# Module 2: Foundations in chemistry

This module acts as an important bridge into AS and A Level Chemistry from the study of chemistry within science courses at GCSE level.

This module provides learners with a knowledge and understanding of the important chemical ideas that underpin the study of A Level Chemistry:

- atomic structure
- quantitative chemistry: formulae, equations, amount of substance and the mole
- reactions of acids
- oxidation number and redox reactions
- bonding and structure.

The importance of these basic chemical concepts is seen as a prerequisite for all further chemistry modules, and it is recommended that this module should be studied first during this course.

This module allows learners to develop important quantitative techniques involved in measuring masses, gas and solution volumes, including use of volumetric apparatus.

Learners are also able to develop their mathematical skills during their study of amount of substance and when carrying out quantitative practical work.

# 2.1 Atoms and reactions

This section builds directly from GCSE Science, starting with basic atomic structure and isotopes.

Important basic chemical skills are developed: writing chemical formulae, constructing equations and calculating chemical quantities using the concept of amount of substance.

The role of acids, bases and salts in chemistry is developed in the context of neutralisation reactions.

Finally, redox reactions are studied within the context of oxidation number and electron transfer.

# 2.1.1 Atomic structure and isotopes

# **Learning outcomes**

Learners should be able to demonstrate and apply their knowledge and understanding of:

# Atomic structure and isotopes

- (a) isotopes as atoms of the same element with different numbers of neutrons and different masses
- (b) atomic structure in terms of the numbers of protons, neutrons and electrons for atoms and ions, given the atomic number, mass number and any ionic charge

# Additional guidance

HSW1 Different models for atomic structure can be used to explain different phenomena, e.g. the Bohr model explains periodic properties.

HSW7 The changing accepted models of atomic structure over time. The use of evidence to accept or reject particular models.

#### **Relative mass**

explanation of the terms relative isotopic mass (mass compared with 1/12th mass of carbon-12) and relative atomic mass (weighted mean mass compared with 1/12th mass of carbon-12), based on the mass of a <sup>12</sup>C atom, the standard for atomic masses

Definitions required.

(d) use of mass spectrometry in:

> the determination of relative isotopic masses and relative abundances of the isotope,

isotopes

(ii) calculation of the relative atomic mass of an element from the relative abundances of its

M0.2, M1.2, M3.1

Knowledge of the mass spectrometer **not** required.

Limited to ions with single charges.

use of the terms relative molecular mass, M<sub>r</sub>, and (e) relative formula mass and their calculation from relative atomic masses.

For simple molecules, the term relative molecular mass will be used.

For compounds with giant structures, the term relative formula mass will be used.

Definitions of relative molecular mass and relative formula mass will **not** be required.

# 2.1.2 Compounds, formulae and equations

# **Learning outcomes** Additional guidance Learners should be able to demonstrate and apply their knowledge and understanding of: Formulae and equations (a) the writing of formulae of ionic compounds from Note that 'nitrate' and 'sulfate' should be assumed ionic charges, including: to be $NO_3^-$ and $SO_4^{2-}$ . prediction of ionic charge from the position Charges on ions other than in (i) and (ii) will be of an element in the periodic table provided. recall of the names and formulae for the following ions: $\rm NO_3^-, \, CO_3^{~2-}, \, SO_4^{~2-}, \, OH^-, \, NH_4^{~+}, \, Zn^{2+}$ and $\rm Ag^+$ (b) construction of balanced chemical equations M0.2 (including ionic equations), including state symbols, for reactions studied and for unfamiliar reactions given appropriate information.

# 2.1.3 Amount of substance

#### Learning outcomes Additional guidance Learners should be able to demonstrate and apply their knowledge and understanding of: The mole (a) explanation and use of the terms: M0.0, M0.1, M0.2, M0.4 amount of substance Amount of substance will be used in exams using the (ii) mole (symbol 'mol'), as the unit for amount formula of the substance, of substance e.g. amount of NaCl; amount of O<sub>2</sub>. (iii) the Avogadro constant, $N_{\Delta}$ (the number of The value for $N_{\Delta}$ and the molar gas volume at RTP particles per mole, $6.02 \times 10^{23}$ mol<sup>-1</sup>) are provided on the Data Sheet. (iv) molar mass (mass per mole, units g mol<sup>-1</sup>), (v) molar gas volume (gas volume per mole, units dm<sup>3</sup> mol<sup>-1</sup>) **Determination of formulae** (b) use of the terms: Definitions not required. empirical formula (the simplest whole number ratio of atoms of each element present in a compound) (ii) molecular formula (the number and type of atoms of each element in a molecule) (c) calculations of empirical and molecular formulae, M0.2, M2.2, M2.3, M2.4 from composition by mass or percentage To include calculating empirical formulae from compositions by mass and relative molecular elemental analysis data (see also 6.3.2 e). mass (d) the terms anhydrous, hydrated and water of M0.2, M2.2, M2.3, M2.4 crystallisation and calculation of the formula PAG1 of a hydrated salt from given percentage composition, mass composition or based on experimental results Calculation of reacting masses, gas volumes and mole concentrations calculations, using amount of substance in mol, M0.0, M0.1, M0.4, M1.1, M2.2, M2.3, M2.4 (e) involving: Learners will be expected to express concentration (i) mass in mol $dm^{-3}$ and $g dm^{-3}$ . (ii) gas volume (iii) solution volume and concentration (f) the ideal gas equation: M0.0, M0.1, M0.4, M1.1, M2.2, M2.3, M2.4 pV = nRTThe value for *R* is provided on the *Data Sheet*. Learners will be expected to express quantities in

SI units.

M0.2

use of stoichiometric relationships in calculations

(g)

2

# Percentage yields and atom economy

(h) calculations to determine:

(i) the percentage yield of a reaction or related quantities

(ii) the atom economy of a reaction

(i) the techniques and procedures required during experiments requiring the measurement of mass, volumes of solutions and gas volumes

(j) the benefits for sustainability of developing chemical processes with a high atom economy. M0.2, M1.1, M2.2, M2.3, M2.4

#### PAG1

HSW4 Many opportunities to carry out experimental and investigative work.

HSW10 Use of processes with high atom economy in chemical industry and other areas.

# **2.1.4** Acids

# **Learning outcomes**

Learners should be able to demonstrate and apply their knowledge and understanding of:

# Acids, bases, alkalis and neutralisation

- (a) the formulae of the common acids (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and CH<sub>3</sub>COOH) and the common alkalis (NaOH, KOH and NH<sub>3</sub>) and explanation that acids release H<sup>+</sup> ions in aqueous solution and alkalis release OH<sup>-</sup> ions in aqueous solution
- **(b)** qualitative explanation of strong and weak acids in terms of relative dissociations
- (c) neutralisation as the reaction of:
  - (i) H<sup>+</sup> and OH<sup>-</sup> to form H<sub>2</sub>O
  - (ii) acids with bases, including carbonates, metal oxides and alkalis (water-soluble bases), to form salts, including full equations

# Acid-base titrations

- (d) the techniques and procedures used when preparing a standard solution of required concentration and carrying out acid–base titrations
- (e) structured and non-structured titration calculations, based on experimental results of familiar and non-familiar acids and bases.

# Additional guidance

# PAG2

HSW4 Many opportunities to carry out experimental and investigative work.

M0.1, M0.2, M1.1, M1.2, M2.2, M2.3, M2.4

# 2.1.5 Redox

# Learning outcomes Additional guidance Learners should be able to demonstrate and

#### Oxidation number

(a) rules for assigning and calculating oxidation number for atoms in elements, compounds and ions

apply their knowledge and understanding of:

- **(b)** writing formulae using oxidation numbers
- (c) use of a Roman numeral to indicate the magnitude of the oxidation number when an element may have compounds/ions with different oxidation numbers

Learners will be expected to know oxidation numbers of O in peroxides and H in metal hydrides.

HSW8 Appropriate use of oxidation numbers in written communication.

Examples should include, but not be limited to, iron(II) and iron(III).

Learners will be expected to write formulae from names such as chlorate(I) and chlorate(III) and *vice* 

Note that 'nitrate' and 'sulfate', with no shown oxidation number, are assumed to be  ${\rm NO_3}^-$  and  ${\rm SO_4^{\ 2^-}}$ .

HSW8 Systematic and unambiguous nomenclature.

# **Redox reactions**

- (d) oxidation and reduction in terms of:
  - (i) electron transfer
  - (ii) changes in oxidation number
- (e) redox reactions of metals with acids to form salts, including full equations (see also 2.1.4 c)
- (f) interpretation of redox equations in (e), and unfamiliar redox reactions, to make predictions in terms of oxidation numbers and electron loss/

Should include examples of s-, p- and d-block elements.

Metals should be from s-, p- and d-blocks e.g. Mg, A*l*, Fe, Zn.

Ionic equations not required.

In **(e)**, reactions with acids will be limited to those producing a salt and hydrogen. Reactions involving nitric acid or concentrated sulfuric acid could be assessed in the context of **(f)**.

M0.2

gain.

# 2.2 Electrons, bonding and structure

This section introduces the concept of atomic orbitals and develops a deeper understanding of electron configurations linked to the periodic table.

The central role of electrons in ionic and covalent bonding is then studied. The important role of

molecules is studied, including an explanation of polarity and intermolecular forces. Finally, this section looks at how bonding and structure contribute to properties of substances.

# 2.2.1 Electron structure

# **Learning outcomes**

#### Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

# Energy levels, shells, sub-shells, atomic orbitals, electron configuration

- (a) the number of electrons that can fill the first four shells
- (b) atomic orbitals, including:
  - (i) as a region around the nucleus that can hold up to two electrons, with opposite spins
  - (ii) the shapes of s- and p-orbitals
  - (iii) the number of orbitals making up s-, p- and d-sub-shells, and the number of electrons that can fill s-, p- and d-sub-shells
- (c) filling of orbitals:
  - (i) for the first three shells and the 4s and 4p orbitals in order of increasing energy
  - (ii) for orbitals with the same energy, occupation singly before pairing
- (d) deduction of the electron configurations of:
  - (i) atoms, given the atomic number, up to Z = 36
  - (ii) ions, given the atomic number and ionic charge, limited to s- and p-blocks up to Z = 36.

HSW1,7 Development of models to explain electron structure.

Learners are expected to be familiar with the 'electrons in box' representations.

HSW1 Development of refined models for electron structure.

Learners should use sub-shell notation, i.e. for oxygen: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>.

# 2.2.2 Bonding and structure

# **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

# Ionic bonding

- ionic bonding as electrostatic attraction between positive and negative ions, and the construction of 'dot-and-cross' diagrams
- (b) explanation of the solid structures of giant ionic lattices, resulting from oppositely charged ions strongly attracted in all directions e.g. NaCl
- (c) explanation of the effect of structure and bonding on the physical properties of ionic compounds, including melting and boiling points, solubility and electrical conductivity in solid, liquid and aqueous states

HSW1 Use of ideas about ionic bonding to explain macroscopic properties.

# **Covalent bonding**

- (d) covalent bond as the strong electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms
- (e) construction of 'dot-and-cross' diagrams of molecules and ions to describe:
  - (i) single covalent bonding
  - (ii) multiple covalent bonding
  - (iii) dative covalent (coordinate) bonding
- (f) use of the term average bond enthalpy as a measurement of covalent bond strength

'Dot-and-cross' diagrams of up to six electron pairs (including lone pairs) surrounding a central atom.

