms of safety, pollution and the use of finite resources.

Elements are created in the stars from simple elements by nuclear fusion.

All naturally occurring elements, including those found in our bodies, originated in stars.