

SAE / 015 / 0054 / 16

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lents should attempt to determine the enthalpy of combustion of an or themselves.  
ield Advanced Science: Chemistry, Students' Book I, Experiment 7.3.  
of bomb calorimeter should be described.

**Comparison of heat values ('calorific' values) of selected fuels and foods**  
venience in supply and use of fuels.  
ents could be told to find out heat values for themselves, and to do some  
'money' comparisons.

**Use of obtaining electrical energy from chemical reactions**  
ls, secondary cells and fuel cells.  
n of Ordinary level syllabus to include standard electrode potentials.  
work should include the measurement of the e.m.f.'s of cells composed of  
electrodes. Measurements involving the use of the hydrogen electrode are  
required.  
n of thermal and electrical energy obtained.  
k would lead to the potential advantages of fuel cells. See Revised Nuffield  
ry: Teachers' Guide II, Topic 23.

**Nuclear energy.** Nuclear fission and fusion. Advantages and disadvantages.  
Einstein's equation  $E = mc^2$ .  
h section 1.1.

**POLLUTION**  
a separate section on pollution has been included in the syllabus, the  
aspects of chemistry to society should be stressed. Throughout this  
the emphasis should be on the chemical aspects of pollution. It is not  
that this section be taught as a separate section but that the subject  
could be raised when appropriate throughout the course. Candidates will  
be expected to memorize for examination purposes the complex formulae of  
pesticides, detergents, etc., but they should nevertheless be introduced to these  
in a familiar with structural principles.

**Pollution of the air**  
n of carbon compounds: composition and products of combustion of  
on fuels from the internal combustion engine. Mention should be made of  
carbon monoxide, carbon dioxide, lead compounds and oxides of nitrogen  
with unburnt hydrocarbons. The particular problem in urban areas.  
of exhaust gases. Products of combustion of coal—in particular sulphur  
leading to the formation of acids and erosion of limestone buildings.  
n sections 2.3 and 4.2. Mention should be made of the 'greenhouse' effect  
of carbon dioxide.

**Pollution of the land**  
orine compounds, e.g. DDT.  
uses, non-biodegradability and accumulation in fatty tissue. Link with  
1.1. Candidates should be introduced to structural formulae and be aware  
of structural principles.

**Radioactive pollution:** radioactivity. Strontium-90, caesium-137 and iodine-131.  
of radioactive waste from nuclear power stations.  
h section 1.1.  
n of Periodic Table studies at Ordinary level to emphasize resemblances  
between elements, e.g. of strontium to calcium.

**5.3 Pollution of rivers and the sea**

Detergents: use of earlier branched carbon chain structures leads to foaming in  
rivers. Change to bio-degradable straight chain compounds.

Link with sections 1.7 and 3.5.  
See Nuffield Advanced Science; Chemistry, Students' Book II, 18.1.

Excess fertilizers and agricultural waste washed from land: nitrates, phosphates and  
waste from intensive farming.

Oil pollution: dispersal of oil slicks.  
Link with sections 1.7, 2.2 and 3.5.

Thermal pollution: release of waste heat into the environment and effect on river life.  
Link with section 4.

A booklist is available on request to the Secretary (see **General Information**).

**ADVANCED LEVEL**

**Chemistry 081**

*The syllabus in this subject incorporates the agreed inter-Board common core as in the  
booklet published by the GCE Boards - 'A Statement of the Agreed Common Cores in  
Certain Subjects at the Advanced Level of the General Certificate of Education'.*

**Aims**

This syllabus has been designed to enable schools and colleges to develop courses in  
Advanced level Chemistry which will:

1. follow on directly from the Ordinary level syllabus in Chemistry, both in  
knowledge and approach,
2. provide a firm foundation for the further study of Chemistry and give an  
adequate basis for the study of related disciplines at the tertiary level,
3. provide a balanced and satisfying course for those who will cease formal  
education in Chemistry at this level,
4. enable students to gain a knowledge and understanding of Chemistry  
appropriate to this level and the ability to apply this knowledge and understanding  
to both familiar and unfamiliar situations,
5. develop skills in laboratory procedures and techniques, the ability to assess the  
uses and limitations of these, and to acquire good habits for health and safety,
6. enable students to recognize and appreciate the interlinking patterns which  
form a distinguishing feature of Chemistry,
7. foster imaginative and critical thinking as well as the acquisition of knowledge,
8. present Chemistry as a field of enquiry in which students can recognize the  
intellectual discipline which the subject provides,
9. relate the study of chemistry to everyday life and to the society in which we live.

It is envisaged that a course based on this syllabus should reflect the experimental  
nature of Chemistry and present chemical theory and experimental work in an  
integrated approach. The practical work should offer scope for students to develop  
skills in common laboratory procedures and techniques. These include simple  
preparative work, volumetric analysis, electrochemical measurements, techniques  
for purification and separation including crystallization, distillation and chromato-

graphy, and the use of melting and boiling points as criteria for purity. It is expected that students will develop the ability to devise simple experiments, to assess the uses and limitations of experimental methods, to make and record accurate observations, and interpret results.

### Objectives

The theory examination will seek to test the ability of candidates to:

1. demonstrate knowledge and understanding of the subject matter specified in the syllabus,
2. apply their knowledge and understanding of Chemistry to problem solving in familiar and unfamiliar situations,
3. analyse and evaluate chemical information of a qualitative or quantitative nature and to draw valid conclusions,
4. organize their chemical knowledge to produce a reasoned and/or critical response in which information is presented in a clear and logical form.

