AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1993

CHEMISTRY — HIGHER LEVEL

MONDAY, 21 JUNE — AFTERNOON, 2.00 to 5.00

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, O = 16, F = 19, Na = 23, P = 31, S = 32, Cl = 35.5, Ca = 40, Cr = 52, Zn = 65.

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 number of marks. *Keep your answers short.*

(*a*) What is meant by an atomic orbital? Indicate the shape of a p orbital.

(*b*) Distinguish between *isotopes* and *allotropes* of an element.

(*c*) What mass of oxygen would occupy the same volume as 1.52 grams of fluorine under the same conditions of temperature and pressure?

(*d*) State Graham's Law of Diffusion.

(*e*) The molecular formula of an organic compound is $C_2H_4O_2$. Give the name of the compound (i) if it is an ester, (ii) if it is a carboxylic acid.

(*f*) What have the ions K^+, Ca^{2+}, Cl^-, S^{2-} in common?

(*g*) Name (i) a technique commonly used in the purification of solids,
(ii) a technique commonly used in the purification of liquids.

(*h*) What type of bond exists (i) between the atoms in a molecule of hydrogen chloride, (ii) between molecules of hydrogen chloride?

(*i*) Write a balanced equation for the reaction of aluminium chloride with water.

(*j*) State the temperature and the catalyst used in the conversion of sulphur dioxide to sulphur trioxide in the manufacture of sulphuric acid.

(*k*) What reagents would you use to confirm the presence of chloride ions in aqueous solution?

(*l*) Why does the Winkler method for determining the concentration of dissolved oxygen in water give an inaccurate result for water that has been chlorinated?

(*m*) Give the names *or* formulae of the two compounds from which the polymer terylene is made.

(*n*) What is the function of aluminium sulphate in the purification of water for drinking? Why is the presence of this compound in drinking water causing some concern at the present time?

(*o*) The mass of 2.8 dm^3 of a gaseous hydrocarbon at S.T.P. is 3.75 grams. Identify the compound.

(11 × 6)

2. A certain mass of ethanedioic acid crystals ($C_2H_2O_4.2H_2O$) was weighed out accurately on a clock glass and then dissolved in deionised water in a beaker. The solution was transferred to a 500 cm^3 volumetric flask, observing the usual precautions, and made up carefully to the mark with deionised water. The concentration of this solution was found by titrating it in 25.0 cm^3 volumes against a 0.020 mol dm^{-3} solution of potassium manganate (VII) which had just been standardised. The average titre was found to be 15.0 cm^3. The equation for the reaction is:

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

(i) What are the precautions followed in transferring the ethanedioic acid solution from the beaker to the volumetric flask? (6)

(ii) What was done to the volumetric flask and its contents immediately after the solution had been made up to the mark with deionised water? Why was it important to do this? (9)

(iii) Why was the potassium manganate (VII) solution standardised before carrying out the titration? (6)

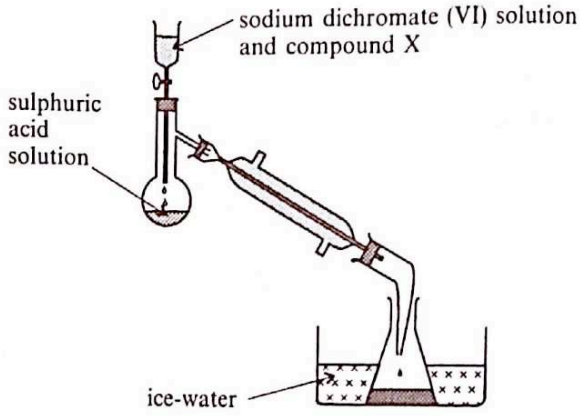
(iv) The 25.0 cm^3 volumes of ethanedioic acid solution were acidified before carrying out the titrations. Why was this necessary? Would you have used nitric acid, sulphuric acid or hydrochloric acid for the acidification? Give a reason for your choice. (12)

(v) After acidifying the ethanedioic acid solution, another procedure is necessary before carrying out the titration. What is this procedure and why is it necessary? (9)

(vi) How was the end-point of the titration identified? (6)

(vii) Calculate the concentration of the ethanedioic acid solution in the volumetric flask (*a*) in mol dm^{-3}, (*b*) in g dm^{-3}. What mass of ethanedioic acid crystals was weighed out at the beginning of the experiment? (18)

3. Two groups of students, group A and group B, carried out the following organic preparations. Group A prepared ethanal by reacting an excess of compound X with acidified sodium dichromate (VI) solution using the apparatus shown in the diagram. Group B prepared propanone by a similar method using an excess of compound Y, but did not surround the collecting flask with ice-water. Both groups used 11.92 g of sodium dichromate (VI) crystals ($Na_2Cr_2O_7.2H_2O$) and about 10 cm^3 of concentrated sulphuric acid dissolved in 25 cm^3 of water. After purification of the products, the yields obtained were 2.75 g of ethanal and 5.15 g of propanone.



