AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1983

CHEMISTRY—HIGHER LEVEL

TUESDAY, 21 JUNE—AFTERNOON, 2 to 5

Six questions to be answered
All questions carry the same number of marks.

Relative atomic masses: H = 1, C = 12, N = 14, O = 16, Na = 23, P = 31, S = 32, Cl = 35·5, K = 39, Fe = 56, I = 127
Molar volume at S.T.P. = 22·4 litres (dm^3)
Avogadro constant (number) = 6×10^{23}

1. Answer *eleven* of the following items, (*a*), (*b*), (*c*), *etc.* All the items carry the same marks. *Keep your answers short.*

(*a*) Define a mole of a substance.

(*b*) A gas occupies 500 cm^3 at 273 K and $1{\cdot}01 \times 10^5$ Nm^{-2} pressure. What volume will it occupy at 819 K and $2{\cdot}02 \times 10^5$ Nm^{-2} pressure?

(*c*) Give two important items of information about an element that can be obtained using a mass spectrometer.

(*d*) The following reagents, in dilute aqueous solution, are used in qualitative analysis:

$$HCl, \quad HNO_3, \quad BaCl_2, \quad FeSO_4, \quad AgNO_3$$

Which reagent, or combination of reagents, would best give a positive identification test for (i) the sulphate ion, (ii) the bromide ion?

(*e*) For what synthetic polymer is $NH_2(CH_2)_6NH_2$ one of the starting materials?

(*f*) For which of the following processes is the energy change known as the first ionisation energy of an element X?

$$X^+_{(g)} + e^- \rightarrow X_{(g)}, \qquad X_{(g)} + e^- \rightarrow X^-_{(g)}, \qquad X_{(g)} \rightarrow X^+_{(g)} + e^-, \qquad X^-_{(g)} \rightarrow X_{(g)} + e^-$$

(*g*) Define the lattice energy of an ionic compound.

(*h*) Write the equilibrium constant expression for the reaction:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2\,(g)}$$

(*i*) What is the concentration of potassium ions, in moles per litre (mol dm^{-3}), in an aqueous solution containing 6·9 g potassium carbonate (K_2CO_3) per 100 cm^3 of the solution?

(*j*) What is the oxidation number of

(i) iron in K_2FeO_4, (ii) vanadium in VO_2^+?

(*k*) Which one of the following is a conjugate acid/base pair?

NH_4^+ and NH_2^-, $H_2NO_3^+$ and HNO_3, NH_3 and NH_2OH, H_3O^+ and OH^-

(*l*) Write an equation for the reaction which occurs when dilute hydrochloric acid is added to ferrous sulphide (iron (II) sulphide).

(*m*) Indicate what shape you expect each of the following molecules to have on the basis of electron pair repulsion theory:

(i) PCl_3, (ii) CO_2

(*n*) Give the name and structural formula of the product formed when acetylene (ethyne) is passed into warm dilute sulphuric acid containing a little mercuric sulphate (mercury (II) sulphate).

2. Indicate briefly how the study of spectra provided experimental evidence for the existence of energy levels in atoms.

What is meant by (i) the ground state of an atom, (ii) an atomic orbital?

The electronic arrangement of the boron atom in its ground state can be shown as follows (where each arrow signifies an electron):

1s	2s	$2p_x$	$2p_y$	$2p_z$
↑↓	↑↓	↑		

Show in a similar manner the ground state electronic arrangement of an atom of (i) carbon, (ii) nitrogen, (iii) oxygen.

Name and state the rule illustrated by the electronic configurations you have shown.

Write the s,p,d ground state configuration of the atom with atomic number 21, putting the sub-levels in the order in which they are filled.
Describe and explain as fully as you can the shape of the methane molecule.
What is meant by the electronegativity of an element?
Why does methane not have a dipole moment although the electronegativities of carbon and hydrogen are different?

3. **A** is a colourless organic liquid which mixes with water in all proportions. When excess of **A** is heated with concentrated sulphuric acid at 140°C (413 K) a low boiling-point liquid, **B**, is obtained. However, when **A** is heated with excess concentrated sulphuric acid at 170°C (443 K) a gas, **C**, is formed which decolorises bromine-water forming an oily liquid, **D**, as a separate lower layer. When **A** is refluxed for a short time with moderately concentrated sulphuric acid and sodium dichromate the colour of the solution changes from orange to green and a liquid, **E**, of relative molecular mass (molecular weight) 60 can be isolated from the reaction mixture. When **E** is purified it will react with **A** on heating in the presence of a little concentrated sulphuric acid to give a sweet-smelling liquid, **F**.