The practical test will seek to test the ability of candidates to:

1. manipulate apparatus and chemicals in quantitative and qualitative exercises,
2. observe the results of experimental work, both quantitative and qualitative, and to record these observations accurately,
3. interpret their observations and arrive at valid inferences and conclusions, including those reached through the calculation of results in quantitative exercises,
4. devise and plan experiments of a simple kind.

### The Examination

The examination will consist of three theory papers and a practical test.

In addition to the official grade representing performance in the examination as a whole (see Regulation 24), candidates will be awarded an unofficial subsidiary practical grade representing performance on Paper 4 alone (the practical test).

**Paper 1 (1½ hours).** This will be a multiple-choice objective test of 50 compulsory questions and will provide a wide and systematic coverage of both subject matter and abilities to be tested. The test will contain classification questions (Section I), multiple completion questions (Section II) and multiple choice questions (Section III); there will be no separate section of laboratory based questions.

An electronic calculator may be used in this paper, but other calculating aids, e.g. slide rules or mathematical tables, may not be used.

**Paper 2 (2 hours).** This will contain about seven compulsory structured questions. Each question will be divided into a number of parts and answers will be recorded by the candidates on the question paper.

**Paper 3 (2 hours).** This will contain seven questions and candidates will be required to answer three. Candidates will be required to organize material and present ideas in a clear and logical form; they may be expected to discuss critically a variety of statements, handle and evaluate experimental information and to apply knowledge to unfamiliar or open ended situations.

**Paper 4 (3 hours)** This will be a practical test with two compulsory questions. Candidates may use any notebooks or textbooks they wish in the practical test.

A Special paper (3 hours) is also available. This will contain nine questions and candidates will be required to answer four. (See also Regulation 8 for further information about Special papers.)

In Papers 1 and 2, the following abilities will be tested in the approximate weightings shown:

3	Knowledge	35%	Application	25%
3	Comprehension	30%	Analysis/evaluation	10%

The three major sections of the syllabus (Principles, Periodic Table and Related Studies, Carbon Compounds) will be weighted approximately in the ratio 3: 2: 2, respectively, on Papers 1 and 2 collectively.

The main areas of Chemistry covered in the theory examination will be the specific behaviour of substances (single substances or groups of substances), experimental techniques and procedure (including the design of experiments), patterns in chemistry, quantitative aspects (including calculation) and concepts and principles. In the practical test (Paper 4) quantitative and observational skills will be tested. Familiarity with the practical aspects of the Ordinary level Chemistry syllabus and the ability to use numerical and other data and to make deductions will be expected. Candidates should also be familiar with common techniques in practical inorganic, organic, physical and analytical chemistry, appropriate to their overall chemical education at Advanced level standard, and should be able to use common items of chemical apparatus. Quantitative exercises including the measurement of mass, volume, temperature, time and length will be set. Volumetric analysis, performed with due regard to accuracy and precision, is an important technique and will be examined along with other topics. Candidates will also be required to carry out qualitative investigations of chemical substances. The ability to record observations, in chemical terms, and to make appropriate deductions, will be expected. The examination will primarily attempt to test *practical* skills.

30% of the marks will be allocated to Paper 1, 30% to Paper 2, 20% to Paper 3 and 20% to Paper 4.

Information on SI units, chemical nomenclature and mathematical requirements is given at the beginning of the Chemistry syllabuses.

Four-figure mathematical tables will be provided by the Board for use in all papers except Paper 1. Candidates will be expected to have an electronic calculator conforming to Regulation 22.4 when answering papers in this subject. In calculations candidates are advised to show all the steps in their working, giving their answers at each stage. It is recommended that candidates have available a calculator with at least the following keys:

$+$ ,  $-$ ,  $\times$ ,  $\div$ ,  $\pi$ ,  $x^2$ ,  $\sqrt{x}$ ,  $\frac{1}{x}$ ,  $x^y$ ,  $\ln x$ ,  $e^x$ ,  $\log x$ ,  $10^x$ , memory.

### Syllabus

Many of the principles underlying Chemistry are collected together at the beginning of the syllabus. It is not intended that these should be understood before attempting other material but rather that they should be encountered and applied during the course. It is envisaged that studies of the principles of Chemistry, the Periodic Table and carbon compounds should be closely co-ordinated. Frequent cross-references have been made to other relevant parts of the syllabus but they are by no means exhaustive.

### INTRODUCTION

#### 1. Chemical background

The definitions, concepts, general background and detailed knowledge of elements and compounds set out in the Ordinary level Chemistry syllabus.

