3.4 A2 Unit F324: *Rings, Polymers and Analysis*

This unit builds upon the chemical concepts that have been developed during AS Chemistry.

This unit consists of **three** teaching modules:

- Module 1: **Rings, Acids and Amines**
    - 4.1.1 Arenes
    - 4.1.2 Carbonyl Compounds
    - 4.1.3 Carboxylic Acids and Esters
    - 4.1.4 Amines

- Module 2: **Polymers and Synthesis**
    - 4.2.1 Amino Acids and Proteins
    - 4.2.2 Polyesters and Polyamides
    - 4.2.3 Synthesis

- Module 3: **Analysis**
    - 4.3.1 Chromatography
    - 4.3.2 Spectroscopy

Candidates are expected to apply knowledge, understanding and other skills gained in this unit to new situations and/or to solve related problems.

Recommended Prior Knowledge

Candidates should:

- have studied AS Chemistry.

4.1 Module 1: Rings, Acids and Amines

This module provides candidates with a deeper knowledge and understanding of how organic chemistry shapes the natural world and how organic chemicals provide many important materials.

This module provides candidates with a knowledge and understanding of organic chemistry:

4.1.1 Arenes

- structure of benzene, electrophilic substitution;
- phenols.

4.1.2 Carbonyl Compounds

- reactions and characteristic tests.

4.1.3 Carboxylic Acids and Esters

- properties;
- esters, triglycerides, unsaturated and saturated fats.

4.1.4 Amines

- basicity and preparation;
- azo dyes.

The material covered in this module builds on, and develops, the knowledge and understanding of functional groups encountered in AS Chemistry.

Unit F322 should be consulted for important information about formulae (2.1.1) and reaction mechanisms (2.1.1.h–j).

Links

AS Unit F321: *Atoms, Bonds and Groups*

- 1.1.2 Moles and Equations
- 1.2.2 Bonding and Structure

AS Unit F322: *Chains, Energy and Resources*

- 2.1.1 Basic Concepts
- 2.1.2 Alkanes
- 2.1.3 Alkenes
- 2.2.1 Alcohols
- 2.2.2 Halogenoalkanes
- 2.4.1 Chemistry of the Air

4.1.1 Arenes

Context and exemplification	Assessable learning outcomes
Structure of benzene How Science Works 1, 7a: • The development and acceptance of models for the structure of benzene. • Students may represent the structure of benzene as  or  in equations and mechanisms.	Candidates should be able to: (a) compare the Kekulé and delocalised models for benzene in terms of p-orbital overlap forming π bonds; (b) review the evidence for a delocalised model of benzene in terms of bond lengths, enthalpy change of hydrogenation and resistance to reaction [see also (e) below];
Electrophilic substitution of arenes • Halogen carriers include iron, iron halides and aluminium halides.	(c) describe the electrophilic substitution of arenes with (i) concentrated nitric acid in the presence of concentrated sulfuric acid,

• For nitration, candidates should include equations for formation of NO_2^+ • For halogenation, candidates should include equations for formation of X^+ or $^{\delta+}X–AlX_3{}^{\delta-}$.	(ii) a halogen in the presence of a halogen carrier; (d) outline the mechanism of electrophilic substitution in arenes, using the mononitration and monohalogenation of benzene as examples (see also unit F322: 2.1.1.h–j); (e) explain the relative resistance to bromination of benzene, compared with alkenes, in terms of the delocalised electron density of the π bonds in benzene compared with the localised electron density of the C=C bond in alkenes;
Phenols	(f) describe the reactions of phenol: (i) with aqueous alkalis and with sodium to form salts, (ii) with bromine to form 2,4,6-tribromophenol; (g) explain the relative ease of bromination of phenol compared with benzene, in terms of electron-pair donation to the benzene ring from an oxygen *p*-orbital in phenol; (h) state the uses of phenols in production of plastics, antiseptics, disinfectants and resins for paints.

4.1.2 Carbonyl Compounds

Context and exemplification	Assessable learning outcomes
Reactions of carbonyl compounds • In equations for organic redox reactions, [O] and [H] should be used. • The nucleophile can be considered as being the hydride ion, $H^–$, with subsequent protonation of the organic intermediate from H_2O.	Candidates should be able to: (a) describe the oxidation of alcohols (see also unit F322: 2.2.1.f) using $Cr_2O_7^{2–}/H^+$ (ie $K_2Cr_2O_7/H_2SO_4$), including: (i) the oxidation of primary alcohols to form aldehydes and carboxylic acids; the control of the oxidation product using different reaction conditions, (ii) the oxidation of secondary alcohols to form ketones; (b) describe the oxidation of aldehydes using $Cr_2O_7^{2–}/H^+$ to form carboxylic acids; (c) describe the reduction of carbonyl compounds using $NaBH_4$ to form alcohols; (d) outline the mechanism for nucleophilic addition reactions of aldehydes and ketones with hydrides, such as $NaBH_4$ (see also unit F322: 2.1.1.h–j);
Characteristic tests for carbonyl compounds	(e) describe the use of 2,4-dinitrophenylhydrazine to: (i) detect the presence of a carbonyl group in

• The equation for this reaction is not required. • Structure of derivative not required.	an organic compound, (ii) identify a carbonyl compound from the melting point of the derivative;
• In equations involving Tollens' reagent, [O] is acceptable.	(f) describe the 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.