Learners should appreciate that the larger the value of the average bond enthalpy, the stronger the covalent bond.

Definition and calculations **not** required. Average bond enthalpies and related calculations are covered in detail in **3.2.1** f.

# The shapes of simple molecules and ions

- (g) the shapes of, and bond angles in, molecules and ions with up to six electron pairs (including lone pairs) surrounding the central atom as predicted by electron pair repulsion, including the relative repulsive strengths of bonded pairs and lone pairs of electrons
- (h) electron pair repulsion to explain the following shapes of molecules and ions: linear, non-linear, trigonal planar, pyramidal, tetrahedral and octahedral

# M4.1, M4.2

Learners should be able to draw 3-D diagrams to illustrate shapes of molecules and ions.

HSW1,2 Using electron pair repulsion theory to predict molecular shapes.

Learners are expected to know that lone pairs repel more than bonded pairs and the bond angles for common examples of each shape including  $CH_4$  (109.5°),  $NH_3$  (107°) and  $H_2O$  (104.5°).

# **Electronegativity and bond polarity**

 electronegativity as the ability of an atom to attract the bonding electrons in a covalent bond; interpretation of Pauling electronegativity values Learners should be aware that electronegativity increases towards F in the periodic table.

HSW1,2 Using ideas about electronegativity to predict chemical bond type.

(j) explanation of:

- a polar bond and permanent dipole within molecules containing covalently-bonded atoms with different electronegativities
- (ii) a polar molecule and overall dipole in terms of permanent dipole(s) and molecular shape

A polar molecule requires polar bonds with dipoles that do not cancel due to their direction. E.g. H<sub>2</sub>O and CO<sub>2</sub> both have polar bonds but only H<sub>2</sub>O has an overall dipole.

#### Intermolecular forces

 (k) intermolecular forces based on permanent dipole–dipole interactions and induced dipole– dipole interactions Permanent dipole–dipole and induced dipole–dipole interactions can **both** be referred to as van der Waals' forces.

Induced dipole–dipole interactions can also be referred to as London (dispersion) forces.

HSW1,2 Dipole interactions as a model to explain intermolecular bonding.

 hydrogen bonding as intermolecular bonding between molecules containing N, O or F and the H atom of –NH, –OH or HF Including the role of lone pairs.

- (m) explanation of anomalous properties of H<sub>2</sub>O resulting from hydrogen bonding, e.g.:
  - (i) the density of ice compared with water
  - (ii) its relatively high melting and boiling points
- (n) explanation of the solid structures of simple molecular lattices, as covalently bonded molecules attracted by intermolecular forces, e.g. I<sub>2</sub>, ice
- (o) explanation of the effect of structure and bonding on the physical properties of covalent compounds with simple molecular lattice structures including melting and boiling points, solubility and electrical conductivity.

HSW1 Use of ideas about hydrogen bonding to explain macroscopic properties.

# Module 3: Periodic table and energy

The focus of this module is inorganic and physical chemistry, the applications of energy use to everyday life and industrial processes, and current environmental concerns associated with sustainability.

The content within this module assumes knowledge and understanding of the chemical concepts developed in Module 2: Foundations in chemistry.

This module provides learners with a knowledge and understanding of the important chemical ideas that underpin the study of inorganic and physical chemistry:

- the periodic table: periodic and group properties
- enthalpy changes and their determination
- rates of reaction
- reversible reactions and chemical equilibrium
- consideration of energy and yield in improving sustainability.

This module allows learners to develop important qualitative practical skills, especially observational skills required for analysis, and accurate quantitative

techniques involved in determination of energy changes and reaction rates.

There are opportunities for developing mathematical skills when studying enthalpy changes and reaction rates and when carrying out quantitative practical work.

# Synoptic assessment

This module provides a context for synoptic assessment and the subject content links strongly with content encountered in Module 2: Foundations in chemistry.

- Atoms, moles and stoichiometry
- Acid and redox reactions
- Bonding and structure

Knowledge and understanding of Module 2 will be assumed and examination questions will be set that link its content with this module and other areas of chemistry.

# 3.1 The periodic table

Periodic trends are first studied to extend the understanding of structure and bonding. Group properties are then studied using Group 2 and the halogens as typical metal and non-metal groups respectively, allowing an understanding of redox reactions to be developed further.

Finally, this section looks at how unknown ionic compounds can be analysed and identified using simple test-tube tests.

# 3.1.1 Periodicity

# **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

# The structure of the periodic table

- (a) the periodic table as the arrangement of elements:
  - (i) by increasing atomic (proton) number
  - (ii) in periods showing repeating trends in physical and chemical properties (periodicity)
  - (iii) in groups having similar chemical properties

HSW1,7,11 The development of the Periodic Law and acceptance by the scientific community.

HSW7,11 The extension of the periodic table through discovery and confirmation of new elements.

# Periodic trend in electron configuration and ionisation energy

- (b) (i) the periodic trend in electron configurations across Periods 2 and 3 (see also 2.2.1 d)
  - (ii) classification of elements into s-, p- and d-blocks
- (c) first ionisation energy (removal of 1 mol of electrons from 1 mol of gaseous atoms) and successive ionisation energy, and:
  - explanation of the trend in first ionisation energies across Periods 2 and 3, and down a group, in terms of attraction, nuclear charge and atomic radius
  - (ii) prediction from successive ionisation energies of the number of electrons in each shell of an atom and the group of an element

#### M3.1

Definition required for first ionisation energy only. Explanation to include the small decreases as a result of s- and p-sub-shell energies (e.g. between Be and B) and p-orbital repulsion (e.g. between N and O).

HSW1,2 Trends in ionisation energy support the Bohr model of the atom.

# Periodic trend in structure and melting point

- (d) explanation of:
  - metallic bonding as strong electrostatic attraction between cations (positive ions) and delocalised electrons
  - (ii) a giant metallic lattice structure, e.g. all metals
- (e) explanation of the solid giant covalent lattices of carbon (diamond, graphite and graphene) and silicon as networks of atoms bonded by strong covalent bonds

No details of cubic or hexagonal packing required.

HSW1,9 Use of ideas about bonding to explain the strength and conductive properties of graphene, and its potential applications and benefits.

(f) explanation of physical properties of giant metallic and giant covalent lattices, including melting and boiling points, solubility and electrical conductivity in terms of structure and bonding Explanations should be in terms of the types of particle present in a lattice, the relative strength of forces and bonds, and the mobility of the particles involved, as appropriate.

(g) explanation of the variation in melting points across Periods 2 and 3 in terms of structure and bonding (see also 2.2.2 o).

HSW1 Use of ideas about bonding to explain macroscopic properties.

M3.1

Trend in structure from giant metallic to giant covalent to simple molecular lattice.

# 3.1.2 Group 2

#### Learning outcomes

Learners should be able to demonstrate and apply their knowledge and understanding of:

# Redox reactions and reactivity of Group 2 metals

- (a) the outer shell s<sup>2</sup> electron configuration and the loss of these electrons in redox reactions to form 2+ ions
- (b) the relative reactivities of the Group 2 elementsMg → Ba shown by their redox reactions with:
  - (i) oxygen
  - (ii) water
  - (iii) dilute acids
- (c) the trend in reactivity in terms of the first and second ionisation energies of Group 2 elements down the group (see also 3.1.1 c)

# Additional guidance

Reactions with acids will be limited to those producing a salt and hydrogen.

#### M3.1

Definition of second ionisation energy is **not** required, but learners should be able to write an equation for the change involved.

# **Reactions of Group 2 compounds**

- (d) the action of water on Group 2 oxides and the approximate pH of any resulting solutions, including the trend of increasing alkalinity
- (e) uses of some Group 2 compounds as bases, including equations, for example (but not limited to):
  - (i) Ca(OH)<sub>2</sub> in agriculture to neutralise acid soils
  - (ii) Mg(OH)<sub>2</sub> and CaCO<sub>3</sub> as 'antacids' in treating indigestion.

# 2

# **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

# Characteristic physical properties

a) existence of halogens as diatomic molecules and explanation of the trend in the boiling points of  ${\rm C}l_2$ ,  ${\rm Br}_2$  and  ${\rm I}_2$ , in terms of induced dipole–dipole interactions (London forces) (see also 2.2.2 k)

# Redox reactions and reactivity of halogens and their compounds

(b) the outer shell s<sup>2</sup>p<sup>5</sup> electron configuration and the gaining of one electron in many redox reactions to form 1– ions

Throughout this section, explanations of redox reactions should emphasise electron transfer and oxidation number changes and include full and ionic equations (see also 2.1.5 Redox).

(c) the trend in reactivity of the halogens  ${\rm C}l_2$ ,  ${\rm Br}_2$  and  ${\rm I}_2$ , illustrated by reaction with other halide ions

Including colour change in aqueous and organic solutions.

- (d) explanation of the trend in reactivity shown in
   (c), from the decreasing ease of forming 1– ions, in terms of attraction, atomic radius and electron shielding
- (e) explanation of the term disproportionation as oxidation and reduction of the same element, illustrated by:
  - the reaction of chlorine with water as used in water treatment
  - (ii) the reaction of chlorine with cold, dilute aqueous sodium hydroxide, as used to form bleach
  - (iii) reactions analogous to those specified in (i) and (ii)
- (f) the benefits of chlorine use in water treatment (killing bacteria) contrasted with associated risks (e.g. hazards of toxic chlorine gas and possible risks from formation of chlorinated hydrocarbons)

# HSW9,10,12 Decisions on whether or not to chlorinate water depend on balance of benefits and risks, and ethical considerations of people's right to choose. Consideration of other methods of purifying drinking water.

# Characteristic reactions of halide ions

(g) the precipitation reactions, including ionic equations, of the aqueous anions  $Cl^-$ ,  $Br^-$  and  $I^-$  with aqueous silver ions, followed by aqueous ammonia, and their use as a test for different halide ions.

Complexes with ammonia are **not** required other than observations.

PAG4 (see also 3.1.4 a) HSW4 Qualitative analysis.

# 3.1.4 Qualitative analysis

# **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

#### **Tests for ions**

- (a) qualitative analysis of ions on a test-tube scale; processes and techniques needed to identify the following ions in an unknown compound:
  - (i) anions:
    - CO<sub>3</sub><sup>2-</sup>, by reaction with H<sup>+</sup>(aq) forming CO<sub>2</sub>(g) (see 2.1.4 c)
    - $SO_4^{2-}$ , by precipitation with  $Ba^{2+}$ (aq)
    - Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> (see 3.1.3 g)
  - (ii) cations: NH<sub>4</sub><sup>+</sup>, by reaction with warm NaOH(aq) forming NH<sub>3</sub>.

Sequence of tests required is carbonate, sulfate then halide. (BaCO<sub>3</sub> and Ag<sub>2</sub>SO<sub>4</sub> are both insoluble.)

#### PAG4

HSW4 Qualitative analysis.

# 3.2 Physical chemistry

This section introduces physical chemistry within the general theme of energy.

Learners first learn about the importance of enthalpy changes, their uses and determination from experimental results including enthalpy cycles.

This section then investigates the ways in which a change in conditions can affect the rate of a chemical reaction, in terms of activation energy, the Boltzmann distribution and catalysis.

