## LEAVING CERTIFICATE EXAMINATION, 1987

### CHEMISTRY—HIGHER LEVEL

**Question 1** and **five** other questions must be answered. These five *must* include question 2 or question 3 but may include *both* question 2 and question 3.
All the questions carry the same number of marks.

Relative atomic masses: H = 1, C = 12, N = 14, O = 16, Na = 23, S = 32, Ca = 40, Cu = 63·5
Avogadro constant = $6 \times 10^{23}$ $mol^{-1}$
Molar volume at S.T.P. = 22·4 $dm^3$
1 Faraday = 96,500 C

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

(*a*) How many (i) neutrons, (ii) electrons, are there in the ion $^{58}_{28}Ni^{2+}$ ?

(*b*) Identify the species represented by each of the following structures.
(i) $[1s^22s^22p^63s^23p^6]^{2-}$ (ii) $1s^22s^22p^63s^23p^63d^34s^2$

(*c*) How many *atoms* are there in 840 $cm^3$ of ethane at S.T.P.?

(*d*) What particles occupy the latice points in a crystal of iodine? Name the forces that bind the crystal.

(*e*) What is the systematic (IUPAC) name for $CH_3CCl_2CH_2COOH$?

(*f*) How would you show the presence of the thiosulphate ion in aqueous solution?

(*g*) On reduction, 1·99 g of a sulphide of copper yielded 1·59 g of the pure metal. What is the empirical formula of the sulphide?

(*h*) State briefly the contribution of Newlands to the classification of the elements.

(*i*) Define bond energy.

(*j*) Give any *two* advantages of the cracking of hydrocarbons.

(*k*) Using a mass spectrometer, it was found that bromine consisted of 54·5% $^{79}_{35}Br$ and 45·5% $^{81}_{35}Br$. Estimate the relative atomic mass of bromine.

(*l*) What names are normally given to the energy changes represented by (i) $X \rightarrow X^+ + e^-$, (ii) $X^+ \rightarrow X^{2+} + e^-$?

(*m*) The melting point of benzoic acid is 395 K. After preparing a sample in the laboratory the acid was found to melt in the range 388—392 K. Suggest a reason for this.

(*n*) Draw a simple sketch graph to indicate the relationship between T and V/T for a definite mass of an ideal gas at constant pressure.

(*o*) Balance the equation: $SO_4^{2-} + I^- + H^+ \rightarrow SO_2 + I_2 + H_2O$

(11 × 6)

**2.** A mass of 3·80 g of powdered limestone (impure calcium carbonate) was weighed on a clock-glass and then dissolved in 100 $cm^3$ of a 1·0 mol $dm^{-3}$ solution of hydrochloric acid in a beaker. The solution was transferred to a 250 $cm^3$ volumetric flask and made up carefully to the mark with deionised water. A burette was filled with this solution and its concentration was determined by titration with 25 $cm^3$ volumes of a 0·090 mol $dm^{-3}$ solution of sodium hydroxide (previously standardised). A pipette was used to measure the sodium hydroxide solution. Four titrations were carried out and the burette readings were as shown.

| Titration | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| 1st reading ($cm^3$) | 0 | 23·1 | 0 | 22·6 |
| 2nd reading ($cm^3$) | 23·1 | 45·6 | 22·6 | 45·0 |

The reactions may be represented:

$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$; $HCl + NaOH \rightarrow NaCl + H_2O$

(i) How would you have ensured that all of the powdered limestone had been transferred from the clock glass to the beaker? (6)

(ii) What, if anything, would you have noticed as the powder dissolved? (6)

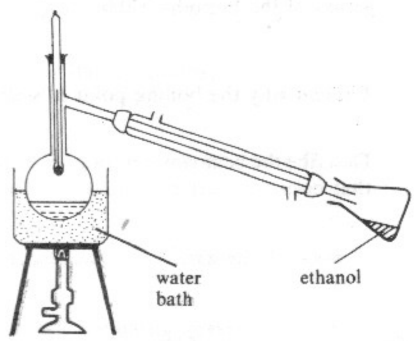
(iii) Why was the solution diluted to 250 $cm^3$ before the titrations were carried out? In many parts of Ireland, dilution with tap water would have caused a slight inaccuracy in the result of the experiment. What is the reason for this? (9)

