LEAVING CERTIFICATE EXAMINATION, 1986

CHEMISTRY—HIGHER LEVEL

TUESDAY, 24 JUNE—AFTERNOON 2 to 5

Question 1 and **five** other questions must be answered. These five questions *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, P = 31, S = 32, Cl = 35·5, K = 39, Cr = 52, Mn = 55, Br = 80.

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 marks. *Keep your answers short.*

(*a*) How many moles of PO_4^{3-} ions are there in two moles of $Ca_3(PO_4)_2$?

(*b*) Write the conjugate acid of each of the following base species:

(i) CrO_4^{2-} (ii) HS^-

(*c*) State Dalton's Law of Partial Pressures.

(*d*) How many *atoms* are there in 560 cm^3 of nitrogen at S.T.P.?

(*e*) Write down the structural formula for (i) benzene, (ii) methylbenzene.

(*f*) Give an example of a covalent crystal. What particles occupy its lattice points?

(*g*) The reactions taking place when carbon dioxide is bubbled through limewater are shown in the following scheme:

$$Ca(OH)_{2(aq)} \xrightarrow{+CO_2} A + H_2O \xrightarrow{+CO_2} B$$

Give the formula of A and the formula of B.

(*h*) Write the structural formula of 3-ethylpent-1-ene.

(*i*) Calculate the percentage by mass of ammonium ion (NH_4^+) in ammonium sulphate.

(*j*) State briefly the contribution of Döbereiner to the classification of the elements.

(*k*) How would you distinguish between sulphite and sulphate ions in aqueous solution?

(*l*) Give the chemical equation for the reaction between a ketone and 2,4-dinitrophenylhydrazine.

(*m*) What technique, used in the purification of solids, is based on the fact that these solids are usually more soluble in hot solvent than in cold?

(*n*) The bond energies in kJ mol^{-1} of HCl, HBr and HI are 432, 366 and 299 respectively. Suggest a reason for the decrease.

(*o*) How many Faradays would be required to discharge 10·4 g of Cr^{3+} ions at an inert electrode?

(11 × 6)

2. A standard solution of sodium thiosulphate was prepared as follows. About 33 g of slightly impure sodium thiosulphate crystals were dissolved in water and made up to 1·0 dm^3 (litre). A burette was rinsed and then filled with this solution using a funnel. The funnel was removed, the tap of the burette was opened briefly and then closed again and the reading noted. A pipette and conical flask were rinsed and then the pipette was used to measure 25·0 cm^3 of a 0·05 mol dm^{-3} iodine solution (previously standardised) into the conical flask. The thiosulphate solution was run in from the burette until the end-point was near. Then a few drops of starch solution were added as indicator and the titration was completed. Further titrations were carried out until two titres agreed closely. The average of these two titres was 20·0 cm^3.

The reaction between iodine and thiosulphate is

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

(i) Why was it not necessary to know the precise mass of the sodium thiosulphate crystals? (6)

(ii) Why was (*a*) the funnel removed, (*b*) the tap of the burette opened briefly and then closed again before the reading was noted? (6)

(iii) What is the difference in the procedure used in rinsing the conical flask from that used in rinsing the pipette and the burette? Give a reason for the difference. (9)

(iv) Mention any *two* steps (other than the addition of the starch indicator) of the procedure carried out on the conical flask and its contents *during the titration*. (6)

(v) How was it possible to recognise that the end-point of the titration was near? What was observed (*a*) when the starch solution was added, (*b*) when the end-point was reached? (9)

