LEAVING CERTIFICATE EXAMINATION, 1985

CHEMISTRY–HIGHER LEVEL

TUESDAY, 25 JUNE–AFTERNOON, 2 to 5

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, Ne = 20, Na = 23, Mg = 24, S = 32, Ca = 40, Cr = 52
Avogadro constant = 6×10^{23} mol^{-1}
Molar volume at S.T.P. = 22·4 dm^3

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

   (*a*) How many *atoms* of hydrogen would be contained in 280cm^3 of hydrogen gas at S.T.P.?
   (*b*) State Avogadro's Law.
   (*c*) Describe the shape of each of the following species as linear, trigonal (planar) or tetrahedral:

       (i) CHCl$_3$, (ii) HCHO.

   (*d*) How would you distinguish between carbonate and hydrogencarbonate ions in aqueous solution?
   (*e*) Which of the following gases would diffuse fastest through the same porous plug at the same temperature and pressure:

   $$C_2H_2, \quad N_2O, \quad O_2, \quad CO_2, \quad Ne ?$$

   (*f*) What mass of magnesium oxide would be obtained from the thermal decomposition of 21g magnesium carbonate?
   (*g*) Define the activation energy of a reaction.
   (*h*) Name the two main products formed when water is added to sodium peroxide at room temperature.
   (*i*) Complete and balance the equation,

   $$FeCl_2 + Cl_2 \rightarrow$$

   (*j*) Why does methyl ethanoate have a much lower boiling point than butan-1-ol which has the same relative molecular mass?
   (*k*) Write the structural formula for 2-methylpropanoic acid.
   (*l*) Which of the following oxides is rapidly oxidised to a higher oxide in air at room temperature:

   $$CO, \quad Na_2O, \quad FeO, \quad Cu_2O ?$$

   (*m*) Write an equation for the *overall* reaction taking place in a hydrogen/alkali/oxygen fuel cell.
   (*n*) Name one metallic element, in each case, the salts of which would impart (i) a lilac colour, (ii) a green colour, to a Bunsen flame.
   (*o*) Show in terms of electron transfer the reaction taking place at the anode when an electric current is passed through a solution of copper(II) sulphate using copper electrodes.

   $$(11 \times 6)$$

2. The following experiment was carried out to estimate the percentage of available ammonia (as NH$_4^+$) in fertiliser. 3·0 g of the crushed fertiliser was placed in a 250 cm^3 flask fitted with a tap funnel and containing silica granules. About 50 cm^3 of a 2·0 mol dm^{-3} solution of sodium hydroxide was added and the flask was boiled gently. The ammonia and steam evolved were passed through a spray-trap into a sloping condenser and then into 50 cm^3 of a 1·0 mol dm^{-3} solution of hydrochloric acid in a beaker using a suitable adaptor. After 20 minutes the adaptor was disconnected and the heating stopped. Both the condenser and the adaptor were rinsed into the beaker. The contents of the beaker were cooled to room temperature and transferred to a 250 cm^3 volumetric flask. When the washings had been added the solution was made up to the mark with water and the flask was stoppered and shaken well.

   25 cm^3 of this solution was titrated against a 0·1 mol dm^{-3} solution of sodium hydroxide using a suitable indicator. The following readings were obtained:

1st reading (cm^3)	0	20·6	0	20·1
2nd reading (cm^3)	20·6	40·6	20·1	40·0
Volume added (cm^3)	20·6	20·0	20·1	19·9

   The reactions may be represented:

   $$NH_4^+ + OH^- \rightarrow NH_3 + H_2O; \quad NH_3 + HCl \rightarrow NH_4Cl; \quad NaOH + HCl \rightarrow NaCl + H_2O$$
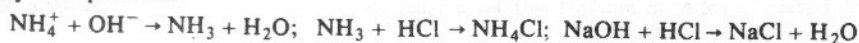
   (i) What mean titration reading should be taken? (6)

   (ii) Why is it desirable to crush the fertiliser granules in a mortar before starting the experiment? (6)

   (iii) Ammonia is very soluble in hydrochloric acid. Mention one precaution that could be taken to ensure that the contents of the beaker were not sucked back into the apparatus. (9)

   (iv) Why is it necessary to cool the solution to room temperature before making it up to the mark in the volumetric flask? (6)

   (v) When the solution is made up to the mark with water the volumetric flask must be shaken well. What is the purpose of this operation and what feature of the volumetric flask makes the operation very necessary? (9)

(vi) Calculate the concentration of the hydrochloric acid solution in the volumetric flask in mol dm^{-3}.
How many moles of hydrogen chloride were contained (a) in 250 cm^3 of this solution, (b) in 50 cm^3 of a 1·0 mol dm^{-3} solution?
How many moles of hydrogen chloride were used up in neutralising the ammonia and hence how many moles of ammonia were displaced? (15)

(vii) Calculate the percentage by mass of (a) ammonium ion (NH$_4^+$), (b) nitrogen, in the fertiliser. (15)

3. A sample of propanone was prepared as follows: 8 cm^3 of concentrated sulphuric acid were mixed carefully with 20 cm^3 water in a beaker and transferred to a distillation flask. Some anti-bump granules were added. 15g sodium dichromate (VI) (Na$_2$Cr$_2$O$_7$.2H$_2$O) were dissolved in 20 cm^3 water in another beaker and 10 cm^3 of propan-2-ol were added. This solution was placed in a dropping funnel fitted to the flask. A condenser was attached for distillation and the receiver was cooled in iced water.
The flask was heated until the contents showed signs of boiling. The heating was stopped and the dichromate (VI)/alcohol mixture was run in at approximately the same rate as distillate collected in the receiver. The distillate was shaken for 10 minutes in a stoppered flask with anhydrous sodium sulphate. It was then filtered and re-distilled on a water bath, collecting the fraction boiling between 327K and 330K. The reaction, which is exothermic, may be represented:

$$3\,CH_3CH(OH)CH_3 + Cr_2O_7{}^{2-} + 8H^+ \rightarrow 3\,CH_3COCH_3 + 2Cr^{3+} + 7H_2O.$$

(i) What precautions would you take when mixing concentrated sulphuric acid with water? Why are these precautions necessary? (6)

(ii) Why was the heating stopped before starting to add the dichromate (VI)/alcohol mixture? (6)

(iii) State and explain the colour change you would see occurring as the reaction proceeds. (9)

(iv) What was the purpose of shaking the crude product with anhydrous sodium sulphate? (6)

(v) A student used propan-1-ol instead of propan-2-ol. Write the name and structural formula of one of the products the student would have obtained if the instructions had otherwise been followed. (9)

(vi) Given that the density of propan-2-ol is 0·785 g cm^{-3} calculate, to two decimal places, the number of moles of (a) sodium dichromate (VI), (b) propan-2-ol, used in the experiment. Explain whether or not you think there is sufficient dichromate (VI) present to oxidise all the propan-2-ol. (15)

(vii) The propanone obtained at the end had a mass of 6·07g. Calculate, to the nearest whole number, the percentage yield of propanone. (15)

4. (i) Write the s, p etc. configuration for (a) the calcium atom, (b) the bromide ion. (6)

(ii) Show, indicating the number of electrons in each main shell and the charges where appropriate, the electronic structure of calcium bromide. (9)

(iii) Arsenic is in the same group as phosphorus. Show the electronic structure of the simplest chloride you would expect arsenic to form. (9)

(iv) Give reasons why the atomic radius of calcium is smaller than that of potassium. Explain why the atomic radii of iron, cobalt and nickel are almost the same. (12)

(v) What electronic structural feature common to iron, cobalt and nickel results in their being classed as transition elements? Mention two general properties of transition elements or their compounds which are not usually shown by non-transition elements. (9)

(vi) The variation of first ionisation energy with atomic number for six successive elements is shown:

Give reasons for the general increase indicated and explain why the increase is interrupted at one point.


First Ionisation Energy (kJ mol^{-1})

Atomic Number (9)
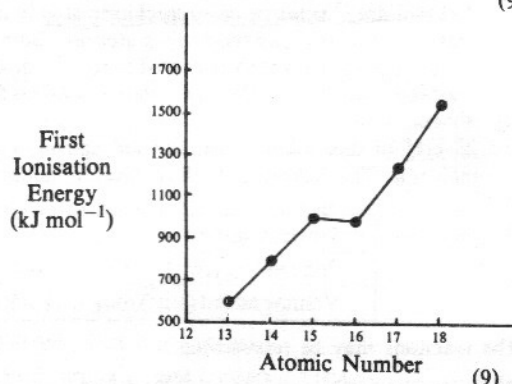
(vii) Using a mass spectrograph it was found that nickel consisted of 70% of $^{58}_{28}$Ni, 26% of $^{60}_{28}$Ni and 4% of $^{62}_{28}$Ni. Calculate the relative atomic mass of nickel as based on the given figures. (12)

5. (i) Define (a) heat of formation, (b) bond energy. (12)

(ii) Calculate the standard heat of formation of ethyne gas from the following data:

$$\begin{array}{llll}
C_2H_{2(g)} & + \ 2\tfrac{1}{2}O_{2(g)} & \rightarrow \ 2CO_{2(g)} \ + \ H_2O_{(l)} & \Delta H = -1299 \ kJ \ mol^{-1} \\
C_{(s)} & + \ O_{2(g)} & \rightarrow \ CO_{2(g)} & \Delta H = -394 \ kJ \ mol^{-1} \\
H_{2(g)} & + \ \tfrac{1}{2}O_{2(g)} & \rightarrow \ H_2O_{(l)} & \Delta H = -286 \ kJ \ mol^{-1}
\end{array}$$
(12)

(iii) If the standard heat of formation of benzene is +49 kJ mol^{-1} calculate the heat change for the reaction,

$$3C_2H_{2(g)} \rightarrow C_6H_{6(l)}$$
(15)

2.

(iv) The bond energy value for the C—H bond is $412 \, \text{kJ mol}^{-1}$ and for C≡C bond is $837 \, \text{kJ mol}^{-1}$. If the heat change for the reaction,
$3C_2H_{2(g)} \rightarrow C_6H_{6(g)}$ is $-591 \, \text{kJ}$, calculate the bond energy of the carbon to carbon bond in benzene. (15)

(v) Suggest why the value obtained in (iv) is different from the bond energy values of the C—C bond $(348 \, \text{kJ mol}^{-1})$ and the C=C bond $(612 \, \text{kJ mol}^{-1})$.
How is the benzene molecule usually represented to show this type of bonding? (12)

6. (a) (i) Explain the term eutrophication of water. What are its causes and effects? (9)

(ii) Outline briefly the principles involved in the (a) primary, (b) secondary, treatment of sewage. (15)

(iii) The effluent from secondary treatment is sometimes subjected to a further purification process. What is the purpose of this tertiary treatment? (6)

(b) A sample of hard water from a dolomite ($MgCO_3.CaCO_3$) district was analysed as follows:
To $50 \, \text{cm}^3$ of the sample 1cm^3 of a buffer solution of pH=10 and 5 drops of a solution of Eriochrome Black T (Solochrome Black T) indicator were added. The solution required $15.0 \, \text{cm}^3$ of a $0.01 \, \text{mol dm}^{-3}$ solution of EDTA for complete complexing of the metal ions. Using H_2Y^{2-} to represent the EDTA anion the reaction may be represented,
$$H_2Y^{2-} + M^{2+} \rightarrow YM^{2-} + 2H^+$$

(i) State the type of hardness involved and how it could be removed. (6)

(ii) Explain, using equations where necessary, how either Mg^{2+} or Ca^{2+} ions could get into solution from the insoluble dolomite in quantity sufficient to cause hardness. (9)

(iii) What colour change would indicate the end-point in the above titration? (6)

(iv) Calculate the hardness of the water expressed as parts per million (p.p.m.) of calcium carbonate. (15)

7. Sulphuric acid is made industrially from sulphur trioxide obtained by the catalytic oxidation of sulphur dioxide using a vanadium pentoxide catalyst.

