LEAVING CERTIFICATE EXAMINATION, 1981

C1

CHEMISTRY—HIGHER LEVEL

MONDAY, 22 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, Al = 27, S = 32, Cl = 35·5, K = 39, Mn = 55, Fe = 56
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) Select (i) a covalent crystal, (ii) an ionic crystal from the following:
diamond, potassium sulphate, naphthalene, sulphur, sodium.

(b) What is meant by a metallic bond?

(c) What does n represent in the general gas equation PV = nRT?

(d) The radioactive isotope $^{32}_{15}P$ decays by emission of a β–particle (electron) from the nucleus to form the isotope $^{Y}_{16}X$.
(i) What is the element represented by the symbol X?
(ii) What is the value of Y? (Refer to Mathematics Tables p.44)

(e) If 42·5 g of sodium nitrate are dissolved in 891 g water, what is the mole fraction of nitrate ions in the solution?

(f) When dilute hydrochloric acid was added to a sodium salt a gas was evolved which turned limewater milky. A solution of the salt formed a precipitate with magnesium sulphate solution. Which of the following could represent the formula of the salt:
$NaBr$, $NaHCO_3$, $NaNO_3$, Na_2CO_3, Na_2SO_4?

(g) Name the compounds, (i) CH_3COONH_4, (ii) CH_3CONH_2.

(h) Define the lattice energy of an ionic compound.

(i) Which one of the following would be most likely to act as a base in aqueous solution:
NH_4^+, C_6H_5OH, $(CH_3)_2NH$, CH_3COOH, CH_3OH?

(j) State Hund's Rule.

(k) Write down two repeating units of the polymer that the ethylene (ethene) derivative, $CH_2=CHCl$, could form.

(l) Which one of the following has a shape which differs from the shape of the other three:
NH_3, BF_3, PCl_3, H_3O^+ ? Justify your choice.

(m) A mixture of equal volumes of air and hydrogen in a vessel exerts a pressure of $10^5\ Nm^{-2}$. What is the partial pressure of oxygen in the mixture given that oxygen constitutes 1/5 of the volume of air?

(n) Why does an ammonium acetate (ethanoate) aqueous solution have a pH of about 7?

2. *(a)* (i) Define the term, isotopes.
(ii) State the number of protons and the number of neutrons in the isotopes of copper, $^{63}_{29}Cu$ and $^{65}_{29}Cu$.
(iii) It was found using a mass spectrometer that copper consists of 70% $^{63}_{29}Cu$ and 30% $^{65}_{29}Cu$. Calculate the relative atomic mass of copper.
(iv) For many years the standard for atomic masses was the oxygen atom which was taken as 16 units. Why was the use of this standard discontinued?

(b) (i) Write the s, p, d configuration for *(a)* iron, *(b)* copper.
(ii) What is meant by the oxidation number of an element?
What is the oxidation number of *(a)* iron in $K_3[Fe(CN)_6]$, *(b)* copper in $[CuCl_2]^-$?
(iii) Using oxidation numbers show that either one of the following reactions is an oxidation-reduction reaction.

$$Fe^{2+} + H^+ + HNO_3 \longrightarrow Fe^{3+} + NO_2 + H_2O.$$
$$Cu_2O + 2H_3O^+ \longrightarrow Cu^{2+} + Cu + 3H_2O.$$

3. *(a)* What is a hybrid orbital?
Describe the shape of the acetylene (ethyne) molecule and discuss the bonding in terms of hybrid orbitals.

(b) Outline the spectroscopic evidence available for the existence of atomic energy levels.

(c) What is meant by the first ionisation energy of an element?

Explain (i) the decrease in first ionisation energies down a group of the Periodic Table e.g. Be to Ba,
(ii) the increase in electronegativity values across a row of the Periodic Table e.g. Li to F.
(Refer to Mathematics Tables p.45 and p.46)

4. Explain each of the following terms and illustrate your answers by one suitable example in each case, using structural formulae for the compounds mentioned:
(i) a saturated hydrocarbon, (ii) an unsaturated hydrocarbon, (iii) a carbonyl group, (iv) an ester.
In each case mention one reaction which is typical of that type of compound, giving an equation for each reaction.

