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EXAMINATION SYLLABUSES FOR

1984

CHEMISTRY

UNIVERSITY OF CAMBRIDGE LOCAL EXAMINATIONS SYNDICATE INTERNATIONAL EXAMINATIONS

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INTRODUCTION

In studying Chemistry, it needs to be emphasised that man's interest in the subject is essentially a practical one; to use or convert materials for his own purpose and to discover the most appropriate methods of doing so.

As understanding of the subject grows, it becomes possible to renew study of problems that were formerly not amenable. This is especially relevant in modern times since the advent of more advanced techniques means that more and more phenomena can be studied experimentally. It is of interest, therefore, that, at Advanced level, candidates should be taken towards some of the boundaries of a scientific subject. This is not merely to aid potential graduates but to try to give some relevant understanding of a science to a greater number of people, especially in an age when the pace of research means that new ideas can have important social consequences within a life-time or even a decade.

The understanding of Chemistry must depend on knowing a sufficient but minimal number of facts and their relation to the fundamental principles derived from them with due emphasis on modern concepts. The present syllabus is an attempt to realise this idea, with the underlying theme that Chemistry is a study of the ways in which energy is associated with mass, chemical structure and chemical

In particular, it is hoped that the Advanced level Chemistry course will promote the qualities summarised as follows.

A. Basic qualities.

- 1. Knowledge of chemical facts and terminology.
- 2. Knowledge of physical and chemical principles.
- 3. Confidence in using scientific equipment properly and safely.
- 4. The ability to perform experiments.
- 5. The ability to observe and record.
- 6. The ability to formulate and perform relevant calculations.
- 7. The ability to organise ideas and facts and to present them clearly.

B. Higher qualities.

- 1. The ability to devise good experiments and draw conclusions from them.
- 2. The ability to understand and interpret scientific information presented in verbal, mathematical, diagrammatic or graphical form and to translate such information from one form to another.
- 3. The ability to formulate and test hypotheses.
- 4. The ability to interpret phenomena in terms of models, laws and principles.
- 5. The ability to solve problems which are unfamiliar or presented in a novel manner.
- 6. A critical approach to information and ideas.

It is hoped that the course will cultivate the following attitudes:

- 1. objectivity and impartiality;
- 2. an awareness of the consequences, e.g. social, industrial, economic, of the practice of chemistry;
- 3. safety consciousness;
- 4. an awareness of science as a construct of the human mind and of the philosophical dependence of science on scientific method-observation (establishing facts or laws of experience); hypothesis and theory; testing of hypotheses and predictions from theory; investigation by experiment; new facts.

At Ordinary level, a student should have a good grounding of elementary facts and principles, and it is intended that the Advanced level syllabus should build on this foundation by introducing such facts or ideas as will develop the student's elementary knowledge towards fuller understanding of modern Chemistry.

The scope of the practical examination is indicated in the Practical Chemistry syllabus printed at the end of the theory syllabus. The Practical Chemistry syllabus should be regarded as part of the 'core' syllabus.

The syllabus as set out applies to both Advanced and Special level papers for the G.C.E. and it should also be taken to include the syllabus for the subject at Ordinary level. Reference to a named chemical in a syllabus does not necessarily imply that candidates will be expected to have direct experience of the chemical in practical work. Although there are no topics that are specifically included only for the Special paper, it is expected in this paper that greater evidence of a real grasp of the subject will be shown by the candidate. Note that the questions in the Special paper will be based only on the core syllabus. The mathematics involved in the Advanced level syllabus is set out at the end of the syllabus.

Options basis of the syllabus.

The syllabus has been constructed on a 'core plus options' basis in which the core represents 80% of the whole. Candidates will be expected to follow two options each representing 10%. The full range of options has not yet been developed and schools will be kept informed as options are developed.

The options fall into three categories.

- (i) There are two standard options, Phase Equilibria and Further Transition Metal Chemistry, which together with the core may be regarded as equivalent to a 'normal' syllabus.
- (ii) Six specialised options are currently available: (a) Biochemistry, (b) Chemical Engineering, (c) Soil Chemistry, (d) Food Chemistry, (e) Polymers, (f) Spectroscopy.

An option on Petrochemicals is being pretested on a trials basis before being made generally available.

(iii) A teacher-assessed 'Individual Study'. See page 63. Details of the external moderation system will be announced in due course. (N.B. This option will be available only to school candidates and only in the June examinations).

Schools/candidates will ultimately be able to offer any combination of two options, e.g. the two standard options, one standard plus one specialised option, two specialised options, one option (either standard or specialised) with the individual study option.

The structure of the examination has been so designed that the options can be added as they become available without seriously interferring with the general style of the question papers—see below.

ARRANGEMENT OF PAPERS

At Advanced level there will be three theory papers and a 31/4 hour Practical test. The Practical test will carry one fifth of the total marks for the subject.

Paper 1 (21/2 hours, 100 marks)—free response questions.

Section A will contain three questions based mainly on the Physical sections of the syllabus. At least one of the questions will be non-mathematical.

Section B will contain two questions based mainly on the Inorganic sections of the syllabus.

Section C will contain three questions based mainly on the Organic sections of the syllabus.

Section D will contain one question on each option, i.e. on each of the standard and the specialised options as they become available.

Candidates will be required to attempt five questions, including one from each section and any one other.

Paper 2 (11/2 hours, 60 marks)—structured questions.

Section A will contain five questions ranging over the whole core syllabus.

Section B will contain one question based on each option, i.e. on each of the standard and the specialised options as they become available.

Candidates will be required to attempt six questions including at least four from

N.B. When the modified scheme for individual studies becomes available, those candidates offering an individual study will be required

(a) in Paper 1 (i) to attempt four questions, including one from each of Sections A, B, and C and any one other,

(ii) to leave the examination room after 2 hours,

(b) in Paper 2 (i) to attempt five questions (including at least four from Section

A),

(ii) to leave the examination room after 1 1/4 hours.

Paper 3 (1 hour, 40 marks)—multiple choice questions.

The paper will consist of forty compulsory questions of two types in the approximate ratio three to one, based only on the core of the syllabus. (Credit is given for the number of correct answers with no adjustment being made in respect of incorrect answers).

Practical Test (31/4 hours, 50 marks).

The questions will include:

(i) a volumetric analysis problem, based on one set of titrations;

(ii) a simple problem (see Practical syllabus, p.58); this problem may be combined with (i);

(iii) an observational problem, in which the candidate will be asked to investigate by specified experiments an unknown substance or mixture. Systematic analysis will not be required.

Semi-micro methods will be accepted where appropriate. An apparatus list of items which the examiners will assume to be available is printed on p.59.

Schools are reminded that candidates re-entering in the November examination have the option of carrying forward their Practical Test mark from the June examination.

The Special Paper will be a 2½ hour paper containing harder questions, based only on the core syllabus, arranged in three sections. Section A will contain three questions on Physical Chemistry, Section B will contain three questions on Inorganic Chemistry and Section C will contain three questions on Organic Chemistry. Candidates will be required to answer five questions of which not more than two may be selected from any one section.

A Data Booklet (dated October 1980) is available for use in Papers 1 and 2 and the Special Paper. The booklet contains a copy of the Periodic Table as shown on page 62.

A set of references to possible practical work is available on request.

DETAILS OF SYLLABUS

(CORE: Sections I to 13 inclusive)

PHYSICAL CHEMISTRY

1. Relative Masses of Atoms and Molecules

(a) Relative atomic, isotopic, molecular and formula masses, based on the ¹²C scale.

The term relative formula mass will be used for ionic compounds.

- (b) The mole, the Avogadro constant.
- (c) The determination of relative masses

- (i) by mass-spectrometry, treated simply,
- (ii) for gases and volatile liquids by a syringe or other simple laboratory method based on pV = nRT.

Details of the physics of mass spectrometry are not required but interpretation of spectrographs (in relation to isotopic abundances and the presence of molecular fragments) is included.

(d) The calculation of empirical and molecular formulae, using composition by

2. Atomic Structure

2.1 ELECTRONS, PROTONS AND NEUTRONS

Considered as the fundamental particles of major importance in chemistry; their relative charges and relative masses.

- 2.2 THE NUCLEUS OF THE ATOM
- (a) Isotopes and mass number.
- (b) Stable and unstable isotopes; radioactivity.
- (i) The nature of α and β -particles and of y-rays.

Differences in penetrating ability should be mentioned but a treatment of the detailed physical evidence establishing the nature of a- and eta-particles and y-rays is not intended.

(ii) Half-life, as a measure of the relative stability of the nucleus. Simple calculations on half-life may be set.

See note to section 7(a).

(iii) The effect of q- and β -particle emission on mass number and atomic number. The balancing of nuclear equations is included.

2.3 THE ELECTRONIC STRUCTURE OF THE ATOM

- (a) The principle of the determination of ionisation energies by electron bombardment: their relevance to electronic configuration.
- (b) The concept of electronic energy levels, treated qualitatively and illustrated by the characteristic line spectra of atomic hydrogen.

Detailed treatment of principal quantum numbers, n and of the spectral series, $1/\lambda = R(1/n_1^2 - 1/n_2^2)$, for hydrogen is not required except that the relation between the convergence limit of the Lyman series and the ionisation energy of hydrogen should be appreciated.

- (c) Atomic orbitals. The number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3: the shape and symmetry of s and p orbitals.
- (d) Extranuclear structure as the basis of periodicity. The filling of orbitals according to their energy and the pairing of electrons.

3. Chemical Bonding

An appreciation of the dependence of the properties of solids, liquids and gases on formula mass and also on types of chemical bonding involved is expected. The theory of resonance is not required.

- (a) Electrovalent bonds between ions.
- (b) Covalent bonds; the pairing of electrons and the overlapping of orbitals.

See section 2.3(c). Reference should be made to the co-ordinate bond as a form of covalent bond.

The qualitative model of repulsion between electron pairs. The shapes of simple molecules, including CO2 (linear), CH4 (tetrahedral), NH, (pyramidal), H,O (non-linear), SO, (trigonal only), SF, (octahedral).

See also section 11(a).

Bond energy as a qualitative indication of the strength of a covalent bond.

See section 8(c).

(c) Metallic bonds.

A simple treatment of metals as consisting of a lattice of positive ions surrounded by mobile electrons is intended.

(d) Intermolecular bonds.

A simple treatment based on permanent and induced dipoles, e.g. as in liquid trichloromethane, solid carbon dioxide, and in the liquid noble gases and solid iodine.

(e) Hydrogen bonding and its influence on properties.

The following examples are useful: (i) the physical properties of water, (ii) the boiling points of the hydrides of elements in groups V, VI and VII.

4. Gases, Liquids and Solids

4.1 GASES

The Gas Laws, Kinetic Theory

Graphical representation of the Boltzmann distribution of molecular speeds. See also section 7(b).

The use and derivation of $pV = \frac{1}{3}Nme^2$ is not required.

- (a) pV = nRT: Dalton's law.
- (b) Deviations from ideality; their qualitative explanation in terms only of intermolecular forces and molecular size.

No treatment or use of Van der Waals' equation is required.

4.2 LIQUIDS

No study of the liquid phase is required beyond appreciation of the fact that, in a liquid, individual molecules have an environment similar to that in a solid but have freedom of motion.

4.3 SOLIDS

(a) Lattice structure and spacing.

Generally, only the qualitative idea that the particles are situated at fixed points in a regular pattern is expected, but for the examples quoted below, a knowledge of the geometry (but not the dimensions) of the actual lattice is required. It should, however, be appreciated that the individual particles may be atoms, molecules or ions.

- (i) NaC1 as a simple cubic ionic lattice and iodine as a simple molecular lattice.
- (ii) Cu as a close-packed metal lattice.
- (iii) Graphite and diamond as examples of macromolecular structures.
- (b) Lattice energy.