**PRINCIPLES****2. Atomic structure****2.1 The atomic nucleus**

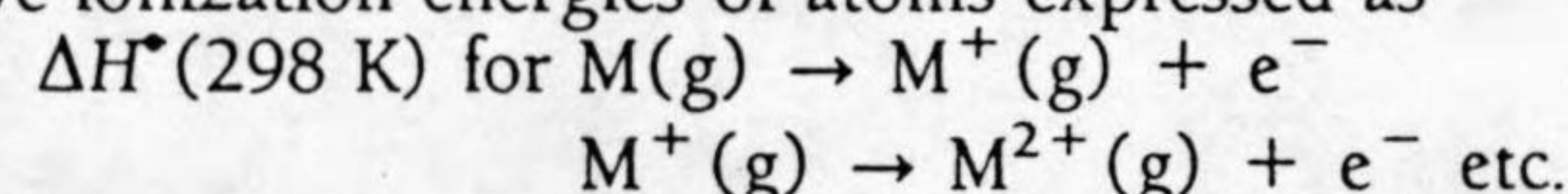
Protons and neutrons as constituents of the nucleus. Nuclear charge and atomic number ( $Z$ ). Isotopes and isotopic mass ( $^{12}\text{C} = 12.000$  scale). The use of the mass spectrometer in recognizing the existence of isotopes. Relative atomic mass as the weighted mean of the isotopic masses, and its determination from suitable data. (See also section 12.5 for applications of mass spectrometry to molecules). Radioactive decay, nature of  $\alpha$ - ( $^4_2\text{He}^{2+}$ ) and  $\beta$ - ( $\text{e}^-$ ) particles and of  $\gamma$ -radiation. Simple treatment of half-life. Representation of radioactive changes by means of equations but detailed knowledge of specific changes is not required.

**2.2 Hydrogen atom and atomic electrons**

Atomic spectrum of hydrogen providing experimental evidence of electronic energy levels; quantitative treatment is not required. Appreciation that the energy difference between states involved in a transition can be found from the frequency of the emitted or absorbed radiation, and that the first ionization energy can be obtained spectroscopically.

**2.3 Ionization energy (enthalpy of ionization)**

First and successive ionization energies of atoms expressed as



Plots of first ionization energy versus atomic number for  $Z = 1$  to 20 (see section 9.2) and of successive ionization energies against number of electrons removed. Relation to electronic configuration.

**2.4 Electron affinity**

First electron affinities of halogen atoms, expressed as  $\Delta H^\circ(298\text{ K})$  for  $\text{X}(\text{g}) + \text{e}^- \rightarrow \text{X}^-(\text{g})$ . Experimental determination not required. First and second electron affinities of oxygen atoms.

**2.5 Electronic configurations of atoms**

Building-up principle and electronic configurations of isolated atoms up to krypton, including those of the first transition series (see section 9.2). The 1s, 2s, 2p, etc. notation of electrons. The 'electrons-in-boxes' representation. An appreciation that atomic electrons are characterized by their energies and are not localized in fixed orbits. A simple charge cloud representation of s- and p-orbitals and of  $\sigma$ - and  $\pi$ - molecular orbitals should be discussed but will be examined only in relation to section 12.

**3. Bonding and structure****3.1 Nature of forces holding atoms together**

Electrostatic interactions between electrons and nuclei leading to different types of bond. Relative energies involved in different types of bond. Relationships between structure and properties.

**3.2 Metallic bonds**

Simple treatment of cationic lattice and mobile valency electrons. Close packing of spheres. Metallic radii (see section 9.2).

**3.3 Ionic bonds**

Electron transfer. Tendency for metals to form cations and for non-metals in Groups 6 and 7 to form anions. Ionic radii. Arrangement of ions in three

dimensions, using sodium chloride and caesium chloride as examples. Cleavage planes in crystals. Differences in physical properties between salts and metals.

**3.4 Covalent bonds**

Electron sharing in single and multiple bonds. Shapes of simple molecules and ions related to pairs of bonding and non-bonding electrons, e.g.  $\text{BF}_3$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{SF}_6$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_2$ ,  $\text{NO}_3^-$ ,  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$ . Covalent radii (see section 9.2). Delocalization of electrons in, e.g. benzene and graphite. Polar covalency and electronegativity (scales not required). Polar molecules as electric dipoles.

**3.5 Dative bonds**

Dative (co-ordinate) bonds treated as special examples of covalent bonds. Molecular addition compounds. Complex ions (see section 11). Hydration of cations in aqueous solution and in crystals.

**3.6 Hydrogen bonds**

Introductory account of hydrogen bonding. Comparison of boiling points of simple hydrides with Groups 4, 5, 6 and 7. Ice and water. Hydration of anions in aqueous solution and in crystals. Carboxylic acid dimers.

**3.7 Van der Waals' attractions**

Simple picture of intermolecular attractions in liquid and solid states. Concept of induced polarity of molecules; existence of crystals of noble gases. Van der Waals' radii.

**4. Energetics****4.1 Energy changes and conservation of energy**

Simple consideration of transfer of heat and work. Standard enthalpy changes. Appreciation that the sign of an enthalpy change does not always indicate the direction of spontaneous change.

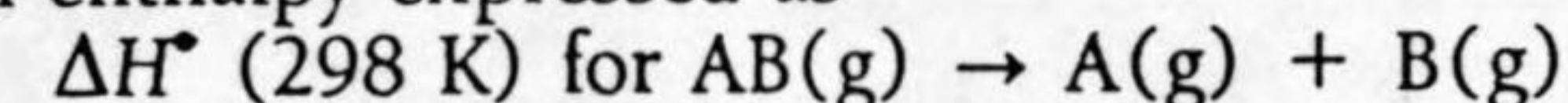
Principle of conservation of energy; applications of Hess's law. Enthalpy changes for reactions in solution and for combustion of organic compounds. Simple enthalpy-level diagrams.

**4.2 Standard enthalpy of formation**

Direct and indirect determination of standard enthalpy of formation of atoms, ions, molecules and of ions in solution. Use of tabulated data of  $\Delta H^\circ(298\text{ K})$  values for calculation of enthalpy of reaction.