The equation for the reaction carried out by group A is:

$$3X + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$$

The equation for the reaction carried out by group B is:

$$3Y + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3CH_3COCH_3 + 2Cr^{3+} + 7H_2O$$

(i) Identify compounds X and Y. (6)

(ii) Having set up the apparatus shown above, what procedure should be followed in carrying out the preparations? (9)

(iii) What features of groups A's preparation were designed to ensure that the main product was ethanal? Were these features equally important in group B's preparation? Explain your reasoning. (12)

(iv) Why was it essential for group A to surround the collection flask with ice-water? (6)

(v) Both groups tested their product with ammoniacal silver nitrate solution (Tollens' reagent). What, if anything, was observed in each case? Write an equation for any reaction that occurred. (12)

(vi) Calculate the percentage yields of ethanal and propanone, giving your answers correct to the nearest whole number. Suggest a reason for the higher percentage yield of propanone. (21)

4. Answer the following questions with reference to the eight elements labelled (a) to (h) in the part of the Periodic Table shown below. (Refer where necessary to Mathematics Tables p. 44 to p. 46).

1 (a)																	2
3	4											5	6	7 (b)	8	9	10
11	12 (c)											13 (d)	14	15 (e)	16	17	18
19	20	21	22	23	24	25	26 (f)	27	28	29 (g)	30	31	32	33	34	35 (h)	36

(i) Which element exists as a liquid at room temperature? At temperatures below $-7.2°C$ this element is a crystalline solid. What type of crystal is it and what binding forces hold the crystal together? (9)

(ii) Write the electronic configurations (s,p) for elements (c) and (d). Explain, in terms of these configurations, why there is a drop in the value of the first ionisation energy from (c) to (d). (12)

(iii) Write the formula for the compound formed between elements (a) and (e), and also for the compound formed between elements (d) and (h). State the shapes of the molecules of these two compounds and account for the difference between them. (18)

(iv) Explain clearly why the compound formed between elements (a) and (b) is much more soluble in water than the compound formed between elements (a) and (e). (9)

(v) Element (e) and two of the other elements commonly exhibit variable valence. Identify the two elements. In the case of either *one* of them state two of the valences exhibited and explain, in terms of electronic configuration, how these valences arise. (18)

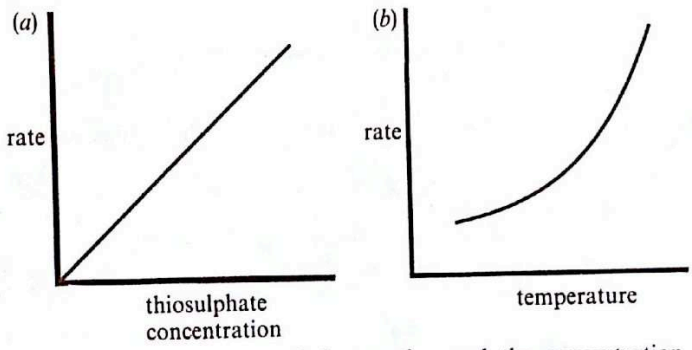
5. Define (i) rate of reaction, (ii) activation energy. (9)

The reaction between sodium thiosulphate solution and dilute hydrochloric acid results in the gradual formation of an insoluble solid. The reaction can therefore be conveniently used to illustrate the effects of concentration or temperature on reaction rate. The other products of the reaction are sodium chloride, water and a colourless gas.

(i) Identify the insoluble solid and the colourless gas and write a balanced equation for the reaction. (12)

(ii) Outline the experimental procedures you would follow in order to show (*a*) the effect of concentration, (*b*) the effect of temperature, on the rate of a reaction. You may use the above reaction between sodium thiosulphate solution and dilute hydrochloric acid or any other suitable reaction. (21)

(iii) The following graphs were obtained from the results of rate of reaction experiments using sodium thiosulphate solution and dilute hydrochloric acid:



State the relationship between the rate of the reaction and the concentration of sodium thiosulphate solution (graph (a)). Explain why the rate of the reaction increases with thiosulphate concentration. (9)

Give *two* reasons why the rate of the reaction between sodium thiosulphate solution and dilute hydrochloric acid increases with temperature as shown in graph (*b*). Which of the two reasons you have given is the more significant? Explain your answer. (15)