Reversible reactions are then studied, including the dynamic nature of chemical equilibrium and the influence of conditions upon the position of equilibrium.

Finally, the integrated roles of enthalpy changes, rates, catalysts and equilibria are considered as a way of increasing yield and reducing energy demand, improving the sustainability of industrial processes.

# 3.2.1 Enthalpy changes

# **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

#### Enthalpy changes: $\Delta H$ of reaction, formation, combustion and neutralisation

- (a) explanation that some chemical reactions are accompanied by enthalpy changes that are exothermic ( $\Delta H$ , negative) or endothermic ( $\Delta H$ , positive)
- (b) construction of enthalpy profile diagrams to show the difference in the enthalpy of reactants compared with products

M3.1

- (c) qualitative explanation of the term activation energy, including use of enthalpy profile diagrams
- (d) explanation and use of the terms:
  - (i) standard conditions and standard states (physical states under standard conditions)
  - (ii) enthalpy change of reaction (enthalpy change associated with a stated equation,  $\Delta_r H$ )
  - (iii) enthalpy change of formation (formation of 1 mol of a compound from its elements,  $\Delta_{\epsilon}H$ )
  - (iv) enthalpy change of combustion (complete combustion of 1 mol of a substance,  $\Delta_c H$ )
  - (v) enthalpy change of neutralisation (formation of 1 mol of water from neutralisation,  $\Delta_{\rm neut} H$ )
- (e) determination of enthalpy changes directly from appropriate experimental results, including use of the relationship:  $q = mc\Delta T$

# **Bond enthalpies**

- (f) (i) explanation of the term average bond enthalpy (breaking of 1 mol of bonds in gaseous molecules)
  - (ii) explanation of exothermic and endothermic reactions in terms of enthalpy changes associated with the breaking and making of chemical bonds
  - (iii) use of average bond enthalpies to calculate enthalpy changes and related quantities (see also 2.2.2 f)

#### Hess' law and enthalpy cycles

- (g) Hess' law for construction of enthalpy cycles and calculations to determine indirectly:
  - (i) an enthalpy change of reaction from enthalpy changes of combustion
  - (ii) an enthalpy change of reaction from enthalpy changes of formation
  - (iii) enthalpy changes from unfamiliar enthalpy cycles
- (h) the techniques and procedures used to determine enthalpy changes directly and indirectly.

#### M3.1

Activation energy in terms of the minimum energy required for a reaction to take place.

Definitions required for enthalpy changes of formation, combustion and neutralisation only.

Standard conditions can be considered as 100 kPa and a stated temperature, 298 K.

M0.0, M0.2, M2.2, M2.3, M2.4

#### PAG3

M0.0, M0.2, M2.2, M2.3, M2.4

Definition of average bond enthalpy **not** required.

Learners are expected to understand that an actual bond enthalpy may differ from the average value.

M0.0, M0.2, M1.1, M2.2, M2.3, M2.4, M3.1

Definition of Hess' law **not** required. Unfamiliar enthalpy cycles will be provided.

HSW2 Application of the principle of conservation of energy to determine enthalpy changes.

M3.1, M3.2

To include the enthalpy changes covered in **5.2.1 c**.

#### DVC3

HSW4 Opportunities for carrying out experimental and investigative work.

# 3.2.2 Reaction rates

#### Learning outcomes Additional guidance Learners should be able to demonstrate and apply their knowledge and understanding of: Simple collision theory the effect of concentration, including the (a) pressure of gases, on the rate of a reaction, in terms of frequency of collisions calculation of reaction rate from the gradients M3.1, M3.2, M3.5 of graphs measuring how a physical quantity Suitable physical quantities to monitor could include changes with time concentration, gas volume, mass, etc. **Catalysts** explanation of the role of a catalyst: Details of processes are not required. (c) in increasing reaction rate without being used up by the overall reaction in allowing a reaction to proceed via a different route with lower activation energy, as shown by enthalpy profile diagrams (d) explanation of the terms homogeneous and heterogeneous catalysts (ii) explanation that catalysts have great HSW9,10 Benefits to the environment of improved economic importance and benefits for sustainability weighed against toxicity of some increased sustainability by lowering catalysts. temperatures and reducing energy demand from combustion of fossil fuels with resulting reduction in CO<sub>2</sub> emissions the techniques and procedures used to PAG9 (e) investigate reaction rates including the HSW4 Many opportunities to carry out experimental measurement of mass, gas volumes and time and investigative work. The Boltzmann distribution (f) qualitative explanation of the Boltzmann M3.1 distribution and its relationship with activation energy (see also 3.2.1 c) explanation, using Boltzmann distributions, M3.1 (g) of the qualitative effect on the proportion of HSW1,2,5 Use of Boltzmann distribution model to molecules exceeding the activation energy and explain effect on reaction rates. hence the reaction rate, for:

(i) temperature changes

(ii) catalytic behaviour (see also 3.2.2 c).

# 3.2.3 Chemical equilibrium

# Learning outcomes Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

# Dynamic equilibrium and le Chatelier's principle

- (a) explanation that a dynamic equilibrium exists in a closed system when the rate of the forward reaction is equal to the rate of the reverse reaction and the concentrations of reactants and products do not change
- (b) le Chatelier's principle and its application for homogeneous equilibria to deduce qualitatively the effect of a change in temperature, pressure or concentration on the position of equilibrium
- (c) explanation that a catalyst increases the rate of both forward and reverse reactions in an equilibrium by the same amount resulting in an unchanged position of equilibrium
- (d) the techniques and procedures used to investigate changes to the position of equilibrium for changes in concentration and temperature.
- (e) explanation of the importance to the chemical industry of a compromise between chemical equilibrium and reaction rate in deciding the operational conditions

# The equilibrium constant, $K_c$

- (f) expressions for the equilibrium constant,  $K_c$ , for homogeneous reactions and calculations of the equilibrium constant,  $K_c$ , from provided equilibrium concentrations
- (g) estimation of the position of equilibrium from the magnitude of  $K_c$ .

Definition for le Chatelier's principle **not** required.

HSW1,2,5 Use of le Chatelier's principle to explain effect of factors on the position of equilibrium.

Qualitative effects only.

HSW4 Opportunities to carry out experimental and investigative work.

HSW6 Balancing the effects of equilibrium, rate, safety and economics to determine the conditions used in industrial reactions e.g. Haber process.

M0.2, M1.1, M2.3, M2.4

Learners will **not** need to determine the units for  $K_c$ .

M0.3

A qualitative estimation only is required.

# Module 4: Core organic chemistry

This module introduces organic chemistry and its important applications to everyday life, including current environmental concerns associated with sustainability.

The module assumes knowledge and understanding of the chemical concepts developed in Module 2: Foundations in chemistry.

The module provides learners with a knowledge and understanding of the important chemical ideas that underpin the study of organic chemistry:

- nomenclature and formula representation, functional groups, organic reactions and isomerism
- aliphatic hydrocarbons
- · alcohols and haloalkanes
- · organic practical skills and organic synthesis
- instrumental analytical techniques to provide evidence of structural features in molecules.

This module also provides learners with an opportunity to develop important organic practical skills, including use of Quickfit apparatus for distillation, heating under reflux and purification of organic liquids.

In the context of this module, it is important that learners should appreciate the need to consider responsible use of organic chemicals in the environment. Current trends in this context include reducing demand for hydrocarbon fuels, processing plastic waste productively, and preventing use of ozone-depleting chemicals.

# Synoptic assessment

This module provides a context for synoptic assessment and the subject content links strongly with the content encountered in Module 2: Foundations in chemistry.

- Atoms, moles and stoichiometry
- Acid and redox reactions
- Bonding and structure

Knowledge and understanding of Module 2 will be assumed and examination questions will be set that link its content with this module and other areas of chemistry.

# 4.1 Basic concepts and hydrocarbons

This section is fundamental to the study of organic chemistry.

This section introduces the various types of structures used routinely in organic chemistry, nomenclature, and the important concepts of homologous series,

functional groups, isomerism and reaction mechanisms using curly arrows.

The initial ideas are then developed within the context of the hydrocarbons: alkanes and alkenes.

# 4.1.1 Basic concepts of organic chemistry

# **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

# Naming and representing the formulae of organic compounds

(a) application of IUPAC rules of nomenclature for systematically naming organic compounds

Nomenclature will be limited to the functional groups within this specification.

E.g.  $\mathrm{CH_3CH_2CH(CH_3)CH_2OH}$  has the systematic name: 2-methylbutan-1-ol.

Learners will be expected to know the names of the first ten members of the alkanes homologous series and their corresponding alkyl groups.

HSW8 Use of systematic nomenclature to avoid ambiguity.

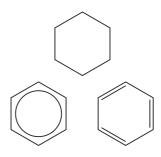
HSW11 The role of IUPAC in developing a systematic framework for chemical nomenclature.

**See also 2.1.3 b** for empirical formula and molecular formula.

Definitions **not** required.

In structural formulae, the carboxyl group will be represented as COOH and the ester group as COO.

The symbols below will be used for cyclohexane and benzene:



HSW8 Communication using organic chemical structures; selecting the appropriate type of formula for the context.

- (b) interpretation and use of the terms:
  - (i) general formula (the simplest algebraic formula of a member of a homologous series) e.g. for an alkane:  $C_nH_{2n+2}$
  - (ii) structural formula (the minimal detail that shows the arrangement of atoms in a molecule) e.g. for butane: CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> or CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>
  - (iii) displayed formula (the relative positioning of atoms and the bonds between them) e.g. for ethanol:

(iv) skeletal formula (the simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional groups) e.g. for butan-2-ol:



# **Functional groups**

- (c) interpretation and use of the terms:
  - homologous series (a series of organic compounds having the same functional group but with each successive member differing by CH<sub>2</sub>)
  - (ii) functional group (a group of atoms responsible for the characteristic reactions of a compound)
  - (iii) alkyl group (of formula  $C_nH_{2n+1}$ )
  - (iv) aliphatic (a compound containing carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings)
  - (v) alicyclic (an aliphatic compound arranged in non-aromatic rings with or without side chains)
  - (vi) aromatic (a compound containing a benzene ring)
  - (vii) saturated (single carbon–carbon bonds only) and unsaturated (the presence of multiple carbon–carbon bonds, including C=C, C≡C and aromatic rings)
- (d) use of the general formula of a homologous series to predict the formula of any member of the series

Isomerism

(e) explanation of the term structural isomers (compounds with the same molecular formula but different structural formulae) and determination of possible structural formulae of an organic molecule, given its molecular formula

Reaction mechanisms

- (f) the different types of covalent bond fission:
  - (i) homolytic fission (in terms of each bonding atom receiving one electron from the bonded pair, forming two radicals)
  - (ii) heterolytic fission (in terms of one bonding atom receiving both electrons from the bonded pair)

Definition required for homologous series only.

R may be used to represent alkyl groups, but also other fragments of organic compounds not involved in reactions.

The terms saturated and unsaturated will be used to indicate the presence of multiple carbon–carbon bonds as distinct from the wider term 'degree of saturation' used also for any multiple bonds and cyclic compounds.

M4.2

- (g) the term *radical* (a species with an unpaired electron) and use of 'dots' to represent species that are radicals in mechanisms
- (h) a 'curly arrow' described as the movement of an electron pair, showing either heterolytic fission or formation of a covalent bond
- (i) reaction mechanisms, using diagrams, to show clearly the movement of an electron pair with 'curly arrows' and relevant dipoles.