**4.3 Bond enthalpy term**

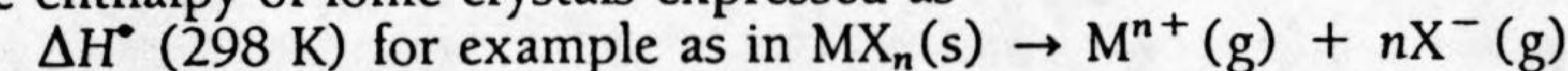
Bond dissociation enthalpy expressed as



Concept of *mean* bond dissociation enthalpy in polyatomic molecules  $\text{AB}_n$  as bond enthalpy term. Approximate transferability and additivity of bond enthalpy terms. Use in estimating enthalpies of formation or reaction.

**4.4. Lattice enthalpy**

Lattice enthalpy of ionic crystals expressed as



Use of the Born - Haber cycle in calculations.

**5. The gaseous state****5.1 The ideal gas equation**

$pV = nRT$  as a generalization from the gas laws and Avogadro's theory. Use of ideal gas equation in calculations, including the determination of relative molecular

mass. Simple experimental determination of the density of a gas or vapour. Dalton's law of partial pressures.

## 5.2 Kinetic theory

Qualitative kinetic theory. Model of ideal gas as a collection of point mass particles in random motion. Graphical representation of the distribution of speeds in a gas. Effect of temperature change on the distribution. Qualitative explanation of deviations of real gases from ideal gas behaviour.

## 6. Phase equilibria

Simple pressure/temperature phase diagram for a one component system showing one solid phase only, illustrated by  $H_2O$ . A discussion of critical phenomena is not required. Representation by phase diagrams of systems of two volatile liquids in which Raoult's law is obeyed: variations of boiling point and vapour pressure with composition at constant temperature or constant pressure. Brief discussion of the principles of fractional distillation. The existence of positive and negative deviations from Raoult's law to be explained in terms of molecular interactions for which enthalpy changes on mixing provide evidence. The treatment of azeotropy is excluded.

## 7. Chemical equilibria

### 7.1 The equilibrium state

The equilibrium state and its dynamic nature. Equilibria in the gaseous state. Equilibrium constants,  $K_c$  and  $K_p$  (relationship not required). Equilibria in solution. Heterogeneous equilibria. Expression of concentration terms for pure solid and pure liquid phases as constants. Solubility products.

Effect of pressure changes on gaseous equilibria. Effect of concentration changes on equilibria. Qualitative effect of temperature changes on equilibrium constants in relation to the sign of enthalpy of reaction. Le Chatelier's principle.

### 7.2 Equilibria at electrodes

Metal/metal ion equilibria and redox equilibria at electrodes. Electron transfer; representation by equations, existence of a potential difference between electrode and solution. Cells: distinction between e.m.f. and p.d. of a cell. Importance of storage cells as a source of energy. Use of e.m.f. values to compare relative tendency of ions to accept electrons; need for a reference electrode. Hydrogen electrode. IUPAC convention for sign of e.m.f. and for writing electrode couples. Qualitative treatment of effect of concentration changes on electrode potential. Standard electrode potentials (standard reduction potentials). The electrochemical series. Use of standard electrode potentials to calculate the standard e.m.f. of cells. Prediction of the direction of oxidation-reduction reactions.

### 7.3 Equilibria in aqueous systems

Qualitative discussion of conductivity as a measure of ionic concentration. Use of Brønsted-Lowry theory to correlate acid/base phenomena. Definition and measurement of pH. Calculation of pH from hydrogen ion concentration and vice-versa. the ionization of water,  $K_w$ . Variation of pH during titrations of strong and weak acids and bases. Dissociation constant  $K_a$  for acids and  $K_b$  for bases. Calculation of pH from  $K_a$  and  $K_b$  from pH.

Buffer systems and their uses; special case of  $pH = pK_a$ . Simple theory of indicators as weak acids or bases; pH range of colour changes.

## 8. Rates of chemical reactions

### 8.1 Homogeneous reactions

Factors which affect the rate of a reaction. Order of reaction; total order and order with respect to a given substance. Graphical presentation and interpretation of results of kinetic measurements, leading to simple rate laws. Integrated form of rate laws will not be required. Rate constants and their units. Concept of half-life for first order reactions. Use of chemical and physical techniques for following a reaction. Variation of rate constant with temperature.

The Arrhenius equation  $k = Ae^{-E/RT}$ ; activation energy.

Complex nature of many common reactions. Presence of several elementary indivisible steps, illustrated by simple examples of mechanism (see section 13.2). Qualitative introduction to ideas of collision processes, activation energy as a barrier to reaction and concept of a transition state.

## 8.2 Catalysis

Catalysis as the creation of a new reaction route for which the energy barrier is lower. Homogeneous and heterogeneous catalysis. A catalyst as a reagent which undergoes regeneration. Examples of catalysis, including those of industrial importance.

## THE PERIODIC TABLE AND RELATED STUDIES

The study of inorganic chemistry should be closely linked to the Periodic Table to emphasize the idea of chemical periodicity as one of the major unifying themes in Chemistry and to lessen the student's need for committing to memory isolated details of factual information.