(iv) After correctly filling the pipette with the sodium hydroxide solution, how would you have ensured that the volume delivered to the titration flask was exactly 25 $cm^3$? (9)

(v) What mean titration reading should be taken? Use this reading to calculate the concentration of the hydrogen chloride solution in the volumetric flask in mol $dm^{-3}$. How many moles of hydrogen chloride were used up in the reaction with the powdered limestone? (21)

(vi) How many (*a*) moles, (*b*) grams, of calcium carbonate were present in the 3·80 g of powdered limestone? What was the percentage of calcium carbonate in the limestone sample? (15)

3. To 6·6 $cm^3$ of ethyl ethanoate (density = 0·9 g $cm^{-3}$), 30 $cm^3$ of 20% (w/v) sodium hydroxide solution were added and the mixture was boiled in a suitable apparatus for about 45 minutes. The mixture was then distilled using the apparatus shown in the diagram. The solution remaining in the flask was cooled and excess dilute sulphuric acid was added in order to liberate the ethanoic acid. The ethanoic acid was recovered by further distillation but a different method of heating was used on this occasion.




The reactions may be represented:

(*a*) $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

(*b*) $2CH_3COONa + H_2SO_4 \rightarrow 2CH_3COOH + Na_2SO_4$

(i) What term is used to describe the reaction between ethyl ethanoate and sodium hydroxide? (6)

(ii) Draw a labelled diagram of a suitable apparatus for boiling the reaction mixture. (9)

(iii) At times the boiling became uneven, causing the whole apparatus to shake. What term is used to describe what was happening? How could it have been prevented? (6)

(iv) Explain why the ethanol obtained as a result of the first distillation was not pure. (6)

(v) Why was the water bath not used for the second distillation? What method of heating could have been used in its place? (9)

(vi) What is meant by a 20% (w/v) solution of sodium hydroxide? How many (*a*) grams, (*b*) moles, of sodium hydroxide are contained in 30 $cm^3$ of this solution? Show clearly that the sodium hydroxide is in excess in the reaction with ethyl ethanoate. (15)

(vii) Following further purification, 3·1 g of pure ethanoic acid were obtained. Calculate the percentage yield. (15)

4. The Haber—Bosch Process for the manufacture of ammonia is an example of artificial nitrogen fixation. The main reaction is

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -94 \text{ kJ}$$

(i) What is meant by nitrogen fixation? Why is it important? (12)

(ii) Give *one* source of the nitrogen and *one* source of the hydrogen used in the production of ammonia. (6)

(iii) Discuss the factors, chemical and economic, involved in the choice of a suitable temperature for the reaction. (12)

(iv) The catalytic oxidation of ammonia to nitrogen monoxide (NO) and water is the first stage in the industrial production of nitric acid. Write a balanced equation for this reaction and name the catalyst used. What further steps are necessary to convert the nitrogen monoxide to nitric acid? (18)

(v) Ammonia and nitric acid combine to give ammonium nitrate. How would you show the presence of the nitrate ion in a solution of this salt?
Calculate the N value of an NPK compound fertiliser containing 20% by mass of ammonium nitrate and no other nitrogenous material.
Why is the widespread use of fertilisers, especially those containing nitrogen, causing increased concern in recent years? (18)

**5.** Define (i) ionic bond, (ii) polar bond, (iii) hydrogen bond. Give one example of (i) and (ii). (15)

What is meant by electronegativity? How are the electronegativities of elements related in general, to their positions in the Periodic Table? Give reasons in support of your answer. (12)

Explain (i) the strong dissociation of hydrogen chloride in aqueous solution;
(ii) the weakly acidic nature of hydrogen fluoride.