Radical mechanisms will be represented by a sequence of equations.

Dots, •, are required in all instances where there is a single unpaired electron (e.g.  $Cl ext{ • }$  and  $CH_3 ext{ • }$ ). Dots are **not** required for species that are diradicals (e.g. O).

'Half curly arrows' are not required, see 4.1.2 f.

HSW1,8 Use of the 'curly arrow' model to demonstrate electron flow in organic reactions.

Any relevant dipoles should be included. Curly arrows should start from a bond, a lone pair of electrons or a negative charge.

HSW1,2,8 Use of reaction mechanisms to explain organic reactions.

# 4.1.2 Alkanes

# **Learning outcomes**

(see also 2.2.2 g-h)

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

# **Properties of alkanes**

(a) alkanes as saturated hydrocarbons containing single C–C and C–H bonds as  $\sigma$ -bonds (overlap of orbitals directly between the bonding atoms); free rotation of the  $\sigma$ -bond

(b) explanation of the tetrahedral shape and bond angle around each carbon atom in alkanes in terms of electron pair repulsion

(c) explanation of the variations in boiling points of alkanes with different carbon-chain length and branching, in terms of induced dipole—dipole interactions (London forces) (see also 2.2.2 k)

Hybridisation not required.

HSW1 Use of model of orbital overlap to explain covalent bonding in organic compounds.

M4.1, M4.2

Learners should be able to draw 3-D diagrams.

M3.1

# **Reactions of alkanes**

(d) the low reactivity of alkanes with many reagents in terms of the high bond enthalpy and very low polarity of the σ-bonds present (see also 2.2.2 j) HSW1 Use of ideas about enthalpy and polarity to explain macroscopic properties of alkanes.

- (e) complete combustion of alkanes, as used in fuels, and the incomplete combustion of alkane fuels in a limited supply of oxygen with the resulting potential dangers from CO
- (f) the reaction of alkanes with chlorine and bromine by radical substitution using ultraviolet radiation, including a mechanism involving homolytic fission and radical reactions in terms of initiation, propagation and termination (see also 4.1.1 f-g)
- (g) the limitations of radical substitution in synthesis by the formation of a mixture of organic products, in terms of further substitution and reactions at different positions in a carbon chain.

Learners are **not** required to use 'half curly arrows' in this mechanism.

Equations should show which species are radicals using a single 'dot', •, to represent the unpaired electron.

2

# 4.1.3 Alkenes

# **Learning outcomes**

# Learners should be able to demonstrate and apply their knowledge and understanding of:

# **Properties of alkenes**

- alkenes as unsaturated hydrocarbons containing a C=C bond comprising a π-bond (sideways overlap of adjacent p-orbitals above and below the bonding C atoms) and a σ-bond (overlap of orbitals directly between the bonding atoms) (see also 4.1.2 a); restricted rotation of the π-bond
- (b) explanation of the trigonal planar shape and bond angle around each carbon in the C=C of alkenes in terms of electron pair repulsion (see also 2.2.2 g-h, 4.1.2 b)

#### Stereoisomerism in alkenes

- (c) (i) explanation of the terms:
  - stereoisomers (compounds with the same structural formula but with a different arrangement in space)
  - E/Z isomerism (an example of stereoisomerism, in terms of restricted rotation about a double bond and the requirement for two different groups to be attached to each carbon atom of the C=C group)
  - cis-trans isomerism (a special case of E/Z isomerism in which two of the substituent groups attached to each carbon atom of the C=C group are the same)
  - (ii) use of Cahn–Ingold–Prelog (CIP) priority rules to identify the *E* and *Z* stereoisomers

(d) determination of possible *E/Z* or *cis–trans* stereoisomers of an organic molecule, given its structural formula

# Additional guidance

Hybridisation is **not** required.

HSW1 Use of model of orbital overlap to explain covalent bonding in organic compounds.

M4.1, M4.2

M4.2, M4.3

$$H_3C$$
 $H$ 
 $C$ 
 $C$ 
 $C$ 
 $C$ 
 $C$ 
 $C$ 
 $C$ 
 $C$ 
 $C$ 
 $E$ -but-2-ene

(trans)

(cis)

Use of *E* as equivalent to *trans* and *Z* as equivalent to *cis* is only consistently correct when there is an H on each carbon atom of the C=C bond.

Assigning CIP priorities to double or triple bonds within R groups is **not** required:

M4.2, M4.3

#### Addition reactions of alkenes

- (e) the reactivity of alkenes in terms of the relatively low bond enthalpy of the  $\pi$ -bond
- (f) addition reactions of alkenes with:
  - (i) hydrogen in the presence of a suitable catalyst, e.g. Ni, to form alkanes
  - (ii) halogens to form dihaloalkanes, including the use of bromine to detect the presence of a double C=C bond as a test for unsaturation in a carbon chain
  - (iii) hydrogen halides to form haloalkanes
  - (iv) steam in the presence of an acid catalyst, e.g. H<sub>3</sub>PO<sub>4</sub>, to form alcohols
- (g) definition and use of the term *electrophile* (an electron pair acceptor)
- (h) the mechanism of electrophilic addition in alkenes by heterolytic fission (see also 4.1.1 h-i)
- (i) use of Markownikoff's rule to predict formation of a major organic product in addition reactions of H–X to unsymmetrical alkenes, e.g. H–Br to propene, in terms of the relative stabilities of carbocation intermediates in the mechanism

# Polymers from alkenes

- (j) addition polymerisation of alkenes and substituted alkenes, including:
  - the repeat unit of an addition polymer deduced from a given monomer
  - (ii) identification of the monomer that would produce a given section of an addition polymer

PAG7 (see also 6.3.1 c)

For the reaction with halogens, either a carbocation or a halonium ion intermediate is acceptable.

HSW1,2,8 Use of reaction mechanisms to explain organic reactions.

Limited to stabilities of primary, secondary and tertiary carbocations.

Explanation for relative stabilities of carbocations **not** required.

HSW1,2,5 Use of stability to explain products of organic reactions.

# Waste polymers and alternatives

- (k) the benefits for sustainability of processing waste polymers by:
  - (i) combustion for energy production
  - use as an organic feedstock for the production of plastics and other organic chemicals
  - (iii) removal of toxic waste products, e.g. removal of HCl formed during disposal by combustion of halogenated plastics (e.g. PVC)
- (I) the benefits to the environment of development of biodegradable and photodegradable polymers.

HSW9,10 Benefits of cheap oil-derived plastics counteracted by problems for environment of landfill; the move to re-using waste, improving use of resources.

HSW9,10 Benefits of reduced dependency on finite resources and alleviating problems from disposal of persistent plastic waste.

# 4.2 Alcohols, haloalkanes and analysis

This section introduces two further functional groups: alcohols and haloalkanes, and considers the importance of polarity and bond enthalpy to organic reactions.

Throughout this section, there are many opportunities for developing organic practical skills, including preparation and purification of organic liquids.

Finally, the important techniques of infrared spectroscopy and mass spectrometry are used to illustrate instrumental analysis as a valuable tool for identifying organic compounds.

# 4.2.1 Alcohols

#### **Learning outcomes**

Learners should be able to demonstrate and apply their knowledge and understanding of:

#### **Properties of alcohols**

- (i) the polarity of alcohols and an explanation, in terms of hydrogen bonding, of the water solubility and the relatively low volatility of alcohols compared with alkanes (see also 2.2.2 l and 4.1.2 c)
  - (ii) classification of alcohols into primary, secondary and tertiary alcohols

# **Reactions of alcohols**

(b) combustion of alcohols

# Additional guidance

(c) oxidation of alcohols by an oxidising agent, e.g.  $Cr_2O_7^{\ 2^-}/H^+$  (i.e.  $K_2Cr_2O_7/H_2SO_4$ ), including:

Equations should use [O] to represent the oxidising agent.

 the oxidation of primary alcohols to form aldehydes and carboxylic acids; the control of the oxidation product using different reaction conditions PAG7 (see also 6.3.1 c)

- (ii) the oxidation of secondary alcohols to form
- (iii) the resistance to oxidation of tertiary alcohols
- (d) elimination of  $\rm H_2O$  from alcohols in the presence of an acid catalyst (e.g.  $\rm H_3PO_4$  or  $\rm H_2SO_4$ ) and heat to form alkenes

Mechanism **not** required.

(e) substitution with halide ions in the presence of acid (e.g. NaBr/H<sub>2</sub>SO<sub>4</sub>) to form haloalkanes.

Mechanism not required.

#### 4.2.2 Haloalkanes

# **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

#### Substitution reactions of haloalkanes

- (a) hydrolysis of haloalkanes in a substitution reaction:
- PAG7 (see also 6.3.1 c)
- (i) by aqueous alkali
- (ii) by water in the presence of AgNO<sub>3</sub> and ethanol to compare experimentally the rates of hydrolysis of different carbon– halogen bonds
- **(b)** definition and use of the term *nucleophile* (an electron pair donor)
- (c) the mechanism of nucleophilic substitution in the hydrolysis of primary haloalkanes with aqueous alkali (see also 4.1.1 h-i)
- (d) explanation of the trend in the rates of hydrolysis of primary haloalkanes in terms of the bond enthalpies of carbon–halogen bonds (C–F, C–Cl, C–Br and C–I)

HSW1,2 Use of reaction mechanisms to explain organic reactions.

# Environmental concerns from use of organohalogen compounds

- (e) production of halogen radicals by the action of ultraviolet (UV) radiation on CFCs in the upper atmosphere and the resulting catalysed breakdown of the Earth's protective ozone layer, including equations to represent:
  - (i) the production of halogen radicals
  - (ii) the catalysed breakdown of ozone by Cl• and other radicals e.g. •NO.

Simple equations of the breakdown process are required, e.g.

$$CF_2Cl_2 \rightarrow CF_2Cl \bullet + \bullet Cl$$

$$\bullet Cl + O_3 \rightarrow \bullet ClO + O_2$$

$$\bullet ClO + O \rightarrow \bullet Cl + O_2$$

Learners could be expected to construct similar equations for other stated radicals.

HSW9,10,11,12 Benefits of CFCs; acceptance of scientific evidence explaining ozone depletion leading to government legislation against CFC use.

# 4.2.3 Organic synthesis

#### Learning outcomes

Learners should be able to demonstrate and apply their knowledge and understanding of:

# **Practical skills**

- (a) the techniques and procedures for:
  - use of Quickfit apparatus including for distillation and heating under reflux
  - (ii) preparation and purification of an organic liquid including:
    - use of a separating funnel to remove an organic layer from an aqueous layer
    - drying with an anhydrous salt (e.g. MgSO<sub>4</sub>, CaCl<sub>2</sub>)
    - redistillation

# Additional guidance

# PAG5

HSW4 Opportunities to carry out experimental and investigative work.

# Synthetic routes

- (b) for an organic molecule containing several functional groups:
  - (i) identification of individual functional groups
  - (ii) prediction of properties and reactions
- (c) two-stage synthetic routes for preparing organic compounds.

Learners will be expected to identify the functional groups encountered in Module 4.

HSW3 Development of synthetic routes.