Name the reagents and mention any essential conditions (temperature, catalyst etc.) required at each stage to bring about any *two* of the following conversions. Each conversion requires two stages.

(i) ethanol to ethylene dibromide (1,2–dibromoethane),

(ii) benzene to aniline (phenylamine),

(iii) isopropyl alcohol (propan–2–ol) to acetone (propanone) phenylhydrazone.

5. Define (i) heat of formation of a compound,
(ii) heat change for a reaction.

Explain in general terms why most chemical reactions involve a heat change.
If the heats of formation of $CH_{4(g)}$, $H_2O_{(g)}$ and $CO_{(g)}$ are –74 kJ mol^{-1}, –242 kJ mol^{-1} and –111 kJ mol^{-1} respectively find the heat change for the reaction,

$$CH_{4(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3H_{2(g)}$$

Explain the significance of the sign of the ΔH value found.
The above reaction is actually reversible and represents the first stage in the industrial preparation of hydrogen from methane. Explain, giving your reasoning, how you would expect the yield of hydrogen to be affected by

(i) high temperature,

(ii) high pressure,

(iii) the use of a catalyst,

6. Explain the following observations as fully as you can, giving equations for any chemical reactions involved:

(i) Sodium monoxide dissolves in water to give a solution which turns litmus paper blue but phosphorus pentoxide (phosphorus (v) oxide) dissolves in water to give a solution which turns litmus paper red.

(ii) Sodium chloride is a solid with a high melting-point but carbon tetrachloride (tetrachloromethane) is a liquid at room temperature.

(iii) Silane (silicon tetrahydride) reacts with water to give a white precipitate but lithium hydride reacts with water giving a clear solution.

(iv) Ammonium chloride gives an acidic gas when concentrated sulphuric acid is added but an alkaline gas is obtained when sodium hydroxide solution is added.

(v) Magnesium oxide and aluminium oxide both dissolve in hydrochloric acid solution. Aluminium oxide will dissolve but magnesium oxide will not dissolve in sodium hydroxide solution.

7. *(a)* 9·6 g of pure iron pyrites were completely oxidised according to the equation

$$4\,FeS_{2(s)} + 11O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

(i) What mass of iron (III) oxide is obtained?

(ii) What volume of sulphur dioxide (sulphur (IV) oxide), measured at S.T.P., is obtained?

(iii) How many molecules of sulphur dioxide does this volume contain?

Sulphur dioxide can be converted to sulphuric acid according to the scheme

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

(iv) How many kg of pure sulphuric acid could be obtained from 180 kg of pure iron pyrites if the process were completely efficient?

(b) The oxidation of sulphur dioxide to sulphur trioxide (sulphur (VI) oxide) in industry proceeds at a satisfactory rate when it is passed with air over a catalyst of vanadium pentoxide (vanadium (V) oxide) at a pressure of one atmosphere and at a temperature of 720 K. Explain briefly how

(i) the presence of the catalyst, (ii) the relatively high temperature contribute to a satisfactory reaction rate.

8. Some benzoic acid crystals were prepared as follows:
About 5 g toluene (methylbenzene) were placed in a flask. 50 cm³ water, 3·95 g potassium permanganate (potassium manganate (VII)) crystals and 5 cm³ of a 2 M solution of potassium hydroxide were added along with some silica granules. The mixture was refluxed for three hours until all the potassium permanganate had reacted.
On cooling the manganese dioxide (manganese (IV) oxide) formed was filtered and the excess toluene in the filtrate was separated from the aqueous layer using a separating funnel. The colourless aqueous solution was acidified with dilute hydrochloric acid. The white crystals of benzoic acid were recrystallised from boiling water and dried between filter papers. 1·22 g benzoic acid was obtained and it was found to melt sharply at the correct melting point (395K). The overall reaction may be represented

$$2MnO_4^- + C_6H_5CH_3 \longrightarrow 2MnO_2 + C_6H_5COOH + 2OH^-$$

(i) What type of reaction did the toluene undergo?