Only a qualitative appreciation that energy is required to break up the structure of a lattice is expected. This should be related to the fact that the solubility of solids usually increases with temperature. Reference should be made to the qualitative differences in the forces of attraction between the particles in atomic, molecular and ionic lattices. See Note 18 on page 5.

5. Electrochemistry

(a) Electrolysis; the factors affecting the mass of substance liberated during electrolysis.

The relationship between the Faraday and the Avogadro constants and the charge on the electron, F = Le, should be given though details of Millikan's experiment are not required.

(b) Electrode potentials.

The I.U.P.A.C. convention will be used. No treatment of overpotentials is required.

(i) Standard electrode and redox potentials.

Only the principles of their measurement are required.

(ii) The electrochemical and redox series.

See also sections 10.1(b) and 10.7(b) (i).

(iii) Standard cell potentials as the combination of two standard electrode potentials, illustrated by the Zn(s)|Zn2*(aq)|Cu2*(aq)|Cu(s) cell.

6. Equilibria

6.1 CHEMICAL EQUILIBRIA

Reversible reactions, dynamic equilibrium.

(a) Factors affecting chemical equilibria: Le Chatelier's principle.

The following examples are useful: (i) the synthesis of hydrogen iodide, (ii) the dissociation of dinitrogen tetraoxide, (iii) the hydrolysis of simple esters, (iv) the Contact process for the manufacture of sulphuric acid, (v) the synthesis of ammonia, (vi) acid and base dissociation constants.

(b) Equilibrium constants, in terms of partial pressures and concentrations. The qualitative effect of temperature on equilibrium constants.

Careful distinction should be drawn between those cases where a change in the composition of the equilibrium mixture occurs (i) with the constant unchanged, e.g. in response to a change in pressure, (ii) because of a change in the value of the equilibrium constant, e.g. in response to a change in temperature.

The relationship between K_c and K_n is not required.

6.2 IONICEQUILIBRIA

(a) Bronsted-Lowry theory of acids and bases. Qualitative distinction between strong and weak electrolytes in terms of conductivity.

See also the note in section 10.

An appreciation that strong electrolytes, in contrast to weak electrolytes, are effectively fully dissociated in all but the most concentrated solutions is expected. Definition and details of the measurement of any form of conductivity are not required.

Degree of dissociation of weak electrolytes: dissociation constants.

Degree of dissociation, described in terms of the actual concentration of hydrogen (or hydroxide) ion relative to maximum theoretical concentration. Candidates should be familiar with the notation pK_a and pK_b .

(b) The ionic product of water.

(c) pH.

CHEMISTRY (A)

(i) pH indicators: choice of indicators; use of pH meters.

Knowledge of the technical details and working, of the electrodes of a pH meter is not required.

(ii) Buffer solutions.

Simple calculations may be set.

Reference should be made to the importance of buffers in biological

(d) Solubility product and the common ion effect.

Simple calculations may be set, e.g. involving direct substitution into a standard formula of the form [X"] [Y]". (Ionic equations should be used, where suitable, throughout the course.)

7. Reaction Kinetics

(a) Simple rate equations; order of reaction; rate constants.

Rate = $k[A]^n[B]^m$. Treatment should be limited to simple cases of single step reactions and of multi-step processes with a rate-determining step, for which n and m are both integral and the overall order is either 1 or 2. The use of the integrated forms of first- and second-order rate equations is not required but the use of constancy of half-life as a test for first order kinetics is included. Simple calculations on half-life may be set. Questions will not be set requiring candidates to determine the order or rate constant of a reaction using methods that involve drawing tangents to curves but the principles of such methods should be understood.

The use of order of reaction in checking that a given reaction mechanism is consistent with the observed kinetics.

(b) The qualitative effect of temperature on rate constants; concept of activation energy as an energy barrier.

> Interpreted qualitatively in terms of the variation with temperature of the Boltzmann distribution.

(c) Catalysis.

It should be appreciated that in the presence of a catalyst a reaction follows an alternative path, i.e. a different (usually lower) energy barrier is involved.

8. Thermochemistry and Chemical Energetics

(a) Enthalpy changes of formation, combustion, solution, neutralisation, fusion, atomisation; Hess' law.

The acquisitive convention should be used, i.e. ΔH is negative for an exothermic reaction. No treatment of enthalpy changes at constant volume (ΔU) is required.

Candidates will be expected to appreciate that all chemical reactions involve energy transfer and to appreciate, therefore, the importance of energy considerations, e.g. the wide applications of Hess' law.

- (b) Lattice energies for simple ionic crystals. A qualitative appreciation of the effects of ionic charge and ionic radius on the magnitude of a lattice energy.
- (c) Born-Haber cycles for the formation of simple ionic crystals and their aqueous solutions.

Calculation of bond energies is not required.

31

INORGANIC CHEMISTRY

9. The Periodic Table: Principles of Chemical Periodicity

It is envisaged that the Periodic Table studies outlined below will be closely co-ordinated with other sections of the syllabus, particularly section 10.

9.1 PERIODICITY OF PHYSICAL PROPERTIES

A qualitative appreciation of the variation in physical properties with atomic number across the second and third periods (lithium to neon, sodium to argon).

The variation in atomic radii, melting points, boiling points, enthalpy changes of vaporisation, electrical conductivities.

> Interpretation and explanation of the above trends and gradations in terms of structure and bonding of the elements sodium to argon.

Ionisation energies as further evidence of periodicity.

9.2 PERIODICITY OF CHEMICAL PROPERTIES

An examination of the reaction of the elements sodium to argon with oxygen and with chlorine.

> Interpretation in terms of their ability to act as oxidising and reducing agents. No treatment of peroxides or superoxides is required.

9.3 PERIODIC PATTERNS IN THE PROPERTIES OF COMPOUNDS

Study in this sub-section should be restricted to the oxides, chlorides and simple hydrides (also excluding 'MgH2' and 'AlH2') of the elements sodium to chlorine.

The patterns and gradations in properties should be interpreted in terms of key atomic and electronic factors such as atomic and ionic radii, ionisation energies and electronegativities.

- (a) Variation in oxidation number illustrated by the oxides, chlorides and simple hydrides.
- (b) (i) Reaction of oxides, chlorides and simple hydrides with water.
 - (ii) Acid/base behaviour of oxides.

No treatment of peroxides or superoxides is required.

(c) Bonding as an aid in the interpretation of properties.

Details of lattice structures are not required.

10. A Study of the Elements in Some Groups of the Periodic Table

It is intended that study should (i) be concerned primarily with selected aspects of the chemistry of a range of elements and their compounds, (ii) be firmly based on the Periodic Table and on other important unifying themes in inorganic chemistry such as redox, acid-base and complexing behaviour. Definitions (i) of redox in terms of electron transfer and of change of oxidation state, (ii) of acids and bases in terms of proton donation and acceptance, are included.

10.1 GROUP II

The elements beryllium, magnesium, calcium, strontium and barium.

A group of reactive metals which are essentially similar to each other with only gradual changes as their atomic numbers increase.

(a) The fixed oxidation number of Group II elements in their compounds.

Interpretation in terms of the electronic structure of the elements.

(b) Chemical properties of the elements as strong reducing agents.

Reference should be made to standard electrode potentials.

(c) Thermal decomposition of nitrates, carbonates and hydroxides.

Qualitative interpretation in terms of charge density and the change from a large anion to the smaller oxide anion.

(d) The variation in solubilities of the sulphates, explained in terms of the relative magnitudes of the enthalpy change of hydration for the relevant ions and the corresponding lattice energies.

10.2 ALUMINIUM

CHEMISTRY (A)

No treatment of Group III as such is required.

(a) Extraction and manufacture of aluminium.

The purification of bauxite is excluded.

- (b) The bonding in, and properties of, the oxide and chloride related to the charge density of the Al3+ ion.
- (c) Corrosion resistance of aluminium.
- (d) Uses of aluminium related to its low density, corrosion resistance and electrical conductivity.
- (e) Acidic character of aqueous aluminium salts and their reaction with concentrated aqueous alkali.

10.3 GROUP IV

The elements carbon, silicon, germanium, tin and lead.

A group in which the character of the elements changes considerably (from non-metals through metalloids to metals) as the atomic number

(a) Variation in selected physical properties of the elements—melting point, electrical conductivity and ionisation energy.

Interpretation in terms of structure and bonding.

- (b) The uses of diamond and graphite related to their properties and structure.
- (c) The bonding, molecular shape, volatility, thermal stability and hydrolysis of the tetrachlorides.
- (d) The bonding, nature (acid/base character) and thermal stability of oxides of oxidation states II and IV.
- (e) Relative stability of higher and lower oxidation states for the elements carbon to lead in their oxides, chlorides and aqueous cations.

10.4 Natrogen

No treatment of Group V as such is required.

- (a) The element: reasons for its lack of reactivity. Principle of its extraction from air.
- (b) Ammonia.
- (i) Manufacture by the Haber process.

Reference should be made to the application of the principles of kinetics and equilibria to this process.

- (ii) Formation from ammonium salts.
- (iii) Properties as a base.
- (iv) Uses, particularly in the manufacture of nitric acid and fertilisers.

(c) Oxides of nitrogen: NO, NO, and N₂O₄. Equilibria between these oxides with particular reference to the manufacture of nitric acid.

Study of the preparation and properties of these oxides is *not* required but see section 9.3(b).

- (d) Nitric acid.
- (i) Manufacture from ammonia.
- (ii) Its properties as an acid, a nitrating agent and an oxidising agent (towards sulphur, copper, iron(II) ions).
- (iii) The importance of nitric acid, particularly in the manufacture of fertilisers and explosives.

10.5 SULPHUR

No treatment of Group VI as such is required.

- (a) The α and β allotropes considered only in terms of different arrangements of S_8 rings.
- (b) Oxides of sulphur: SO₂, SO₃. Equilibrium between these oxides with particular reference to the manufacture of sulphuric acid.
- (c) Sulphuric acid.
- (i) Its manufacture by the Contact process from various sources of sulphur dioxide (from the element, sulphide ores).
- (ii) Its properties as an acid, a dehydrating agent and an oxidising agent (towards copper, halide ions).

Reference should be made to the use made of the non-volatility of the acid. No treatment of other oxo-acids of sulphur is intended but see paragraph 19 of the Practical Syllabus.

(iii) Uses of sulphuric acld in manufacturing industry.

10.6 GROUP VII

Chlorine, bromine and iodine.

A group of reactive non-metals which are essentially similar to each other with only gradual changes as their atomic numbers increase.

(a) Variations in the volatility and colour intensity of the elements.

Interpretation of volatility in terms of structure and bonding in the element.

- (b) The relative reactivity of the elements as oxidising agents. Reactions of the elements with hydrogen and the relative stability of the hydrides.
- (c) Reactions of halide ions (i) with aqueous silver ions followed by aqueous ammonia, (ii) with concentrated sulphuric acid.
- (d) The manufacture of chlorine by the electrolysis of brine either by a mercury cathode cell or diaphragm cell (diagrams of cells are not required).
- (e) The important uses of the halogens and halogen compounds. See also section 13,2

10.7 AN INTRODUCTION TO THE CHEMISTRY OF SOME d-BLOCK BLEMENTS

The first row d-block (transition) elements chromium, manganese, iron, nickel and copper.

Emphasis should be placed on the similarity of the elements to each other and the interpretation of their properties in terms of bonding, electronic structures, standard electrode potentials, metallic and ionic radii.

- (a) The physical properties of transition metals: melting points, density, successive ionisation energies (up to the fourth, where appropriate).
- (b) Characteristic chemical properties of these elements.
- (i) Variable oxidation state and colour: the principal oxidation states/numbers of these elements in their common cations, oxides and oxo-anions, the relative stabilities of these oxidation states: the use of standard redox potentials in predicting the relative stabilities of aqueous ions. (See section 5(b).)
- (ii) Formation of complex ions by exchange of ligands.

No treatment of stability constants is expected.