Learners will be expected to be able to devise twostage synthetic routes by applying transformations between all functional groups encountered up to this point of the specification.

Extra information may be provided on exam papers to extend the learner's toolkit of organic reactions.

HSW3 Development of synthetic routes.

# 4.2.4 Analytical techniques

# **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

# Infrared spectroscopy

- (a) infrared (IR) radiation causes covalent bonds to vibrate more and absorb energy
- (b) absorption of infrared radiation by atmospheric gases containing C=O, O-H and C-H bonds (e.g. H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub>), the suspected link to global warming and resulting changes to energy usage
- (c) use of an infrared spectrum of an organic compound to identify:
  - an alcohol from an absorption peak of the O-H bond
  - (ii) an aldehyde or ketone from an absorption peak of the C=O bond
  - (iii) a carboxylic acid from an absorption peak of the C=O bond and a broad absorption peak of the O-H bond
- (d) interpretations and predictions of an infrared spectrum of familiar or unfamiliar substances using supplied data
- (e) use of infrared spectroscopy to monitor gases causing air pollution (e.g. CO and NO from car emissions) and in modern breathalysers to measure ethanol in the breath

# Mass spectrometry

(f) use of a mass spectrum of an organic compound to identify the molecular ion peak and hence to determine molecular mass HSW9,10,11,12 Acceptance of scientific evidence explaining global warming has prompted governments towards policies to use renewable energy supplies.

#### M3.1

In examinations, infrared absorption data will be provided on the *Data Sheet*.

Learners should be aware that most organic compounds produce a peak at approximately 3000 cm<sup>-1</sup> due to absorption by C–H bonds.

#### M3.1

Restricted to functional groups studied in this specification (see also 6.3.2 e).

HSW3,5 Analysis and interpretation of spectra.

HSW12 Use of analytical techniques to provide evidence for law courts, e.g. drink driving.

#### M3.1

Limited to ions with single charges. Learners will **not** be expected to interpret mass spectra of organic halogen compounds.

Limited to organic compounds encountered in this specification (see also 6.3.2 e).

Learners should be aware that mass spectra may contain a small M+1 peak from the small proportion of carbon-13.

HSW3,5 Analysis and interpretation of spectra.

(g) analysis of fragmentation peaks in a mass spectrum to identify parts of structures.

# M3.1

Learners should be able to suggest the structures of fragment ions.

HSW3,5 Analysis and interpretation of spectra.

# **Combined techniques**

(h) deduction of the structures of organic compounds from different analytical data including:

(i) elemental analysis (see also 2.1.3c)

(ii) mass spectra

(iii) IR spectra.

# M3.1

Limited to functional groups encountered in this specification.

Learners will **not** be expected to interpret mass spectra of organic halogen compounds.

HSW3,5,6 Analysis and interpretation of different analytical data.

# Module 5: Physical chemistry and transition elements

The content within this module assumes knowledge and understanding of the chemical concepts developed in Module 2: Foundations in chemistry and Module 3: Periodic table and energy.

This module extends the study of energy, reaction rates and equilibria, and the periodic table.

The main areas of physical chemistry studied include:

- rate equations, orders of reaction, the ratedetermining step
- equilibrium constants,  $K_c$  and  $K_n$
- acid-base equilibria including pH, K<sub>a</sub> and buffer solutions
- lattice enthalpy and Born–Haber cycles
- entropy and free energy
- electrochemical cells.

The main areas of inorganic chemistry studied include:

- redox chemistry
- transition elements.

# Synoptic assessment

This module provides a context for synoptic assessment and the subject content links strongly with the content encountered in Module 2: Foundations in chemistry and Module 3: Periodic table and energy.

- Atoms, moles and stoichiometry
- Acid and redox reactions
- Bonding and structure
- Periodicity, Group 2 and the halogens
- Enthalpy changes
- Reaction rates
- Chemical equilibrium

Knowledge and understanding of Module 2 and Module 3 will be assumed and examination questions will be set that link their content with this module and other areas of chemistry.

# 5.1 Rates, equilibrium and pH

The largely qualitative treatment of reaction rates and equilibria encountered in Module 3 is developed within a quantitative and graphical context.

This section also allows learners to develop practical quantitative techniques involved in the determination of reaction rates and pH.

There are many opportunities for developing mathematical skills, including use of logarithms and exponents, when studying the content of this section and when carrying out quantitative practical work.

# 2

# 5.1.1 How fast?

#### **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

#### Orders, rate equations and rate constants

- (a) explanation and use of the terms: rate of reaction, order, overall order, rate constant, half-life, rate-determining step
- (b) deduction of:
  - (i) orders from experimental data
  - (ii) a rate equation from orders of the form: rate =  $k[A]^m[B]^n$ , where m and n are 0, 1 or 2
- (c) calculation of the rate constant, k, and related quantities, from a rate equation including determination of units

# M0.2

Learners are expected to interpret initial rates data to determine orders with respect to reactants. Integrated forms of rate equations are **not** required.

#### PAG10

HSW8 Use of rate equations.

M0.0, M0.1, M0.4, M1.1, M2.2, M2.3, M2.4

#### Rate graphs and orders

- (d) from a concentration—time graph:
  - (i) deduction of the order (0 or 1) with respect to a reactant from the shape of the graph
  - (ii) calculation of reaction rates from the measurement of gradients (see also 3.2.2 b)
- (e) from a concentration—time graph of a first order reaction, measurement of constant half-life,  $t_{1/2}$
- (f) for a first order reaction, determination of the rate constant, k, from the constant half-life,  $t_{1/2}$ , using the relationship:  $k = \ln 2/t_{1/2}$
- **(g)** from a rate–concentration graph:
  - deduction of the order (0, 1 or 2) with respect to a reactant from the shape of the graph
  - (ii) determination of rate constant for a first order reaction from the gradient

M0.1, M0.4, M1.1, M3.1, M3.2, M3.3, M3.4, M3.5

Concentration—time graphs can be plotted from continuous measurements taken during the course of a reaction (continuous monitoring).

M3.1, M3.2

Learners should be aware of the constancy of half-life for a first order reaction.

M0.1, M0.4, M1.1, M2.3, M2.4, M2.5

Learners will **not** be required to derive this equation from the exponential relationship between concentration and time,  $[A] = [A_n]e^{-kt}$ .

M0.1, M0.4, M1.1, M3.1, M3.2, M3.3, M3.4, M3.5

Rate—concentration data can be obtained from initial rates investigations of separate experiments using different concentrations of one of the reactants. Clock reactions are an approximation of this method where the time measured is such that the reaction has not proceeded too far.

HSW5 Link between order and rate.

(h) the techniques and procedures used to investigate reaction rates by the initial rates method and by continuous monitoring, including use of colorimetry (see also 3.2.2 e)

# PAG9,10

HSW4 Opportunities to carry out experimental and investigative work.

# **Rate-determining step**

- (i) for a multi-step reaction, prediction of,
  - a rate equation that is consistent with the rate-determining step
  - (ii) possible steps in a reaction mechanism from the rate equation and the balanced equation for the overall reaction

HSW1 Use of experimental evidence for the proposal of reaction mechanisms.

# Effect of temperature on rate constants

- (j) a qualitative explanation of the effect of temperature change on the rate of a reaction and hence the rate constant (see 3.2.2 f–g)
- (k) the Arrhenius equation:
  - (i) the exponential relationship between the rate constant, k and temperature, T given by the Arrhenius equation,  $k = Ae^{-Ea/RT}$
  - (ii) determination of  $E_a$  and A graphically using:  $\ln k = -E_a/RT + \ln A$  derived from the Arrhenius equation.

M0.3

M0.1, M0.4, M2.2, M2.3, M2.4, M2.5, M3.1, M3.2, M3.3, M3.4

E<sub>a</sub> = activation energy,
 A = pre-exponential factor,
 R = gas constant (provided on the *Data Sheet*)
 Explanation of A is **not** required.
 Equations provided on the *Data Sheet*.

HSW5 Link between k and T.

# 5.1.2 How far?

	Lea	rning outcomes	Additional guidance	
		rners should be able to demonstrate and bly their knowledge and understanding of:		
Equilibrium				
(a)		of the terms mole fraction and partial ssure	See also 3.2.3 Chemical Equilibrium.	
(b)		culation of quantities present at equilibrium, en appropriate data	M0.2	
(c)	the techniques and procedures used to determine quantities present at equilibrium		<b>Not</b> for $K_p$ .	
			HSW4 Opportunities to carry out experimental and investigative work.	
(d)	expressions for $K_c$ and $K_p$ for homogeneous and heterogeneous equilibria (see also 3.2.3 f)		M0.2	
			Note: liquid and solid concentrations are constant and are omitted in heterogeneous $K_{\rm c}$ and $K_{\rm p}$ expressions.	
(e)	calculations of $K_{\rm c}$ and $K_{\rm p}$ , or related quantities, including determination of units (see also 3.2.3 f)		M0.0, M0.1, M0.2, M0.4, M2.2, M2.3, M2.4	
			Learners will <b>not</b> be required to solve quadratic equations.	
(f)	(i)	the qualitative effect on equilibrium constants of changing temperature for exothermic and endothermic reactions	M0.3	
	(ii)	the constancy of equilibrium constants with changes in concentration, pressure or in the presence of a catalyst		
(g)	explanation of how an equilibrium constant controls the position of equilibrium on changing concentration, pressure and temperature		M0.3	
(h)	application of the above principles in <b>5.1.2 How</b> far? for $K_c$ , $K_p$ to other equilibrium constants, where appropriate (see also <b>5.1.3</b> c etc.).			

# 5.1.3 Acids, bases and buffers

# **Learning outcomes** Additional guidance Learners should be able to demonstrate and apply their knowledge and understanding of: Brønsted-Lowry acids and bases a Brønsted-Lowry acid as a species that Learners should be able to identify acid-base pairs (a) in equations for acid-base equilibria. donates a proton and a Brønsted-Lowry base as a species that accepts a proton HSW1,7 Development of different models over time (see also 2.1.4 Acids) to explain acid-base behaviour. (ii) use of the term conjugate acid-base pairs (iii) monobasic, dibasic and tribasic acids the role of H<sup>+</sup> in the reactions of acids with (b) metals and bases (including carbonates, metal oxides and alkalis), using ionic equations (see also 2.1.4 c, 2.1.5 e) the acid dissociation constant, $K_a$ , for the (c) M0.1, M0.2, M0.4, M2.3, M2.4, M2.5 extent of acid dissociation (see also 2.1.4 b) the relationship between $K_a$ and $pK_a$ pH and [H+(aq)] use of the expression for pH as: M0.1, M0.4, M2.2, M2.3, M2.4, M2.5 $pH = -log[H^+]$ HSW8 pH as convenient terminology for communicating [H<sup>+</sup>]. $[H^+] = 10^{-pH}$ (e) use of the expression for the ionic product of M0.1, M0.4, M2.2, M2.3, M2.4 water, $K_{\rm w}$ calculations of pH, or related quantities, for: (f) M0.1, M0.4, M2.2, M2.3, M2.4, M2.5 strong monobasic acids (ii) strong bases, using $K_{\rm w}$ calculations of pH, $K_{\rm a}$ or related quantities, for a (g) M0.1, M0.4, M2.1, M2.2, M2.3, M2.4, M2.5 weak monobasic acid using approximations Approximations for weak acid calculations: [HA]<sub>equilibrium</sub> ~ [HA]<sub>undissociated</sub> i.e. [HA] >> [H+] [H<sup>+</sup>] <sub>equilibrium</sub> ~ [A<sup>-</sup>] <sub>equilibrium</sub> i.e. negligible dissociation of H<sub>2</sub>O. Learners will **not** be required to solve quadratic equations.