Studies of the physical and chemical properties of the elements and their compounds should be based on the long form of the Periodic Table and should emphasize horizontal and vertical relationships.

In the discussion of the trends within the main groups of the Periodic Table, emphasis should be given to group similarities in Groups 1, 2, and 7, and to the transition from non-metallic to metallic character in Group 4. For Groups 3, 5 and 6, the considerable differences between the first two members of each group should be stressed.

## 9. Chemical periodicity

### 9.1 Electronic configuration

Relationship between electronic configurations of atoms and their positions in the full Periodic Table. Classification into s- and p- block elements (main groups), d-block elements (transition metals) and f-block elements (inner transition metals). Treatment of f-block elements to be limited to their existence as part of this classification system.

### 9.2 Periodic relationships amongst the elements Li to Ar

A study, based largely on data collected from the literature, of the variation of melting point, boiling point, atomic volume and radii with atomic number. A qualitative structural interpretation of these data in terms of the number and nature of atomic interactions for the elements at room temperature and atmospheric pressure. Ionization energies as additional evidence of periodicity (see section 2.3).

### 9.3 Periodic relationships amongst the oxides, chlorides and simple hydrides of the elements Li to Ar

A comparative study of the stoichiometric composition of the oxides, chlorides and simple hydrides of the above elements. The practical determination of the composition of an oxide or halide formed by one of the elements from Na to S.

General methods for the preparation of the principal oxides and chlorides of the elements from Li to Cl, including action of heat on suitable compounds for metal oxides, direct combination for oxides of reactive non-metals, neutralization for highly ionic chlorides and direct combination for covalent chlorides.

The reactions of the oxides, chlorides and hydrides with water: acid/base behaviour of the oxides, hydrolytic behaviour of the chlorides and hydrides.

Bonding in simple ionic and covalent chlorides and its relationship to chemical and macroscopic physical properties (see section 3).

## 10. Study of the characteristics of the main groups within the Periodic Table

### 10.1 Hydrogen

Existence of ionic and covalent hydrides (see section 9.3) and complex hydrides exemplified by  $\text{LiAlH}_4$  only. Acids in aqueous solution (see section 7.3). Hydrogen bonding (see section 3.6).

### 10.2 Groups 1 and 2

Selected properties of the elements Li, Na, K, Be, Mg, Ca, Sr, and Ba and some of their important compounds. An extension of the work in sections 9.2 and 9.3 to include elements not mentioned there. Fixed oxidation states of the elements and interpretation in terms of electronic configurations. Solubilities of hydroxides, carbonates, sulphates and nitrates: thermal stabilities of hydroxides, carbonates and nitrates. The study of beryllium and its compounds to be limited to that detailed in sections 9.2 and 9.3; the covalent nature of  $\text{BeCl}_2$  and the amphoteric nature of  $\text{BeO}$ .

### 10.3 Group 3

Comparison of boron and aluminium and their chlorides and hydroxides to illustrate the non-metallic character of boron and the metallic character of aluminium. The detailed chemistry of boron and its compounds is not required, except as detailed in section 9.3.

Amphoteric nature of  $\text{Al}_2\text{O}_3$ , the acidic character of the  $\text{Al}^{3+}(\text{aq})$  ion and its interaction with the hydroxide ion.

### 10.4 Group 4

An extension of the material covered in sections 9.2 and 9.3 to include the variations in melting points, boiling points and ionization energies of the elements C to Pb and their interpretation. Composition and hydrolytic behaviour of the chlorides. The principal oxides, their composition and acidic, basic, amphoteric or neutral nature. Physical state of the oxides at room temperature interpreted in terms of their molecular or giant structures. Brief review of hydrides, limited to range of hydrides and stability. Reducing action of  $\text{Sn}^{2+}(\text{aq})$ .

### 10.5 Groups 5 and 6

Brief comparison of the physical properties of oxygen and sulphur and of nitrogen and phosphorus, based on information covered in section 9.2. Readiness of oxygen and sulphur to combine with many other elements directly forming oxides and sulphides which are abundant in nature. Formation of sulphides by precipitation with  $\text{H}_2\text{S}$  should be mentioned, but conditions necessary for the precipitation of particular sulphides need not be discussed, nor is practical work expected. Contrast between physical properties of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  related to hydrogen bonding (see section 3.6).

Stoichiometry of the principal oxides, chlorides and hydrides of Group 5 and Group 6 elements as specified in section 9.3. Methods of formation (excluding details of experimental procedure) of the following: NO (by action of dilute nitric

acid on copper),  $\text{NO}_2$  (by action of heat on some nitrates),  $\text{NH}_3$  (from elements),  $\text{SO}_2$  (from elements) and conversion into  $\text{SO}_3$ ,  $\text{PCl}_3$  and  $\text{PCl}_5$  (link with section 9.3). Principal oxo-anions of nitrogen and sulphur to illustrate variable oxidation states. Redox reactions involving  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{S}_2\text{O}_8^{2-}$ .

### 10.6 Group 7

Trends in the properties of the elements F, Cl, Br and I, including electron affinities (see section 2.4). The reactions between ionic halides and sulphuric acid, phosphoric acid and silver ions. The acidic properties of the hydrogen halides and the abnormal behaviour of  $\text{HF}(\text{aq})$  and  $\text{F}^-(\text{aq})$ . Comparison of bond dissociation enthalpies for the series of compounds  $\text{X}_2$  and  $\text{HX}$ . Displacement reactions of halogens. Existence of  $\text{I}_3^-$ . Variable oxidation states, illustrated by the oxo-anions of chlorine. Disproportionation of  $\text{Cl}_2$  and  $\text{ClO}^-$ .