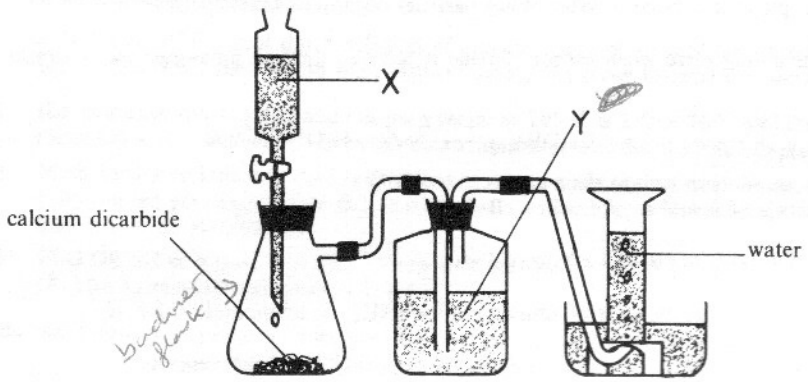
(vi) Calculate the concentration of the thiosulphate solution (*a*) in mol dm^{-3}, (*b*) in g dm^{-3} of crystalline sodium thiosulphate ($Na_2S_2O_3.5H_2O$). (18)

(vii) Acidified solutions of potassium manganate(VII) liberate iodine from iodide solutions according to the equation

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

When excess potassium iodide was added to 25·0 cm^3 of an acidified solution of potassium manganate(VII), it required 22·5 cm^3 of the sodium thiosulphate solution to reduce the iodine liberated.
Calculate the mass of potassium manganate(VII) in the 25·0 cm^3 of solution. (12)

3. A student prepared a sample of ethyne gas using the following apparatus:



Answer the following questions in relation to ethyne.

(i) Describe the physical appearance of calcium dicarbide. (6)

(ii) Name the substance X. Write a balanced equation for the reaction between substance X and calcium dicarbide. (9)

(iii) Describe what the student observes in the flask as X is dropped on to the calcium dicarbide. (6)

(iv) A small quantity of acidified potassium manganate(VII) is added to a gas jar of ethyne and the jar shaken for a short time. State what is observed and what deduction may be made. (6)

(v) Ethyne prepared using the above method, normally contains impurities which can be removed by bubbling the gas through solution Y. Name Y and mention any one of the impurities removed. Name one substance in the calcium dicarbide which could give rise to this impurity. (9)

(vi) Name the reagents used and describe the conditions under which ethyne is converted to ethanal. What reagent and conditions are used to convert ethyne to propenonitrile (acrylonitrile) industrially? (15)

(vii) Ethyne was hydrogenated using a palladium/barium sulphate catalyst and 8·4 mg of the product gave 26·4 mg of carbon dioxide and 10·8 mg of water vapour on complete combustion. Find the molecular formula of the hydrocarbon. What other hydrocarbon could be obtained by the hydrogenation of ethyne? (15)

4. Answer this question by referring where necessary to the first thirty-six elements of the Periodic Table (Mathematics Tables p.44 to p.46).

(i) Distinguish clearly between mass number (A) and relative atomic mass (A_r). (12)

(ii) Give the formula of an oxide of copper that is predominantly ionic, and write the electronic configuration (s, p etc.) of the copper ion. (6)

(iii) Suggest two possible shapes for molecules of general formula QX_3 where X is an atom of a monovalent element. Give a reason for the difference between these shapes. (9)

(iv) How are the electrons in the 4p sublevel arranged in orbitals (*a*) in a germanium atom, (*b*) in an arsenic atom? Show the arrangement of these orbitals relative to each other in the arsenic atom. (9)

(v) Write the formula of the compound formed by the reaction between chlorine and the metallic element of atomic number 31. How would you expect this compound to react with water? (9)

(vi) Give *two* reasons why ammonia (NH_3) is very soluble in water. Why is the solubility of phosphine (PH_3) in water very low? (12)

(vii) The first and second ionisation energies of sodium and magnesium are shown in the table.

Ionisation energy (kJ mol^{-1})	Na	Mg
First	494	736
Second	4,550	1,450

Explain why sodium has a lower first ionisation energy but a much higher second ionisation energy than magnesium. (9)

5. State Le Chatelier's Principle. (6)

The thermal decomposition of phosphorus pentachloride is represented by the following equation.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

A mass of 20·85 g of phosphorus pentachloride was heated at 523 K in a closed 8 dm^3 vessel. When the reaction had come to equilibrium at that temperature, it was found that 80% of the pentachloride had dissociated. The pressure in the reaction vessel at equilibrium was one atmosphere.