4.1.3 Carboxylic Acids and Esters

Context and exemplification	Assessable learning outcomes
Properties of carboxylic acids • Comparison of acidity of different carboxylic acids not required.	Candidates should be able to: (a) explain the water solubility of carboxylic acids in terms of hydrogen bonding and dipole–dipole interaction; (b) describe the reactions of carboxylic acids with metals, carbonates and bases;
Esters, triglycerides, unsaturated and saturated fats How Science Works 6b: • Examples: octadecanoic acid,18,0; octadec-9-enoic acid, 18,1(9); octadec-9,12-enoic acid, 18,2(9,12) • Link between unsaturated and saturated fats and current concerns about heart disease and obesity. How Science Works 7c: • Use of biodiesel as a fuel to increase contribution to energy requirements from renewable fuels.	(c) describe esterification of carboxylic acids with alcohols, in the presence of an acid catalyst (see also 2.2.1.g); of acid anhydrides with alcohols; (d) describe the 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; (e) state the uses of esters in perfumes and flavourings; (f) describe a *triglyceride* as a triester of glycerol (propane-1,2,3-triol) and fatty acids; (g) compare the structures of saturated fats, unsaturated fats and fatty acids, including *cis* and *trans* isomers, from systematic names and shorthand formulae; (h) compare the link between *trans* fatty acids, the possible increase in 'bad' cholesterol and the resultant increased risk of coronary heart disease and strokes; (i) describe and explain the increased use of esters of fatty acids as biodiesel.

4.1.4 Amines

Context and exemplification	Assessable learning outcomes
Basicity of amines • Comparison of basicity of different amines not required.	Candidates should be able to: (a) explain the basicity of amines in terms of proton acceptance by the nitrogen lone pair; (b) describe the reactions of amines with acids to form salts;
Preparation of amines	(c) describe the preparation of: (i) aliphatic amines by substitution of halogenoalkanes with excess ethanolic ammonia, (ii) aromatic amines by reduction of nitroarenes using tin and concentrated hydrochloric acid;
Synthesis of azo dyes • Nitrous acid is generated *in situ* from $NaNO_2$/HCl.	(d) describe the synthesis of an azo dye by reaction of an aromatic amine with nitrous acid (<10 °C), with formation of a diazonium ion, followed by coupling with a phenol under alkaline conditions; (e) state the use of reactions, such as (d), in the formation of dyestuffs.

Practical Skills are assessed using OCR set tasks. The practical work suggested below may be carried out as part of skill development. Centres are not required to carry out all of these experiments:

- Preparation and identification of a 2,4-DNPH derivative.
- $NaBH_4$ reduction of a carbonyl compound, eg 1,2-diphenylethanedione.
- Nitration of methyl benzoate.
- Preparation of an ester, eg ethyl ethanoate and methyl 2-hydroxybenzoate.
- Synthesis of antifebrin.
- Hydrolysis of an ester, eg methyl benzoate.
- Synthesis of aspirin.

4.2 Module 2: Polymers and Synthesis

This module provides candidates with a knowledge and understanding of how amino acids are the building blocks of polypeptides and proteins, the preparation of synthetic condensation polymers and the importance of synthetic organic chemistry.

4.2.1 Amino Acids and Chirality

- amino acids, proteins and optical isomerism.

4.2.2 Polyesters and Polyamides

- polymerisation;
- hydrolysis of polymers.

4.2.3 Synthesis

- synthetic routes;
- the importance of chirality in pharmaceutical synthesis.

The material covered in this module builds on, and develops, the knowledge and understanding of functional groups encountered in AS Chemistry.

Links

AS Unit F321**:** *Atoms, Bonds and Groups*

- 1.1.3 Acids.

AS Unit F322: *Chains, Energy and Resources*

- 2.1.1 Basic Concepts.

A2 Unit F324: *Rings, Polymers and Analysis*

- 4.1.3 Carboxylic Acids and Esters;
- 4.1.4 Amines.