### 10.7 Group 8 (noble gases)

Treatment limited to the general inertness of the noble gases, trends in ionization energy and knowledge of the existence of a few xenon compounds.

## 11. d-Block elements

### 11.1 General features

A general survey only is required, to be undertaken with reference to those chemical and physical properties considered in sections 9.2 and 9.3. Emphasis is to be given to those features which are common to most transition metals: their electronic configurations (see section 9.1), metallic character, variable oxidation states, formation of coloured ions and complexes (see section 11.2). The terms *transition metal* and *d-block element* will be used interchangeably and will include those elements from Sc and Zn inclusive. Detailed chemistry will not be examined except as set out in section 11.3.

### 11.2 Complex ions

The formation of complex ions in solution and their existence in the solid state. Brief discussion of shapes of complex ions (limited to tetra- and hexa-coordinated systems). General treatment of bonding in terms of either donation of lone pairs of electrons by ligands (using electrons in boxes notation) or in terms of electrostatic interaction between centres of negative charge on the ligand and the positive central metal ion.

### 11.3 Detailed chemistry

Simple aqueous chemistry of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , including the formation of the ion from the metal by the action of suitable acids, precipitation of hydroxides and interconversions between oxidation states. Cu(I) chemistry, limited to the formation of  $\text{Cu}_2\text{O}$  in Fehling's test and the disproportionation of  $\text{Cu}^+$  in aqueous solution. Evidence for the fixed oxidation state of zinc in its compounds.

Redox chemistry and oxidation states of V and Mn. Oxidizing action of  $\text{Cr}_2\text{O}_7^{2-}$ . Complex ions to be studied should include  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{CuCl}_4]^{2-}$ ,  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Zn}(\text{OH})_4]^{2-}$ .

## CARBON COMPOUNDS

It is intended that there should be an emphasis on the behaviour of functional groups rather than of individual compounds. General synthetic pathways should be emphasized throughout, and wherever possible reaction mechanisms should contribute to understanding and rationalization of the factual basis of the subject.

Opportunity should be given for the biological aspects of substances to be brought out where these cases arise.

In dealing with practical aspects, small scale work may be more convenient for many operations but it would be expected that some experience of dealing with materials on a large scale (macro, e.g. about 10 g) would be included.

## 12. Structure and reactivity in organic compounds

### 12.1 Saturated compounds

Tetravalent carbon in saturated compounds. Spatial distribution of bonds (e.g.  $\text{CCl}_4$ ,  $\text{CH}_4$ ); treatment in terms of electron-pair repulsion. Unbranched and branched chains. Isomerism of butanes. A treatment of carbocyclic compounds is not intended. Hybridization may be discussed but will not be examined.

### 12.2 Unsaturated compounds

Double and triple bonds. Spatial distribution of bonds in ethene and ethyne. Relationship between electronic structure and unsaturated character. The reactivity and unsaturated character of the double bond to be explained in terms of the overlap of p orbitals, and the  $\pi$  bond.

### 12.3 Aromatic compounds

Special case of benzene. Stability of structure, leading to aromatic character outweighing degree of unsaturation. Electronic structure and spatial distribution of bonds.

Simple reactions of arenes compared with those of alkanes and alkenes (with, e.g.  $\text{Br}_2$  and  $\text{H}_2\text{SO}_4$ ). (See section 12.2.)

### 12.4 Functional groups

Concept of functional groups in any of the above frameworks. The groups  $-\text{Hal}$ ,  $-\text{OH}$ ,  $-\text{CHO}$ ,  $>\text{C}=\text{O}$ ,  $-\text{CO}_2\text{H}$ ,  $-\text{NO}_2$ ,  $-\text{CN}$  and  $-\text{NH}_2$ , should be discussed. Effect of group and hydrocarbon residue on physical properties. Homologous series. Isomerism of unbranched and branched chain (e.g. propyl and butyl) compounds, of disubstituted benzenes and of ethers and alcohols, ketones and aldehydes, acids and esters, etc. Effect of chain branching on physical properties (e.g. boiling points) of the butyl alcohols.

### 12.5 Determination of structure

Calculation of empirical formulae from analytical data. Molecular formula. Structure deduced from reactions of functional groups and physical properties. Use of mass spectrometry and infrared spectroscopy in the elucidation of structures of some simple organic compounds; only a brief treatment is required. Infrared spectroscopy, used solely as a means of identification, stressing the concept of characteristic group/bond frequencies.

## 13. Chemistry of the functional groups

### 13.1 Hydrocarbons

Petroleum distillation and cracking. Petroleum as an industrial source of alkanes, alkenes and aromatic hydrocarbons. Halogenation of alkanes (homolytic mechanism). Addition of halogens and hydrogen halides to alkenes (electrophilic mechanism). Nitration and halogenation of benzene (electrophilic mechanism). Electrophilic and homolytic mechanisms to be discussed without reference to orientation.

### 13.2 Halogeno-compounds

Replacement of halogen by  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{CN}$ . Comparison of rates of hydrolysis of halogenoalkanes and halogenobenzenes. Heterolytic mechanisms of replacement

of halogens in halogenoalkanes. Elimination of hydrogen halides to form alkenes and alkynes. Chloroethene polymerization: applications and homolytic (chain) mechanism.