6. Explain the terms (*a*) oxidation number, (*b*) tribasic (triprotic) acid. (12)

What do you understand by a conjugate pair in the Bronsted-Lowry theory of acids and bases? (6)

The following are the formulae of three compounds of phosphorus, two of which are used in the making of fertilisers:

$$H_3PO_4 \qquad PCl_3 \qquad Ca(H_2PO_4)_2$$

(i) In the case of each of the three phosphorus compounds, find the oxidation number of the phosphorus atom (or atoms) present. (12)

(ii) Orthophosphoric acid, H_3PO_4, is a tribasic acid. The equation for the first dissociation of the acid in aqueous solution is

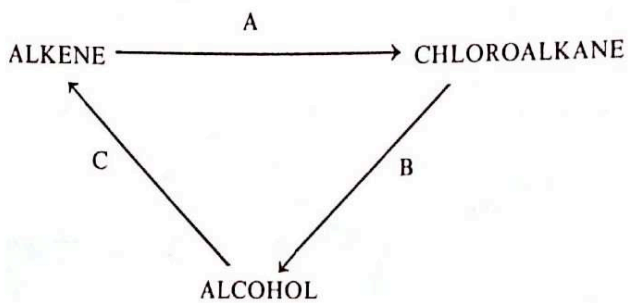
$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

Write an equation for the second dissociation in aqueous solution. Indicate the conjugate pairs present in the second dissociation. (12)

(iii) A compound (NPK) fertiliser was produced containing 5.3% phosphorus by mass. If the only phosphorus compound used was $Ca(H_2PO_4)_2$, how many kilograms of it were required to make one tonne (1000 kg) of the fertiliser? (12)

(iv) Give the name *and* the formula (*a*) of a nitrogen compound, (*b*) of a potassium compound, that could have been used to supply the nitrogen and potassium for the compound fertiliser in (iii). (12)

7. The alkenes are a homologous series of <u>unsaturated</u> hydrocarbons which take part in the following series of reactions:



(i) Explain the underlined term. Name any alkene and write its structural formula. (15)

(ii) Illustrate reaction B by means of a balanced equation. Give the name and structural formula of the alcohol formed. (12)

(iii) Describe with reference to the alcohol you have named in (ii) how you would carry out reaction C in the laboratory. What term is used for this type of reaction? (12)

(iv) Which of the reactions is an addition reaction? Name the reagent used to bring about the reaction. Describe briefly the mechanism of the reaction. (15)

(v) Give the name of (*a*) an aromatic substituted alkene, (*b*) a nitrogen-containing substituted alkene, each of which is used in polymer production. Write the structural formula for one of the compounds you have named. (12)

8. The following experiment was carried out to find the equilibrium constant (K_c) for the reaction

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

A mixture of 9.00 grams of ethanoic acid and 6.90 grams of ethanol was allowed to come to equilibrium in a sealed vessel at 373 K. It was found by titration that the ethanoic acid present in the equilibrium mixture required 0.05 moles of sodium hydroxide for neutralisation.

(i) Write the equilibrium constant expression (K_c) for the reaction. (6)

(ii) Write an equation for the reaction between sodium hydroxide and ethanoic acid. Name an indicator that would have been suitable for the titration and explain clearly the reasons for your choice. (15)

(iii) Calculate the numbers of moles of ethanoic acid, ethanol, ethyl ethanoate and water present in the equilibrium mixture and the value of the equilibrium constant (K_c) at 373 K. In calculating K_c, why was it not necessary to know the volume of the reaction mixture? (24)

(iv) Assuming that the heat change ($\triangle H$) for the equilibrium reaction is zero, what change, if any, would there have been in the value of K_c if the reaction had been carried out at 298 K? Explain your reasoning. (9)

(v) In a similar experiment at 373 K, using quantities of ethanoic acid and ethanol identical to those used in the experiment above, a little concentrated hydrochloric acid was added to the reaction mixture. State and explain the effect of the hydrochloric acid (*a*) on the time taken for the reaction to reach equilibrium, (*b*) on the value obtained for K_c. (Neglect the effect of the small amount of water present in the concentrated hydrochloric acid.) (12)