(i) Identify each of the compounds **A** to **F** by giving its name and its structural formula.

(ii) Write an equation for the reaction of **E** with **A**.

(iii) Write an equation for one other reaction, not mentioned, which **A** might undergo.

(iv) Explain why the colour changes from orange to green while **A** is being converted to **E**.

(v) Mention one everyday use outside the laboratory for each of any *two* of the compounds **A** to **F**.

(vi) Explain why **A** is soluble in water while **D** is insoluble.

4. (*a*) State (i) Dalton's Law of Partial Pressures, (ii) Graham's Law of Diffusion.

100 cm^3 of methane, of relative molecular mass (molecular weight) 16, took 40 seconds to diffuse through a porous plug. Under the same conditions 100 cm^3 of nitrogen dioxide took 80 seconds to diffuse through the same plug.

(i) State two conditions that must be kept constant.

(ii) Calculate the apparent relative molecular mass of nitrogen dioxide.

(iii) Suggest why the value obtained in (ii) differs from the value expected from its formula.

(*b*) The reduction of ferric oxide (iron (III) oxide) by carbon monoxide is shown by the equation

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

(i) What mass of iron could, in theory, be obtained from 1 kg of iron (III) oxide?

(ii) What volume of carbon dioxide, measured at S.T.P., would be formed in (i)?

(iii) How many molecules of carbon dioxide would this volume contain?

(iv) What mass of carbon would have to react to form the carbon monoxide necessary to reduce 1 kg of iron (III) oxide?

5. Define (i) heat of formation, (ii) bond energy, (iii) heat of reaction.
The bond energies of the C—Cl, C—Br and C—I bonds are respectively 338 kJ mol^{-1}, 276 kJ mol^{-1} and 238 kJ mol^{-1}. Why do these values show a decrease?

(i) Calculate the heat change for the reaction

$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$$

given the following bond energies:

$$\begin{aligned} E(H-H) &= 436 \text{ kJ mol}^{-1} \\ E(C-C) &= 348 \text{ kJ mol}^{-1} \\ E(C=C) &= 612 \text{ kJ mol}^{-1} \\ E(C-H) &= 412 \text{ kJ mol}^{-1} \end{aligned}$$

(ii) Calculate again the heat change for the reaction

$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$$

using the following data:

$$\begin{aligned} C_{(s)} + O_{2(g)} &\rightarrow CO_{2(g)} & \Delta H &= -394 \text{ kJ mol}^{-1} \\ H_{2(g)} + \tfrac{1}{2}O_{2(g)} &\rightarrow H_2O_{(l)} & \Delta H &= -286 \text{ kJ mol}^{-1} \\ C_2H_{6(g)} + 3\tfrac{1}{2}O_{2(g)} &\rightarrow 2CO_{2(g)} + 3H_2O_{(l)} & \Delta H &= -1542 \text{ kJ mol}^{-1} \\ 2C_{(s)} + 2H_{2(g)} &\rightarrow C_2H_{4(g)} & \Delta H &= +54 \text{ kJ mol}^{-1} \end{aligned}$$

Suggest one reason for the difference in the values obtained in (i) and (ii).

6. (*a*) 7·84 g of ferrous ammonium sulphate (ammonium iron (II) sulphate), $FeSO_4(NH_4)_2SO_4 . xH_2O$, were dissolved in dilute sulphuric acid and the solution made up to 250 cm^3 with distilled water.
25 cm^3 of this solution required 20 cm^3 of 0·02 moles per litre (mol dm^{-3}) potassium permanganate (potassium manganate (VII)) for complete reaction according to the equation

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

(i) Why was dilute sulphuric acid used in making up the iron (II) salt solution?

(ii) Find the concentration, in moles per litre (mol dm^{-3}), of Fe^{2+} ions in the solution.

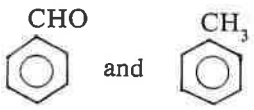
(iii) Find the value of x.

(iv) Show clearly any changes in oxidation number which have occurred in the reaction.

(*b*) Sodium is obtained by the electrolysis of molten sodium chloride using an iron cathode and a carbon anode.
Show the electron changes occurring (i) at the cathode, (ii) at the anode, during this process.
Explain why iron is not used in both electrodes.
If 5 faradays of electricity were passed through molten sodium chloride (i) what mass of sodium, (ii) what volume of chlorine gas, measured at S.T.P., would be obtained?