### 13.3 Hydroxy compounds

Comparison of properties and reactions of hydroxyl group when attached to (a) a saturated carbon framework and (b) an aromatic nucleus. Primary, secondary and tertiary alcohols. Reactions of alcohols: oxidation of primary and secondary alcohols, dehydration, halide formation, ether formation, and the haloform reaction. Influence of electron displacement in increasing acidity of phenols and reactivity of nucleus towards electrophiles. Electrophilic bromination of phenol. Ethane-1,2-diol as example of a dihydric alcohol; formation from ethene (excluding practical details), properties and uses.

The stability of ethers in contrast to hydroxy-compounds.

### 13.4 Introduction to optical isomerism

Asymmetry and optical isomerism: butan-2-ol and 2-hydroxypropanoic acid (lactic acid) as examples. Chemistry (apart from stereochemistry) and preparation of hydroxy-acids are not required.

### 13.5 Carbonyl compounds

Structures and formation of simple aliphatic and aromatic aldehydes and ketones by oxidation of alcohols. Addition reactions with hydrogen,  $\text{HCN}$ ,  $\text{NaHSO}_3$ . Contrast between aldehydes and ketones in oxidation and reduction. Reactions with hydroxylamine and 2,4-dinitrophenylhydrazine. Polarization of carbonyl group and simple mechanistic interpretation of addition reactions. Preparation and purification of derivatives of carbonyl compounds and their use for characterization.

### 13.6 Carboxylic acids and their derivatives

Formation of carboxyl group from nitriles, alcohols and aldehydes and by oxidation of aromatic side chains. Reasons for acidity. Influence of substituents on acidity. Comparative unreactivity of carbonyl function in these compounds. Comparison of dissociation constants of ethanoic and homologous acids, benzoic acid, and mono-, di- and trichloroethanoic acids.

Decarboxylation. Esterification and ester hydrolysis; isotopic evidence for position of fission treated briefly. Polyester formation e.g. from benzene-1,4-dicarboxylic acid (terephthalic acid) and ethane-1,2-diol. Formation and simple reactions of acid chlorides, amides and amino acids. Existence of polyamide structure in proteins. Proteins and their hydrolysis, treated briefly.

The formation of nylon from hexanedioic acid (adipic acid) and hexane-1,6-diamine (hexamethylene diamine). Reduction of the carboxyl function. Ethanedioic acid (oxalic acid). *Cis*- and *trans*-butenedioic acids (maleic and fumaric acids) as an example of geometrical isomerism.

### 13.7 Nitriles

Formation from halides and from amides. Hydrolysis and reduction.

### 13.8 Nitro-compounds

Aromatic nitration in sulphuric acid (see section 13.1).

### 13.9 Amino-compounds

Formation of primary amines from nitro compounds, nitriles and amides. Alkylation of amines. Basicity. Comparison of basicities of ammonia, aliphatic primary amines, aromatic primary amines, and amides. Reactions of aminoethane

**Test on Unit 22 Sulphur**

*Questions 1–4. There are various forms of sulphur. These include:  $\alpha$ -sulphur,  $\beta$ -sulphur, plastic sulphur. Which one of these forms of sulphur:*

- 1 does not consist of an arrangement of  $S_8$  rings?
- 2 is most stable at room temperature?
- 3 is formed when a solution of sulphur evaporates at  $40^\circ\text{C}$ ?
- 4 is formed when molten sulphur is rapidly cooled by pouring into cold water?
- 5 Name the compound formed when a mixture of iron and sulphur is heated.

*Questions 6–10. Complete the following passage:*

Sulphur is extracted from underground deposits by the \_\_\_\_\_ (6) process.  
 A hole is drilled down to the deposits and a pump is placed in the hole. Superheated \_\_\_\_\_ (7) at  $170^\circ\text{C}$  is pumped down the \_\_\_\_\_ (8) tube to \_\_\_\_\_ (9) the sulphur. Hot compressed \_\_\_\_\_ (10) is pumped down the middle pipe to force the sulphur to the surface.

**Test on Unit 23 Sulphides and hydrogen sulphide**

*Questions 1–3. When hydrogen sulphide was passed through a solution of zinc sulphate, a white precipitate was formed.*

- 1 Name the white precipitate.
- 2 Write a symbol equation for this reaction.

*The precipitate was filtered off and added to dilute sulphuric acid.*

- 3 Name the gas evolved.
- 4 The salts produced by replacing hydrogens in hydrogen sulphide are called \_\_\_\_\_.
- 5 Hydrogen sulphide cannot be dried using concentrated sulphuric acid. True or false?
- 6 Natural gas has to have hydrogen sulphide removed before it can be used for combustion. Name the product of combustion of hydrogen sulphide which can lead to pollution problems.

*Questions 7–10. Name the products of the following reactions:*

- 7 Hydrogen sulphide and iron(III) chloride.
- 8 Hydrogen sulphide and chlorine.
- 9 Hydrogen sulphide and lead(II) nitrate.
- 10 Hydrogen sulphide and sulphur dioxide.

