

Course content

The course content includes the following areas of chemistry:

Inorganic chemistry

The topics covered are:

- ◆ electromagnetic radiation and atomic spectra
- ◆ atomic orbitals, electronic configurations and the periodic table
- ◆ transition metals

Physical chemistry

The topics covered are:

- ◆ chemical equilibrium
- ◆ reaction feasibility
- ◆ kinetics

Organic chemistry and instrumental analysis

The topics covered are:

- ◆ molecular orbitals
- ◆ synthesis
- ◆ stereo chemistry
- ◆ experimental determination of structure
- ◆ pharmaceutical chemistry

Researching chemistry

The topics covered are:

- ◆ common chemical apparatus
- ◆ skills involved in experimental work
- ◆ stoichiometric calculations
- ◆ gravimetric analysis
- ◆ volumetric analysis
- ◆ practical skills and techniques

Skills, knowledge and understanding

Skills, knowledge and understanding for the course

The following provides a broad overview of the subject skills, knowledge and understanding developed in the course:

- ◆ extending and applying knowledge of chemistry to new situations, interpreting and analysing information to solve complex problems
- ◆ planning and designing chemical experiments/investigations, including risk assessments, to make a discovery, demonstrate a known fact, illustrate particular effects or test a hypothesis
- ◆ carrying out complex experiments in chemistry safely, recording systematic detailed observations and collecting data
- ◆ selecting information from a variety of sources and presenting detailed information appropriately, in a variety of forms
- ◆ processing and analysing chemical information and data (using calculations, significant figures and units, where appropriate)
- ◆ making reasoned predictions and generalisations from a range of evidence and/or information
- ◆ drawing valid conclusions and giving explanations supported by evidence and/or justification
- ◆ critically evaluating experimental procedures by identifying sources of uncertainty and suggesting and implementing improvements
- ◆ drawing on knowledge and understanding of chemistry to make accurate statements, describe complex information, provide detailed explanations and integrate knowledge
- ◆ communicating chemical findings and information fully and effectively
- ◆ analysing and evaluating scientific publications and media reports

Skills, knowledge and understanding for the course assessment

The following provides details of skills, knowledge and understanding sampled in the course assessment:

Inorganic chemistry
(a) Electromagnetic radiation and atomic spectra
<p>Electromagnetic radiation can be described in terms of waves and characterised in terms of wavelength and/or frequency.</p> <p>The relationship between these quantities is given by $c = f\lambda$.</p> <p>The different types of radiation arranged in order of wavelength is known as the electromagnetic spectrum.</p> <p>Wavelengths of visible light are normally expressed in nanometres (nm).</p> <p>Electromagnetic radiation can be described as a wave (has a wavelength and frequency), and as a particle, and is said to have a dual nature.</p> <p>When electromagnetic radiation is absorbed or emitted by matter it behaves like a stream of particles. These particles are known as photons.</p> <p>A photon carries quantised energy proportional to the frequency of radiation.</p> <p>When a photon is absorbed or emitted, energy is gained or lost by electrons within the substance.</p> <p>The photons in high frequency radiation can transfer greater amounts of energy than photons in low frequency radiation.</p> <p>The energy associated with a single photon is given by:</p> $E = hf \text{ or } E = \frac{hc}{\lambda}$ <p>The energy associated with one mole of photons is given by:</p> $E = Lhf \text{ or } E = \frac{Lhc}{\lambda}$ <p>Energy is often in units of kJ mol^{-1}.</p> <p>When energy is transferred to atoms, electrons within the atoms may be promoted to higher energy levels.</p> <p>An atom emits a photon of light energy when an excited electron moves from a higher energy level to a lower energy level.</p> <p>The light energy emitted by an atom produces a spectrum that is made up of a series of lines at discrete (quantised) energy levels. This provides direct evidence for the existence of these energy levels.</p>

Inorganic chemistry (continued)

(a) Electromagnetic radiation and atomic spectra (continued)

Each element in a sample produces characteristic absorption and emission spectra. These spectra can be used to identify and quantify the element.

In absorption spectroscopy, electromagnetic radiation is directed at an atomised sample. Radiation is absorbed as electrons are promoted to higher energy levels.

An absorption spectrum is produced by measuring how the intensity of absorbed light varies with wavelength.

In emission spectroscopy, high temperatures are used to excite the electrons within atoms. As the electrons drop to lower energy levels, photons are emitted.

An emission spectrum of a sample is produced by measuring the intensity of light emitted at different wavelengths.

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

(b) Atomic orbitals, electronic configurations and the periodic table

The discrete lines observed in atomic spectra can be explained if electrons, like photons, also display the properties of both particles and waves.

Electrons behave as standing (stationary) waves in an atom. These are waves that vibrate in time but do not move in space. There are different sizes and shapes of standing wave possible around the nucleus, known as orbitals. Orbitals can hold a maximum of two electrons.

The different shapes of orbitals are identified as s, p, d and f (knowledge of the shape of orbitals is not required).

Electrons within atoms have fixed amounts of energy called quanta.

It is possible to describe any electron in an atom using four quantum numbers:

- ◆ the principal quantum number n indicates the main energy level for an electron and is related to the size of the orbital
- ◆ the angular momentum quantum number l determines the shape of the subshell and can have values from zero to $n - 1$
- ◆ the magnetic quantum number m_l determines the orientation of the orbital and can have values between $-l$ and $+l$
- ◆ the spin magnetic quantum number m_s determines the direction of spin and can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$

Inorganic chemistry (continued)

(b) Atomic orbitals, electronic configurations and the periodic table (continued)

Electrons within atoms are arranged according to:

- ◆ the aufbau principle — electrons fill orbitals in order of increasing energy ('aufbau' means 'building up' in German)
- ◆ Hund's rule — when degenerate orbitals are available, electrons fill each singly, keeping their spins parallel before spin pairing starts
- ◆ the Pauli exclusion principle — no two electrons in one atom can have the same set of four quantum numbers, therefore, no orbital can hold more than two electrons and these two electrons must have opposite spins

In an isolated atom the orbitals within each subshell are degenerate.

The relative energies corresponding to each orbital can be represented diagrammatically using orbital box notation for the first four shells of a multi-electron atom.

Electronic configurations using spectroscopic notation and orbital box notation can be written for elements of atomic numbers 1 to 36.

The periodic table is subdivided into four blocks (s, p, d and f) corresponding to the outer electronic configurations of the elements within these blocks.