It is expected that candidates will be familiar with the common aqueous ions of the above elements, including the corresponding ammine complexes, where appropriate, together with

[Fe(CN)₆]⁴⁻, [Fe(CN)₆]³⁻, [Fe(H₂O)₅(SCN)]²⁺.

The use of these ions and of the insoluble hydroxides, where appropriate, in identification—see section 19, page 58—should be appreciated.

Knowledge of the bonding in, or the geometry of, a particular ion is not required.

(iii) Catalytic properties: transition metals and their compounds as important industrial catalysts, especially V₂O₅ in the Contact process, Fe/Fe₂O₃ in the Haber process, Ni in the hydrogenation of alkenes.

ORGANIC CHEMISTRY

Throughout the whole of the following section, technical details of manufacturing processes are not required.

11. Structural Considerations

(a) The shapes of the ethane, ethene and benzene molecules.

The concepts of hybridisation and delocalisation may be found helpful, particularly with regard to giving a mental picture of the benzene molecule. Although candidates will be expected to know that the carbon atoms in the benzene molecule are all equivalent, questions calling for explanation of this aspect will not be set. In question papers, the notations 'C₆H₅' or 'O' for aromatic compounds will be used.

(b) Isomerism; structural, cis-trans and optical.

Cis-trans isomerism considered primarily in relation to alkenes containing one double bond. Reference should be made to the effect of restricted rotation about the double bond in preventing the direct interconversion of cis-trans isomers.

Optical activity in chiral species, i.e. those lacking both a centre and a plane of symmetry. The simplest examples are those containing a single asymmetric C-atom, e.g. 2-aminopropanoic acid and 2-hydroxy-propanoic acid. The meaning of the terms enantiomer and racemic/racemate is included but methods of racemisation and of resolution are not required.

(c) Structure elucidation.

The interpretation of infra-red spectra to identify the presence of functional groups in organic molecules as an aid in structure elucidation.

Knowledge of the structure and working of an infra-red spectrometer is not required. See the Data Booklet. Specimen questions are available on request.

(d) Structure—its influence on acidity and basicity.
The influence of structure on the relative strength as acid or base, i.e. proton donor or acceptor, in ethylamine, phenylamine, ethanol, phenol and in the chlorine substituted ethanoic acids.

12. Common Mechanisms in Organic Reactions

- (a) Free radical reactions, illustrated in alkanes by the chlorine/methane reaction.
- (b) Addition by electrophilic reagents, illustrated in alkenes by either bromine/ ethene or hydrogen bromide/ethene.
- (c) Electrophilic substitution, illustrated by the nitration of benzene.

The effect of the delocalisation of electrons on the behaviour of benzene should be considered.

(d) Nucleophilic attack at a carbon atom as in halogenoalkanes.

Reference to S_N1 and S_N2 mechanisms is not required.

13. General Organic Chemistry

13.1 HYDROCARBONS

- (a) Alkanes, typified by ethane; substitution by halogens, combustion. Crude oil as a source of aliphatic and aromatic hydrocarbons. Cracking reactions as a means of obtaining light fractions from heavier ones and as a means of obtaining alkenes. Reference should be made to the lack of reactivity of alkanes towards polar reagents.
- (b) Alkenes, typified by ethene; addition of hydrogen, halogens, hydrogen halides, combustion, oxidation to diol and to epoxyalkane, polymerisation.

Practical details for the preparation of ethene by the dehydration of ethanol. Simple tests for alkenes by decolorisation of manganate(VII) ions and of bromine in an inert solvent. The industrial importance of ethene. Its reaction to form important industrial chemicals: with chlorine to form 1,2-dichloroethane and hence chloroethene, with oxygen to form epoxyethane and hence ethane-1,2-diol, with itself to form poly(ethene). See section 13,7.

(c) Arenes, typified by benzene and methylbenzene. Substitution reactions with halogens (not fluorine), nitration, oxidation of side-chain to give carboxylic acid.

Halogenation in side chain or aromatic nucleus depending on reaction conditions.

Consideration of addition to the benzene ring is excluded. Consideration of 'rules' describing the orientating influence of substituents on further substitution in aromatic molecules is not required but knowledge that methylbenzene gives 1,2 and 1,4 products is expected. The reactions of disubstituted compounds in which the substituents may be regarded as mutually independent are included.

Polycyclic arenes are excluded.

The industrial importance of benzene. Its Friedel-Crafts reaction with propene to form (1-methylethyl)benzene (cumene) and hence phenol and propanone. Nitration to nitrobenzene and hence phenylamine.

13.2 HALOGEN DERIVATIVES

Halogenoalkanes, typified by bromoethane. Hydrolysis, formation of nitriles, formation of primary amines by reaction with ammonia.

Reference should be made to the fact that secondary and tertiary amines and quaternary ammonium salts are also formed in the reaction of halogenoalkanes with ammonia.

It is not intended that a detailed study of fluoroalkanes should be undertaken but reference should be made to their less reactive nature (compared to chloroalkanes) and to the uses of fluoroand chlorofluoroalkanes as inert materials for aerosol propellants, refrigerants and fire-extinguishers.

Reference should be made to the marked contrast in reactivity of chlorobenzene compared with chloroalkanes and the extreme difficulty of hydrolysis of the former.

13.3 HYDROXY COMPOUNDS

Hydroxy compounds, typified by ethanol and phenol. Classification of alcohols as primary, secondary and tertiary (the last characterised by resistance to mild oxidation). Reactions of alcohols: to give halogenoalkanes; with sodium; combustion; oxidation to carbonyl compounds and carboxylic acids; dehydration to alkenes and lethers; esterification; acylation. The use of the trihalogenomethane (haloform) test. The acidity of phenols; reactions with sodium; acylation; the ease of halogenation and nitration of the aromatic ring.

Manufacture of industrial ethanol from ethene.

Manufacture of phenol from (1-methylethyl)benzene (cumene). Importance of phenol in the manufacture of cyclohexanol and hence aylon 66 (see section 13.7).

13.4 CARBONYL COMPOUNDS

- (a) Aldehydes, typified by ethanal and benzaldehyde; intermediate product of oxidation of primary alcohol, oxidation to carboxylic acid, reduction to alcohol, condensation (2,4-dinitrophenylhydrazine).
- (b) Ketones, typified by propanone and phenylethanone; oxidation product of secondary alcohol, reduction to alcohol, condensation (2,4-dinitrophenylhydrazine).

Characterisation of aldehydes and ketones in terms of reactivity towards [Ag(NH₃)₂)*, alkaline Cu²⁺ complex, and 2,4-dinitrophenylhydrazine and of the trihalogenomethane test.

13.5 CARBOXYLIC ACIDS AND DERIVATIVES

(a) Carboxylic acids, typified by ethanoic acid and benzoic acid. Formation by the oxidation of primary alcohols and by the hydrolysis of nitriles. Salt, ester and acyl chloride formation, reduction to alcohol.

Oxidation and dehydration of methanoic acid and ethanedioic acid are included.

Industrial importance of carboxylic acids in the production of esters.

- (b) Acyl chlorides, their ease of hydrolysis compared with alkyl and aryl chlorides. Reactions with alcohols, phenols and primary amines.
- (c) Acid anhydrides as important industrial acylating agents, illustrated by the use of ethanoic anhydride in aspirin manufacture.

Methods for obtaining acid anhydrides are not required.

(d) Esters, typified by ethyl ethanoate and phenyl benzoate, formation from carboxylic acids and from acyl chlorides; hydrolysis (acid and base), reduction.

Polyesters as important synthetic fibres (see section 13.7).

Practical details for the preparation of ethyl ethanoate and phenyl benzoate to illustrate the general principles of purifying liquid and solid products.

13.6 NITROGEN COMPOUNDS

(a) Primary amines, typified by ethylamine and phenylamine: formation by the reduction of nitriles (and phenylamine from nitrobenzene); salt formation and reaction with nitrous acid. The reaction of phenylamine with aqueous bromine.

Brief reference should be made to the fact that, with nitrous acid, the relatively high yield of $C_2H_3NH_2 \rightarrow C_2H_5OH$ is atypical and that higher aliphatic amines yield a variety of products, e.g. alkenes and secondary alcohols.

The manufacture of dyes illustrated by the coupling reaction of benzenediazonium chloride with phenol.

- (b) Amides, their formation by RNH2/R1COCl and their hydrolysis.
- (c) Amino-acids, typified by aminoethanoic acid: acid and base properties, zwitterion formation.
 Outline of structure of proteins based on the peptide linkage; the hydrolysis of proteins.

13.7 POLYMERS

Addition and condensation polymerisation, illustrated by reference to poly-(ethene), poly(chloroethene) (PVC), poly(phenylethene) (polystyrene), nylon 66 and a typical polyester (*Terylene*).

Mechanisms of polymerisation and technical details of commercial production are not required.

OPTIONS SYLLABUSES

Candidates are expected to study two options and they should be instructed to attempt only those questions on options for which they have been prepared.

STANDARD OPTIONS

14. PHASE EQUILIBRIA (Standard Option A)

Notes for Guidance for this option can be purchased from the Syndicate. See page 65.

14.1 VAPOUR PRESSURE DIAGRAMS

(a) Pure compounds

Illustrated by water (including reference to its atypical behaviour).

- (i) As graphical plots of experimental determinations.
- (ii) As curves describing the conditions of equilibrium between phases; the qualitative relationships between boiling point, enthalpy change of vaporisation and intermolecular forces.
- (iii) As regions representing single phases.

(b) Solutions

CHEMISTRY (A)

- (i) Qualitative treatment of the effect of a non-volatile solute on the vapour pressure of a solvent and hence on freezing point and boiling point. Simple eutectic diagrams illustrated by tin/lead, sodium chloride/water (knowledge of dihydrate formation not required), camphor/naphthalene.
- (ii) Solubility of solids in liquids.

The qualitative influence on solubility of the relationship between enthalpy change of solution, lattice energy of the solid, hydration or other solvent/solute interaction.

- (c) Liquid Mixtures
- (i) Mixtures of two miscible liquids: Raoult's law applied to the vapour pressures of miscible liquids; boiling point/composition curves; fractional distillation; azeotropic mixtures.
- (ii) Mixtures of two immiscible liquids. Steam distillation.

Calculations may be set.

- 14.2 DISTRIBUTION OF SOLUTES (INCLUDING GASES) BETWEEN TWO PHASES
- (a) Partition coefficient: solvent extraction illustrated by ether extraction. (A suitable example to illustrate partition/solvent extraction is the distribution of an organic acid in 2-methylpropan-1-ol/water.)

It should be appreciated that the partition law only applies when the solute is in the same molecular state in the two solutions. The quantitative effect of association or dissociation of the solute is not required.

(b) Chromatography: a qualitative treatment, in terms of adsorption and/or partition, but with an indication of its use as a tool in analysis.

Practical experience should be given in paper, thin-layer and column chromatography. The widespread application of these methods and of gas chromatography in industry and medicine should be noted.

15. FURTHER TRANSITION METAL CHEMISTRY (Standard Option B)

References to the following texts are given in this option syllabus:

- 1. Modern Inorganic Chemistry—Chambers and Holliday (Butterworths).
- 2. Modern Inorganic Chemistry-Liptrot (Mills and Boon).
- 3. Education in Chemistry (1980) Vol. 17, No. 4.
- 4. Chemistry in Context-Hill and Holman (Nelson).
- 5. Inorganic Chemistry through Experiment-Liptrot (Mills and Boon).
- 6. Introduction to Inorganic Chemistry-Brown (Longman).

Notes for Guidance that cover both this option and section 10.7 can be purchased from the Syndicate. See page 65.

If this Option is to be studied, it may be desirable to integrate it with section 10.7. (An introduction to the chemistry of some d-block elements).

Topic

Notes

Reference

- 15.1 STRUCTURE AND STABILITY OF COMPLEX IONS
 - (a) Bonding: simple descriptive discussion of coordinate bond formation between ligand and central metal atom/ion.