**Test on Unit 24 Oxides of sulphur**

*Questions 1–7. Identify the substances A–G in the following statements:*

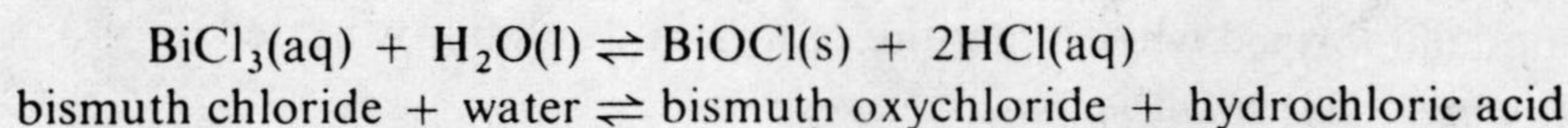
- 1 A colourless gas A, with a pungent odour, when passed through an orange solution of potassium dichromate, turns the solution green, and forms a white precipitate.
- 2–3 A colourless gas B forms needle-shaped crystals when cooled in an ice-salt mixture. When these crystals are added to water, a strongly acidic solution C is produced.
- 4 When the mixture, resulting from the preparation of sulphur dioxide, is poured into water a blue solution D is produced.
- 5 A yellowish solid E is formed when burning magnesium is added to sulphur dioxide.
- 6 A white precipitate F is formed when sulphur dioxide is passed through limewater (calcium hydroxide).
- 7 A colourless gas G turns potassium dichromate green and does not form any precipitate.
- 8 Sulphur dioxide can be prepared by heating copper and dilute sulphuric acid. True or false?
- 9 Sulphur dioxide can act as an oxidising agent or a reducing agent. True or false?
- 10 Sulphur trioxide can be produced by burning sulphur in excess oxygen. True or false?

- (iii) a greater mass of magnesium were used with the same volume of acid,  
 (iv) a larger volume of acid were used with the same mass of magnesium?

(East Anglian Examinations Board—South)

### Test on Unit 21 Reversible reactions and equilibrium

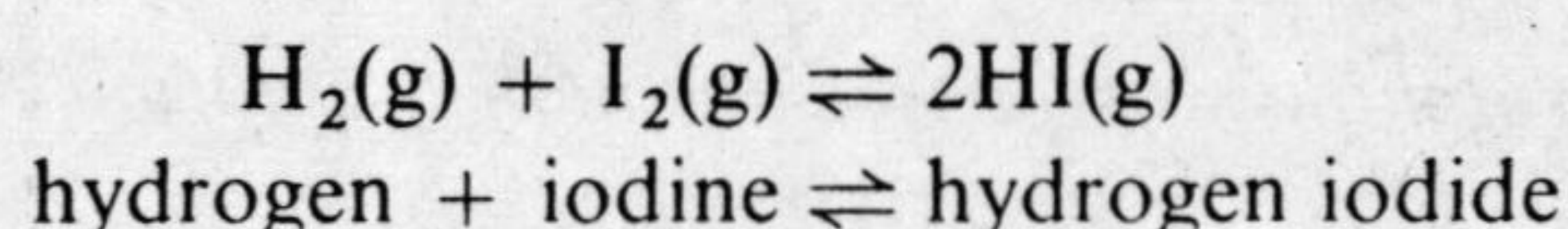
Questions 1–3 refer to the following reaction:



A solution of bismuth chloride was prepared by adding solid bismuth chloride to concentrated hydrochloric acid.

- 1 What would be observed if water was added to this solution of bismuth chloride?
- 2 In which direction (left or right) does the equilibrium move when water is added?
- 3 Suggest one method of reversing this equilibrium change.
- 4 An equilibrium can only be established in reversible reactions. True or false?

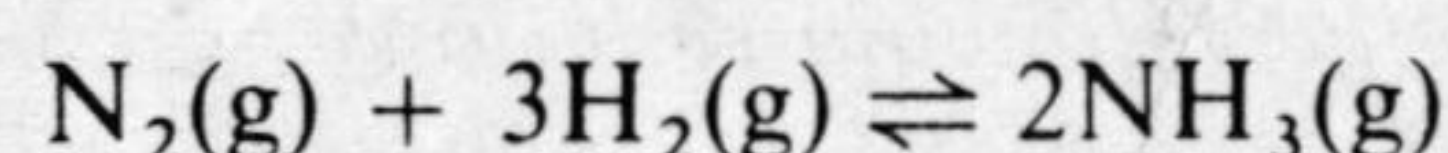
Questions 5–8 refer to the following reaction:



The forward reaction is endothermic. A mixture of hydrogen, iodine and hydrogen iodide were in equilibrium. What would be the effect on the equilibrium (move to left, move to right or unchanged) of each of the following changes?

- 5 Adding additional hydrogen to the equilibrium mixture.
- 6 Removing hydrogen iodide from the equilibrium mixture.
- 7 Increasing the pressure.
- 8 Increasing the temperature.

Questions 9–10 refer to the reaction:



The table below shows the effects of changes of temperature and pressure on the yield of ammonia.

Temp. °C	Percentage of ammonia in equilibrium mixture at pressures of:			
	1 atmosphere	100 atmospheres	200 atmospheres	1000 atmospheres
200	15.3	80.6	85.8	98.3
400	0.44	25.1	36.3	79.8
600	0.05	4.5	8.3	31.4
800	0.01	1.2	2.2	—
1000	0.004	0.4	0.9	—

Using the table:

- 9 What is the effect of increasing pressure on the equilibrium?
- 10 What is the effect of increasing temperature on the equilibrium?