The variation in first, second and subsequent ionisation energies with increasing atomic number for the first 36 elements can be explained in terms of the relative stability of different subshell electronic configurations. This provides evidence for these electronic configurations. Anomalies in the trends of ionisation energies can be explained by considering the electronic configurations.

There is a special stability associated with half-filled and full subshells. The more stable the electronic configuration, the higher the ionisation energy.

VSEPR (valence shell electron pair repulsion) theory can be used to predict the shapes of molecules and polyatomic ions.

The number of electron pairs surrounding a central atom can be found by:

- ◆ taking the total number of valence (outer) electrons on the central atom and adding one for each atom attached
- ◆ adding an electron for every negative charge
- ◆ removing an electron for every positive charge
- ◆ dividing the total number of electrons by two to give the number of electron pairs

Electron pairs are negatively charged and repel each other. They are arranged to minimise repulsion and maximise separation.

Inorganic chemistry (continued)

(b) Atomic orbitals, electronic configurations and the periodic table (continued)

The arrangement of electron pairs around a central atom is:

- ◆ linear for two electron pairs
- ◆ trigonal planar for three electron pairs
- ◆ tetrahedral for four electron pairs
- ◆ trigonal bipyramidal for five electron pairs
- ◆ octahedral for six electron pairs

Shapes of molecules or polyatomic ions are determined by the shapes adopted by the atoms present based on the arrangement of electron pairs. Electron dot diagrams can be used to show these arrangements.

Electron pair repulsions decrease in strength in the order:

non-bonding pair/non-bonding pair > non-bonding pair/bonding pair > bonding pair/bonding pair

(c) Transition metals

The d-block transition metals are metals with an incomplete d subshell in at least one of their ions.

The filling of the d orbitals follows the aufbau principle, with the exception of chromium and copper atoms.

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

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

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

The oxidation number can be determined by the following:

- ◆ uncombined elements have an oxidation number of 0
- ◆ ions containing single atoms have an oxidation number that is the same as the charge on the ion
- ◆ in most of its compounds, oxygen has an oxidation number of -2
- ◆ in most of its compounds, hydrogen has an oxidation number of +1
- ◆ the sum of all the oxidation numbers of all the atoms in a neutral compound must add up to zero
- ◆ the sum of all the oxidation numbers of all the atoms in a polyatomic ion must be equal to the charge on the ion

Inorganic chemistry (continued)

(c) Transition metals (continued)

A transition metal can have different oxidation states in its compounds.

Compounds of the same transition metal in different oxidation states may have different colours.

Oxidation can be defined as an increase in oxidation number. Reduction can be considered as a decrease in oxidation number.

Changes in oxidation number of transition metal ions can be used to determine whether oxidation or reduction has occurred.

Compounds containing metals in high oxidation states are often oxidising agents, whereas compounds with metals in low oxidation states are often reducing agents.

Ligands may be negative ions or molecules with non-bonding pairs of electrons that they donate to the central metal atom or ion, forming dative covalent bonds.

Ligands can be classified as monodentate, bidentate, up to hexadentate.

It is possible to deduce the ligand classification from a formula or structure of the ligand or complex.

The total number of bonds from the ligands to the central transition metal is known as the coordination number.

Names and formulae can be written according to IUPAC rules for complexes containing:

- ◆ central metals that obey the normal IUPAC rules
- ◆ copper (cuprate) and iron (ferrate)
- ◆ ligands, including water, ammonia, halogens, cyanide, hydroxide, and oxalate

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

Splitting of d orbitals to higher and lower energies occurs when the electrons present in approaching ligands cause the electrons in the orbitals lying along the axes to be repelled.

Ligands that cause a large difference in energy between subsets of d orbitals are strong field ligands. Weak field ligands cause a small energy difference.

Ligands can be placed in an order of their ability to split d orbitals. This is called the spectrochemical series.

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

Light is absorbed when electrons in a lower energy d orbital are promoted to a d orbital of higher energy.

Inorganic chemistry (continued)

(c) Transition metals (continued)

If light of one colour is absorbed, then the complementary colour will be observed.

Electrons transition to higher energy levels when energy corresponding to the ultraviolet or visible regions of the electromagnetic spectrum is absorbed.

Transition metals and their compounds can act as catalysts.

Heterogeneous catalysts are in a different state to the reactants.

Heterogeneous catalysis can be explained in terms of the formation of activated complexes and the adsorption of reactive molecules onto active sites. The presence of unpaired d electrons or unfilled d orbitals is thought to allow activated complexes to form. This can provide reaction pathways with lower activation energies compared to the uncatalysed reaction.

Homogeneous catalysts are in the same state as the reactants.

Homogeneous catalysis can be explained in terms of changing oxidation states with the formation of intermediate complexes.

Physical chemistry

(a) Chemical equilibrium

A chemical reaction is in equilibrium when the composition of the reactants and products remains constant indefinitely.

The equilibrium constant (K) characterises the equilibrium composition of the reaction mixture.

For the general reaction $aA + bB \rightleftharpoons cC + dD$ the equilibrium expression is:

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

$[A], [B], [C]$ and $[D]$ are the equilibrium concentrations of A, B, C and D and a, b, c and d are the stoichiometric coefficients in the balanced reaction equation.

The value of equilibrium constants can be calculated.

The value of an equilibrium constant indicates the position of equilibrium.

Equilibrium constants have no units.

The concentrations of pure solids and pure liquids at equilibrium are taken as constant and given a value of 1 in the equilibrium expression.

The numerical value of the equilibrium constant depends on the reaction temperature and is independent of concentration and/or pressure.

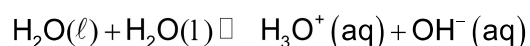
For endothermic reactions, a rise in temperature causes an increase in K and the yield of the product is increased.

For exothermic reactions, a rise in temperature causes a decrease in K and the yield of the product is decreased.

The presence of a catalyst does not affect the value of the equilibrium constant.

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

This ionisation of water can be represented by:



$\text{H}_3\text{O}^+(\text{aq})$ represents a hydronium ion, a hydrated proton. A shorthand representation of $\text{H}_3\text{O}^+(\text{aq})$ is $\text{H}^+(\text{aq})$.

Physical chemistry (continued)

(a) Chemical equilibrium (continued)

Water is amphoteric (can react as an acid and a base).

The dissociation constant for the ionisation of water is known as the ionic product and is represented by K_w :

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

The value of the ionic product varies with temperature.