Candidates will not be asked to specify which orbitals are involved in any particular complex ion.

Topic

Notes

Reference

(b) Stereochemistry

The structure of typical hexa-(octahedral) and tetra-(tetrahedral and square-planar) co-ordinated complex ions.

Explanations of occurrence of 'tetrahedral' and 'square-planar' symmetry in particular cases are not required.

Isomerism: structural, cis-trans and optical in 1,380; 2,365; complex ions as illustrated by $CrC1_1.6H_2O$; 3,115; 4,269- $[Cr(NH_3)_4C1_2]^*$ and $[Cr(C_2O_4)_3]^{3-}$ respectively.

(c) Stoichiometry of complex ions.

This should be investigated by a colorimetric or 5,173-177; titrimetric method, e.g. Ni²⁺/edta or Fe³⁺/SCN⁻ or 4,203-204,267-Cu²⁺/NH₃.

(d) Relative stabilities of complex ions, illustrated by 6,311-312 Cu²⁺ with H₂O, Cl⁻, NH₃, edta.

Qualitative reference should be made to stability constants in predicting the stability of ions.

15.2 CATALYTIC PROPERTIES

Heterogeneous catalysis (e.g. the hydrogenation of 4,273-274 alkenes). 5,158-59

Explained in terms of the availability of d-orbitals resulting in a different mechanism of lower activation energy.

Homogeneous catalysis: illustrated by the catalysis, by Fe³⁺ions, of the reaction

$$2I^{-} + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

2,354; 6,330

Explained in terms of the reduction of Fe³⁺ by iodide ions and the subsequent re-oxidation by S₂O₄²⁻ions.

15.3 A CHEMICAL STUDY OF THE ELEMENTS Ti, V. Fe, Co, Ni, Cu

Considered in terms of variable oxidation states and colour as characteristic properties.

(a) Titanium

The chemical principles of the extraction of the 1,369-370 metal from TiO₂ involving the reduction of TiCl₄ using magnesium and the subsequent recycling of magnesium chloride. The uses of alloys of the metal 2,356 related to its chemical and physical properties.

(b) Vanadium

Common oxidation states of vanadium in its 5,157-158 aqueous ions and their interconversion. $VO_3 \hookrightarrow [VO_3(H_2O)_4]^* \Rightarrow [VO(H_2O)_4]^{2^*}$

$$[V(H_2O)_6]^{2+} \neq [V(H_2O)_6]^{3+}$$

Explained, where appropriate, in terms of redox potentials.

Topic

Notes

Reference

(c) Iron

Study of the reaction of iron with air, water and acids.

The corrosion of iron and its prevention including 1,398-400 reference to their electrochemical aspects. 4,284-285

The effect of pH and of cyanide ligands on the relative stability of Fe³⁺ and Fe²⁺. 1,395; 4,282

Reference should be made to redox potentials.

The biochemical importance of iron: illustrated by 1,397; 4,204-the oxygen-carrying properties of haemoglobin. 205

(d) Cobalt

The effect of ligands and/or temperature on the stability and geometry of complex ions illustrated by:

$$[Co(H_2O)_6]^{2^*} \rightleftharpoons [CoCl_4]^{2^*}$$

1,404-405

[Co(NH₁)₆]²⁺→{Co(NH₁)₆]³⁺

The biochemical importance of cobalt: illustrated 1,401 by its occurrence as a complex in vitamin B_{12} .

(e) Nickel

The extraction of pure nickel from nickel(II) oxide 2,386 using the volatile neutral complex Ni(CO)₄.

The uses of nickel (i) as a hydrogenation catalyst, (ii) in alloys.

(f) Copper

The relative stabilities of Cu(I) and Cu(II) 1,409-416 compounds in aqueous solution and the solid state. The 4,287-289 energetics of formation of $Cu^+(aq)$ and of $Cu^{2+}(aq)$.

The reduction of Cu(II) to Cu(I).

Discussion should be in terms of redox potentials.

The disproportionation of Cu(I) in aqueous solution. 2,496-412
Discussed in terms of redox potentials and 5,180-185
relevant enthalpy cycles.

SPECIAL OPTIONS

These syllabuses, because of their new nature, are given in more detail than those of the standard options.

Copies of specimen questions are available on request.

Home Centres should indicate on Circular 114 in the September preceding the examination for which special options they intend to prepare candidates.

All other Centres should inform the Syndicate, at least three months prior to the examinations, for which special options candidates have been prepared.

Candidates are not permitted to answer both the Biochemistry and the Food chemistry questions on any one paper.

The aims of the syllabus are to:

1. show that the principles which apply to test tube reactions also apply to reactions in living systems:

2. consider the similarity of the chemical constituents and chemical processes in all living systems (animals, plants and micro-organisms):

3. study the structure, properties and functions of the major chemical constituents in living systems:

4. investigate the nature of control processes in biochemical reactions;

5. consider energy conversions in living organisms;

6. appreciate some of the industrial, agricultural and medical applications of biochemistry.

The syllabus which follows is designed to develop the aims outlined above and extend the fundamental concepts of structure, bonding, reaction rates and energetics met earlier in the 'A' level Chemistry course. This option is not intended to provide an introduction to university Biochemistry and students will not be expected to memorise the formulae and structure of complex substances such as proteins. polysaccharides and nucleic acids. Students studying Biology will inevitably have met some of the ideas in this special option, but it is important to emphasise that this course lays stress on the chemical interpretation of biological processes at a molecular level.

Students might find the following books useful.

- 1. The Chemistry of Proteins-Unilever Educational Booklet-R. J. Taylor (Unilever Ltd)
- 2. Biochemistry—A Special Study—Nuffield Advanced Science (Longman)
- 3. Guidebook to Biochemistry—Yudkin and Offord (Oxford University Press). Teachers might find the following material useful:

4. The Chemistry of Glycerides-Unilever Educational Booklet-R. J. Taylor (Unilever Ltd)

5. Teachers' Guide to the Special Studies-Chemistry-Nuffield Advanced Science (Longman)

6. Modern Topics in Biochemistry—Bennett and Frieden (Macmillan)

7. The Living Cell-Readings from Scientific American-D. Kennedy (W. H. Freeman)

8. Enzymes—Moss (Oliver and Boyd)

9. Proteins and nucleic acids-Perutz (Elsevier)

10. Matter, Energy and Life-Baker and Allen (Addison-Wesley)

11. Practical Biochemistry-An Introductory Course-F. Frais (Butterworths)

SYLLABUS

Reference

1. BIOCHEMISTRY IN ITS BIOLOGICAL CONTEXT.

Biochemistry as the study of chemical processes in living things.

Review of the attributes of living systems.

Living organisms as intricate systems of chemical reactions.

The basic structure of an animal cell (limited to those structures required elsewhere in the syllabus). Candidates will be expected to be familiar with diagrams of cells (see ref. 9) but will not be required to reproduce such drawings in the examination.

Topic

Notes

Reference

Location within the cell of the compounds and processes referred to below, the cell being the fundamental unit of life within which energy transformations, synthesis and replication can occur. Limited conditions for biochemical reactions (i.e. between 5 °C and 40 °C, between pH 3 and 9 and in aqueous media).

2. THE STRUCTURES, FUNCTIONS AND PROPERTIES OF THE MAJOR CHEMICALS IN LIVING SYSTEMS.

2.1 Proteins

General formula of an amino-acid, proteins as 1, 2, 5, 9 condensation polymers (approx. relative molecular masses and number of monomer units). Peptide links, disulphide bridges, hydrogen bonding, salt link in protein structure-primary, secondary (helical) and tertiary structure. Solubility of proteins. Effects of pH and heavy metal ions on proteins. Function of proteins as structural polymers (e.g. muscle, hair) and in control of metabolism (e.g. enzymes) (see topic 4).

2.2 Carbohydrates

a- and β-ring structure of glucose. Polysaccharides 2, 5, 6 as condensation polymers (approx. relative molecular masses and number of monomer units). Glycogen, starch and cellulose as typical polysaccharides.

High water solubility of monosaccharides and disaccharides due to hydrogen bonding.

High AHC (i.e. combustion) for polysaccharides. Easily reversible polymerisation by enzymes.

Function of carbohydrates as structural polymers (e.g. cellulose) and as energy storage chemicals (e.g. starch, glycogen).

General structure of a triglyceride fat. Hydro- 2, 4, 5 phobic and hydrophilic portions of the fat molecule. The low solubility of fats in water and their high $\Delta H_{\rm c}^{\rm o}$ related to their function in energy storage.

Approximate relative molecular masses for fats.

2.4 Nucleic Acids

2.3 Fats

General formula of a nucleotide and of nucleic 2.5.6.9, 10 acids as Base-Sugar-Phosphate. Nucleic acids as condensation polymers (approx. relative molecular masses and number of monomer units). The existence and importance of hydrogen bonding in the structure of nucleic acids-basic structure and simple idea of replication of double-stranded DNA. Relative solubilities of nucleic acids as a consequence of their sugar-phosphate structure.

Function of nucleic acids in the control of metabolism.

The structures of DNA and RNA considered merely in terms of units. In particular, the structures of A (= adenine), T (= thymine), C (= cytosine) and G (= guanine) are not required but the spatial reason for AT and CG occurring as pairs should be understood, together with the idea that the hydrogen bonds occur as N-H....N and N-H....O. The number of such bonds is not required.

It is instructive to compare and contrast proteins, nucleic acids, carbohydrates and fats in terms of structure, properties and their important functions.

Notes

Reference

3. METABOLISM AND ENERGY CHANGES IN LIVING SYSTEMS.

An elementary discussion of metabolism restricted 5, 58-69 to glycolysis, the citric acid cycle and the role of ATP/ADP. Recall of the details of mechanisms and intermediates in these processes is not required. Where necessary, diagrams will be given in the question papers.

Digestion of food as the simple hydrolysis of large molecules catalysed by enzymes. Glycolysis resulting in the conversion of glucose to 2-oxopropanoate (pyrayate).

The fate of 2-oxopropanoate:

- (i) under anaerobic conditions (fermentation) forming ethanol in micro-organisms and 2-hydroxypropanoic (lactic) acid in mammals;
- (ii) under aerobic conditions—its oxidation to carbon dioxide and water.

4. CONTROL OF METABOLISM.

4.1 Control of catalysis

Comparison and contrast of enzymes with 5,8 inorganic catalysts. Enzymes as catalysts of high activity and specificity, their proteinaceous nature. The influence of temperature and pH on enzyme catalysed reactions.

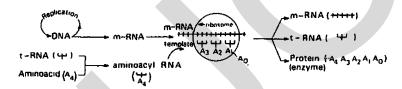
The factors affecting the rate of an enzymecontrolled reaction.

The concept of, and evidence for, an active site together with the 'lock and key' model to explain enzyme activity particularly specificity, reversible and irreversible inhibition.

Brief reference should be made to the importance of co-factors and of feedback mechanism in the control of metabolism. *Detailed consideration of co-factors is not intended*.

4.2 The control of metabolism by the ability of chemicals to store and transmit information.

DNA as the primary determinant of metabolism by 3, chap. 20; 10 its control on the production of enzymes (limited to the diagram below).



t-RNA = transfer RNA m-RNA = messenger RNA

5. APPLICATIONS.

It is intended that brief reference should be made to the applications of biochemistry in industry, agriculture and medicine, e.g. the use of pesticides, the use of micro-organisms for the production of penicillin and for the degradation of sawage, methane being a side product. Approximate time allocation, including practical work, for the sections of the syllabus:

Section 1, 2 periods (may be omitted for the students studying Biology); Section 2, 16 periods; Section 3, 6 periods; Section 4, 12 periods; Section 5, 2 periods.

(It may be found desirable to integrate some of the teaching of this option with related sections in the core syllabus.)

PRACTICAL WORK

Candidates should carry out (i) an analysis, (ii) a metabolism study, (iii) an enzyme study, chosen from those listed below.