(h) limitations of using approximations to  $K_a$  related calculations for 'stronger' weak acids

M0.3

Including reasons why

[HA]<sub>equilibrium</sub> ~ [HA]<sub>undissociated</sub> may no longer be

HSW6 Understanding of the circumstances under which  $K_a$  approximations break down.

# **Buffers: action, uses and calculations**

- a buffer solution as a system that minimises pH changes on addition of small amounts of an acid or a base
- (j) formation of a buffer solution from:
  - (i) a weak acid and a salt of the weak acid, e.g. CH<sub>3</sub>COOH/CH<sub>3</sub>COONa
  - (ii) excess of a weak acid and a strong alkali, e.g. excess CH<sub>3</sub>COOH/NaOH
- (k) explanation of the role of the conjugate acid-base pair in an acid buffer solution, e.g. CH<sub>3</sub>COOH/CH<sub>3</sub>COO<sup>-</sup>, in the control of pH
- (I) calculation of the pH of a buffer solution, from the  $K_{\rm a}$  value of a weak acid and the equilibrium concentrations of the conjugate acid—base pair; calculations of related quantities
- (m) explanation of the control of blood pH by the carbonic acid—hydrogencarbonate buffer system

M0.1, M0.4, M2.2, M2.3, M2.4, M2.5

The H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub><sup>-</sup> buffer is present in blood plasma, maintaining a pH between 7.35 and 7.45.

#### Neutralisation

- (n) pH titration curves for combinations of strong and weak acids with strong and weak bases, including:
  - (i) sketch and interpretation of their shapes
  - (ii) explanation of the choice of suitable indicators, given the pH range of the indicator
  - (iii) explanation of indicator colour changes in terms of equilibrium shift between the HA and A<sup>-</sup> forms of the indicator
- (o) the techniques and procedures used when measuring pH with a pH meter.

M3.1

No indicator is suitable for a weak acid/weak base titration

The indicator should be considered as a weak acid, HA.

#### PAG11

HSW4 Opportunities to carry out experimental and investigative work.

# 5.2 Energy

Born–Haber cycles are used as a theoretical model to illustrate the energy changes associated with ionic bonding.

Entropy and free energy are then introduced as concepts used to predict quantitatively the feasibility of chemical change.

Redox chemistry permeates chemistry and the introductory work in Module 2 is developed further within this section, including use of volumetric analysis for redox titrations and an introduction of electrochemistry in the context of electrode potentials.

# 5.2.1 Lattice enthalpy

# Additional guidance **Learning outcomes** Learners should be able to demonstrate and apply their knowledge and understanding of: Lattice enthalpy explanation of the term lattice enthalpy Definition required. (formation of 1 mol of ionic lattice from gaseous ions, $\Delta_{LF}H$ ) and use as a measure of the strength of ionic bonding in a giant ionic lattice (see also 2.2.2 b-c) Born-Haber and related enthalpy cycles use of the lattice enthalpy of a simple ionic solid M2.2, M2.3, M2.4, M3.1 (e.g. NaCl, MgC $l_2$ ) and relevant energy terms for: Relevant energy terms: enthalpy change of (i) the construction of Born-Haber cycles formation, ionisation energy, enthalpy change of (ii) related calculations atomisation and electron affinity. Definition required for first ionisation energy (see also 3.1.1 c) and enthalpy change of formation (see also 3.2.1 d) only. HSW2 Application of conservation of energy to determine enthalpy changes. Definitions required. (c) explanation and use of the terms: Details of infinite dilution **not** required. enthalpy change of solution (dissolving of 1 mol of solute, $\Delta_{\mathrm{sol}}H$ ) enthalpy change of hydration (dissolving of 1 mol of gaseous ions in water, $\Delta_{\text{hvd}} H$ ) (d) use of the enthalpy change of solution of a M2.2, M2.3, M2.4, M3.1 simple ionic solid (e.g. NaCl, MgCl<sub>2</sub>) and relevant HSW2 Application of conservation of energy to energy terms (enthalpy change of hydration and determine enthalpy changes. *lattice enthalpy*) for: the construction of enthalpy cycles (ii) related calculations

(e) qualitative explanation of the effect of ionic charge and ionic radius on the exothermic value of a lattice enthalpy and enthalpy change of hydration.

# 5.2.2 Enthalpy and entropy Learning outcomes

	Learners should be able to demonstrate and apply their knowledge and understanding of:		
Entro	ру		
(a)	explanation that entropy is a measure of the dispersal of energy in a system which is greater, the more disordered a system	HSW1 The model of entropy to explain thermodynamic stability.	
(b)	explanation of the difference in magnitude of the entropy of a system:		
	(i) of solids, liquids and gases		
	(ii) for a reaction in which there is a change in the number of gaseous molecules		
(c)	calculation of the entropy change of a system, $\Delta \textit{S},$ and related quantities for a reaction given the entropies of the reactants and products	M2.2, M2.3, M2.4	
Free	energy		
(d)	explanation that the feasibility of a process depends upon the entropy change and temperature in the system, $T\Delta S$ , and the enthalpy change of the system, $\Delta H$	HSW1,5,6 Use of entropy, enthalpy and temperature for predicting feasibility.	
(e)	explanation, and related calculations, of the free	M0.0, M2.2, M2.3, M2.4	
	energy change, $\Delta G$ , as: $\Delta G = \Delta H - T\Delta S$ (the Gibbs' equation) and that a process is feasible when $\Delta G$ has a negative value	HSW5 Link between $\Delta G$ and feasibility.	
(f)	the limitations of predictions made by $\Delta G$ about	M0.3	
	feasibility, in terms of kinetics.	HSW6 The relative effects of entropy and rate in determining feasibility of processes.	

Additional guidance

### 5.2.3 Redox and electrode potentials

### **Learning outcomes** Additional guidance Learners should be able to demonstrate and apply their knowledge and understanding of: Redox (a) explanation and use of the terms oxidising agent and reducing agent (see also 2.1.5 Redox) construction of redox equations using half-M0.2 (b) equations and oxidation numbers interpretation and prediction of reactions (c) involving electron transfer **Redox titrations** the techniques and procedures used when HSW4 Opportunities to carry out experimental and carrying out redox titrations including those investigative work. involving $Fe^{2+}/MnO_4^-$ and $I_2/S_2O_3^{2-}$ (see also 2.1.5 e-f) structured and non-structured titration (e) M0.1, M0.2, M0.4, M1.1, M1.2, M2.2, M2.3, M2.4 calculations, based on experimental results of Non-structured titration calculations could be redox titrations involving: examined in the context of both acid-base and (i) $Fe^{2+}/MnO_4^-$ and $I_2/S_2O_3^{2-}$ redox titrations (see also 2.1.4 d-e). (ii) non-familiar redox systems **Electrode potentials** use of the term standard electrode (redox) $E^{\Theta}$ data will be provided on examination papers. potential, $E^{\Theta}$ including its measurement using a hydrogen electrode the techniques and procedures used for the For measurement of standard cell potentials, ions (g) measurement of cell potentials of: of the same element can have concentrations of 1 mol dm<sup>-3</sup> or be equimolar. metals or non-metals in contact with their ions in aqueous solution PAG8 (ii) ions of the same element in different HSW4 Opportunities to carry out experimental and oxidation states in contact with a Pt investigative work. electrode (h) calculation of a standard cell potential by combining two standard electrode potentials (i) prediction of the feasibility of a reaction using M0.3 standard cell potentials and the limitations HSW6 The relative effects of standard electrode of such predictions in terms of kinetics and potential, rate and concentration in determining concentration

feasibility of processes.

### Storage and fuel cells

(j) application of principles of electrode potentials to modern storage cells

Details of storage cells and required equations will be provided. Relevant electrode potentials and other data will be supplied.

HSW9 Benefits of electrochemical cells counteracted

by risks from toxicity and fire from Li-based cells.

Recall of fuel cells and equations will **not** be required. Relevant electrode potentials and other data will be supplied.

(k) explanation that a fuel cell uses the energy from the reaction of a fuel with oxygen to create a voltage and the changes that take place at each electrode.

### 5.3 Transition elements

This section provides learners with a deeper knowledge and understanding of the periodic table within the context of the transition elements.

This section includes the role of ligands in complex ions, stereochemistry, precipitation, ligand substitution and redox reactions. The colour changes and observations in these reactions increase the toolkit of qualitative inorganic tests for identifying unknown ionic compounds.

### 5.3.1 Transition elements

## Learning outcomes

# Learners should be able to demonstrate and apply their knowledge and understanding of:

# **Properties**

- (a) the electron configuration of atoms and ions of the d-block elements of Period 4 (Sc–Zn), given the atomic number and charge (see also 2.2.1 d)
- (b) the elements Ti–Cu as transition elements i.e. d-block elements that have an ion with an incomplete d-sub-shell
- (c) illustration, using at least two transition elements, of:
  - the existence of more than one oxidation state for each element in its compounds (see also 5.3.1 k)
  - (ii) the formation of coloured ions (see also 5.3.1 h, j-k)
  - (iii) the catalytic behaviour of the elements and their compounds and their importance in the manufacture of chemicals by industry (see 3.2.2 d)

### Additional guidance

Learners should use sub-shell notation e.g. for Fe:  $1s^22s^22p^63s^23p^63d^64s^2$ .

No detail of how colour arises required.

Practical examples of catalytic behaviour include:  $Cu^{2+}$  for reaction of Zn with acids;  $MnO_2$  for decomposition of  $H_2O_2$ .

No detail of catalytic processes required.

HSW9 Benefits of reduced energy usage; risks from toxicity of many transition metals.

### Ligands and complex ions

- (d) explanation and use of the term ligand in terms of coordinate (dative covalent) bonding to a metal ion or metal, including bidentate ligands
- (e) use of the terms *complex ion* and *coordination number* and examples of complexes with:
  - six-fold coordination with an octahedral shape
  - (ii) four-fold coordination with either a planar or tetrahedral shape (see also 2.2.2 g-h)
- (f) types of stereoisomerism shown by complexes, including those associated with bidentate and multidentate ligands:
  - (i) cis-trans isomerism e.g.  $Pt(NH_3)_2Cl_2$  (see also 4.1.3 c-d)
  - (ii) optical isomerism e.g.  $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ (see also 6.2.2 c)
- (g) use of *cis*-platin as an anti-cancer drug and its action by binding to DNA preventing cell division

### Ligand substitution

- (h) ligand substitution reactions and the accompanying colour changes in the formation of:
  - (i)  $[Cu(NH_3)_4(H_2O)_2]^{2+}$  and  $[CuCl_4]^{2-}$  from  $[Cu(H_2O)_6]^{2+}$
  - (ii)  $[Cr(NH_3)_6]^{3+}$  from  $[Cr(H_2O)_6]^{3+}$ (see also 5.3.1 j)
- explanation of the biochemical importance of iron in haemoglobin, including ligand substitution involving O<sub>2</sub> and CO

# **Precipitation reactions**

- (j) reactions, including ionic equations, and the accompanying colour changes of aqueous Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup> and Cr<sup>3+</sup> with aqueous sodium hydroxide and aqueous ammonia, including:
  - (i) precipitation reactions
  - (ii) complex formation with excess aqueous sodium hydroxide and aqueous ammonia

Examples should include: monodentate:  $H_2O$ ,  $Cl^-$  and  $NH_3$  bidentate:  $NH_2CH_2CH_2NH_2$  ('en').