(Refer to Mathematics Tables p. 46). (15)

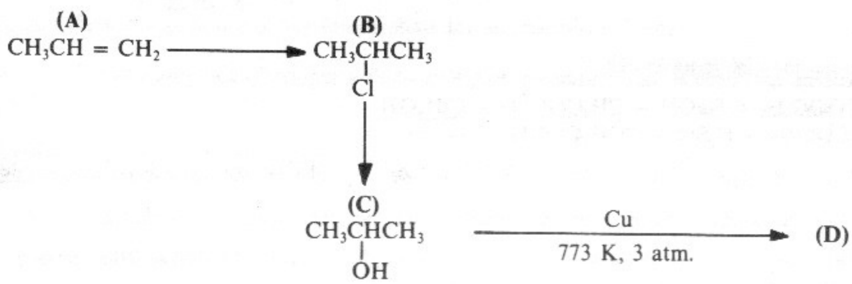
The table shows boiling points in degrees kelvin (K) of the chlorides of three elements from the third period of the Periodic Table.

| Empirical formula | NaCl | $AlCl_3$ | $PCl_3$ |
|---|---|---|---|
| Boiling point (K) | 1790 | 453 | 349 |

Explain why the boiling point of sodium chloride is so much higher than those of the other two chlorides. (9)

Describe the behaviour in water of each of the three chlorides, giving balanced equations for any chemical reactions that occur. (15)

**6.**




(i) Name **A, B, C.** (9)

(ii) What reagent is used (*a*) to convert **A** to **B**, (*b*) to convert **B** to **C**? In the case of (*a*) *or* (*b*) write a balanced equation for this reaction. (12)

(iii) **C** is a secondary alcohol. Explain what this means and give the name and structural formula of the corresponding primary alcohol. (12)

(iv) Identify **D** and describe briefly how it could be converted back to **C**. Write the structural formula of another named member of the homologous series to which compound **D** belongs. (15)

(v) Which of the three compounds **A, B, C** would you expect to undergo addition polymerisation? Give a reason for your choice and outline a possible mechanism for the polymerisation reaction. (18)

**7.** (*a*) Define (i) acid, (ii) base, (iii) conjungate pair, in terms of the Bronsted-Lowry Theory. (9)
In each of the following, indicate the acids, bases and conjugate pairs.

$$HSO_4^- + OH^- \rightleftharpoons SO_4^{2-} + H_2O$$

$$CH_3NH_2 + HClO_4 \rightleftharpoons CH_3NH_3^+ + ClO_4^-$$ (12)

(*b*) The dissociation of methanoic acid in dilute aqueous solution is represented

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

(i) Write the expression for the acid dissociation constant ($K_a$). (6)

(ii) If methanoic acid is 1·3% dissociated in a 1·0 mol dm$^{-3}$ aqueous solution, show clearly that the approximate value of the acid dissociation constant is $1{\cdot}7 \times 10^{-4}$. (6)

(iii) Calculate the pH of the 1·0 mol dm$^{-3}$ solution of methanoic acid. (9)

(*c*) To determine the B.O.D. (Biochemical Oxygen Demand) of lake water, a sample was well aerated by shaking it thoroughly and then divided into two portions. One was immediately analysed for dissolved oxygen by the Winkler method; the other was kept for a period of time under certain conditions and then analysed for dissolved oxygen by the same method.

(i) Why was the sample well aerated? (6)

(ii) In carrying out the analyses, the addition of two reagents to the water resulted in the formation of a brown precipitate. What were the two reagents? (6)

(iii) For how long and under what conditions was the second portion kept before analysis? How was the B.O.D. calculated from the results of the two analyses? (12)

**8.** State (*a*) Dalton's Law of Partial Pressures, (*b*) Avogadro's Law. (12)

Nitrogen dioxide may be obtained in the laboratory by heating lead(II) nitrate and passing the mixture of gases produced through a U-tube immersed in a freezing mixture. The other products are lead(II) oxide and oxygen. Write a balanced equation for the reaction. What was the function of the freezing mixture? (9)

Dinitrogen tetroxide dissociates on heating into nitrogen dioxide. The equation for the reaction is