Analysis of grass or of milk-Ref. 5.

(≈6 periods)

Model making to illustrate the structures of proteins, carbohydrates and nucleic acids.

A comparison of the metabolism of glucose by yeast under aerobic and anaerobic conditions (Ref. 5, pages 58-69). (~4 periods)

Studies on the acidic and enzymic hydrolysis of starch. Ref. 5. 8.

Investigation of the specificity and kinetics of an enzyme catalysed reaction and the effects of pH, temperature, concentration and heavy metal ions. See also the practical work suggested in 5, pages 33-51.

Suitable systems for study include urease with urea and other amides, a-amylase with starch, rennin and pancreatin with milk. (≈5 periods)

Details of some suitable experiments are given in: Biology: A Functional Approach, Students' Manual—M. B. V. Roberts (Nelson), chapters 2, 5, 6, 7 and 30

CHEMICAL ENGINEERING

This option has two main aims: firstly, to give an insight into the nature of an area of applied chemistry where the scale of operation is much greater than that encountered in school laboratories; secondly, to show how considerations other than the basic chemistry of the process itself affect the chemical engineer. Such considerations involve some topics that are somewhat physical rather than chemical, questions of cost and efficiency, of safety and other social importance. Where topics of a physical nature are involved, it is not intended that these should be treated 'from first principles'—to do so would overload the option. It is hoped that, where possible, schools might arrange visits to local chemical industry and it is intended that suitable practical work should be undertaken in the school laboratory to illustrate some aspects of the option.

Although the use of SI units is not uniform in industry, it is intended that qualitative work in the syllabus should be restricted to SI units, it being assumed that an A-level student entering chemical industry should be readily able to convert to other units that may be in use.

Particular attention is drawn to: Chemical Engineering and Industrial Processes (B.P. Educational Service).

Reference to the following books and material (some of which is provided by manufacturers) may also be found helpful:

- 1. The Chemical Economy (Reuben and Burstall, Longman)*
- 2. A case study of the acetic acid process (BP Educational Service)
- 3. A petroleum chemical plant and the environment (Esso Chemical Information)
- 4. Industrial processes for Sixth-form Chemistry (BP Educational Service)
- 5. Chemical Engineering (Unilever)
- 6. Inorganic Chemicals (ICI Publications)
- 7. Chemical Processing in Industry (RIC Monograph 16)
- 8. Sulphuric acid (Schools Information Centre on the Chemical Industry)
- 9. Ammonia (Schools Information Centre on the Chemical Industry)
- 10. The Modern Inorganic Chemical Industry (The Chemical Society)

Topic

11. Fluid Dynamics (Both, Chanel and Waite, Heinemann)

- 12. Why Chemical Engineering? (Institution of Chemical Engineers, Railway Terrace, Rugby)
- 13. Broaden your horizons through Chemical Engineering (Institution of Chemical Engineers, Railway Terrace, Rugby)
- 14. Thinking on your feet (Esso Petroleum Company Ltd).

Schools having access to computing facilities may be interested in the Schools Council package "Computers in the Chemistry curriculum" (Arnold) which includes a program to simulate the Contact process.

*Currently out of print.

SYLLABUS

Topic

Notes

Reference

1. THE SCOPE OF CHEMICAL ENGINEERING.

A simple review of the range of materials in produc- 12, 13, 14 tion is intended, e.g. chemicals, steel and other bulk metals, plastics, man-made fibres, food, coment, building materials, paints, fine chemicals such as pharmaceuticals.

2. THE ROLE OF THE CHEMICAL ENGINEER.

To devise, design, maintain and advise on efficient 2 production, i.e. optimum yield at minimum cost bearing in mind external considerations such as safety, pollution, local amenities, etc.

3. THE BASIC ASPECTS OF LARGE-SCALE PRODUCTION.

- (a) Reagents, their sources and locations, purification.
- (b) Operating conditions, e.g.
 - (i) nature of reaction, gas or liquid phase, homogeneous or heterogeneous.
 - (ii) continuous v batch methods.
 - (iii) completion v equilibrium v maximising yield within shortest time, recycling,
 - (iv) control of heat input and output,
 - (v) separation and purification of product.
 - (vi) packaging and distribution.

This section is intended to summarise aspects dealt 1, chap 15 with more fully in other sections. In view of the 10, chap 1, 2 wide scope outlined in Section 1, it is intended that attention should be concentrated on particular examples, i.e.

Continuous processing Ammonia

1, 365-376. 10. chap 9

1, 379-385. 10, chap 10

Batch processing

Iron Poly(phenylethene) (polystyrene)

1, 239-242, 407

Pharmaceuticals Titanium(IV) oxide

Sulphuric acid

1.345-350 1, 281, 282

See also 11.3

4. RESEARCH AND DEVELOPMENT.

- (a) Recognition of need and demand for product.
- (b) Laboratory studies in finding appropriate chemical route and yields.
- (c) Pilot stage.
- (d) Full scale operation.



Notes

Reference

182-184

191~194

159-162 (oil)

(natural gas)

(fermentation)

5. FUELS.

A brief outline of the major sources of fuel, coal, 1, 184-191 (coal) oil, natural gas, radioactive elements. Their sources, supply and utilisation: combustion, nuclear power, carbonation. Thermochemical calculations of the relative efficiencies (energy output/mass of fuel) may be set. For carbonation, a qualitative review of the variety of conditions and products is intended.

Fuel engineering as an integral part of chemical engineering both in its own right and as an essential aspect of many chemical industries.

Brief reference should be made to other sources of energy (hydroelectric, tidal, wind, solar and geothermal power) and to the reasons why increasing attention is being paid to their possible exploitation.

6. OPERATIONS.

Heat transfer, mass transfer and fluid flow as 2, 11 relevant to

- (a) sedimentation and washing (flow of solids through fluids),
- (b) filtration, extraction, fluidisation (flow of fluids through solids).
- (c) evaporation and distillation (flow of gas through liquid).

Qualitative reference should be made to the importance of the design of reaction vessels and furnaces.

7. CONCEPTS IN CHEMICAL ENGINEERING.

(a) Mass balance: fluid flow. Rate of mass flow of fluid in = rate of mass flow of fluid out (fluids treated as non-viscous)

 $V_1A_1Q_1 = V_2A_2Q_2$, where V =volume per time, $A = cross-sectional area, \rho = density.$

(b) Energy balance. Total energy input = total energy output.

(c) Rate equation. Production rate =

8. FLUID FLOW.

8.1 Streamline and turbulent flow: velocity profiles, critical velocity. Reynolds number.

Streamline flow-no turbulence or eddies 1,408 $\bar{\nu} = 0.5 \ \nu_{\text{max}}$. Turbulent flow $\bar{\nu} = 0.8 \ \nu_{\text{max}}$. The 11 coefficient of viscosity treated merely as a property measuring resistance to flow. Revnolds number

equation treated as empirical:

 $R_0 = \bar{v} D_0 / \eta$ where $\bar{v} = \text{mean velocity}$, D = diameterof tube, q = density, n = coefficient of viscosity. Characteristic ranges of Reynolds number for

circular duct. <2000-laminar, streamline flow; 2000 to 4000.

transitional: >4000 turbulent.

Discontinuity at $R_e \approx 2000$ in plot of $(p_1 - p_2)$ 5, 6-8, 10, 11 against ν , where p = hydrostatic pressure at

different planes in duct.

8.2 Measurement of fluid flow. The treatment is intended to be essentially descriptive with no technical details.

Measurement by absolute method, i.e. mass/time, displacement, hydrodynamic. Advantages of hydrodynamic methods, e.g. orifice plate, nozzle, venturi tube, pitot tube, rotameter, in giving instantaneous values.

between liquid and vapour. Azeotropic mixtures.

mass and vapour pressure.

distillation under reduced pressure.

components.

Consequent limitations on separating the two

Qualitative advantages and disadvantages of

Steam distillation: proportions by mass of the liquids in distillate dependent on relative molecular

Notes Topic Reference Qualitative discussion of such factors as filter 11.2 Filtration. medium; cake thickness during filtration; size of particles. Factors that determine whether batch or continuous 11.3 Batch and continuous methods are adopted. processing Control procedures.

Suggested teaching allocation/periods: 'What is chemical engineering?', 1: 'What does a chemical engineer do?'. 1; Fuels, 4; Operations/fluid flow, 10; Heat transfer, 8: Mass transfer/Unit operations, 8; Applications (including possible visit), 8.

PRACTICAL WORK: Sets of details of possible experiments are available on request.

SOIL CHEMISTRY

This option has two main aims. Firstly, to provide an area of applied chemistry where the theoretical principles met at A-level can be shown to be of importance in a more practical context, and secondly, to provide some links with both geography and biology. No attempt has been made to offer a comprehensive introduction to soil science, embracing as it does so many areas of geography, biology, physics and chemistry. Instead, areas of soil chemistry have been selected which seem to provide a suitable extension to the basic chemistry met at A-level. Additional material has only been added to provide an overall coherence. It is hoped that such fundamental concepts as rates, redox potentials, structures and bonding, solubility products and oH will all be further illustrated by the intricate chemistry of soils.

Particular attention is drawn to:

1. Introduction to the Principles and Practice of Soil Science—R. E. White (Blackwell).

Reference is also made to the following books:

- 2. An Introduction to Soil Science—B. A. FitzPatrick (Oliver and Boyd)
- 3. Fundamentals of Soil Science—H. D. Foth and L. M. Turk (Wiley)
- 4. Environmental chemistry-R. W. Raiswell, P. Brimblecombe, D. L. Dent and P.
- S. Liss (Arnold)

CHEMISTRY (A)

N.B. Notes for Guidance for this option are available on request, see page 65. Only those copies dated June 1981 should be used, all previous editions should be destroyed.

SYLLABUS		
Topic	Notes	Reference
1. INTRODUCTION		
	(i) Soil—a definition. (ii) Introduction to a soil profile.	1, 3, 4
	(Note: Only a very general account in terms of the steady generation of more stable materials from less stable ones is intended.)	2, 1-6
2. SILICATES.	·	
	(The recall of formulae of named minerals is not required)	
	(i) The SiO,4 tetrahedron as a primary structural	1, 13-21
	unit. Simple silicates (e.g. olivine). (ii) The joining of these units to form chains	3, 178-183, 160-167
	(pyroxenes, amphiboles); sheets (mica) and	2, 8-11
	framework structures (quartz). The increasing weathering resistance of these structures. The calculation of Si/O ratios is included.	4, 49-56
	(iii) Isomorphous substitution relating the struc-	

silicates (see 4(i)).

tures of the feldspars to the three-dimensional

Topic Notes Reference (iv) An outline of the structures of kaolinite and 3, 184-193 montmorillonite to illustrate the formation of 4, 69-70 1:1 and 2:1 clays. The structure of montmorillonite should be related to kaolinite but its ability to expand and contract and its consequent high cation exchange capacity should be appreciated. Gibbsite and brucite sheet as possibilities in sheet silicates. (Note: Specific geometry is not required but the importance of hydrogen bonding in the 1:1 clays should be noted.) 3. SOIL FORMATION. 2.1 The weathering The influence of (a) the parent rock (surface area 1, 55-56, 113-114 and permeability), (b) temperature, (c) moisture, 2, 12-20, 105-125 of inorganic (d) oxygen circulation in the weathering process. materials 4, 56-69, 72-74 An appreciation of the following generalised stages of weathering: (i) Early weathering stages. The release of group I and group II metal ions. The precipitation of carbonates. The alkaline nature of the soil. (ii) The breakdown of the silicate anions. The relationship between their structure and their resistance to weathering. The acidic nature of (iii) The presence of 2:1 sheet silicates (indicative of a potentially fertile soil) and, in more extreme conditions, 1:1 sheet silicates. (iv) Advanced weathering stages. Gibbsite/bauxite and iron oxide/hydroxide. 3.2 Organic (i) The importance of fungi and bacteria in the 1, 24-25 processes decomposition of organic material. (Note: Such processes may maintain growth on very poor soil as in tropical forests.) (Specific names are not required.) (ii) The importance of pH for the satisfactory operation of fungi and bacteria (see 5(vi)), (iii) The use of the C/N ratio to assess the potential value of organic material. 4. ION EXCHANGE. (i) Isomorphous substitution (Al1 for 'Si4"; 1, 22-23 Mg2 for Al3) leading to a permanent cation 4, 75 exchange capacity. Definition of cation exchange capacity. (ii) The pH-dependent cation exchange capacity 1, 32-34, 84-86 of the edges of silicate clays and of organic material. (iii) The strength of cation adherence in terms of 1, 86-87 the size of charge and size of hydrated ion. Selectivity coefficients. (iv) The ideal timing of fertilizer application 1, 158-167 related to the ability of soil to hold the fertilizer ions. (v) Anion exchange. A brief mention that this 1, 91-92 usually occurs by the surface substitution of silicate clays. The possibility of anion adherence in very acidic soils (see 4(ii)). 5. SOIL ACIDITY. (i) The causes of soil acidity and its variation with the degree of weathering. (i) The instability of silicate clays at lower pH 1,87 leading to the predominance of Al3+ at

exchange sites and hence to increased acidity.