(ii) How many moles of $KMnO_4$ does 3·95 g represent?

(iii) Why was it possible to use a separating funnel to get rid of the excess toluene?

(iv) How do you know that all the potassium permanganate had reacted?

(v) If excess potassium permanganate had remained state one method by which it could be removed.

(vi) Show, by an equation or otherwise, why it was necessary to acidify the solution to obtain crystals of benzoic acid.

(vii) If the crystals had been found to melt gradually over the range 370 K to 375 K what would you have concluded?

(viii) Calculate the yield of benzoic acid as a percentage of the theoretical yield.

9. A potassium salt of oxalic (ethanedioic) acid has the formula, $KH_x(C_2O_4)_y.2H_2O$.
To 25 cm³ of a solution of this salt in water 20 cm³ of a 1M solution of sulphuric acid was added and the solution was heated to about 350 K. It required 30 cm³ of a 0·02 M solution of potassium permanganate (manganate (VII)) for complete oxidation of the oxalate according to the equation,

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O.$$

(i) Why was the sulphuric acid added?

(ii) Calculate the molarity of the solution with respect to $C_2O_4^{2-}$.

Another 25 cm³ of the salt solution required 22·5 cm³ of a 0·1M solution of sodium hydroxide for complete neutralisation according to the equation

$$H^+ + OH^- \longrightarrow H_2O.$$

Phenolphthalein was used as indicator.

(iii) Explain why methyl orange would not have been a suitable indicator.

(iv) Calculate the molarity of the solution with respect to H^+ ions available to react with the base.

(v) Calculate the ratio of moles of available H^+ to moles of $C_2O_4^{2-}$ from the results obtained in (iv) and (ii).

(vi) Hence, given that the relative molecular mass of the potassium salt is 254, deduce the values of x and y in the formula $KH_x(C_2O_4)_y.2H_2O$.

10. Answer any *two* of the following: c4

(a) Show the structures of maleic and fumaric (butenedioic) acids. Name the type of isomerism they illustrate and explain why it arises.
Name the type of stereoisomerism shown by lactic (2–hydroxypropanoic) acid and explain how it arises.
Write down the formulae of the three compounds in the following list which might show stereoisomerism and, in each case, name the type of stereoisomerism expected:

$ClCH = CHCl$, $CH_3CH_2CH_2CH_3$, $(CH_3)_2\,C = CH_2$,

$CH_3CH(OH)C \equiv N$, $CF_3CHClBr$, CF_2ClCH_2Cl.

(b) Define the terms, (i) electrolysis, (ii) electrolyte.
Show clearly, indicating the electron changes involved, the reactions taking place (i) at the cathode, (ii) at the anode, during the electrolysis of molten calcium chloride. Where does oxidation occur in the electrolysis?
How many moles of each of the products are formed when 10 Faradays of electricity are passed through the molten calcium chloride? Name a suitable anode material and give a reason for your choice.

(c) What is a Brønsted acid?
What is the conjugate acid of each of the following bases, (i) $HCOO^-$, (ii) PO_4^{3-} ?
The first dissociation of H_3PO_4 is represented as

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$$

Write (i) the equilibrium constant expression for this dissociation,

(ii) the equation for the second dissociation of H_3PO_4.

Given that the acidity of the H_3PO_4 solution is due mostly to its first dissociation and given also that $K_a = 8 \times 10^{-3}$ for this dissociation, calculate the pH of a 0·01 M aqueous solution of H_3PO_4.
[Assume that the concentration of the acid (·01 M) remains unchanged as a result of the dissociation].

(d) What is Raoult's Law?
State one limitation in each case in respect of (i) the type of compound that obeys the law, (ii) its use in the determination of the relative molecular mass (molecular weight) of a compound.
The vapour pressure of water at 349 K is 30 cm. A solution containing 180 g of water and 36 g of glucose has a vapour pressure of 29·4 cm at the same temperature. What is the relative molecular mass of the glucose?