At 25°C the value of K_w is approximately 1×10^{-14} .

The relationship between pH and the hydrogen ion concentration is given by:

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] \text{ and } [\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

In water and aqueous solutions with a pH value of 7 the concentrations of $\text{H}_3\text{O}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ are both $10^{-7} \text{ mol l}^{-1}$ at 25°C.

If the concentration of $\text{H}_3\text{O}^+(\text{aq})$ or the concentration of $\text{OH}^-(\text{aq})$ is known, the concentration of the other ion can be calculated using K_w or by using $\text{pH} + \text{pOH} = 14$.

The Brønsted-Lowry definitions of acids and bases state that an acid is a proton donor and a base is a proton acceptor.

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

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

Strong acids and strong bases are completely dissociated into ions in aqueous solution.

Weak acids and weak bases are only partially dissociated into ions in aqueous solution.

Examples of strong acids include hydrochloric acid, sulfuric acid and nitric acid.

Ethanoic acid, carbonic acid and sulfurous acid are examples of weak acids.

Solutions of metal hydroxides are strong bases.

Ammonia and amines are examples of weak bases.

The weakly acidic nature of solutions of carboxylic acids, sulfur dioxide and carbon dioxide can be explained by reference to equations showing the equilibria.

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

Physical chemistry (continued)

(a) Chemical equilibrium (continued)

Equimolar solutions of weak and strong acids (or bases) have different pH values, conductivity, and reaction rates, but the stoichiometry of reactions are the same.

The acid dissociation constant is represented by K_a :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

or by:

$$\text{p}K_a \text{ where } \text{p}K_a = -\log_{10} K_a$$

The approximate pH of a weak acid can be calculated using:

$$\text{pH} = \frac{1}{2}\text{p}K_a - \frac{1}{2}\log_{10} c.$$

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.

The name of the salt produced depends on the acid and base used.

Using the appropriate equilibria, the changes in concentrations of H_3O^+ and OH^- ions of salt solutions can be explained.

A buffer solution is one in which the pH remains approximately constant when small amounts of acid, base or water are added.

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

In an acid buffer solution the weak acid provides hydrogen ions when these are removed by the addition of a small amount of base. The salt of the weak acid provides the conjugate base, which can absorb excess hydrogen ions produced by the addition of a small amount of acid.

A basic buffer consists of a solution of a weak base and one of its salts.

In a basic buffer solution the weak base removes excess hydrogen ions, and the conjugate acid provided by the salt supplies hydrogen ions when these are removed.

Physical chemistry (continued)

(a) Chemical equilibrium (continued)

An approximate pH of an acid buffer solution can be calculated from its composition and from the acid dissociation constant:

$$\text{pH} = \text{p}K_a - \log_{10} \frac{[\text{acid}]}{[\text{salt}]}$$

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



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

$$K_{\text{in}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

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

The colour of the indicator is determined by the ratio of $[\text{HIn}]$ to $[\text{In}^-]$.

The theoretical point at which colour change occurs is when $[\text{H}_3\text{O}^+] = K_{\text{in}}$.

The colour change is assumed to be distinguishable when $[\text{HIn}]$ and $[\text{In}^-]$ differ by a factor of 10.

The pH range over which a colour change occurs can be estimated by the expression:

$$\text{pH} = \text{p}K_{\text{in}} \pm 1$$

Suitable indicators can be selected from pH data, including titration curves.

(b) Reaction feasibility

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

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

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

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

Physical chemistry (continued)

(b) Reaction feasibility (continued)

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

The greater the degree of disorder, the greater the entropy.

Solids have low disorder and gases have high disorder.

Entropy increases as temperature increases.

There is a rapid increase in entropy at the melting point of a substance and an even more rapid and larger change in entropy at the boiling point.

The second law of thermodynamics states that the total entropy of a reaction system and its surroundings always increases for a spontaneous process.

Heat energy released by the reaction system into the surroundings increases the entropy of the surroundings.

Heat energy absorbed by the reaction system from the surroundings decreases the entropy of the surroundings.

The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero.

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

The change in standard entropy for a reaction system can be calculated from the standard entropies of the reactants and products:

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

The change in free energy for a reaction is related to the enthalpy and entropy changes:

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

If the change in free energy (ΔG°) between reactants and products is negative, a reaction may occur and the reaction is said to be feasible. A feasible reaction is one that tends towards the products rather than the reactants. This does not give any indication of the rate of the reaction.

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

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

The feasibility of a chemical reaction under standard conditions can be predicted from the calculated value of the change in standard free energy (ΔG°).

The temperatures at which a reaction may be feasible can be estimated by considering the range of values of T for which $\Delta G^\circ < 0$.

Physical chemistry (continued)

(b) Reaction feasibility (continued)

Under non-standard conditions any reaction is feasible if ΔG is negative.

At equilibrium, $\Delta G = 0$.

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

(c) Kinetics

The rate of a chemical reaction normally depends on the concentrations of the reactants.

Orders of reaction are used to relate the rate of a reaction to the reacting species.

If changing the concentration of a reactant A has no effect on the rate of the reaction, then the reaction is zero order with respect to A .

If doubling the concentration of a reactant A doubles the rate of the reaction, then the reaction is first order with respect to A . The rate can be expressed as:

rate = $k[A]$ where k is the rate constant and $[A]$ is the concentration of reactant A in mol l^{-1}

If doubling the concentration of a reactant A increases the rate of the reaction fourfold, then the reaction is second order with respect to A . The rate can be expressed as:

rate = $k[A]^2$

The order of a reaction with respect to any one reactant is the power to which the concentration of that reactant is raised in the rate equation.

The overall order of a reaction is the sum of the powers to which the concentrations of the reactants are raised in the rate equation.

The order of a reaction can only be determined from experimental data.

The rate equation and the rate constant, including units, can be determined from initial rate data for a series of reactions in which the initial concentrations of reactants are varied. These can be zero, first, second or third order.

Reactions usually occur by a series of steps called a reaction mechanism.

The rate of reaction is dependent on the slowest step, which is called the 'rate determining step'.

Experimentally determined rate equations can be used to determine possible reaction mechanisms.