(iii) The distinction between reserve and active

acidity.

Topic

Notes

Reference

- (iv) Liming of soils to raise the pH. The use of 1, 147-148 ammonium sulphate or sulphur to lower the pH.
- (v) The base saturation (no formal definition 1, 87 required) of soils at higher pH.
- (vi) An appreciation of the effects of acidity on the activity of bacteria and fungi.
- (vii) The effect of pH on the availability of iron, 3, 206-208 calcium, nitrogen and phosphorus. (Note: The 4, 77 pH also affects the form of the phosphate ion.) It should also be noted that the effects of pH may be more significant biologically than chemically.

6. REDOX PROCESSES.

- (i) The effects of anaerobic conditions (primarily 1, 108 waterlogging) on the redox potential of soils 3 with particular reference to the processes NO₃⁻→NO₃⁻→NH₄⁺and Fe³⁺→Fe³⁺.
- (ii) The loss of nutrients from and toxicity of soils under extreme reducing conditions. (CH₄, H₂S, N₂O and N₂ may be produced.)

7. THE SUPPLY OF IONS.

- (i) The roles and relative importance of organic 1, 129-143 and inorganic materials in the supply of 2, 81-88 nitrogen, phosphorus and potassium. The 3, 293-325 mineralisation and immobilisation of ions in organic processes.
- (ii) The nitrogen cycle.

8. THE ROLE OF IONS IN PLANT GROWTH.

- (i) A simple explanation of the means by which 1, 129-143 plants absorb ions from the soil.
- (ii) The roles of the elements N, P, K, Ca, Mg, S and Fe in plant growth.
- (iii) The mobility of the ions of the elements mentioned in 8(ii) in plants.
- (iv) The use of an understanding of 8(ii) and 8(iii) as well as soil acidity in explaining the effects of a deficiency of these ions in plants.

9. GENERAL ASPECTS.

- (i) The limits of the application of fertilizers in obtaining economic growth and avoiding ionic pollutions.
- (ii) An appreciation of the types of chemical 1, 167-172 control available for pest and weed control. 4, 128-129 An understanding of the problems of toxicity and degradability of these materials.

PRACTICAL WORK

Section 2 The estimation of organic carbon by dichromate(VI) titration.

Section 3 Making models of kaolinite and montmorillonite structures. (Optional)

Section 4 The measurement of overall cation exchange capacity for a soil.

Section 5 The use of indicators or a pH meter in determining soil acidity.

The estimation of soil lime content. (Optional)

The measurement of reserve acidity.

Section 7 The quantitative assessment of nitrate, phosphate and potassium in a given soil sample.

Section 8 Plants (maize perhaps) could be grown in culture solutions to show the effects of N, P or K deficiency. (Optional)

N.B. A complete set of experimental details is available on request. Questions may be set on the specified practical work.

Reference

Candidates are not permitted to answer both the Food Chemistry and the Biochemistry questions on any one paper.

The aims of this option are:

- 1. to consider what substances are used as foodstuffs and their chemical nature, where appropriate.
- 2. to study some reactions and their importance to Food Science,
- 3. to study practically methods of analysis appropriate to foodstuffs.
- 4. to study some aspects of the processing of food.

The option seeks to reinforce previously acquired material and simultaneously introduce new practical techniques. Of necessity, certain 'biological' aspects have been included as to have omitted them would lead to the presentation of an imbalanced area of study. Detailed metabolic processes are beyond the scope of this option.

Candidates will not be expected to reproduce complex molecular and structural formulae from memory. They will, however, be expected to appreciate the consequences of the presence of certain functional groups within a given molecular structure.

Particular attention is drawn to the following texts.

- 1. Food Science—A Chemical Approach—Fox & Cameron (Hodder & Stoughton)
- 2. Foods and Nutrition-Rankin & Hildreth (Mills & Boon)
- 3. Experimental Work in Food Science—Salfield (Heinemann)

Reference is also made to the following:

- 4. Chemistry in the Market Place—Selinger (John Murray)
- 5. Plant Protein Food—(Unilever)
- 6. New Protein—(I.C.I.)
- 7. The Chemistry of Proteins—(Unilever)
- 8. Vegetable Oils and Fats—(Unilever)
- 9. Margarine and Cooking Fats—(Unilever)
- 10. The Chemistry of Glycerides-(Unilever)
- 11. Micronutrients—(Unilever)
- 12. Food Preservation—(Unilever)

Notes for Guidance for this option will be available in due course, see p.65.

SYLLABUS

Notes Topic I. THE CHEMICAL NATURE OF FOOD

Constituents of food and their main functions in

Occurrence, to be considered as a sequence 1, 2, 5, 6, 7 1.2 Proteins

1.1 Introduction

(unspecified) of aminoacids joined by peptide links (see 'core' syllabus, section 13.6(c)). Reference should be made to the fact that some aminoacids are 'essential'. Recall of the names and structures of particular aminoacids not required. Classification into four main types, i.e. simple, conjugate, globular, fibrous. Enzymes as globular proteins (to be considered in food deterioration (section 2.1) and in the digestive process).

Principles of a suitable method for %N analysis.

e.g. colorimetric, Kjeldahl.

Practical:

Biuret test, denaturation by changes of temperature and of pH. Aminoacid separations.

1.3 Carbohydrates

Occurrence, classified as mono-, di- and poly- 1, 2 saccharides as exemplified by glucose, fructose, sucrose, maltose, starch and cellulose. The detailed stereochemistry of these sugars is not required.

CHEMISTRY (A) Topic

Notes

Reference

Candidates should be aware of the ring v open chain equilibrium for glucose/fructose. Particular reference should be made to their reducing/nonreducing properties. A consideration of α and β linkages with particular reference to cellulose as an indigestible polysaccharide compared to starch. Principles of a suitable method for sugars analysis. total glucose and sucrose determinations, e.g. in iam.

Practical:

Hydrolysis of starch. Test for distinguishing between reducing and non-reducing sugars.

1.4 Fats and oils

Occurrence. Classification, considered as solid and 1, 2, 8, 9 liquid tri-glycerides with varying degrees of unsaturation in the acid chain. Hardening of oils by hydrogenation (e.g. as in margarine production). Rancidity

(a) hydrolytic rancidity.

(b) oxidative rancidity (linked to the degree of unsaturation). No detailed treatment is required.

The concept of calorific value. Simple calculations may be set but no practical work is intended.

Stain tests, iodine value of an oil. Practical:

1.5 Vitamins

Practical:

Classification as fat soluble or water soluble. 1, 2, 11 Limited to vitamins A, B (one only), C, D and K. Candidates will not be required to recognise the structure of a particular vitamin. Refer to one disease caused through severe deficiency in each case, where appropriate.

Vitamin C determination (knowledge of the under-

lying chemistry not required).

Awareness of the importance of Na, K, Ca and P I, 2, 11 1.6 Minerals

(for bones), Fe in haemoglobin, F and I. Candidates should be aware of the hazards caused by contaminant toxic metals such as Cu, Cd, Hg

and Pb.

Solvent properties; colloidal systems as illustrated 2 1.7 Water by milk and butter, treated qualitatively as aggregates of large molecules that themselves are

insoluble in water but have hydrophilic groups. The simple idea of emulsifying agents as having unspecified functional groups which have affinities for the two solvents is included. A suitable method of moisture analysis.

A practical investigation of milk in terms of those components detailed in section 1, where appropriate.

2. FOOD PRESERVATION AND FOOD ADDITIVES

2.1 Food deterioration

Practical:

Types of food deterioration; bacterial, fungal, 1, 2, 12 oxidation, hydrolysis, dehydration.

2.2 Food preservation

Principles underlying the following methods of preservation (technical details of the actual processing of foods not required).

(a) Osmotic methods: use of sodium chloride and sucrose, e.g. for fish and jam respectively.

(b) Thermal methods: canning and bottling, e.g. fruit, vegetables, meat.

(c) Dehydration including freeze drying, e.g. peas.

(d) Freezing, e.g. meat and vegetables.

(e) Other methods: smoking e.g. bacon; use of sulphur 1, 2, 4 dioxide, e.g. fruit squash; nitrate/nitrite ion methods, e.g. bacon; ethanoic acid, e.g. pickling.

Reasons for and disadvantages of:

(a) colouring agents,

(b) antioxidants,

(c) texturizing and emulsifying agents.

(d) flavourings.

Names and structures are not required. Practical: Chromatographic separations, especially for

colouring agents.

Suggested time allocation, including practical work: Section one, 26 periods; Section two, 10

Notes

Questions may be set on the specified practical work.

POLYMERS

The option is intended to provide a link between pure and applied chemistry as well as illustrating the influence of structure on properties.

It is envisaged that practical work will be supported by model-making and industrial visits, where appropriate. The visits could indicate the production of the polymer and/or its fabrication. It is also hoped that the students will conduct a detailed examination of one polymer-from starting materials to finished product-poly(phenylethene) (polystyrene) being a particularly good example since it affords opportunities to carry out reactions in the laboratory similar to those employed on a large scale.

IUPAC nomenclature will be used, but, where appropriate, the names commonly used in industry will also be given.

Particular attention is drawn to:

1. High Polymers-P. Tooley (John Murray)

Reference to the following material may be found helpful:

- 2. Experiments in Polymer Chemistry-H. S. Finlay (Shell Education Service, Shell Centre, London SEI 7NA)
- 3. Polymers: I. Long Chain Molecules; 2. Synthetic Fibres; 3. Plastics (Sixth Form Topics) (I.C.I. Publications for Schools)*
- 4. Industrial Processes for Sixth Form Chemistry: Book 1 (BP Educational Service)
- 5. Polymer Kit: (Griffin and George)
- 6. Filmstrip: Plastics (Griffin and George)
- 7. Film Loops: Nuffield—Giant Molecules: Proteins. Bothen Films (International) Ltd, 70 Furzehill Road, Boreham Wood, Herts-Polymerization by addition

*Currently out of print but copies of current I.C.I. Publications and other material on polymers can be obtained from ESPRI, Department of Creative Design, University of Technology, Loughborough.