In exams, other ligands could be introduced.

M4.1, M4.2

Examples:

Octahedral: many hexaaqua complexes, e.g.  $[\mathrm{Cu}(\mathrm{H_2O})_6]^{2+}$ ,  $[\mathrm{Fe}(\mathrm{H_2O})_6]^{3+}$  Tetrahedral: many tetrachloro complexes, e.g.  $\mathrm{CuC}l_4^{\ 2-}$  and  $\mathrm{CoC}l_4^{\ 2-}$  Square planar: complexes of Pt, e.g. platin:  $\mathrm{Pt}(\mathrm{NH_3})_2\mathrm{C}l_2$  (see also 5.3.1 g).

M4.1, M4.2, M4.3

Learners should be able to draw 3-D diagrams to illustrate stereoisomerism.

HSW8

HSW9 Benefits of chemotherapy; risks from unpleasant side effects.

Complexed formulae should be used in ligand substitution equations.

For precipitation, non-complexed formulae or complexed formulae, are acceptable e.g.  $\mathrm{Cu}^{2+}(\mathrm{aq})$  or  $[\mathrm{Cu}(\mathrm{H}_2\mathrm{O})_6]^{2+}$ ;  $\mathrm{Cu}(\mathrm{OH})_2(\mathrm{s})$  or  $\mathrm{Cu}(\mathrm{OH})_2(\mathrm{H}_2\mathrm{O})_4$ . With excess NaOH, only  $\mathrm{Cr}(\mathrm{OH})_3$  reacts further forming  $[\mathrm{Cr}(\mathrm{OH})_6]^{3-}$ . With excess NH $_3$ , only  $\mathrm{Cr}(\mathrm{OH})_3$  and  $\mathrm{Cu}(\mathrm{OH})_2$  react forming  $[\mathrm{Cr}(\mathrm{NH}_3)_6]^{3+}$  and  $[\mathrm{Cu}(\mathrm{NH}_3)_4(\mathrm{H}_2\mathrm{O})_2]^{2+}$  respectively (see also 5.3.1 h).

### **Redox reactions**

- (k) redox reactions and accompanying colour changes for:
  - (i) interconversions between Fe<sup>2+</sup> and Fe<sup>3+</sup>
  - (ii) interconversions between Cr<sup>3+</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>
  - (iii) reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> and disproportionation of Cu<sup>+</sup> to Cu<sup>2+</sup> and Cu

 $\rm Fe^{2+}$  can be oxidised with  $\rm H^+/MnO_4^-$  and  $\rm Fe^{3+}$  reduced with  $\rm I^-, Cr^{3+}$  can be oxidised with  $\rm H_2O_2/OH^-$  and  $\rm Cr_2O_7^{2-}$  reduced with Zn/H<sup>+</sup>, Cu<sup>2+</sup> can be reduced with I<sup>-</sup>. In aqueous conditions, Cu<sup>+</sup> readily disproportionates.

Learners will **not** be required to recall equations but may be required to construct and interpret redox equations using relevant half-equations and oxidation numbers (see 5.2.3 b-c).

 interpretation and prediction of unfamiliar reactions including ligand substitution, precipitation, redox.

### 5.3.2 Qualitative analysis

### **Learning outcomes**

Learners should be able to demonstrate and apply their knowledge and understanding of:

### **Tests for ions**

- (a) qualitative analysis of ions on a test-tube scale: processes and techniques needed to identify the following ions in an unknown compound:
  - (i) anions:  $CO_3^{2-}$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $SO_4^{2-}$  (see 3.1.4 a)
  - (ii) cations:  $NH_4^+$ ;  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Cr^{3+}$  (see 3.1.4 a, 5.3.1 j).

### Additional guidance

### PAG4

HSW4 Qualitative analysis.

### Module 6: Organic chemistry and analysis

The content within this module assumes knowledge and understanding of the chemical concepts developed in Module 2: Foundations in chemistry and Module 4: Core organic chemistry.

This module introduces several new functional groups and emphasises the importance of organic synthesis. This module also adds NMR spectroscopy to the instrumentation techniques used in organic and forensic analysis.

The main areas of organic chemistry studied include:

- · aromatic compounds
- carboxylic acids and esters
- organic nitrogen compounds: amines and amino acids
- polymerisation: addition polymers and condensation polymers
- synthetic organic chemistry and further development of practical skills
- the importance of modern analytical techniques in organic analysis.

### Synoptic assessment

This module provides a context for synoptic assessment and the subject content links strongly with the content encountered in Module 2: Foundations in chemistry and Module 4: Core organic chemistry.

- Atoms, moles and stoichiometry
- Acid and redox reactions
- Bonding and structure
- Organic nomenclature and structures
- Hydrocarbons
- Alcohols and haloalkanes
- Synthesis and analysis

Knowledge and understanding of Module 2 and Module 4 will be assumed and examination questions will be set that link their content with this module and other areas of chemistry.

### 6.1 Aromatic compounds, carbonyls and acids

This section extends the range of functional groups encountered in Module 4.

Aromatic compounds are first introduced, including the central role of delocalisation within the chemistry of arenes and phenols. Directing groups are also introduced, including their importance to organic synthesis.

The important carbonyl compounds, aldehydes and ketones, are then studied.

Finally, carboxylic acids and their related functional groups, acyl chlorides and esters, are studied. The importance of acyl chlorides in organic synthesis is emphasised.

### 6.1.1 Aromatic compounds

### **Learning outcomes**

### Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

### Benzene and aromatic compounds

the comparison of the Kekulé model of benzene with the subsequent delocalised models for benzene in terms of p-orbital overlap forming a delocalised π-system Learners may represent the structure of benzene in equations and mechanisms as:



over time.



(b) the experimental evidence for a delocalised, rather than Kekulé, model for benzene in mode terms of bond lengths, enthalpy change of support

hydrogenation and resistance to reaction (see also 6.1.1 f)

(c) use of IUPAC rules of nomenclature for

HSW11 Acceptance of the delocalised benzene model by the scientific community in light of supporting experimental evidence.

HSW1,7 Development of the model for benzene

 use of IUPAC rules of nomenclature for systematically naming substituted aromatic compounds Use of locant numbers to identify positions of substitution e.g. 2,4-dinitromethylbenzene.

HSW8 Introduction of systematic nomenclature.

# **Electrophilic substitution**

(d) the electrophilic substitution of aromatic compounds with:

 concentrated nitric acid in the presence of concentrated sulfuric acid

- (ii) a halogen in the presence of a halogen carrier
- (iii) a haloalkane or acyl chloride in the presence of a halogen carrier (Friedel–Crafts reaction) and its importance to synthesis by formation of a C–C bond to an aromatic ring (see also 6.2.4 d)

Halogen carriers include iron, iron halides and aluminium halides.

(e) the mechanism of electrophilic substitution in arenes for nitration and halogenation(see also 4.1.1 h-i)

For nitration mechanism, learners should include equations for formation of  $\mathrm{NO_2}^+$ .

Halogen carriers include iron, iron halides and aluminium halides.

For the halogenation mechanism, the electrophile can be assumed to be X<sup>+</sup>.

HSW1,2,8 Use of reaction mechanisms to explain organic reactions.

(f) the explanation of the relative resistance to bromination of benzene, compared with alkenes, in terms of the delocalised electron density of the  $\pi$ -system in benzene compared with the localised electron density of the  $\pi$ -bond in alkenes (see also 4.1.3 a, 6.1.1 a)

HSW2,5 Use of delocalised benzene model to explain reactivity.

(g) the interpretation of unfamiliar electrophilic substitution reactions of aromatic compounds, including prediction of mechanisms Extra information may be provided on exam papers.

### **Phenols**

(h) the weak acidity of phenols shown by the neutralisation reaction with NaOH but absence of reaction with carbonates (see also 5.1.3 b)

PAG7 (see also 6.3.1 c)

- (i) the electrophilic substitution reactions of phenol:
  - (i) with bromine to form 2,4,6-tribromophenol
  - (ii) with dilute nitric acid to form 2-nitrophenol
- (j) the relative ease of electrophilic substitution of phenol compared with benzene, in terms of electron pair donation to the  $\pi$ -system from an oxygen p-orbital in phenol (see also 4.1.3 a)

Note that nitration with phenol does not require concentrated  ${\rm HNO_3}$  or the presence of a concentrated  ${\rm H_2SO_4}$  catalyst.

Illustrated by reactions with bromine and with nitric acid.

Explanation is only in terms of susceptibility of ring to 'attack' and not in terms of stability of intermediate.

HSW2,5 Use of delocalised benzene model to explain reactivity.

(k) the 2- and 4-directing effect of electrondonating groups (OH, NH<sub>2</sub>) and the 3-directing effect of electron-withdrawing groups (NO<sub>2</sub>) in electrophilic substitution of aromatic compounds Learners will **not** be expected to know further electron-donating or electron-withdrawing groups; relevant additional data will be supplied in examinations.

HSW5 Correlation between substituted group and position of reaction.

 the prediction of substitution products of aromatic compounds by directing effects and the importance to organic synthesis (see also 6.2.5 Organic Synthesis).

# 6.1.2 Carbonyl compounds

### Additional guidance

### **Learning outcomes**

Learners should be able to demonstrate and apply their knowledge and understanding of:

### Reactions of carbonyl compounds

(a) oxidation of aldehydes using  $Cr_2O_7^{2-}/H^+$ (i.e.  $K_2Cr_2O_7/H_2SO_4$ ) to form carboxylic acids In equations for organic redox reactions, [O] and [H] should be used.

PAG7 (see also 6.3.1 c)

- (b) nucleophilic addition reactions of carbonyl compounds with:
  - (i) NaBH<sub>4</sub> to form alcohols
  - (ii) HCN [i.e. NaCN(aq)/H<sup>+</sup>(aq)], to form hydroxynitriles (see also 6.2.4 b)
- (c) the mechanism for nucleophilic addition reactions of aldehydes and ketones with NaBH<sub>4</sub> and HCN

For NaBH $_4$ , the nucleophile can be considered as being the hydride ion, H $^-$ , with subsequent protonation of the organic intermediate from H $_2$ O.

For HCN, initial nucleophilic attack is from  $\rm CN^-$  ions; subsequent protonation stage can be shown using  $\rm H_2O$  or  $\rm H^+$ .

HSW1,2,8 Use of reaction mechanisms to explain organic reactions.

### Characteristic tests for carbonyl compounds

- (d) use of 2,4-dinitrophenylhydrazine to:
  - (i) detect the presence of a carbonyl group in an organic compound
  - (ii) identify a carbonyl compound from the melting point of the derivative
- (e) use of Tollens' reagent (ammoniacal silver nitrate) to:
  - (i) detect the presence of an aldehyde group
  - (ii) distinguish between aldehydes and ketones, explained in terms of the oxidation of aldehydes to carboxylic acids with reduction of silver ions to silver.