Organic chemistry and instrumental analysis

(a) Molecular orbitals

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

Molecular orbitals form when atomic orbitals combine. The number of molecular orbitals formed is equal to the number of atomic orbitals that combine. The combination of two atomic orbitals results in the formation of a bonding molecular orbital and an antibonding orbital. The bonding molecular orbital encompasses both nuclei. The attraction of the positively charged nuclei and the negatively charged electrons in the bonding molecular orbital is the basis of bonding between atoms. Each molecular orbital can hold a maximum of two electrons.

In a non-polar covalent bond, the bonding molecular orbital is symmetrical about the midpoint between two atoms. Polar covalent bonds result from bonding molecular orbitals that are asymmetric about the midpoint between two atoms. The atom with the greater value for electronegativity has the greater share of the bonding electrons. Ionic compounds are an extreme case of asymmetry, with the bonding molecular orbitals being almost entirely located around just one atom, resulting in the formation of ions.

Molecular orbitals that form by end-on overlap of atomic orbitals along the axis of the covalent bond are called sigma (σ) molecular orbitals or sigma bonds.

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

The electronic configuration of an isolated carbon atom cannot explain the number of bonds formed by carbon atoms in molecules. The bonding and shape of molecules of carbon can be explained by hybridisation.

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

In alkanes, the 2s orbital and the three 2p orbitals of carbon hybridise to form four degenerate sp^3 hybrid orbitals. These adopt a tetrahedral arrangement. The sp^3 hybrid orbitals overlap end-on with other atomic orbitals to form σ bonds.

The bonding in alkenes can be described in terms of sp^2 hybridisation. The 2s orbital and two of the 2p orbitals hybridise to form three degenerate sp^2 hybrid orbitals. These adopt a trigonal planar arrangement. The hybrid sp^2 orbitals overlap end-on to form σ bonds. The remaining 2p orbital on each carbon atom of the double bond is unhybridised and lies perpendicular to the axis of the σ bond. The unhybridised p orbitals overlap side-on to form π bonds.

Organic chemistry and instrumental analysis (continued)

(a) Molecular orbitals (continued)

The bonding in benzene and other aromatic systems can be described in terms of sp^2 hybridisation. The six carbon atoms in benzene are arranged in a cyclic structure with σ bonds between the carbon atoms. The unhybridised p orbitals on each carbon atom overlap side-on to form a π molecular system, perpendicular to the plane of the σ bonds. This π molecular system extends across all six carbon atoms. The electrons in this system are delocalised.

The bonding in alkynes can be described in terms of sp hybridisation. The 2s orbital and one 2p orbital of carbon hybridise to form two degenerate hybrid orbitals. These adopt a linear arrangement. The hybrid sp orbitals overlap end-on to form σ bonds. The remaining two 2p orbitals on each carbon atom lie perpendicular to each other and to the axis of the σ bond. The unhybridised p orbitals overlap side-on to form two π bonds.

Molecular orbital theory can be used to explain why organic molecules are colourless or coloured. Electrons fill bonding molecular orbitals, leaving higher energy antibonding orbitals unfilled. The highest bonding molecular orbital containing electrons is called the highest occupied molecular orbital (HOMO). The lowest antibonding molecular orbital is called the lowest unoccupied molecular orbital (LUMO).

Absorption of electromagnetic energy can cause electrons to be promoted from HOMO to LUMO.

Most organic molecules appear colourless because the energy difference between HOMO and LUMO is relatively large. This results in absorption of light from the ultraviolet region of the spectrum.

Some organic molecules contain chromophores. A chromophore is a group of atoms within a molecule that is responsible for absorption of light in the visible region of the spectrum. Light can be absorbed when electrons in a chromophore are promoted from the HOMO to the LUMO.

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

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

Organic chemistry and instrumental analysis (continued)

(b) Synthesis

When an organic reaction takes place, bonds in the reactant molecules are broken and bonds in the product molecules are made. The process of bond breaking is known as bond fission.

There are two types of bond fission, homolytic and heterolytic.

Homolytic fission:

- ◆ results in the formation of two neutral radicals
- ◆ occurs when each atom retains one electron from the σ covalent bond and the bond breaks evenly
- ◆ normally occurs when non-polar covalent bonds are broken

Reactions involving homolytic fission tend to result in the formation of very complex mixtures of products, making them unsuitable for organic synthesis.

Heterolytic fission:

- ◆ results in the formation of two oppositely charged ions
- ◆ occurs when one atom retains both electrons from the σ covalent bond and the bond breaks unevenly
- ◆ normally occurs when polar covalent bonds are broken

Reactions involving heterolytic fission tend to result in far fewer products than reactions involving homolytic fission, and so are better suited for organic synthesis.

The movement of electrons during bond fission and bond making can be represented using curly arrow notation where:

- ◆ a single-headed arrow indicates the movement of a single electron
- ◆ a double-headed arrow indicates the movement of an electron pair
- ◆ the tail of the arrow shows the source of the electron(s)
- ◆ the head of the arrow indicates the destination of the electron(s)
- ◆ two single-headed arrows starting at the middle of a covalent bond indicate homolytic bond fission is occurring
- ◆ a double-headed arrow starting at the middle of a covalent bond indicates heterolytic bond fission is occurring
- ◆ an arrow drawn with the head pointing to the space between two atoms indicates that a covalent bond will be formed between those two atoms

Organic chemistry and instrumental analysis (continued)

(b) Synthesis (continued)

In reactions involving heterolytic bond fission, attacking groups are classified as nucleophiles or electrophiles.

Nucleophiles are:

- ◆ negatively charged ions or neutral molecules that are electron rich, such as Cl^- , Br^- , OH^- , CN^- , NH_3 and H_2O
- ◆ attracted towards atoms bearing a partial (δ^+) or full positive charge
- ◆ capable of donating an electron pair to form a new covalent bond

Electrophiles are:

- ◆ positively charged ions or neutral molecules that are electron deficient, such as H^+ , NO_2^+ and SO_3
- ◆ attracted towards atoms bearing a partial (δ^-) or full negative charge
- ◆ capable of accepting an electron pair to form a new covalent bond

The following reaction types can be identified from a chemical equation:

- ◆ substitution
- ◆ addition
- ◆ elimination
- ◆ condensation
- ◆ hydrolysis
- ◆ oxidation
- ◆ reduction
- ◆ neutralisation

Synthetic routes can be devised, with no more than three steps, from a given reactant to a final product.

The possible reactions of a particular molecule can be deduced by looking at the structural formula.

The structure of any molecule can be drawn as a full, shortened or skeletal structural formula.