4.2.1 Amino Acids and Chirality

Context and exemplification	Assessable learning outcomes
Amino acids • In exam papers, candidates will be provided with isoelectric points.	Candidates should be able to: (a) state the general formula for an α-amino acid as $RCH(NH_2)COOH$; (b) state that an amino acid exists as a zwitterion at a pH value called the isoelectric point; (c) state that different R groups in α-amino acids may result in different isoelectric points; (d) describe the acid–base properties of α-amino acids at different pH values;
Peptide formation and hydrolysis of proteins	(e) explain the formation of a peptide (amide) linkage between α-amino acids by condensation and subsequent condensation polymerisation to form polypeptides and proteins (see also 4.2.2.a–e);

	(f) describe the acid and the alkaline hydrolysis of proteins and peptides to form α-amino acids or carboxylates (see also 4.1.3.d);
Optical isomerism	(g) describe *optical isomers* as non-superimposable mirror images about an organic chiral centre: four different groups attached to a carbon atom; (h) identify chiral centres in a molecule of given structural formula; (i) explain that optical isomerism and *EIZ* isomerism (see also unit F322: 2.1.1.f) are different types of stereoisomerism.

4.2.2 Polyesters and Polyamides

Context and exemplification	Assessable learning outcomes
Condensation polymers • Candidates will not be expected to recall the structures of synthetic polyesters and polyamides or their monomers. • See also polypeptides and proteins from amino acids, 4.2.1.e. • Condensation and addition polymerisation required for (c) and (d).	Candidates should be able to: (a) describe *condensation polymerisation* to form (i) polyesters, eg Terylene from benzene-1,4-dicarboxylic acid and ethane-1,2-diol, poly(lactic acid) from 2-hydroxypropanoic acid (lactic acid) (see (h) below), (ii) polyamides, eg nylon-6,6 from 1,6-diaminohexane and hexane-1,6-dicarboxylic acid, Kevlar from benzene-1,4-diamine and benzene-1,4-dicarboxylic acid; (b) compare condensation polymerisation with addition polymerisation (see also unit F322: 2.1.3.g–i); (c) suggest the type of polymerisation from: (i) a given monomer or pair of monomers, (ii) a given section of a polymer molecule; (d) identify the monomer(s) required to form a given section of a polymer (and *vice versa*); (e) state the use of polyesters and polyamides as fibres in clothing;
Hydrolysis and degradable polymers • Poly(lactic acid) is used for waste sacks, packaging, disposable eating utensils and medical applications such as internal stitches. How Science Works 6b: • Production of degradable polymers from renewable resources.	(f) describe the acid and the base hydrolysis of polyesters and polyamides; (g) outline the role of chemists in minimising environmental waste by development of degradable polymers, similar in structure to poly(lactic acid) [see (a) above]; (h) explain that condensation polymers: (i) may be photodegradable as the C=O bond absorbs radiation, (ii) may be hydrolysed at the ester or amide group.

4.2.3 Synthesis

Context and exemplification	Assessable learning outcomes
Synthetic routes • Candidates will only be expected to identify functional groups encountered in the specification.	Candidates should be able to: (a) for an organic molecule containing several functional groups: (i) identify individual functional groups, (ii) predict properties and reactions; (b) devise multi-stage synthetic routes for preparing organic compounds;
Chirality in pharmaceutical synthesis How Science Works 6a, 6b: • Requirement for chiral drugs and medicines to minimise side effects, for economical reasons and to reduce risk to companies from litigation. • Examples of chemical chiral synthesis use cyclic strained molecules, reagents fixed to a polymer support with reactants flowing over them, and supercritical CO_2.	(c) explain that the synthesis of pharmaceuticals often requires the production of a single optical isomer; (d) explain that molecules prepared synthetically in the laboratory often contain a mixture of optical isomers, whereas molecules of the same compound produced naturally by enzymes in living systems will often be present as one optical isomer only; (e) explain that the synthesis of a pharmaceutical that is a single optical isomer: (i) increases costs due to difficulty in separating the optical isomers, (ii) reduces possible side effects and improves pharmacological activity; (f) explain that modern synthesis of a pharmaceutical with a single optical isomer is often carried out: (i) using enzymes or bacteria which promote stereoselectivity, (ii) using chemical chiral synthesis or chiral catalysts, (iii) using natural chiral molecules, such as L-amino acids or sugars, as starting materials.

Practical Skills are assessed using OCR set tasks. The practical work suggested below may be carried out as part of skill development. Centres are not required to carry out all of these experiments:

- Reactions of glycine.
- Nylon rope trick demonstration.

4.3 Module 3: Analysis

This module provides candidates with a deeper knowledge and understanding of modern analytical techniques for organic chemicals. In addition this module also highlights some of the analytical techniques encountered in many areas of employment and in everyday life. The material covered in this module includes the application of some of the important instrumentation techniques used in organic and forensic analysis.