(i) What is meant by chemical equilibrium? Why is it described as a dynamic process? (6)

(ii) What would be the effect, if any, on the percentage decomposition of the phosphorus pentachloride if the reaction were carried out at a higher pressure? (6)

(iii) Write expressions for K_c and K_p for the reaction. (12)

(iv) Calculate K_c for the reaction. (15)

(v) Calculate K_p for the reaction. Explain why the values of K_c and K_p are not the same. (21)

6. (*a*) Define pH of a solution. What is the hydrogen ion concentration in a solution which has a pH of 3 at room temperature? (6)

Calculate the pH of (i) a solution containing 0·024 g dm^{-3} of potassium hydroxide, (9)

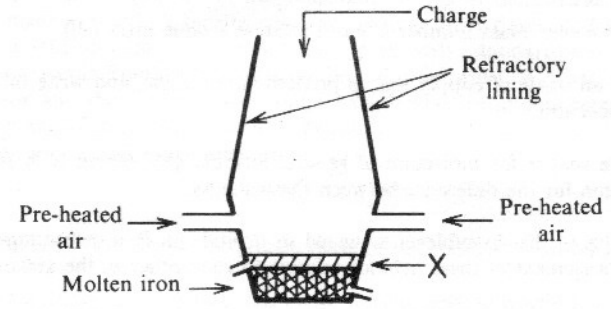
(ii) a solution of ethanoic acid containing 8×10^{-2} mol in 100 cm^3 of solution. (18)
(K_a for ethanoic acid $= 1{\cdot}8 \times 10^{-5}$)

(*b*) (i) What is meant by *flocculation* in the water purification process? At the end of the purification process it is sometimes necessary to adjust the pH of the water. State how this adjustment is carried out. (12)

(ii) What is the difference, if any, between water that has been distilled and water that has been passed through an efficient deionising resin? Explain the function of the resin. (9)

(iii) A student filtered 500 cm^3 of water and found that the mass of the filter paper after drying had increased by 0·68 g. 100 cm^3 of the filtered water were then evaporated to dryness in a beaker and it was found that the mass of the beaker had increased by 0·13 g.
What is the amount of suspended solids and the amount of dissolved solids in the water expressed as parts per million (p.p.m.)? (12)

7. The following is a diagram of a blast furnace used to extract iron from iron ore.



(i) Iron ore and two other materials make up the charge which is fed into the top of the furnace. Name these materials and give one function of each. (12)

(ii) Write a balanced equation for a reaction of iron ore for its conversion to iron. (6)

(iii) Molten iron and another substance, *X*, are tapped off at the bottom of the furnace. Give the name of this other substance and state one of its uses. Also, give the common name for iron which has been obtained directly from the furnace. (9)

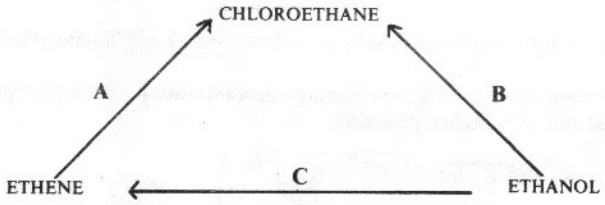
(iv) Steel always contains a small amount of another element mixed with iron. Name this element and give the term commonly used to describe such a mixture. (9)

(v) Suggest one method by which the properties of steel can be varied. Give the name of a process by which steel is made. (6)

(vi) Given the position of aluminium relative to iron in the electrochemical series you would expect aluminium to corrode more easily. Explain (*a*) why aluminium is in fact more resistant to corrosion than iron, (*b*) how this resistance to corrosion can be increased. (9)

(vii) Another commercially important metal, copper, may be obtained in a relatively pure form by a roasting process. Outline how the copper may be further purified by electrolysis, giving equations for the reactions at the electrodes. (15)

8. (*a*)



(i) From the chemical reactions involved in the conversions **A**, **B** and **C** above select an example of each of the following: dehydration, ionic addition, hydrolysis. (9)

(ii) Write a balanced equation for the reaction which illustrates hydrolysis. (6)

(iii) Give the mechanism for the reaction which involves ionic addition. (9)