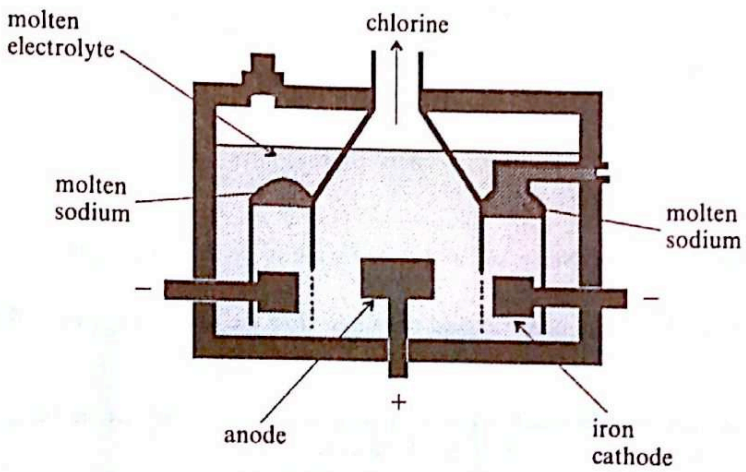
9. Sodium is a more electropositive metal than zinc. This is shown by the greater reactivity of the metal and also by the greater stability of its compounds.

(i) What is meant by saying that sodium is a more electropositive metal than zinc? (6)

(ii) Show that sodium is a more reactive metal than zinc by describing the reactions of the two metals with water or steam. Give the names of the compounds produced in the reactions. (12)

(iii) Show that the compounds of sodium are more stable than those of zinc by stating the effect, if any, of heat on the carbonates and hydroxides of the two metals. Write equations for any reactions that occur. (18)

(iv) Metallic sodium is obtained by electrolysis in the cell shown in the diagram.



(*a*) The molten electrolyte usually consists of sodium chloride mixed with another substance. What is the other substance and why is it used? (6)

(*b*) What material is used for the anode? Explain why iron is not used. (6)

(v) What mass of zinc would be liberated from molten zinc chloride by the quantity of electricity that would liberate 6.9 kg of sodium from molten sodium chloride? What volume of chlorine, measured at S.T.P. would be produced? (18)

10. Answer any *two* of the following.

(*a*) When 1.25×10^{-3} moles of a liquid hydrocarbon were burned completely in oxygen, 350 cm^3 of oxygen were used up and 224 cm^3 of carbon dioxide were produced. (Both volumes were at S.T.P.)

(i) How many moles of oxygen would be used up and how many moles of carbon dioxide would be produced if one mole of the liquid hydrocarbon were burned completely in oxygen? (12)

(ii) Show clearly that the molecular formula of the liquid hydrocarbon is C_8H_{18}. (9)

(iii) As a result of a cracking experiment, a molecule of the liquid hydrocarbon was split into one molecule of a branched-chain alkane and two identical alkene molecules. Give the names *and* structural formulae of these compounds. (12)

(*b*) Define pH. (6)

Calculate the pH of a solution containing 0.049 grams of sulphuric acid in 200 cm^3 of solution. (12)

A solution was obtained by mixing 50 cm^3 of a 0.1 mol dm^{-3} solution of nitric acid with 75 cm^3 of a 0.05 mol dm^{-3} solution of potassium hydroxide. Calculate (i) the number of moles of hydrogen ions (H^+) in the nitric acid solution, (ii) the number of moles of hydroxyl ions (OH^-) in the potassium hydroxide solution, (iii) the pH of the mixture. (15)

(*c*) State Hess's Law. (3)

Calculate the heats of formation of carbon monoxide and nitrogen monoxide from the following data:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -393 \text{ kJ}$$
$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} \quad \Delta H = -570 \text{ kJ}$$
$$N_{2(g)} + 2O_{2(g)} \rightarrow 2NO_{2(g)} \quad \Delta H = 66 \text{ kJ}$$
$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)} \quad \Delta H = -114 \text{ kJ}$$

(18)

From the oxides in the equations above give (i) an example of a neutral oxide, (ii) an example of an acidic oxide. In the case of the acidic oxide, write an equation for its reaction with a base of your choice. (12)

(*d*) What is hard water? (3)

A bucket of water from a stream was divided into three portions, A, B and C. A was left untreated, B was boiled and allowed to cool, and C was passed through a column of deionising resins. The hardness in the three portions was then determined by a titration experiment and the results (expressed in parts per million of calcium carbonate) are given in the following table.

PORTION	A	B	C
HARDNESS	250	110	5

(i) State (*a*) the standard solution, (*b*) the indicator, used in the titration. What was the colour change at the end-point? (12)

(ii) Give the names *or* formulae of two compounds that could have been responsible for the hardness of the water in A. (6)

(iii) Write an equation for a reaction that could explain the drop in hardness from A to B. (6)

(iv) Explain why there was virtually no hardness left in C. (6)