In a skeletal structural formula, neither the carbon atoms, nor any hydrogens attached to the carbon atoms, are shown. The presence of a carbon atom is implied by a 'kink' in the carbon backbone, and at the end of a line.

Given a full or shortened structural formula for a compound, the skeletal structural formula can be drawn.

Given a skeletal structural formula for a compound, the full or shortened structural formula can be drawn.

Molecular formulae can be written from a full, shortened or skeletal structural formula.

Organic chemistry and instrumental analysis (continued)

(b) Synthesis (continued)

Straight and branched chain alkanes; alkenes; alcohols; carboxylic acids; aldehydes and ketones; haloalkanes; and ethers can be systematically named, indicating the position of the functional group where appropriate, from structural formulae containing no more than eight carbon atoms in their longest chain. Straight chain esters can be systematically named from the names of their parent alcohol and carboxylic acid or their structural formula.

Molecular formulae can be written and structural formulae drawn from systematic names of straight and branched chain alkanes; alkenes; alcohols; carboxylic acids; aldehydes and ketones; haloalkanes; and ethers containing no more than eight carbon atoms in their longest chain. Molecular formulae can be written and structural formulae drawn for esters from the systematic name or the structural formulae of their parent alcohol and carboxylic acid.

Haloalkanes (alkyl halides) are substituted alkanes in which one or more of the hydrogen atoms is replaced with a halogen atom.

Monohaloalkanes:

- ◆ contain only one halogen atom
- ◆ can be classified as primary, secondary or tertiary according to the number of alkyl groups attached to the carbon atom containing the halogen atom
- ◆ take part in elimination reactions to form alkenes using a strong base, such as potassium or sodium hydroxide in ethanol
- ◆ take part in nucleophilic substitution reactions with:
 - aqueous alkalis to form alcohols
 - alcoholic alkoxides to form ethers
 - ethanolic cyanide to form nitriles (chain length increased by one carbon atom) that can be hydrolysed to carboxylic acids

A monohaloalkane can take part in nucleophilic substitution reactions by one of two different mechanisms.

S_N1 is a nucleophilic substitution reaction with one species in the rate determining step and occurs in a minimum of two steps via a trigonal planar carbocation intermediate.

S_N2 is a nucleophilic substitution reaction with two species in the rate determining step and occurs in a single step via a single five-centred, trigonal bipyramidal transition state.

The reaction mechanisms for S_N1 and S_N2 reactions can be represented using curly arrows. Steric hindrance and the inductive stabilisation of the carbocation intermediate can be used to explain which mechanism will be preferred for a given haloalkane.

Organic chemistry and instrumental analysis (continued)


(b) Synthesis (continued)

Alcohols are substituted alkanes in which one or more of the hydrogen atoms is replaced with a hydroxyl functional group, -OH group.

Alcohols can be prepared from:

- ◆ haloalkanes by substitution
- ◆ alkenes by acid-catalysed hydration (addition)
- ◆ aldehydes and ketones by reduction using a reducing agent such as lithium aluminium hydride

Reactions of alcohols include:

- ◆ dehydration to form alkenes using aluminium oxide, concentrated sulfuric acid or concentrated phosphoric acid
- ◆ oxidation of primary alcohols to form aldehydes and then carboxylic acids and secondary alcohols to form ketones, using acidified permanganate, acidified dichromate or hot copper(II) oxide
- ◆ formation of alcoholic alkoxides by reaction with some reactive metals such as potassium or sodium, which can then be reacted with monohaloalkanes to form ethers
- ◆ formation of esters by reaction with carboxylic acids using concentrated sulfuric acid or concentrated phosphoric acid as a catalyst
- ◆ formation of esters by reaction with acid chlorides () — this gives a faster reaction than reaction with carboxylic acids, and no catalyst is needed

Hydroxyl groups make alcohols polar, which gives rise to hydrogen bonding. Hydrogen bonding can be used to explain the properties of alcohols including boiling points, melting points, viscosity and solubility or miscibility in water.

Ethers can be regarded as substituted alkanes in which a hydrogen atom is replaced with an alkoxy functional group, -OR , and have the general structure $\text{R}' - \text{O} - \text{R}''$, where R' and R'' are alkyl groups.

Ethers are named as substituted alkanes. The alkoxy group is named by adding the ending 'oxy' to the alkyl substituent, and this prefixes the name of the longest carbon chain.

Ethers can be prepared in a nucleophilic substitution reaction by reacting a monohaloalkane with an alkoxide.

Due to the lack of hydrogen bonding between ether molecules, they have lower boiling points than the corresponding isomeric alcohols.

Organic chemistry and instrumental analysis (continued)

(b) Synthesis (continued)

Methoxymethane and methoxyethane are soluble in water. Larger ethers are insoluble in water due to their increased molecular size.

Ethers are commonly used as solvents since they are relatively inert chemically and will dissolve many organic compounds.

Alkenes can be prepared by:

- ◆ dehydration of alcohols using aluminium oxide, concentrated sulfuric acid or concentrated phosphoric acid
- ◆ base-induced elimination of hydrogen halides from monohaloalkanes

Alkenes take part in electrophilic addition reactions with:

- ◆ hydrogen to form alkanes in the presence of a catalyst
- ◆ halogens to form dihaloalkanes
- ◆ hydrogen halides to form monohaloalkanes
- ◆ water using an acid catalyst to form alcohols

Markovnikov's rule states that when a hydrogen halide or water is added to an unsymmetrical alkene, the hydrogen atom becomes attached to the carbon with the most hydrogen atoms attached to it already. Markovnikov's rule can be used to predict major and minor products formed during the reaction of a hydrogen halide or water with alkenes.

The reaction mechanisms for the addition of a hydrogen halide and the acid-catalysed addition of water can be represented using curly arrows and showing the intermediate carbocation. The inductive stabilisation of intermediate carbocations formed during these reactions can be used to explain the products formed.

The reaction mechanism for the addition of a halogen can be represented using curly arrows and showing the cyclic ion intermediate.

Carboxylic acids can be prepared by:

- ◆ oxidising primary alcohols using acidified permanganate, acidified dichromate and hot copper(II) oxide
- ◆ oxidising aldehydes using acidified permanganate, acidified dichromate, Fehling's solution and Tollens' reagent
- ◆ hydrolysing nitriles, esters or amides

Organic chemistry and instrumental analysis (continued)

(b) Synthesis (continued)

Reactions of carboxylic acids include:

- ◆ formation of salts by reactions with metals or bases
- ◆ condensation reactions with alcohols to form esters in the presence of concentrated sulfuric or concentrated phosphoric acid
- ◆ reaction with amines to form alkylammonium salts that form amides when heated
- ◆ reduction with lithium aluminium hydride to form primary alcohols

Amines are organic derivatives of ammonia in which one or more hydrogen atoms of ammonia has been replaced by an alkyl group.

