

**UNIVERSITY ENTRANCE EXAMINATION  
CHEMISTRY SYLLABUS**

**1 EQUILIBRIA**

**1.1 Chemical Equilibria**

Reversible reactions, dynamic equilibrium.

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

The following examples are useful: (i) the hydrolysis of simple esters, (ii) the synthesis of ammonia, (iii) acid base behaviour.

- (b) Equilibrium constants, their definition and their calculation in terms of 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 concentration, (ii) because of change in the value of the equilibrium constant, in response to a change in temperature.

Calculations may be set involving substitution into such equation as

$$K = \frac{[C][D]}{[A][B]}$$

**1.2 Ionic Equilibria**

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

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  $\alpha$ , described in terms of actual concentration of hydrogen (or hydroxide) ion relative to maximum theoretical concentration. No treatment of  $pK_a$ ,  $K_b$  or  $pK_b$  is required.

- (b) The ionic product of water  $K_w$ .  
(c) pH.

Calculation of pH from concentration for strong acids and from concentration and  $K_a$  for weak acids using  $K_a = \frac{a^2}{v}$  (derivation not required).

pH indicators: choice of indicators.

- (d) Buffer solutions -- a qualitative treatment only. Reference should be made to the importance of buffers in biological systems.

### 1.3 Chromatography

Treated as an equilibrium between a stationary and a moving phase. Practical experience should be given in paper, thin layer and column chromatography. The use of  $R_f$  values. Gas chromatography, the use of peak heights and retention times. The widespread application of these methods in industry and medicine should be noted.

## 2 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 are either 0, 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 of a reaction using methods that involve drawing tangents to curves. Candidates will not be asked to determine the values of rate constants but should be able to construct a rate equation for a reaction by inspection of suitable data.

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 barrier of lower energy is involved.

## 3 THERMOCHEMISTRY AND CHEMICAL ENERGETICS

- (a) Standard enthalpy changes of reaction, formation, combustion, neutralisation; Hess' law. (Candidates will not be required to write formal definitions in the examination.)

The acquisitive convention should be used, i.e.  $\Delta H$  is negative for an exothermic reaction. No calculations involving  $\Delta U$  will be 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. A treatment of the Born-Haber cycle is not required.

#### 4 THE PERIODIC TABLE: PRINCIPLES OF CHEMICAL PERIODICITY

##### 4.1 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 first ionisation energies, atomic radii, melting points.

Interpretation and explanation of the above trends and gradations in terms of structure and bonding of the elements.

##### 4.2 Periodic Patterns in the Chemical Properties of Compounds

Study in this sub-section should be restricted to the oxides, chlorides and simple hydrides (also excluding 'MgH<sub>2</sub>' and 'AlH<sub>3</sub>') 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.

#### 5 A STUDY OF THE ELEMENTS IN SOME GROUPS OF THE PERIODIC TABLE

##### 5.1 Group II

The elements 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) Thermal decomposition of nitrates, carbonates and hydroxides.

## 5.2 Nitrogen

- (a) The element: reasons for its lack of reactivity.

- (b) Ammonia

- (i) Manufacture by the Haber process.

Reference should be made to 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.

## 5.3 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. Reaction 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 important uses of the halogen compounds.

## 5.4 An Introduction to the Chemistry of some d-block Elements

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, where appropriate, in terms of incomplete d sub-shells.

- (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.

- (ii) Formation of complex ions; exchange of ligands.

No treatment of stability constants is expected.

It is expected that candidates will be familiar with the hexa-aquo ions of the above elements, the corresponding ammine complexes, where appropriate, and the  $[\text{CuCl}_4]^{2-}$  ion.

No treatment of the geometry of complexes is required. No treatment of bonding in complexes is required.

- (iii) Catalytic properties, transition metals and their compounds as important industrial catalysts, e.g. Fe/Fe<sub>2</sub>O<sub>3</sub> in the Haber process, Ni in the hydrogenation of alkenes.

## 6 THE STRUCTURES OF ORGANIC MOLECULES

The shapes of the ethane, ethene and benzene molecules. (A treatment of hybridisation is not required.) Structural isomerism in both aliphatic and aromatic compounds. *Cis-trans* isomerism in alkenes.

## 7 ELECTRONIC EFFECTS AND REACTION TYPES

The nature of the  $\begin{array}{c} \diagup \\ \text{C-H} \\ \diagdown \end{array}$ ,  $\begin{array}{c} \diagup \\ \text{C-Br} \\ \diagdown \end{array}$  and  $>\text{C}=\text{C}<$  and  $>\text{C}=\text{O}$  bonds in terms of electron density distribution.

Heterolytic and homolytic bond fission; nucleophiles and electrophiles. Reaction types; addition, substitution and elimination. Addition and substitution classified as electrophilic, nucleophilic (reference to S<sub>N</sub>1 and S<sub>N</sub>2 mechanisms is not required) or free radical.

## 8 GENERAL ORGANIC CHEMISTRY

Wherever possible the above classification of reaction types should be indicated.

### 8.1 Hydrocarbons

**Alkanes** – Cracking reactions as a means of obtaining alkenes from crude oil fractions. Alkanes as being generally characterised by free radical reactions, e.g. reaction with bromine.

**Alkenes** – Characterised by electrophilic addition, e.g. HBr, Br<sub>2</sub>. Simple tests for alkenes by decolourisation of manganate (VII) ions and of bromine in an inert solvent. Catalytic hydrogenation to alkanes.

**Arenes** – Characterised by electrophilic substitution, e.g. AlBr<sub>3</sub>/Br<sub>2</sub>, conc. HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. (Monosubstitution only).

## 8.2 Halogen derivatives

Halogenoalkanes characterised by nucleophilic substitution, e.g.  $\text{OH}^-$ ,  $\text{CN}^-$ . Difficulties of nucleophilic substitution in halogenoarenes.

## 8.3 Hydroxy compounds

Primary, secondary and tertiary alcohols; reactions with acids, e.g.  $\text{HBr}$ ,  $\text{H}_2\text{SO}_4$  leading to substitution and elimination. Oxidisation of primary and secondary alcohols – resistance to mild oxidation by tertiary alcohols. Ester formation with organic acids and acyl chlorides. Tests for presence of hydroxyl group using sodium or phosphorus pentachloride.

Phenols – acidity compared to alcohols and carboxylic acids; ease of electrophilic substitution compared with benzene.

## 8.4 Carbonyl compounds

(a) Aldehydes; ease of oxidation; reduction to primary alcohol; condensation with hydroxylamine.

(b) Ketones; more resistant to oxidation; reduction to secondary alcohol; condensation with hydroxylamine.

Tests based on alkaline  $\text{Cu}^{2+}$  complex to distinguish between aldehydes and ketones.

## 8.5 Carboxylic acids and derivatives

Carboxylic acids; acidity compared to alcohols and phenols. Formation from alcohols. Reduction to alcohols. Conversion to esters, acyl chlorides.

Acyl chlorides; treated as reactive derivatives carboxylic acids widely used in the synthesis of amides and esters.

## 8.6 Amines

Aliphatic primary amines; basic properties. Reaction with nitrous acid. Formation from nitriles. Aromatic primary amines; their formation from aromatic nitro compounds; basic properties. Reaction with nitrous acid and production azo dyes.

### Reading List

*Physical Chemistry* by H. L. Heys

*Organic Chemistry* by B. J. Stokes

*Physical Chemistry* by G. I. Brown

*Inorganic Chemistry* by C. W. Wood & A. L. Holliday