4.3.1 Chromatography

- thin-layer and gas chromatography;
- GC-MS.

4.3.2 Spectroscopy

- NMR spectroscopy;
- combined techniques.

Links

AS Unit F322: *Chains, Energy and Resources*

- 2.2.3 Modern Analytical Techniques.

4.3.1 Chromatography

Context and exemplification	Assessable learning outcomes
Types of chromatography • Paper chromatography can be used to illustrate the separation process.	Candidates should be able to: (a) describe chromatography as an analytical technique that separates components in a mixture between a mobile phase and a stationary phase; (b) state that: (i) the mobile phase may be a liquid or a gas, (ii) the stationary phase may be a solid (as in thin-layer chromatography, TLC) or either a liquid or solid on a solid support (as in gas chromatography, GC); (c) state that: (i) a solid stationary phase separates by adsorption, (ii) a liquid stationary phase separates by relative solubility; (d) explain the term R_f *value*, and interpret one-way chromatograms in terms of R_f values; (e) explain the term *retention time*, and interpret gas chromatograms in terms of retention times and the approximate proportions of the components of a mixture; (f) explain that analysis by gas chromatography has limitations, eg:

	(i) similar compounds often have similar retention times, (ii) unknown compounds have no reference retention times for comparison;
Combining mass spectrometry with chromatography • Mass spectrometry is used with GC as GC-MS and with high pressure liquid chromatography as HPLC-MS; separated components are directed into the mass spectrometer. • Candidates may be expected to interpret provided gas chromatograms and mass spectra (see also unit F322: 2.2.3.f–h). How Science Works 3, 7c: • Use of GC-MS by society in modern analysis and the use of such evidence in courts.	(g) explain that mass spectrometry can be combined with chromatography: (i) to provide a far more powerful analytical tool than from chromatography alone, (ii) to generate mass spectra which can be analysed or compared with a spectral database by computer for positive identification of a component; (h) state the use of GC-MS in analysis, eg in forensics, environmental analysis, airport security and space probes.

4.3.2 Spectroscopy

Context and exemplification	Assessable learning outcomes
NMR Spectroscopy • Background theory will not be tested on examination papers: the emphasis is on the interpretation of spectra. Thus, candidates will not be tested on why nuclear magnetic resonance takes place, the reasons for different chemical shift values, why spin–spin splitting occurs or why ^{13}C NMR requires proton decoupling. • 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*. • Compounds chosen will be limited to those containing any of the following atoms: C, H, N, O and halogens. • Candidates will be expected to identify aromatic protons from chemical shift values but will not be expected to analyse their splitting patterns.	Candidates should be able to: (a) state that NMR spectroscopy involves interaction of materials with the low-energy radiowave region of the electromagnetic spectrum; (b) analyse a carbon-13 NMR spectrum of a simple molecule to make predictions about: (i) the different types of carbon present, from chemical shift values, (ii) possible structures for the molecule; (c) analyse a high resolution proton NMR spectrum of a simple molecule to make predictions about: (i) the different types of proton present, from chemical shift values, (ii) the relative numbers of each type of proton present from relative peak areas, using integration traces or ratio numbers, when required, (iii) the number of non-equivalent protons adjacent to a given proton from the spin–spin splitting pattern, using the $n + 1$ rule, (iv) possible structures for the molecule; (d) predict the chemical shifts and splitting patterns of the protons in a given molecule;

	(e) describe the use of tetramethylsilane, TMS, as the standard for chemical shift measurements; (f) state the need for deuterated solvents, eg $CDCl_3$, when running an NMR spectrum; (g) describe the identification of O–H and N–H protons by proton exchange using D_2O; (h) explain that NMR spectroscopy is the same technology as that used in 'magnetic resonance imaging' (MRI) to obtain diagnostic information about internal structures in body scanners;
Combined techniques • In examinations, infrared absorption values will be provided on the *Data Sheet*. • Rearrangement reactions are not required; unipositive ions only.	(i) For organic compounds containing any of the following atoms: C, H, N and O: (i) analyse infrared absorptions in an infrared spectrum to identify the presence of functional groups in a molecule (see also unit F322: 2.2.3.b), (ii) analyse molecular ion peaks and fragmentation peaks in a mass spectrum to identify parts of structures (see also unit F322: 2.2.3.f–h), (iii) combine evidence from a number of spectra: NMR, IR and mass spectra, to deduce structures.

Practical Skills are assessed using OCR set tasks. The practical work suggested below may be carried out as part of skill development. Centres are not required to carry out all of these experiments:

- Thin-layer or paper chromatography.
- Interpretation of spectra – spectra available at: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng