LEAVING CERTIFICATE EXAMINATION, 1990

CHEMISTRY — HIGHER LEVEL

THURSDAY, 14 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 questions carry the same number of marks.

Relative atomic masses: H = 1, C = 12, N = 14, O = 16, Na = 23, S = 32, K = 39, Ca = 40.

Avogadro constant = 6×10^{23} mol^{-1}

Molar volume at S.T.P. = 22·4 dm^3

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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 $^{37}_{17}Cl^-$?

(*b*) What is (i) the conjugate acid, (ii) the conjugate base, of $HC_2O_4^-$?

(*c*) Which of the following molecules has a shape that is different from the other three?

BF_3 AsH_3 HCHO $AlCl_3$

State the shape of the molecule you have chosen.

(*d*) State *two* ways in which real gases depart from ideal behaviour.

(*e*) It takes $7{\cdot}5 \times 10^{21}$ atoms of neon to completely fill a conical flask at S.T.P. What is the total capacity of the flask in cm^3?

(*f*) What binding forces (i) hold the water molecules together in a crystal of ice, (ii) hold the carbon dioxide molecules together in a crystal of dry ice?

(*g*) Give *one* advantage and *one* disadvantage of fuel cells.

(*h*) Explain briefly how lightning can lead to soil enrichment.

(*i*) What is the valence of scandium in Sc_2O_3? Explain, by reference to the electronic configuration of scandium, how this valence arises.

(*j*) A sodium hydroxide solution is labelled 10% (w/v). What is the concentration of the solution in mol dm^{-3}?

(*k*) In the history of the classification of the elements name (i) the scientist who arranged elements in octaves, (ii) the scientist who predicted the discovery of new elements.

(*l*) Write a balanced equation for the reaction of phosphorus (III) chloride and water.

(*m*) Winkler's reagent (used with manganese (II) sulphate solution in determining the dissolved oxygen content of a water sample) consists of two substances dissolved in water. What are the two substances?

(*n*) Calculate the N value of an NPK compound fertiliser containing 23·6% of ammonium sulphate and no other nitrogenous material.

(*o*) As a result of catalytic cracking, the molecule $C_{10}H_{22}$ produced a molecule of butane (C_4H_{10}) together with a branched and an unbranched alkene molecule. Identify the *two* alkene molecules.

(11 × 6)

2. A mass of 3·34 g of a mixture of anhydrous sodium carbonate (Na_2CO_3) and anhydrous potassium carbonate (K_2CO_3) was weighed accurately on a clock glass. It was then dissolved in warm water in a beaker. When the solution had cooled to room temperature, it was transferred to a 500 cm^3 volumetric flask and made up carefully to the mark with deionised water. The solution was then titrated in 25 cm^3 volumes against a standard solution of hydrochloric acid and the following titration results were obtained: 30·3 cm^3, 30·0 cm^3, 30·0 cm^3.

(i) What is a standard solution? Is hydrochloric acid a primary or a secondary standard? Explain your answer. (9)

(ii) Why would it have been undesirable to have used filter paper instead of a clock glass when weighing the mixture? (6)

(iii) Explain why *warm* water was used to dissolve the mixture. Why was the solution allowed to cool before it was made up to 500 cm^3 in the volumetric flask? (6)

(iv) Describe tests that would enable you (*a*) to distinguish between sodium ions and potassium ions, (*b*) to show that the negative ions in the mixture were carbonate and not hydrogencarbonate ions. (18)

(v) The equation for the titration reaction is

$$CO_3^{2-} + 2HCl \rightarrow 2Cl^- + H_2O + CO_2$$

Given that the concentration of the hydrochloric acid solution was 0·1 mol dm^{-3}, calculate the concentration of carbonate ions (CO_3^{2-}) in the solution in the volumetric flask in mol dm^{-3}. What was (*a*) the number of moles, (*b*) the mass of carbonate ions, in the mixture? (15)

(vi) Calculate the mass of sodium carbonate in the mixture. (12)

3. A student prepared reasonably pure ethyne and converted it to ethanal by bubbling it through a dilute solution of X containing a catalyst Y. The ethanal was then added to a solution of 2,4-dinitrophenylhydrazine and a coloured precipitate was formed. The precipitate was filtered, dried, and its melting point was determined. It melted in the range 163-166°C. It was then recrystallised using ethanol and, after recrystallisation, it melted sharply at 168°C.

(i) Describe, with the aid of a diagram, how you would prepare reasonably pure ethyne. (12)

(ii) Identify X and Y and suggest a suitable temperature for the reaction. (9)

(iii) Give the name and structural formula of the precipitate formed when the ethanal reacted with 2,4-dinitrophenylhydrazine. What colour was the precipitate? After filtering, how was the precipitate dried? (15)

(iv) How would you have measured the melting point of the precipitate? What information concerning the precipitate was suggested (*a*) by the melting point taken before recrystallisation, (*b*) by the melting point taken after recrystallisation? (12)

(v) Outline the procedure involved in recrystallising the precipitate. (12)

(vi) What use is made, in chemical analysis, of the reactions of aldehydes and ketones with 2,4-dinitrophenylhydrazine? (6)

4. (*a*) What use is made of each of the following substances in the production of water for drinking?

(i) aluminium sulphate,

(ii) chlorine,

(iii) dilute sulphuric acid,

(iv) hexafluorosilicic acid. (12)

(*b*) Outline what takes place in the primary and secondary treatment of sewage. (12)

Some sewage treatment plants carry out a tertiary process which further reduces the levels of certain substances. What are these substances and why is the process considered necessary? (9)

(*c*) What is meant by the dissociation constant of an acid (K_a)? (6)

The pH of a 1 mol dm^{-3} solution of ethanoic acid is 2·37.
Calculate the hydrogen ion concentration and show that the approximate value of the dissociation constant is $1{\cdot}8 \times 10^{-5}$. (15)

What is the approximate value of the pH of a 0·05 mol dm^{-3} solution of ethanoic acid? (12)

5. Define (i) exothermic reaction, (ii) kilogram calorific value, (iii) bond energy. (15)

Draw an energy profile diagram for the combustion of methane. (6)

The heat of combustion of methane is -890 kJ mol^{-1}. Calculate its kilogram calorific value. What use can be made of kilogram calorific values? (9)

Use the heat of combustion of methane, together with the following thermochemical data, (where E stands for the molar bond energy) to work out a value for E(C – H) in methane.

$$E(H-H) = 436 \text{ kJ mol}^{-1}$$
$$C_{(s)} \rightarrow C_{(g)} \quad \triangle H = 718 \text{ kJ mol}^{-1}$$
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \triangle H = -394 \text{ kJ mol}^{-1}$$
$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \quad \triangle H = -286 \text{ kJ mol}^{-1}$$

(24)

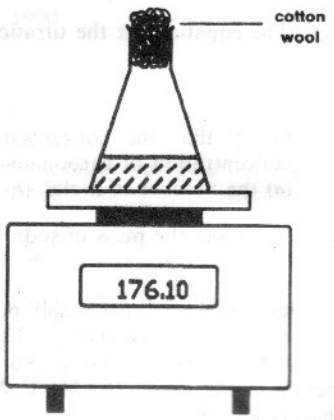
The energy required (per mole) to break just one of the C – H bonds in methane was found by experiment and is given in the following equation.

$$CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)} \quad \triangle H = 432 \text{ kJ mol}^{-1}$$

Explain why the value is not the same as that calculated above. (6)

Linus Pauling used bond energy data to draw up a set of numbers expressing the relative attractions of different elements for bonding electrons. What is this set of numbers called? (6)

6. A mass of 1 g of manganese (IV) oxide was weighed in a small test tube. 100 cm^3 of a hydrogen peroxide solution were measured into a conical flask which was then fitted with a loose plug of cotton wool. The flask was placed on the pan of a direct-reading balance (see diagram) and, after adding the manganese (IV) oxide, the mass was recorded at 1 minute intervals. The results obtained are shown in the following table.



Time (min.)	0	1	2	3	4	5	6	7	8
Mass (g)	176·58	176·34	176·22	176·16	176·12	176·11	176·10	176·10	176·10

(i) What was the function of the cotton wool plug? (6)

(ii) How would you find the mass at 0 minutes i.e. before the reaction had started? (6)

(iii) Using graph paper, plot a graph of *loss in mass* against time. (12)

What difference, if any, would you expect there to be in the graph if 2 g of manganese (IV) oxide had been used? Explain your answer. (6)

(iv) Use the graph to find (*a*) the time required to liberate $8{\cdot}75 \times 10^{-3}$ moles of oxygen, (*b*) the number of moles of oxygen liberated after 2·5 minutes, (*c*) the instantaneous rate of the reaction after 2 minutes. (21)

(v) Write a balanced equation for the reaction taking place in the experiment. Calculate the total number of moles of oxygen produced and hence find the number of moles of hydrogen peroxide initially present in the 100 cm^3 of solution used. (15)

7. The following are some metals in the order in which they appear in the electrochemical series:

K Na Mg Al Zn Fe Sn Pb Cu

Answer the following questions with reference to these metals.

(i) Name one metal that can be found in nature as the free element and explain why this is possible. (6)

(ii) Two of the metals are commonly used as protective coats to help prevent iron from rusting. Identify the two metals. Which of the two is likely to give the better protection? Give a reason for your answer. (15)

(iii) Select (*a*) a metal the nitrate of which is converted to a nitrite on heating, (*b*) a metal the nitrate of which is converted to an oxide on heating. Write balanced equations for the two reactions. (18)

(iv) Show by means of an equation the displacement of one metal from a salt solution by another metal in the series. Show that this is an oxidation-reduction reaction. (12)

(v) Which metals are commonly extracted by an electrolytic method? In the case of one of these metals give a brief description of the electrolytic process involved in its extraction. (15)

8. (i) An alcohol was found on analysis to contain 64·9% carbon, 13·5% hydrogen and 21·6% oxygen. If the relative molecular mass of the alcohol is 74, show that the molecular formula is $C_4H_{10}O$. (12)

(ii) Using the molecular formula $C_4H_{10}O$, write the full structural formula (*a*) for a straight-chain primary alcohol, (*b*) for a branched-chain primary alcohol, (*c*) for a secondary alcohol. Give the systematic (IUPAC) names for the three alcohols. (18)

(iii) Describe briefly how the straight-chain primary alcohol you have given in (ii) could be converted to an acid. What is the name of the acid? (12)

(iv) Name the ester obtained when the straight-chain primary alcohol and the acid produced in (iii) are heated with concentrated sulphuric acid. Write a balanced equation for the reaction. State *two* ways in which the reaction is affected by the presence of the sulphuric acid. (15)

(v) The combustion of organic compounds like the alcohol in (i) tends to increase the level of carbon dioxide in the atmosphere. What natural process is mainly responsible for offsetting this increase? Why is the overall level of carbon dioxide in the atmosphere causing concern among scientists at the present time? (9)

9. What is meant by (i) a reversible reaction, (ii) chemical equilibrium? (6)

Write the equilibrium constant expression in terms of partial pressures for each of the following reactions.

(i) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

(ii) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ (12)

What is the industrial importance of reaction (i)? Under what conditions is it normally carried out? (12)

A mixture of nitrogen, hydrogen and ammonia was allowed to reach equilibrium at a certain temperature. The equilibrium mixture contained 13·5 mol nitrogen, 3·6 mol hydrogen and 0·9 mol ammonia. Calculate K_p for this reaction if the total pressure at equilibrium is 2 atmospheres. (18)

When this reaction is carried out at a lower temperature the value of K_p is higher. What conclusion can be drawn regarding the heat change for the reaction? Explain your answer. (9)

If the equation for the reaction had been written in the form

$$\tfrac{1}{2}N_{2(g)} + 1\tfrac{1}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$$

what change, if any, would there be in the value of K_p? (9)

10. Answer any *two* of the following:

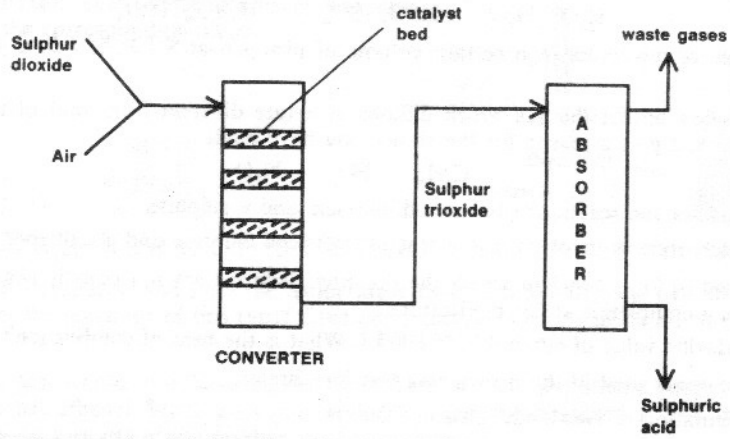
(*a*) Explain the terms (i) energy level, (ii) orbital, (iii) first ionisation energy. (9)

Identify the species $[1s^2]$ and name a compound in which it is found. (9)

Show, by means of a diagram, how the orbitals are arranged in the 4p sublevel of an atom of an element e.g. element 33. (3)

Explain why the first ionisation energy of element 33 is greater (i) than that of element 32, (ii) than that of element 34. (12)

(*b*)



The diagram shows a simplified outline of an industrial plant for the manufacture of sulphuric acid by the Contact process.

(i) In some plants, the sulphur dioxide is obtained as a byproduct of the roasting of sulphide ores e.g. galena (PbS) is roasted in air to produce lead (II) oxide and sulphur dioxide.
Write a balanced equation for this reaction. (6)

(ii) The catalyst beds usually consist of a transition metal oxide. Give the name and formula of the transition metal oxide. What structural feature of transition metal atoms enables them to act as catalysts? (12)

(iii) In the absorber the sulphur trioxide dissolves in a liquid. Name the liquid. What substance is added to the solution in order to complete the process? (6)

(iv) The following reaction may be used to reduce emissions of sulphur dioxide in the waste gases:

$$2CaCO_3 + 2SO_2 + O_2 \rightarrow 2CaSO_4 + 2CO_2$$

What volume of sulphur dioxide (measured at S.T.P.) could be removed from the waste gases by this reaction for every kilogram of calcium carbonate used? (9)

(*c*) Gallium is a metallic element in Group 3 of the Periodic Table (Mathematics Tables, page 44). It is normally trivalent in its compounds.

(i) Write the formula for (*a*) gallium chloride, (*b*) gallium oxide. (6)

(ii) What type of bonding is most likely in gallium chloride? Give a reason for your answer.
What reaction, if any, would you expect between gallium chloride and water? (12)

(iii) Show by means of equations how you would expect gallium oxide to react with (*a*) hydrochloric acid, (*b*) sodium hydroxide. What term is used for oxides that behave in this way? (15)

(*d*) What is a polymer? (6)

Distinguish clearly between addition and condensation polymerisation. (6)

Terylene is an example of a condensation polymer. Write out the full structural formula of the repeating part of terylene. (6)

Give a brief description of how a sample of a named addition polymer may be prepared in the laboratory, and indicate the structure of the polymer by showing two repeating units. (15)