The equation for this reaction is **not** required. Structure of derivative **not** required.

# PAG7 (see also 6.3.1 c)

HSW4 Qualitative analysis.

In equations involving Tollens' reagent, [O] is acceptable.

### PAG7 (see also 6.3.1 c)

HSW4 Qualitative analysis.

### 6.1.3 Carboxylic acids and esters

### **Learning outcomes**

Learners should be able to demonstrate and apply their knowledge and understanding of:

### Properties of carboxylic acids

- (a) explanation of the water solubility of carboxylic acids in terms of hydrogen bonding
- reactions in aqueous conditions of carboxylic acids with metals and bases (including carbonates, metal oxides and alkalis)

Additional guidance

Comparison of acidity of different carboxylic acids **not** required.

PAG7 (see 6.3.1 c)

### **Esters**

- (c) esterification of:
  - carboxylic acids with alcohols in the presence of an acid catalyst (e.g. concentrated H<sub>2</sub>SO<sub>4</sub>)
  - (ii) acid anhydrides with alcohols
- (d) hydrolysis of esters:
  - (i) in hot aqueous acid to form carboxylic acids and alcohols
  - (ii) in hot aqueous alkali to form carboxylate salts and alcohols

### **Acyl chlorides**

- (e) the formation of acyl chlorides from carboxylic acids using SOCl<sub>2</sub>
- (f) use of acyl chlorides in synthesis in formation of esters, carboxylic acids and primary and secondary amides.

Including esterification of phenol, which is not readily esterified by carboxylic acids.

### 6.2 Nitrogen compounds, polymers and synthesis

This section focuses on organic nitrogen compounds, including amines, amides and amino acids. Chirality and optical isomerism is also introduced.

Condensation polymerisation is also introduced and compared with addition polymerisation.

The importance of carbon–carbon bond formation in organic synthesis is stressed. Learners are also able

to consider multi-stage synthetic routes towards an organic product.

This module allows learners many opportunities to further develop their organic practical skills, especially in preparing and purifying organic solids, including recrystallisation and determination of melting points.

### 6.2.1 Amines

# Learning outcomes Learners should be able to demonstrate and apply their knowledge and understanding of: Basicity and preparation of amines (a) the basicity of amines in terms of proton acceptance by the nitrogen lone pair and the reactions of amines with dilute acids, e.g. HCl(aq), to form salts Additional guidance Comparison of basicity of different amines not required. Restricted to inorganic acids.

- (b) the preparation of:
  - (i) aliphatic amines by substitution of haloalkanes with excess ethanolic ammonia and amines
  - (ii) aromatic amines by reduction of nitroarenes using tin and concentrated hydrochloric acid.

Including formation of primary amines from ammonia and secondary/tertiary amines from amines.

See also reduction of nitriles (see 6.2.4 c).

### 6.2.2 Amino acids, amides and chirality

### **Learning outcomes**

Learners should be able to demonstrate and apply their knowledge and understanding of:

### **Reactions of amino acids**

- (a) the general formula for an  $\alpha$ -amino acid as RCH(NH<sub>2</sub>)COOH and the following reactions of amino acids:
  - reaction of the carboxylic acid group with alkalis and in the formation of esters (see also 6.1.3 c)
  - (ii) reaction of the amine group with acids

### Amides

(b) structures of primary and secondary amides (see also 6.1.3 f, 6.2.3 a-b)

### Chirality

- (c) optical isomerism (an example of stereoisomerism, in terms of non-superimposable mirror images about a chiral centre) (see also 4.1.3 c-d)
- (d) identification of chiral centres in a molecule of any organic compound.

# Additional guidance

M4.2, M4.3

Learners should be able to draw 3-D diagrams to illustrate stereoisomerism.

HSW1,8

M4.2, M4.3

### 6.2.3 Polyesters and polyamides

### **Learning outcomes**

### Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

### **Condensation polymers**

- (a) condensation polymerisation to form:
  - (i) polyesters
  - (ii) polyamides

Formation from carboxylic acids/dicarboxylic acids (or respective acyl chlorides) and from alcohols/diols or amines/diamines.

Learners will **not** be expected to recall the structures of synthetic polyesters and polyamides or their monomers.

- (b) the acid and base hydrolysis of:
  - (i) the ester groups in polyesters
  - (ii) the amide groups in polyamides
- (c) prediction from addition and condensation polymerisation of:
  - (i) the repeat unit from a given monomer(s)
  - (ii) the monomer(s) required for a given section of a polymer molecule
  - (iii) the type of polymerisation.

See also 4.1.3 j.

### 6.2.4 Carbon-carbon bond formation

### **Learning outcomes**

### **Additional guidance**

Learners should be able to demonstrate and apply their knowledge and understanding of:

### **Extending carbon chain length**

- the use of C-C bond formation in synthesis to increase the length of a carbon chain(see also 6.1.1 d, 6.1.2 b)
- (b) formation of  $C-C \equiv N$  by reaction of:
  - (i) haloalkanes with CN<sup>-</sup> and ethanol, including nucleophilic substitution mechanism (see also 4.2.2 c)
  - (ii) carbonyl compounds with HCN, including nucleophilic addition mechanism (see also 6.1.2 b-c)
- (c) reaction of nitriles from (b):
  - (i) by reduction (e.g. with H<sub>2</sub>/Ni) to form
  - (ii) by acid hydrolysis to form carboxylic acids

(d) formation of a substituted aromatic C–C by alkylation (using a haloalkane) and acylation (using an acyl chloride) in the presence of a halogen carrier (Friedel–Crafts reaction) (see also 6.1.1 d).

### 6.2.5 Organic synthesis

### **Learning outcomes**

# Additional guidance

Learners should be able to demonstrate and apply their knowledge and understanding of:

### **Practical skills**

- (a) the techniques and procedures used for the preparation and purification of organic solids involving use of a range of techniques (see also 4.2.3 a) including:
  - (i) organic preparation
    - use of Quickfit apparatus
    - · distillation and heating under reflux
  - (ii) purification of an organic solid
    - filtration under reduced pressure
    - recrystallisation
    - measurement of melting points

### PAG6

HSW4 Opportunities to carry out experimental and investigative work.

### Synthetic routes

- (b) for an organic molecule containing several functional groups:
  - (i) identification of individual functional groups
  - (ii) prediction of properties and reactions
- (c) multi-stage synthetic routes for preparing organic compounds.

Learners will be expected to identify functional groups encountered in Module 6 (see also 4.2.3 b).

HSW3 Development of synthetic routes.

Learners will be expected to be able to devise multistage synthetic routes by applying transformations between all functional groups studied throughout the specification.

Extra information may be provided on exam papers to extend the learner's toolkit of organic reactions.

HSW3 Development of synthetic routes.

### 6.3 Analysis

This section develops and complements the spectroscopic areas of organic chemistry previously encountered (see Module 4: Core organic chemistry; 4.2.4 Analytical techniques).

This section demonstrates how analytical techniques introduced in Module 4 (infrared spectroscopy, mass spectrometry and elemental analysis) may be used in combination with NMR spectroscopy to provide evidence of structural features in molecules.

The instrumentation methods of analysis studied during the A level course provide learners with an important base of knowledge, understanding and awareness for further study in Higher Education and in many areas of employment in the broad scientific field.

This section also looks at how unknown organic functional groups can be analysed and identified using simple test-tube tests.

### 6.3.1 Chromatography and qualitative analysis

### Additional guidance **Learning outcomes** Learners should be able to demonstrate and apply their knowledge and understanding of: Types of chromatography interpretation of one-way TLC chromatograms in (a) M3.1 terms of R<sub>f</sub> values PAG6 HSW3 Interpretation of TLC to analyse organic compounds. interpretation of gas chromatograms in terms of: (b) M3.1, M3.2 retention times To include creation and use of external calibration (ii) the amounts and proportions of the curves to confirm concentrations of components. components in a mixture. Peak integration values will be supplied. HSW3 Interpretation of GC to analyse organic compounds. Tests for organic functional groups (c) qualitative analysis of organic functional groups on a test-tube scale: processes and techniques needed to identify PAG7 the following functional groups in an unknown HSW4 Qualitative analysis. compound: alkenes by reaction with bromine (i) (see also 4.1.3 f) (ii) haloalkanes by reaction with aqueous silver nitrate in ethanol (see also 4.2.2 a) (iii) phenols by weak acidity but no reaction with $CO_3^{2-}$ (see also 6.1.1 h) (iv) carbonyl compounds by reaction with 2,4-DNP (see also 6.1.2 d) (v) aldehydes by reaction with Tollens' reagent

(see also 6.1.2 e)

- (vi) primary and secondary alcohols and aldehydes by reaction with acidified dichromate (see also 4.2.1 c, 6.1.2a)
- (vii) carboxylic acids by reaction with CO<sub>3</sub><sup>2-</sup> (see also 6.1.3 b).

### 6.3.2 Spectroscopy

### **Learning outcomes**

Learners should be able to demonstrate and apply their knowledge and understanding of:

### **NMR Spectroscopy**

- (a) analysis of a carbon-13 NMR spectrum of an organic molecule to make predictions about:
  - (i) the number of carbon environments in the molecule
  - (ii) the different types of carbon environment present, from chemical shift values
  - (iii) possible structures for the molecule
- (b) analysis of a high resolution proton NMR spectrum of an organic molecule to make predictions about:
  - the number of proton environments in the molecule
  - (ii) the different types of proton environment present, from chemical shift values
  - (iii) the relative numbers of each type of proton present from relative peak areas, using integration traces or ratio numbers, when required
  - (iv) the number of non-equivalent protons adjacent to a given proton from the spin-spin splitting pattern, using the n + 1 rule
  - (v) possible structures for the molecule
- (c) prediction of a carbon-13 or proton NMR spectrum for a given molecule
- (d) (i) the use of tetramethylsilane, TMS, as the standard for chemical shift measurements
  - (ii) the need for deuterated solvents, e.g.  ${\rm CDC}l_3$ , when running an NMR spectrum
  - (iii) the identification of O–H and N–H protons by proton exchange using D<sub>2</sub>O

### **Additional guidance**

### M3.1

All carbon-13 NMR spectra that are assessed will be proton decoupled.

In examinations, NMR chemical shift values will be provided on the *Data Sheet*.

Restricted to functional groups studied in the A level specification.

HSW3,5 Interpretation of spectra to analyse organic compounds.

M3.1

In examinations, NMR chemical shift values will be provided on the *Data Sheet*.

Restricted to functional groups studied in the A level specification.

Learners will be expected to identify aromatic protons from chemical shift values but will **not** be expected to analyse their splitting patterns.

HSW3,5 Interpretation of spectra to analyse organic compounds.

M3.1

# **Combined techniques**

- (e) deduction of the structures of organic compounds from different analytical data including:
  - (i) elemental analysis (see also 2.1.3 c)
  - (ii) mass spectra (see also 4.2.4 f-g)
  - (iii) IR spectra (see also 4.2.4 d-e)
  - (iv) NMR spectra.

### M3.1

Spectral reference data will be provided on the *Data Sheet*.

Restricted to functional groups studied in the A level specification.

Learners will **not** be expected to interpret mass spectra of organic halogen compounds.

HSW3,5,6 Interpretation of a variety of different evidence to analyse organic compounds.