(iv) Chloroethane can also be obtained by means of a free radical substitution reaction. Show the mechanism involved in this reaction. (12)

(*b*) (i) What is an ester? (6)

The polymer, terylene, is a polyester used in making clothes, curtains, sails, safety belts etc. It is formed by the following condensation reaction

$$X + Y \rightarrow \text{TERYLENE}$$

(ii) What is a condensation reaction? (6)

(iii) Give the names *or* formulae of X and Y. (6)

(iv) Show the structural formula of one of the repeating units of the polymer. (6)

(v) Why is terylene described as a polyester? (6)

9. What is meant by the term *rate of reaction*? (6)

In an experiment, 25 cm^3 of 0·1 M sulphuric acid were added to excess granulated zinc in a reaction vessel. The hydrogen evolved in the reaction was collected and its volume (at room temperature and pressure) measured at regular intervals of time. The results obtained are shown in the following table:

Time (minutes)	0	1	2	3	4	5	6	7	8	9	10	11
Volume of Hydrogen (cm^3)	0	30	45	52·5	56·3	58·2	60	61	61·5	62	62	62

(i) Draw a diagram of the apparatus you would use in this experiment. (12)

(ii) Using the balanced equation for the reaction, calculate the maximum volume of hydrogen gas at S.T.P. which would be evolved in the above experiment. (9)

(iii) Plot on graph paper the results in the above table and comment on the shape of the graph. (15)

(iv) Find, using the graph, the rate of the reaction after two minutes (i.e. the instantaneous rate), expressing the rate in terms of cm^3 of hydrogen liberated per minute. (12)

(v) What changes would you expect in the graph if (*a*) 25 cm^3 of 0·5 M sulphuric acid were used in the experiment, (*b*) if the same quantity of 0·1 M sulphuric acid had been used but the temperature was higher? (12)

10. Answer any *two* of the following.

(*a*) In a reaction 14·7 g of potassium dichromate(VI) reacted completely with concentrated hydrochloric acid according to the equation:

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

(i) How many moles of potassium dichromate(VI) were used? (6)

(ii) How many moles of water were produced? (6)

(iii) What volume of chlorine, measured at S.T.P., was produced? (6)

(iv) How many molecules of chlorine did this volume contain? (6)

(v) If the chlorine produced in the reaction were bubbled through a solution containing excess sodium bromide, what mass of bromine would be liberated? (9)

(*b*) (i) State Hess's Law. (6)

(ii) Ethanoic acid can be manufactured by the catalytic oxidation of butane. The reaction may be represented by the following equation:

$$2C_4H_{10(g)} + 5O_{2(g)} \rightarrow 4CH_3COOH_{(l)} + 2H_2O_{(l)}$$

Given the following values for heats of combustion calculate the heat change (ΔH) per mole of ethanoic acid produced in the reaction.

$$CH_3COOH_{(l)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -876 \text{ kJ mol}^{-1}$$

$$C_4H_{10(g)} + 6\tfrac{1}{2}O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(l)} \qquad \Delta H = -2877 \text{ kJ mol}^{-1}$$

(12)

(iii) Name the catalyst used in the reaction to manufacture ethanoic acid from butane and mention one other necessary condition. (6)

(iv) Explain what is meant by the kilogram calorific value of a fuel. Using the value of the heat of combustion given above, calculate the kilogram calorific value of butane. (9)

(*c*) What is meant by an amphoteric oxide? (6)

From the following list, classify each oxide as acidic, basic, amphoteric or neutral. Describe the reaction (if any) of each oxide with water and with either a dilute mineral acid or base where appropriate giving the balanced equation.

$$Na_2O \ , \ Al_2O_3 \ , \ NO_2$$

(27)

(*d*) Define oxidation in terms of electron transfer. (6)

What is the oxidation number of

(i) nitrogen in NH_4^+, (ii) phosphorus in H_3PO_4, (iii) sulphur in $Na_2S_4O_6$? (9)

Show, using oxidation numbers, that the decomposition of hydrogen peroxide into water and oxygen is an oxidation-reduction reaction. (9)

Using oxidation numbers, balance the following equation:

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

(9)