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

(i) The average relative molecular mass of the above equilibrium mixture was 72. Given that for every 10 molecules of nitrogen dioxide in the equilibrium mixture there were $X$ molecules of dinitrogen tetroxide, find the value of $X$. (12)

(ii) Would the value of $X$ in (i) increase, decrease or remain the same if the total pressure was increased? Explain your answer. (9)

(iii) If the total pressure of the equilibrium mixture was 1·15 atmospheres, calculate the partial pressures of the two gases. (12)

(iv) Write the equilibrium constant expression ($K_p$) for the reaction, and calculate the value of $K_p$ correct to two places of decimals. (12)

**9.** (*a*) Of the three d-block metals iron, copper and zinc, only copper and iron are classed as transition elements.

(i) Explain the underlined terms. Why is zinc not considered to be a transition element? (15)

(ii) Outline the main steps involved in the corrosion of iron. (9)

(iii) Use your knowledge of energy levels to explain briefly why metals like sodium and copper give characteristic colours to the bunsen flame. (9)

(*b*) Sodium is produced industrially by electrolysis of molten sodium chloride to which some calcium chloride has been added. Draw a labelled diagram of the cell in which the electrolysis is carried out and write equations for the reactions taking place at the anode and cathode. What is the reason for adding the calcium chloride? (21)

How long, to the nearest second, would it take to produce 1 kg of sodium, if the current used was $3 \times 10^4$ amperes? (12)

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

(*a*) Define (i) reaction rate, (ii) activation energy. (12)

Draw an energy profile diagram for an endothermic reaction. Indicate clearly on the diagram the likely effect of a catalyst. (12)

It can be shown from the kinetic theory of gases that a 10 K rise in temperature increases the number of collisions between molecules by only about 2% while the rate of the reaction is doubled or even trebled.

(i) Account for the slight increase in the number of collisions.

(ii) Suggest a reason for the much greater increase in the reaction rate. (9)

(*b*) Define heat of neutralisation. (6)

When 50 $cm^3$ of a 1·0 mol $dm^{-3}$ hydrochloric acid solution were added to 50 $cm^3$ of a potassium hydroxide solution in a plastic container of negligible heat capacity, the acid was completely neutralised and the temperature rose. Calculate the rise in temperature, given that the density and specific heat capacity of the resulting solution (assumed equal to those of water) are 1·0 g $cm^{-3}$ and 4·2 kJ $kg^{-1}$ $K^{-1}$ respectively, and that the heat of neutralisation of hydrochloric acid by potassium hydroxide is $\triangle H = -57{\cdot}2$ kJ $mol^{-1}$. (15)

What change, if any, would you expect in the temperature rise if nitric acid were used in place of hydrochloric acid in the above experiment? Explain your answer. (12)

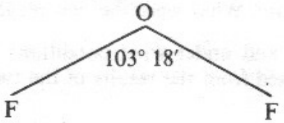
(*c*) Define oxidation number. (6)

What is the oxidation number of oxygen in each of the following species?

(i) $O_3$ (ii) $OF_2$ (iii) $Cl_2O$ (iv) $O_2^{2-}$ (12)

Though (ii) and (iii) above both consist of a halogen combined with oxygen, it is usual to write their formulae with the oxygen first in (ii) and the halogen first in (iii) as shown. Suggest a reason for this. (6)

The diagram shows the $OF_2$ molecule. Use the electron pair repulsion theory to explain the shape and to account for a bond angle of about this value.




(9)

(*d*) When $2{\cdot}5 \times 10^{-3}$ moles of an aromatic hydrocarbon were burned completely in 1 $dm^3$ of oxygen, 392 $cm^3$ of carbon dioxide were produced and the volume of oxygen remaining after the reaction was 496 $cm^3$. (All volumes are at S.T.P.)

(i) Give a chemical test which shows that benzene does not contain double bonds like an alkene. (6)

(ii) How many moles of carbon dioxide were produced and how many moles of oxygen were consumed in the reaction? (12)

(iii) Deduce the molecular formula of the hydrocarbon showing clearly the steps taken in the deduction. (9)

(iv) Identify the compound and write its structural formula. (6)