SYLLABUS		
Topic 1. INTRODUCTION	Notes	Reference
1.1 What are polymers?	Examples of polymers such as poly(ethene) and along and a brief reference to naturally occurring large molecules such as chlorophyll, haemoglobing	
	and polymers (with repeating units of one or more building blocks) such as cellulose, starch, protein, rubber. Details of the structures of chlorophyll, haemoglobin, cellulose and starch are not required.	
I.2 Historical development of polymer production	for example, Bakelite and rayon (from cellulose) in 1909 (small quantities only); the production of poly(ethene) starting in the 1930s leading to the present day production on a vast scale of a wide range of polymers.	1, 22-23 28-29
POLYMERISATION Addition polymerisation	Illustrated by poly(ethene), considered, in outline, in terms of initiation (e.g. by benzoyl peroxide), propagation and termination.	1, 2-7

CHEMISTRY (A)

53

Topic Notes Reference (i) High pressure, high temperature and peroxides. (ii) Ziegler catalyst (considered as AIR, + TiCl.), lower temperature and pressure (no mechanistic details). See also section 3.1. Examples of addition polymerisation: considered as polymers of R₁R₂C=CR₁R₄, e.g. poly(ethene), poly(propene), poly(chloroethene) PVC, poly(propenonitrile), poly-(phenylethene) (polystyrene), poly(methyl-2methylpropenoate) Perspex, poly(tetrafluorethene) (PTFE), poly(butadiene), poly(styrenebutadiene). 2.2 Condensation Illustrated by nylon 6.6., Terylene and phenoi- 1, 8-11 polymerisation methanal resins. in sections 2.1 and 2.2, details of the manufacture of the polymers are not required, except as specified in section 4. 2.3 Energy changes Particularly in addition polymerisationsexothermic reaction and need for cooling of polymer vessei. (A qualitative reference should be made to the breaking and formation of bonds.) 3. CLASSIFICATION OF POLYMERS 3.1 Plastics Thermoplastic materials (relatively little crosslinking), e.g. poly(ethene), PVC, poly(phenylethene), nylon. Effect of length of side chains on density, softening 1, 13-16 point, rigidity, crystallinity and glass point related 1, 32-39 to Van der Waals forces. Candidates should be aware that changing the initiator and/or the temperature usually results in a different degree of polymerisation. Isotactic, syndiotactic and atactic structures and the 1, 43-53 effect of these structures on physical properties (e.g. for poly(propene)). Thermosetting materials (high degree of cross- 1,63-68 linkings), e.g. phenolic and urea resins. 3.2 Fibres 73~76 Synthetic fibres. The drawing of thermoplastics and 1, 13-15 its effect on structure and hence physical 36-39 properties. e.g. polyamides (nylon 6.6 and nylon 6). 86-88 95-99 polyesters (Terylene), 117-133 poly(propene). Regenerated fibres. Brief reference to wood 1, 93-95 144-148 cellulose for rayon (block diagrams only); cellulose ethanoate; uses of rayon and cellulose ethanoate. Structure of cellulose from glucose units: cotton 1,99-102 cellulose 2000 →10000 units, wood cellulose ~1000 units, rayon ~270 units (known as 'cellophane' when in film form), 3.3 Elastomers Structural characteristic of elastomers. (a) Natural 1, 151, 153-159, Advantages-stretch and distort then return to original shape, waterproof, airtight. Disadvantages-soft and sticky when hot, stiff and inflexible when cold. Structure, monomer considered to be 2-methylbuta-1,3-diene (isoprene); cis (natural rubber) and trans (gutta percha). Qualitative reference to extensibility, breaking point, glass point. (No experimental work is intended). Vulcanisation and its effect on structure. Other

4. 14-19

1, 164-169

Topic Reference additives, to improve the quality of the product. i.e. carbon, antioxidants, softeners. (Specific names are not required). 1, 162-166 (b) Synthetic Buta-1.3-diene rubber: more bounce than 169-172 natural rubber. Butadiene copolymers. Styrene-butadiene copolymer; good abrasion resistance and less tendency to skid. Propenonitrile-butadiene copolymer (nitrile rubber); tough, oil and chemical resistant. Polysulphide rubber-from 1,2-dichloroethane and sodium polysulphide; oil and solvent resistant. 3.4 Silicones (a) Formation of silicones by the preparation and 1, 178-184 hydrolysis of di- and tri-chloroalkyl silicon 187-188 compounds. Monochloroalkyl silicon com-194-206 nounds as chain stoppers. (b) Physical and chemical properties of silicones related to their structures: water repellent, thermally and electrically stable, viscostatic, stable to weathering and oils. 4. THE MANUFACTURE AND USES OF POLYMERS

Outline manufacture (i.e. type of initiator, where appropriate, monomer and cooling conditions) and uses of:

(i) the addition polymers; poly(ethene) (both high 1, 32-36, 43-46 and low density forms), poly(phenylethene);

(ii) the condensation polymers; phenol-methanal 1, 63-67, 118-126 (formaldehyde), polyamides (nylon 6.6 and nylon 6).

Manufacture of a synthetic rubber.

Outline manufacture of Styrene-Butadiene Rubber (SBR) from ethylbenzene and but-1-ene to obtain phenylethene (styrene) and buta-1,3-diene which are then polymerised.

Uses of synthetic rubbers: SBR. Nitrile. Polysulphide.

Note: Many properties superior to those of natural rubber.

Silicones. Uses related to properties: rubbers, 1, 187-192 fluids, greases-water repellent surfaces, adhesives. sealing compounds, polishes, lubricants, release agents (for moulds and paper), electrical insulators. thermally resistant coatings.

Advantages and disadvantages of polymers compared with traditional materials.

Suggested Practical Work

- 1. Preparation of Bakelite (phenolic resin), a thermosetting plastic, a condensation polymer.
- 2. Perspex, a thermoplastic, addition polymer. Time of polymerisation and viscosity.
- 3. Plastics: their properties and uses (see 'Which Plastics?'-B.P. Educational Service)

PVC (transparent squash bottles and garden hosepipes); poly(phenylethene) (ball-point pen barrels, yoghurt pots and coffee cups); poly(ethene) (washingup liquid bottles); phenolic resin (dark-coloured electric light fittings and plugs); acrylics (motor car rear-light and indicator covers).

Test samples of each for:

- (i) cutting and/or breaking, (iv) softening by heating, (ii) bending,
- (v) burning.

(iii) floating.

4 Preparation of nylon 6.6 and nylon 6.10.

- 5 Preparation of polyester resin from benzene-1,2-dicarboxylic anhydride (phthalic anhydride) and propane-1,2,3-triol (glycerol).
- 6. Preparation of a synthetic rubber.
- 7 Preparation of a silicone.
- 8. (a) Polymerisation of phenylethene (styrene) at different temperatures.
 - (b) Polymerisation of phenylethene (styrene) using different initiators at different temperatures.
- 9. Silicone treatment of materials (fabric, brick, porous stone) and investigation of properties-heat and water.

SPECTROSCOPY

The aim of this option is to introduce students to the principles and methods of modern structural and quantitative analysis.

The syllabus is designed to develop and complement those areas of the 'A' level course previously encountered and show how the various analytical techniques may be used in combination to provide evidence of structural features in molecules.

Particular attention is drawn to:

- 1. Investigation of Molecular Structure—B. C. Gilbert (Mills and Boon)
- 2. Introduction to Spectroscopy—Pavia, Lampman and Kinz (Saunders Golden
- 3. Organic Chemistry: a Problem Solving Approach—Cane and Tomlinson (Mills and Boon)

Reference to the following books may be found useful:

- 4. The Physics of Chemical Structure-Unilever Educational Booklet-R. J. Taylor (Unilever Ltd.)
- 5. Spectroscopy in Chemistry-R. C. Whitfield (Concepts in Chemistry-Longman)*
- 6. Modern Analytical Methods-Betteridge and Hallman (Chem. Soc. Monographs for Teachers No. 21)
- 7. Applications of Absorption Spectroscopy of Organic Compounds—J. Dyer (Prentice-Hall)
- 8. Organic Spectroscopy: an Introduction—Dyke, Floyd, Sainsbury and Theobold-(Penguin)
- 9. Mass Spectroscopy—R. B. Moyes—School Science Review, 1971, 181, 52, 879
- 10. Mass Spectra of Simple Molecules-D. E. F. Armstead, School Science Review, 1975, 197, 56, 754
- 11. Modern Aspects of Mass Spectroscopy-J. F. J. Todd, Education in Chemistry, 1973, 10, 89
- 12. Absorption of d-block Elements—1. F. Roberts, Education in Chemistry, 1971.
- 13. A Survey of Molecular Spectroscopy—J. H. J. Peet, School Science Review, 1972, 187, 54, 281

Notes for Guidance for this option should be available from July 1982, see page 65.

SYLLABUS

Topic 1. BASIC PRINCIPLES OF SPECTROSCOPY Notes Reference

1.1 The electro-A qualitative understanding of the range of wave- 1, 39 magnetic lengths (frequencies, energies) with different types spectrum of radiation used in spectroscopy (see 'core' syllabus, section 11(c)). Use of E = hv

Distinction between absorption and emission. Refer 5, 32-3, 5-7 1.2 Atomic spectra to the line spectrum of hydrogen (see core syllabus, section 2.3 (b)).

^{*}Currently out of print.

Reference Notes Topic Sodium provides a suitable example of the 5, 14-23 application of this technique in the quantitative analysis of serum. 1.3 Molecular spectra The idea of molecular energy levels-electronic, 1, 70-71 vibrational, rotational (quantal formula and 6, 158-162 selection rules are not required). 2. ULTRA-VIOLET AND VISIBLE SPECTROSCOPY 2.1 The quantitative The Beer-Lambert law, i.e. $\lg(I_0/I) = \epsilon cI$, where ϵ is 5, 13 taken merely as a constant, characteristic of the 1,75 absorption of substance concerned. Knowledge of particular light values of ϵ is not expected. The units of ϵ will be consistent with c and l. No transformation of units will be required. (See section 2.3(a)). Considered simply in terms of transitions between 1, 70-1 2.2 The origin of available energy levels. absorptions in the u.v./visible region. The distribution of electrons in complex ions. The (a) Colour in shape and symmetry of the main lobes of transition d-orbitals. metal Candidates should be aware that vacant d- and complexes. other orbitals on the metal are used to form coordinate bonds with ligands although they will not be asked to specify which orbitals are involved in any particular case. The splitting of degenerate d-orbitals into two energy levels in octahedral complexes, explained in terms of the repulsion experienced by electrons in the orbitals directed along the x-, y- and z-axes. The colour of a complex ion resulting from the absorption of light energy as an electron moves between two non-degenerate d-orbitals. Candidates should be aware that different ligands can produce different splittings and therefore different coloured complexes. Simple test-tube experiments involving the Cu2. 5, 38-42 complexes with water, ammonia and ethane-1, 12 2-diamine can be used in a qualitative investigation of the spectrochemical series. The recall of formulae and structures of particular transition metal complexes and quantitative work on ligand-field splitting is not intended. The idea of chromophores—groups of atoms 1, 76-80 (b) Organic (strictly electrons) responsible for absorption; 5, 42-48 molecules 2, 188-195 C = C, -NO, -N = N - , C = O,Effects of delocalisation (e.g. carotene) Detailed theory of why chromophores have absorptions of appropriate energy is not required. A brief survey of the applications is intended with 1, 80-84 2.3 Applications of appropriate examples. n.v./visible spectroscopy Limited to the estimation of a single compound (a) Quantitative obeving Beer's Law. anaiysis (See 'core' syllabus, section 6.2(c)). (b) Dyes and indicators

3. INFRA-RED SPECTROSCOPY

3.1 Modes of vibration

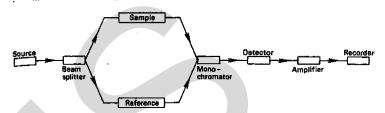
i.r. active and inactive modes should be explained 2, 16 simply in terms of dipoles, using SO2 and CO2 as 7, 23 examples.

CHEMISTRY (A) Topic

Notes

Reference

1.2 Mechanics of Simple explanation of double beam instrument 7, 24-29 messurement represented as



Liquid films, solutions, mulls and discs should be 6, 24-29 mentioned.

3.3 Structure elucidation Using absorptions of common functional groups as in the core 'A' level syllabus (see the Data Book).