Amines can be classified as primary, secondary or tertiary according to the number of alkyl groups attached to the nitrogen atom.

Amines react with acids to form salts.

Primary and secondary amines, but not tertiary amines, display hydrogen bonding. As a result, primary and secondary amines have higher boiling points than isomeric tertiary amines.

Primary, secondary and tertiary amine molecules can hydrogen-bond with water molecules, thus explaining the appreciable solubility of the shorter chain length amines in water.

Amines like ammonia are weak bases and dissociate to a slight extent in aqueous solution. The nitrogen atom has a lone pair of electrons which can accept a proton from water, producing hydroxide ions.

Benzene (C_6H_6) 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 in the conjugated system. The presence of delocalised electrons explains why the benzene ring does not take part in addition reactions.

Bonding in benzene can be described in terms of sp^2 hybridisation, sigma and pi bonds, and electron delocalisation.

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 $-C_6H_5$.

Benzene rings can take part in electrophilic substitution reactions. Reactions at benzene rings include:

- ◆ halogenation by reaction of a halogen using aluminium chloride or iron(III) chloride for chlorination and aluminium bromide or iron(III) bromide for bromination
- ◆ alkylation by reaction of a haloalkane using aluminium chloride
- ◆ nitration using concentrated sulfuric acid and concentrated nitric acid
- ◆ sulfonation using concentrated sulfuric acid

Organic chemistry and instrumental analysis (continued)

(c) Stereo chemistry

Molecules that have the same molecular formula but different structural formulae are called isomers.

Structural isomers occur when the atoms are bonded together in a different order in each isomer.

Stereoisomers occur when the order of the bonding in the atoms is the same but the spatial arrangement of the atoms is different in each isomer. There are two types of stereoisomer, geometric and optical.

Geometric isomers:

- ◆ can occur when there is restricted rotation around a carbon-carbon double bond or a carbon-carbon single bond in a cyclic compound
- ◆ must have two different groups attached to each of the carbon atoms that make up the bond with restricted rotation
- ◆ can be labelled cis or trans according to whether the substituent groups are on the same side (cis) or on different sides (trans) of the bond with restricted rotation
- ◆ have differences in physical properties, such as melting point and boiling point
- ◆ can have differences in chemical properties

Optical isomers:

- ◆ occur in compounds in which four different groups are arranged tetrahedrally around a central carbon atom (chiral carbon or chiral centre)
- ◆ are asymmetric
- ◆ are non-superimposable mirror images of each other
- ◆ can be described as enantiomers
- ◆ have identical physical properties, except for their effect on plane-polarised light
- ◆ have identical chemical properties, except when in a chiral environment such as that found in biological systems (only one optical isomer is usually present)
- ◆ rotate plane-polarised light by the same amount but in opposite directions and so are optically active
- ◆ when mixed in equal amounts are optically inactive because the rotational effect of the plane-polarised light cancels out — this is called a racemic mixture

Organic chemistry and instrumental analysis (continued)

(d) Experimental determination of structure

In organic chemistry a number of experimental techniques are carried out to verify the chemical structure of a substance.

Elemental microanalysis is used to determine the masses of C, H, O, S and N in a sample of an organic compound in order to determine its empirical formula.

An empirical formula shows the simplest ratio of the elements in a molecule.

Elemental microanalysis can be determined from:

- ◆ combustion product masses
- ◆ percentage product by mass

Mass spectrometry can be used to determine the accurate gram formula mass (GFM) and structural features of an organic compound.

In mass spectrometry, a small sample of an organic compound is bombarded by high-energy electrons. This removes electrons from the organic molecule generating positively charged molecular ions known as parent ions. These molecular ions then break into smaller positively charged ion fragments. A mass spectrum is obtained showing a plot of the relative abundance of the ions detected against the mass-to-charge (m/z) ratio.

The mass-to-charge ratio of the parent ion can be used to determine the GFM of the molecular ion, and so a molecular formula can be determined using the empirical formula.

The fragmentation data can be interpreted to gain structural information.

Infrared spectroscopy is used to identify certain functional groups in an organic compound.

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

In infrared spectroscopy, infrared radiation is passed through a sample of the organic compound and then into a detector that measures the intensity of the transmitted radiation at different wavelengths. The absorbance of infrared radiation is measured in wavenumbers, the reciprocal of wavelength, in units of cm^{-1} .

Characteristic absorptions by particular vibrations are given in the data booklet.

Organic chemistry and instrumental analysis (continued)

(d) Experimental determination of structure (continued)

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

^1H nuclei behave like tiny magnets and in a strong magnetic field some align with the field (lower energy), whilst the rest align against it (higher energy). Absorption of radiation in the radio frequency region of the electromagnetic spectrum causes the ^1H nuclei to 'flip' from the lower to the higher energy alignment. As they fall back from the higher to the lower energy alignment the emitted radiation is detected and plotted on a spectrum.

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

Chemical shift values for ^1H in different chemical environments are given in the data booklet.

The area under the peak is related to the number of ^1H atoms in that environment and is often given by an integration curve on a spectrum. The height of an integration curve is proportional to the number of ^1H atoms in that environment, and so a ratio of ^1H atoms in each environment can be determined.

The standard reference substance used in ^1H NMR spectroscopy is tetramethylsilane (TMS), which is assigned a chemical shift value equal to zero.

^1H NMR spectra can be obtained using low-resolution or high-resolution NMR.

High-resolution ^1H NMR uses higher radio frequencies than those used in low-resolution ^1H NMR and provides more detailed spectra.

In a high-resolution ^1H NMR an interaction with ^1H atoms on neighbouring carbon atoms can result in the splitting of peaks into multiplets. The number of ^1H atoms on neighbouring carbon atoms will determine the number of peaks within a multiplet and can be determined using the $n+1$ rule, where n is the number of ^1H atoms on the neighbouring carbon atom.

Low- and high-resolution ^1H NMR spectra can be analysed, and low-resolution ^1H NMR spectra can be sketched for any given compound.

Organic chemistry and instrumental analysis (continued)

(e) Pharmaceutical chemistry

Drugs are substances that alter the biochemical processes in the body.

Drugs that have beneficial effects are used in medicines.

A medicine usually contains the drug plus other ingredients such as fillers to add bulk or sweeteners to improve the taste.

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

Drugs that act on receptors can be classified as agonists or antagonists.

- ◆ An agonist mimics the natural compound and binds to the receptor molecules to produce a response similar to the natural active compound.
- ◆ An antagonist prevents the natural compound from binding to the receptor, and so blocks the natural response from occurring.

Many drugs that act on enzymes are classified as enzyme inhibitors and act by binding to the active site of the enzyme and blocking the reaction normally catalysed there.

The overall shape and size of a drug is such that it interacts with a receptor binding site or to the active site of an enzyme. The types of interactions formed can include van der Waals forces and/or ionic bonds.

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

By comparing the structures of drugs that have similar effects on the body, the structural fragment that is involved in the drug action can be identified.

Researching chemistry

(a) Common chemical apparatus

Candidates must be familiar with the use(s) of the following types of apparatus:

- ◆ conical flask
- ◆ digital balance
- ◆ pipette with safety filler
- ◆ burette
- ◆ volumetric (standard) flask
- ◆ distillation (round-bottomed) flask
- ◆ condenser
- ◆ thermometer
- ◆ Buchner or Hirsch or sintered glass funnel
- ◆ glassware with ground glass joints ('Quickfit' or similar)
- ◆ thin-layer chromatography apparatus
- ◆ colorimeter
- ◆ melting point
- ◆ separating funnel

(b) Skills involved in experimental work

Candidates must be able to:

- ◆ tabulate data using appropriate headings and units of measurement
- ◆ represent data as a scatter graph with suitable scales and labels
- ◆ sketch a line of best fit (straight or curved) to represent the trend observed in the data
- ◆ calculate average (mean) values
- ◆ identify and eliminate rogue points
- ◆ qualitatively appreciate the relative accuracy of apparatus used to measure the volume of liquids
- ◆ comment on the reproducibility of results where measurements have been repeated
- ◆ carry out quantitative stoichiometric calculations
- ◆ interpret spectral data
- ◆ appropriately use a positive control, for example a known substance, to validate a technique or procedure

(c) Stoichiometric calculations

Stoichiometry is the study of mole relationships involved in chemical reactions.

Chemical equations, using formulae and state symbols, can be written and balanced to show the mole ratio(s) of reactants and products, including multi-step reactions.

The mass of a mole of any substance, in grams (g), is equal to the gram formula mass (GFM) and can be calculated using relative atomic masses.

Researching chemistry (continued)

(c) Stoichiometric calculations (continued)

Calculations can be performed using the relationship between the mass and the number of moles of a substance.

For solutions, the mass of solute (grams or g), the number of moles of solute (moles or mol), the volume of solution (litres or l), or the concentration of the solution (moles per litre or mol l^{-1}), can be calculated from data provided.

Percentage by mass is the mass of solute made up to 100 cm^3 of solution.

Percentage by volume is the number of cm^3 of solute made up to 100 cm^3 of solution.

The unit ppm stands for parts per million and refers to 1 mg per kg or 1 mg per litre.

Calculations can be performed using data, including:

- ◆ GFM
- ◆ masses
- ◆ number of moles
- ◆ concentrations and volumes of solutions
- ◆ volumes of gases
- ◆ reactant excess
- ◆ theoretical and percentage yield
- ◆ empirical formulae

Theoretical yields can be calculated and compared with actual yields, leading to determining the percentage yield. The percentage yield is reduced by:

- ◆ mass transfer or mechanical losses
- ◆ purification of product
- ◆ side reactions
- ◆ equilibrium position

Candidates must be able to carry out stoichiometric calculations for all of the skills and techniques in the course where appropriate.

Researching chemistry (continued)

(d) Gravimetric analysis

Candidates must be familiar with the technique of gravimetric analysis, including use of:

- ◆ an accurate electronic balance, including the tare function
- ◆ a weighing boat
- ◆ weighing by difference
- ◆ the term 'weighing accurately approximately'
- ◆ heating to constant mass:
 - heating a substance
 - allowing to cool in a desiccator to prevent absorption of water
 - weighing
 - repeating the steps of heating, cooling and weighing until no further changes in mass are observed

Gravimetric analysis is used to determine the mass of an element or compound in a substance.

The substance is converted into another substance of known chemical composition, which can be readily isolated and purified.

The conversion can occur either through precipitation or volatilisation.

In precipitation conversion the substance undergoes a precipitation reaction. The precipitate is separated from the filtrate and the filtrate tested to ensure the reaction has gone to completion. The precipitate is washed, dried to constant mass and then weighed.

In volatilisation conversion the substance is heated and any volatile products (often water) are evaporated. The substance is heated to constant mass and the final mass recorded.

(e) Volumetric analysis

Candidates must be familiar with use of the technique of volumetric analysis, including:

- ◆ preparing a standard solution
- ◆ accurate dilution
- ◆ standardising solutions to determine accurate concentration
- ◆ titrating to obtain concordancy using burettes, pipettes and volumetric flasks
- ◆ choosing an appropriate indicator

Researching chemistry (continued)

(e) Volumetric analysis (continued)

A solution of accurately known concentration is known as a standard solution.

A standard solution can be prepared by:

- ◆ weighing a primary standard accurately
- ◆ dissolving in a small volume of solvent (usually deionised or distilled water) in a beaker
- ◆ transferring the solution and rinsings into a volumetric flask
- ◆ making up to the graduation mark with solvent
- ◆ stoppering and inverting

Standard solutions can also be prepared by accurate dilution by pipetting an appropriate volume of a standard solution into a volumetric flask, making up to the graduation mark with solvent, stoppering and inverting.

A primary standard must:

- ◆ be available in a high state of purity
- ◆ be stable when solid and in solution
- ◆ be soluble
- ◆ have a reasonably high GFM

Examples of primary standards include:

- ◆ sodium carbonate, Na_2CO_3
- ◆ hydrated oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
- ◆ potassium hydrogen phthalate, $\text{KH}(\text{C}_8\text{H}_4\text{O}_4)$
- ◆ silver nitrate, AgNO_3
- ◆ potassium iodate, KIO_3
- ◆ potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$

Sodium hydroxide is not a primary standard as it has a relatively low GFM, is unstable as a solid (absorbs moisture) and unstable as a solution. Sodium hydroxide solution must be standardised before being used in volumetric analysis.

Researching chemistry (continued)

(e) Volumetric analysis (continued)

Candidates must be familiar with use of the following types of volumetric analysis:

- ◆ acid-base titrations
- ◆ redox titrations based on reactions between oxidising and reducing agents
- ◆ complexometric titrations based on reactions in which complexes are formed — EDTA is an important complexometric reagent and can be used to determine the concentration of metal ions in solution
- ◆ back titrations used to find the number of moles of a substance by reacting it with an excess volume of a reactant of known concentration. The resulting mixture is then titrated to work out the number of moles of the reactant in excess. From the initial number of moles of that reactant, the number of moles used in the reaction can be determined. The initial number of moles of the substance being analysed can then be calculated. A back titration is useful when trying to work out the quantity of substance in a solid with a low solubility.

(f) Practical skills and techniques

Candidates must be familiar with use of the technique of colorimetry, including:

- ◆ preparing a series of standard solutions of appropriate concentration
- ◆ choosing an appropriate colour or wavelength of filter complementary to the colour of the species being tested
- ◆ using a blank
- ◆ preparing a calibration graph

Colorimetry uses the relationship between colour intensity of a solution and the concentration of the coloured species present.

A colorimeter or a spectrophotometer is used to measure the absorbance of light of a series of standard solutions, and this data is used to plot a calibration graph.

The concentration of the solution being tested is determined from its absorbance and by referring to the calibration curve.

The concentration of coloured species in the solution being tested must lie in the straight line section of the calibration graph.

Candidates must be familiar with use of the technique of distillation. Distillation is used for identification and purification of organic compounds.

The boiling point of a compound, determined by distillation, is one of the physical properties that can be used to confirm its identity.

Distillation can be used to purify a compound by separating it from less volatile substances in the mixture.

Researching chemistry (continued)

(f) Practical skills and techniques (continued)

Candidates must be familiar with use of the technique of heating under reflux. Heating under reflux allows heat energy to be applied to a chemical reaction mixture over an extended period of time without volatile substances escaping.

When carrying out heating under reflux, the reaction mixture is placed in a round-bottomed flask with anti-bumping granules and the flask is fitted with a condenser. The flask is then heated using an appropriate source of heat.

Candidates must be familiar with use of the technique of vacuum filtration. Vacuum filtration involves carrying out a filtration under reduced pressure and provides a faster means of separating a precipitate from a filtrate. A Büchner, Hirsch or sintered glass funnel can be used during vacuum filtration.

Candidates must be familiar with use of the technique of recrystallisation to purify an impure solid involving:

- ◆ dissolving an impure solid gently in a minimum volume of a hot solvent
- ◆ hot filtration of the resulting mixture to remove any insoluble impurities
- ◆ cooling the filtrate slowly to allow crystals of the pure compound to form, leaving soluble impurities dissolved in the solvent
- ◆ filtering, washing and drying the pure crystals

The solvent for recrystallisation is chosen so that the compound being purified is completely soluble at high temperatures and only sparingly soluble at lower temperatures.

Candidates must be familiar with use of the technique of solvent extraction. Solvent extraction involves isolating a solute from a liquid mixture or solution by extraction using an immiscible solvent in which the solute is soluble.

When carrying out a solvent extraction, the two immiscible solvents form two layers in the separating funnel. The solute dissolves in both solvents and an equilibrium establishes between the two layers. The ratio of solute dissolved in each layer is determined by the equilibrium constant, K . The lower layer is run off into a container and the upper layer is poured into a second container. This process is repeated to maximise the quantity of solute extracted.

Researching chemistry (continued)

(f) Practical skills and techniques (continued)

The quantity of solute extracted is greater if a number of extractions using smaller volumes of solvent are carried out rather than a single extraction using a large volume of solvent.

The solvent used should be:

- ◆ immiscible with the liquid mixture or solution (usually water)
- ◆ one in which the solute is more soluble in than the liquid mixture or solution (usually water)
- ◆ volatile to allow the solute to be obtained by evaporation of the solvent
- ◆ unreactive with the solute

Candidates must be familiar with use of the techniques of melting point and mixed melting point determination. The melting point of a substance is the temperature range over which the solid first starts to melt, to when all of the solid has melted.

The identity of a pure compound can be confirmed by melting point analysis and a comparison of the experimentally determined melting point with a literature or known melting point value.

Determination of the melting point of a compound can give an indication of the purity of a compound. The presence of impurities in the compound lowers the melting point and broadens its melting temperature range due to the disruption in intermolecular bonding in the crystal lattice.

Determination of a mixed melting point involves mixing a small quantity of the product with some of the pure compound and determining the melting point. The melting point value and the range of the melting temperature can be used to determine if the product and the pure compound are the same substance.

Candidates must be familiar with use of the technique of thin-layer chromatography. Chromatography is a technique used to separate the components present within a mixture. Chromatography separates substances by making use of differences in their polarity or molecular size.

Thin-layer chromatography (TLC) uses a fine film of silica or aluminium oxide spread over glass, aluminium foil or plastic. A small sample of the mixture being tested is spotted onto the base (pencil) line of the chromatogram. A solvent dissolves the compounds in the spot and carries the compounds up the chromatogram. How far the compounds are carried depends on how soluble the compounds are in the chosen solvent and how well they adhere to the plate. A developing agent or ultraviolet light is normally required to visualise the spots on the chromatogram.

Researching chemistry (continued)

(f) Practical skills and techniques (continued)

R_f values can be calculated:

$$R_f = \frac{\text{distance travelled by the sample}}{\text{distance travelled by the solvent}}$$

Under the same conditions (temperature, solvent, and saturation levels) a compound always has the same R_f value (within experimental error).

The identity of a compound can be confirmed by:

- ◆ comparing the experimentally determined R_f values with a literature or known value determined under the same conditions
- ◆ making a direct comparison on a TLC plate between the compound being tested and the pure substance — a co-spot could be used

TLC is used to assess the purity of substances. A pure substance, when spotted and developed on a TLC plate, should appear as a single spot (some impurities may not be visible by TLC analysis). The presence of more than one spot shows that impurities are present.

Skills, knowledge and understanding included in the course are appropriate to the SCQF level of the course. The SCQF level descriptors give further information on characteristics and expected performance at each SCQF level, and are available on the SCQF website.