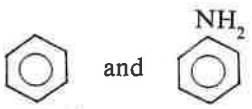
7. Write the structural formula for (i) methylamine, (ii) benzoic acid, (iii) phenol.
Show by equations how phenol reacts with (i) sodium hydroxide solution, (ii) bromine water.
Name the organic product in each case.
Explain why the —OH group in phenol is more acidic than the —OH group in ethanol.

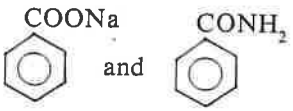
Describe one chemical reaction (other than the use of indicators) which could be used to distinguish between the two compounds in each of any *three* of the following pairs.
State clearly in each case which member of the pair is being identified by the reaction chosen.
Your description should include reagents and conditions and either an equation or a clear statement of the change occurring.

(i) 

(ii) $CH_3CH_2CH_3$ and $CH_3CH = CH_2$

(iii) HCOOH and CH_3COOH

(iv) 

(v) 

8. Distinguish between an ionic and a covalent bond. Give one example of each type and in each case show the electronic arrangement.
Explain why reactions involving ions in solution are usually extremely fast while reactions involving covalent substances often take much longer.
Explain as fully as you can the factor or factors affecting the reaction rate in each of the following:

(i) Limestone chips take much longer than the same mass of powdered limestone to dissolve in excess 2 M (bench) hydrochloric acid.

(ii) 1 g of magnesium ribbon will dissolve faster in 50 cm^3 of 2 M hydrochloric acid than in 100 cm^3 of 1 M hydrochloric acid.

(iii) Sulphur dioxide on heating with oxygen at 450°C (723 K) gives very little sulphur trioxide but in the presence of vanadium pentoxide at this temperature there is a 98% conversion.

(iv) When aluminium powder is added to excess 2 M (bench) sodium hydroxide a slow evolution of hydrogen is observed but after a few minutes the reaction becomes very vigorous and water vapour as well as hydrogen is given off.

(v) When a mixture of methane and chlorine is exposed to diffused sunlight a slow reaction occurs but in direct sunlight the reaction becomes explosive.

9. Name one example of each of the following (i) a strong acid, (ii) a weak acid, (iii) a salt which does not hydrolyse in water, (iv) a salt which hydrolyses in water.
Define the pH of a solution.

(i) Calculate the pH of an aqueous solution of acetic (ethanoic) acid of concentration 0·08 moles per litre (mol dm^{-3}) given that the dissociation constant for acetic (ethanoic) acid is $1{\cdot}8 \times 10^{-5}$.

(ii) Calculate the pH of an aqueous solution of sodium hydroxide of concentration 5×10^{-5} moles per litre (mol dm^{-3}).

(iii) Explain clearly by reference to the equilibria which are present in an aqueous solution of sodium acetate (ethanoate) why the pH of a solution of this salt differs from 7.

(iv) When a solution of acetic (ethanoic) acid is being titrated against a solution of sodium hydroxide, the pH at the end-point changes suddenly from about 6·8 to 9·7. Which one of the following indicators, which change colour in the pH ranges shown, would be most suitable for this titration? Explain your reasoning.

Indicator	pH range
Methyl Orange	3·0 — 4·5
Methyl Red	4·2 — 6·4
Bromothymol Blue	6·0 — 7·4
Phenolphthalein	8·2 — 9·8

10. Answer any *two* of the following.

(*a*) Explain (i) structural isomerism, (ii) stereoisomerism. Give the structural formulae of two structural isomers of molecular formula C_2H_6O.
Show by using structural formulae how stereoisomerism exists in dicarboxylic acids of molecular formula $C_4H_4O_4$. Name the type of stereoisomerism shown and explain how it arises.

(*b*) 1·55 g of white phosphorus lowered the freezing-point of 200 g benzene by 0·32 K. If the freezing-point constant for benzene is 5·12 K mol^{-1} kg^{-1} calculate the relative molecular mass (molecular weight) of white phosphorus in benzene.
What formula would you suggest for the white phosphorus molecule?
What mass of hydrogen iodide would have to be dissolved in 200 g benzene to give the same lowering of freezing-point (0·32 K)?

(*c*) The following are the formulae of three compounds of sodium:

$$NaCl, \quad NaH, \quad Na_2O$$

(i) What type of oxide is Na_2O?

(ii) Show the electronic structure of each negative ion present in the compounds.

(iii) Explain, using equations where possible, how each of the three compounds would behave when placed in water.

(iv) Give the name and formula of one other oxide of sodium.

(*d*) Discuss, with suitable explanations, how the following properties vary across a typical period (e.g. Na to Ar) of the periodic table:

(i) atomic radius,

(ii) first ionisation energy,

(iii) basic and/or acidic character of hydroxy compounds.