(i) Give the equation for one reaction by which sulphur dioxide could be obtained industrially. (6)

(ii) The sulphur dioxide is treated to remove impurities such as hydrogen sulphide, compounds of arsenic etc. Why is it necessary to remove such impurities? (6)

(iii) Give a balanced equation for the overall reaction taking place in the presence of the catalyst. (6)

(iv) How is the sulphur trioxide converted to concentrated sulphuric acid? Give one reason for the use of the procedure you suggest. (12)

(v) Straw for making straw hats is sometimes bleached with sulphur dioxide. What type of reaction is this bleaching process? Suggest why straw bleached with sulphur dioxide turns yellow with age. (6)

(vi) What would you see happening when some concentrated sulphuric acid is dropped on to copper sulphate crystals? What term is used to describe the action of concentrated sulphuric acid in this reaction? How could the reaction be reversed? (12)

(vii) You are given solutions labelled (a) sodium sulphate and (b) sodium sulphite. Describe the effect (if any) at each stage of adding to each of these solutions a few drops of barium chloride solution followed by an excess of dilute hydrochloric acid. Explain by means of equations what is happening. (18)

8. (a) Potassium dichromate (VI) is an orange-red salt which is soluble in water giving an orange solution in which the following dynamic equilibrium is reached,
$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$

(i) Is the reaction shown a redox reaction? Explain your reasoning. (6)

(ii) Explain why the solution turns yellow on the addition of sodium hydroxide solution. (12)

(iii) Explain the visible and chemical effects of adding excess dilute hydrochloric acid to the alkaline solution in (ii). (12)

(b) Dinitrogen tetroxide, which is a gas at temperatures above 294K, dissociates according to the equation,
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

(i) Write the equilibrium constant (Kp) expression for this reaction in terms of partial pressures. (6)

(ii) What would you see happening if some $N_2O_{4(g)}$ were raised from 295K to 330K? (6)

(iii) Some N_2O_4 was placed in a closed vessel and the temperature was raised to 330K, at which temperature N_2O_4 is 50% dissociated. The total pressure in the vessel at equilibrium was found to be 9 atmospheres. Calculate Kp for the reaction at this temperature. (12)

(iv) Some more N_2O_4 was added to the vessel at the same temperature until the partial pressure of $N_2O_{4(g)}$ at equilibrium was 6.75 atmospheres. Calculate the partial pressure of $NO_{2(g)}$ at the new equilibrium. (12)

9. (i) Name two allotropes of carbon. (6)

(ii) Mention two ways in which carbon dioxide is continually being added to the atmosphere and two ways in which it is continually being removed. (12)

3.

(iii) $1 \cdot 8$ dm^3 of a hydrocarbon measured at room temperature and pressure gave $2 \cdot 7$ g water and $6 \cdot 6$ g carbon dioxide when completely burnt in oxygen. If molar volume at room temperature and pressure is $24 \cdot 0$ dm^3 find the molecular formula of the hydrocarbon. (12)

(iv) Describe a simple test which would confirm whether the compound in (iii) is saturated or unsaturated. (6)

(v) Show by an equation how the hydrocarbon in (iii) would react with chlorine gas. Discuss as fully as you can the mechanism of this reaction. (15)

(vi) What do you understand by the term catalytic cracking? Why is it carried out in an oil refinery? An alkane of molecular formula $C_{14}H_{30}$ gave on cracking a branched-chain saturated molecule containing seven carbon atoms, a molecule containing four carbon atoms and one containing three carbon atoms. Show clearly one possible structure in each case for the three molecules formed. (15)

10. Answer any *two* of the following:

(a) Thiosulphate ions react in acid solution as follows:

$$S_2O_{3(aq)}^{2-} + 2H_{(aq)}^+ \rightarrow S_{(s)} + SO_{2(aq)} + H_2O_{(l)}$$
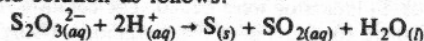
A series of experiments was carried out in identical flasks at room temperature. The concentration of thiosulphate ions was varied but the concentration of the acid and the total volume of the solution were kept constant. The time taken in each case for a cross marked on paper to be obscured by the suspended sulphur was noted. It can be shown that the initial rate of reaction in each case is inversely proportional to the time taken for the cross to disappear. The volume of standard thiosulphate solution used is a measure of the concentration of the thiosulphate ions. Results were tabulated as follows:

Volume of 0·2 mol dm^{-3} solution of Na$_2$S$_2$O$_3$ (cm^3)	Vol. of water added (cm^3)	Vol. of 2 mol dm^{-3} HCl (cm^3)	Time (t) (seconds)	$1/t$ (s^{-1})
60	0	10	40	·025
50	10	10	48	·021
40	20	10	62	·016
30	30	10	80	·0125
20	40	10	120	·008
10	50	10	250	·004

(i) Why is it necessary to use identical flasks? (6)

(ii) Plot on graph paper the volume of thiosulphate solution against $1/t$. (12)

(iii) What conclusion can you draw about the relationship between the rate of the reaction and the concentration of thiosulphate ions? (6)

(iv) If $24 \cdot 0$ cm^3 of $0 \cdot 2$ mol dm^{-3} solution of sodium thiosulphate had been used in one of the above experiments what time would have elapsed before the cross became obscured? (9)

(b) (i) The hydrogen ion concentration in pure water at 298 K is $1 \cdot 0 \times 10^{-7}$ mol dm^{-3} but at 330 K it is about $3 \cdot 0 \times 10^{-7}$ mol dm^{-3}. Does this mean that water is acidic at 330K? Explain your reasoning. (6)

(ii) Methyl red is an indicator used in titrations of strong acids against weak bases. It changes from red to yellow in the pH range $4 \cdot 2$ to $6 \cdot 3$. If it can be regarded as a weak base represented as XOH explain how it acts as an indicator. (9)

(iii) Find the pH of a $0 \cdot 05$ mol dm^{-3} solution of ammonia in water given that the dissociation constant (K_b) for ammonia in solution is $1 \cdot 8 \times 10^{-5}$. (18)

(c) Study the following sequence of reactions and answer the questions which follow.

$$CaC_2 \xrightarrow{H_2O} X \xrightarrow[\substack{HgSO_4 \\ 330K}]{dil. H_2SO_4} Y \xrightarrow[\substack{Ni \\ 410K}]{H_2} Z$$
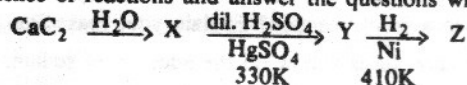
(i) Identify X, Y and Z by name or correct formula. (9)

(ii) Give the name and structural formula for the yellow compound formed when Y reacts with a solution of 2,4-dinitrophenylhydrazine. (6)

(iii) Write an equation for the reaction of Z with phosphorus pentachloride. (9)

(iv) Under suitable conditions X will react with hydrogen cyanide to form a product which is used to make an industrially important polymer. Name this polymer and indicate its structure by showing two repeating units. (9)

(d) Aluminium metal is obtained by the electrolysis of pure aluminium oxide dissolved in molten cryolite using carbon electrodes. The cell operates at a temperature of about 1150 K.

(i) Why is the electrolysis *not* carried out on molten aluminium oxide? (6)

(ii) Write equations, showing the electron changes, for the reactions occurring (a) at the cathode, (b) at the anodes, in the cell. (12)

(iii) What important economic factor, other than the availability of raw materials, might influence the siting of an aluminium smelter? Give a reason for your answer. (6)

(iv) Aluminium metal is sometimes anodised. Explain briefly how this is done. What is the purpose of the operation? (9)

4.