1,53-80 5, 25-80 2,57-68

1, 107-198, 116

Examples of interpretation of simple i.r. spectra of organic molecules, containing no more than three functional groups, should be given.

4. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

4.1 Magnetic proper- Examples of nuclei possessing spin e.g. 'H and '3C 1, 118-9 ties of the nucleus as the most important in organic chemistry. 2.81-2 7, 58-60, 123-5

nuclear spin

(resonance)

(a) The idea of Questions on spectra involving 'C will not be set.

(b) The absorp- A simple, qualitative treatment of nuclear spin 1, 86-7 tion of energy leading to nuclei behaving as magnets that may be 5, 76-7 aligned either with or against an applied magnetic 2, 82-6 field. Resonance considered as the absorption of 7,60-2 energy when a nucleus 'flips' to the higher energy spin state.

(c) The n.m.r. spectrometer

Simplified description of the function of the basic components only as detailed in the Notes for

4.2 The 'H n.m.r. spectrum of organic molecules.deshielding.

The effect of chemical environment in a molecule 1, 89-97 on the position of absorption in terms of 2,86-88 7, 62-66

(a) Chemical chifts

Use of the d scale with T.M.S. as a standard. Particular & values will be given in the examination if required.

Integration of peak area giving the relative numbers of 'H present.

(b) Chemical equivalence and spin-spin splitting

Students should be able to identify protons in 2, 90-91 chemically identical environments in simple molecules.

Spin-spin splitting considered simply as a 1,97-108 diagnostic tool, i.e. to recognise the number of 2, 99-106 adjacent protons.

No knowledge of coupling nor the theory of why 7, 66-71 coupling occurs is required.

4.3 Application of n.m.r. spectroscopy to structure elucidation

Restricted to those functional groups which are detailed in section 13 of 'core' syllabus. Recognition of labile protons by the addition of 1, 114-8

D.O. It is intended that students should be capable of

interpreting 'H n.m.r. spectra of simple organic molecules containing no more than three functional groups. An n.m.r. data sheet for use with this option is available on request.

Topic Notes Reference 5. MASS SPECTROMETRY The section is intended to expand that work already covered in section 1(c)(i) of the core syllabus. 5.1 Basic principles Basic features of double focusing instruments, 4, 20-1 considered as having velocity selection and m/e 1, 10-11 analysing fields. Detailed knowledge of instrumentation is not required, but students should be aware of the functions of the main parts of the instrument. 5.2 Determination Relative isotopic masses, isotopic abundance. 1, 12-14 of relative Distinguishing molecules of similar r.m.m. by high 3, 18-19 atomic/moleresolution mass spectrometry. cular masses 5.3 Mass spectrometry of molecules (a) Basic features Features should include the base peak, the 1,14-19 of a mass molecular ion, and M+1 (and M+2 where 2, 233-39 spectrum appropriate) peaks. Students should be aware of the usefulness of M + 1 peaks. Questions involving an M + I peak will have ''C as the only contributor. (b) Fragmenta-Only simple cleavage need be covered in detail but 1, 19-33 tion patterns students are expected to be aware that rearrange- 5, 65-71 ment accompanying cleavage may occur. No details of mechanism of rearrangement are required. (c) Applications Determination of position of isotopic labelling. 1, 34-37 6. STRUCTURE ELUCIDATION BY COMBINED TECHNIQUES Students should be aware of the information contri- 1, 148-50 buting to evidence of an overall structure which 2, 300-336 each spectrum provides, and its limitations. It is expected, therefore, that students will have attempted to elucidate structures by combined techniques. All data normally available with spectra will be

PRACTICAL SYLLABUS

given in the examination.

16. Questions on the techniques and principles involved in the practical syllabus may be set in the theory papers.

17. A knowledge of the following volumetric determinations will be required: acids and alkalis, using suitable indicators; iron(II), ethanedioic acid (and its salts), and hydrogen peroxide by potassium manganate(VII). Simple titrations involving other reagents, e.g. lodine and sodium thiosulphate may also be set, but if problems are set involving any other reactions sufficient working details will be given. Candidates should normally record their burette readings to the nearest 0.05 cm, or better and they should ensure that they have carried out a sufficient number of titrations, e.g. in an experiment with a good end-point, two accurate titres within 0.10 cm.

18. Candidates will be required, having been given full instructions, to carry out an experiment that may involve the measurement of some quantity, e.g. the enthalpy change of a reaction, the rate of a reaction. Such experiments will depend on the simple manipulation of usual laboratory apparatus.

19. Although systematic analysis and a knowledge of traditional methods of separation will not be required, it will be assumed that candidates will be familiar with the simple reactions of the following ions: NH₄*, Mg^{2*}, Al^{3*}, Ca^{2*}, Cr^{3*}, Mn^{2*}, Fe^{2*}, Fe¹⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ba²⁺, Pb²⁺, CO₃²⁻, NO₃⁻, NO₃⁻, S²⁻, SO₄²⁻, SO₃²⁻, S₂O₃²⁻, Cl⁻, Br*, I*, CrO, 2*.

Candidates will be allowed to refer to note books and text books in the Practical examination.

Exercises requiring a knowledge of simple organic reactions as outlined in Section 13, e.g. test-tube reactions indicating the presence of unsaturation, alcoholic, phenolic and carboxylic groups.

The substances to be investigated may contain ions not included in the above list: in such cases candidates will not be expected to identify the ions but to draw conclusions of a general nature.

APPARATUS LIST

The list given below has been drawn up in order to give guidance to schools and to examiners concerning the apparatus that is expected to be generally available for examination purposes. The list is not intended to be exhaustive: in particular, items (such as bunsen burners, tripods, glass-tubing) that are commonly regarded as standard equipment in a chemical laboratory are not included. Unless otherwise stated, the rate of allocation is 'per candidate'.

Two burettes, 50 cm3 Two pipettes, 25 cm³ One pipette, 10 cm3 Dropping pipette 'Safety' flask for pipetting or, preferably, one pipette filler Conical flasks: 3 within range 150 cm3 to 250 cm3; 1 × 500 cm3 Volumetric flask, 250 cm3 Graduated test tube, 10 cm3 Measuring cylinders, 50 cm³ and 100 cm³ Wash bottle Two filter funnels Porcelain crucible, with lid, 00 size Evaporating basin, at least 30 cm³ Beakers, squat form, with lip: 100 cm3; 250 cm3: 600 cm3 (1 per 3 candidates) Thermometers: -10 °C to + 110 °C at 1 °C; -5 or 10 °C to + 105 or 110 °C at 0.2 °C (1 per 2 or 3 candidates) Vacuum flask, 'polythene' beaker or flask or other suitable alternative.

Clocks (or wall-clock) to measure to an accuracy of about 1 s.

Balance, single-pan, direct reading, 0.01 g or better

MATHEMATICAL NEEDS

It is assumed that candidates will be competent in the techniques described below. The list is intended as a guide but, in essence, no very significant change relative to pre-1978 policy is implied.

For the Basic Advanced level Papers

(1 per 8-12 candidates).

Make calculations involving addition, subtraction, multiplication and division of

Make approximate evaluations of numerical expressions, including the use of approximation such as n≈3.

Express small fractions as percentages, and vice versa.

Calculate an arithmetic mean.

Transform decimal notation to power of ten notation (standard form).

Use tables of logarithms (especially for pH, rate equations), squares, square rots, reciprocals, sines, cosines and tangents.

Change the subject of an equation. (Most such equations involve only the simpler operations but may include positive and negative indices and square roots.)

Substitute physical quantities into equations using consistent units so as to calculate one quantity. Check the dimensional consistency of such calculations, e.g. the units of the gas constant R and of a rate constant k.

Solve simple algebraic equations, including quadratics. (Most are linear but equations involving inverse relations and simultaneous equations may be required.)

Recognise the equivalent forms of the logarithms of ab, a/b, x^a , e^x .

Comprehend and use the symbols/notations <, >, \approx , /, \triangle , ∂ , \equiv , d/dt, x, $\rightarrow 0$.

Make suitable approximations of $(1 \pm x)$ and $(1 \pm x)^2$ as $x \rightarrow 0$.

Test tabulated pairs of values for direct proportionality by a graphical method or by constancy of ratio.

Use of sines, cosines and tangents in problems.

Select appropriate variables and scales for plotting a graph, especially to obtain a linear graph of the form y = mx + c.

Determine and interpret the slope and intercept of a linear graph, including relevant units.

Choose by inspection a straight line that will serve as the 'least bad' linear model for a set of data presented graphically.

Understand and use (i) the slope of a tangent to a curve as a measure of rate of change, (ii) the 'area' below a curve where the area has physical significance.

Construct rate equations of the form $dy/dt = ky^n$.

Estimation of error in measured and derived quantities especially for y = xz and $y = x^n$, i.e. $\Delta y/y = \Delta x/x + \Delta z/z$ and $\Delta y/y = n(\Delta x/x)$.

Comprehend how to handle numerical work so that significant figures are neither lost unnecessarily nor used beyond what is justified.

Be able to estimate orders of magnitude.

Formulate simple algebraic equations as mathematical models and identify failures of such models.

Summary of key quantities

The list below is intended as a guide to the more important quantities which might be encountered in teaching and in question papers. The list is not exhaustive.

Quantity	Usual symbols	SI unit
Base quantities	Osuai symbols	31 talk
mass	m	kg, g
length	ï	~5, β Π
time	,	s
electric current		Å
thermodynamic temperature	r	ĸ
amount of substance	'n	moi
amount of juostance	, "	mor
Other quantities		
temperature	θ, t	°C
area	A, S	m².
volume	ν, _ν	m,
density	e	kg m ⁻¹ , g dm ⁻¹ , g cm ⁻³
velocity	u, v, w	m s-t
mean velocity		m s ⁻¹
mean square velocity	Ži	m²s-²
force	₹ c ² F	N
work, energy	W. E. U	ï
potential energy	V. E.	j
kinetic energy	T, E,	j
pressure	P	Pa
period	T	Š
frequency	v, f	Hz
wavelength	Å.	m, mm, nm
speed of electromagnetic waves	c	m s ⁻¹
Planck constant	h	Js
electric charge		c
electric potential difference	Q V	V

(standard) electrode		
potential	(E [∞]) E	V
redox)		
electromotive force	E	٧
specific charge	e/m	C kg '
molar gas constant	R	J K • mol •
heat capacity	С	J K-1
specific heat capacity	C	J K - 1 kg - 1
radioactive decay constant	λ	S-1
half-life	T_{V_1} , t	S
atomic mass	m _e	kg
(atomic		_
relative (isotopic) mass	A.	_
electron mass	m _e	kg
neutron mass	m,	kg
proton mass	m _p	kg
molecular mass	m	kg
relative molecular mass	M.	~ 5
molar mass	M	kg moi-i
mass number	Ä	KB 11101
atomic number	Z	
neutron number	N	
number of molecules	N	_
number of molecules per unit volume	n	m- [,]
Avogadro constant	ï	mol-i
Faraday constant	ř	
enthalpy of reaction, molar	ΔΗ; ΔΗ _{π;} ΔΗ°	C moi ⁻¹
enthalpy of reaction		J, kJ;
ionisation energy	1	J mol*i, kJ mol*i
lattice energy	<u>.</u>	kJ mol ⁻¹
bond energy	<u></u>	kJ mol ⁻¹
electron affinity	<u> </u>	kJ mol ⁻¹
rate constant	k	kJ mol ⁻¹
equilibrium constant	κ, κ, κ,	as appropriate
acid (and base) dissociation constant	$K_a(K_b)$	as appropriate
order of reaction	- · •·	as appropriate
mole fraction	n, m	-
concentration	x	_
mass concentration	C	mo! dm-)
partition coefficient	C	kg dm-3
degree of dissociation	K	
ionic product, solubility product	œ .	
ionic product of water	K, K _s	as appropriate
pH	K _w	mol² dm ⁴
hr.	рН	