LEAVING CERTIFICATE EXAMINATION, 1989

CHEMISTRY — HIGHER LEVEL

FRIDAY, 16 JUNE — MORNING, 9.30 to 12.30

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, P =31, S = 32, Cr = 52, Fe = 56, Cu = 63·5

Avogadro constant = 6×10^{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 number of marks. *Keep your answers short.*

(*a*) Define relative atomic mass (A_r).

(*b*) What is meant by heterogeneous catalysis? Give an example.

(*c*) Write a balanced equation for the reaction that takes place when copper (II) carbonate is heated.

(*d*) Which of the gases: hydrogen, ammonia, carbon dioxide would you expect to come closest to ideal behaviour? Give a reason for your answer.

(*e*) What is the oxidation number of P in (i) H_3PO_4, (ii) HPO_3^{2-}?

(*f*) A volume of 5 cm^3 of sulphur dioxide diffused through a porous plug in 1 second. What volume of methane would diffuse through the same plug in 1 second under the same conditions?

(*g*) What is flocculation? Name a flocculating agent.

(*h*) Give the systematic (IUPAC) name of the compound

$$CH_3CH_2CH_2C(C_2H_5) = CH_2$$

(*i*) How many *atoms* are there in 1·12 dm^3 of hydrogen sulphide at S.T.P.?

(*j*) State what takes place in the secondary treatment of sewage.

(*k*) Name the product of the reaction between ethyne and hydrogen cyanide. Give one use of this product.

(*l*) Complete and balance the following equation:

$$Na_2O_2 + H_2O \longrightarrow$$

(*m*) What is meant by the *activation energy* of a reaction?

(*n*) What is a *triad* in Dobereiner's classification of the elements?

(*o*) When 4·0 mg of a hydrocarbon were burned completely in oxygen, 13·2 mg of carbon dioxide were produced. Calculate the percentage by mass of carbon in the hydrocarbon.

(11 × 6)

oxalic acid > above 60°C

2. A mass of 8·82 g of ammonium iron (II) sulphate crystals: $(NH_4)_2SO_4.FeSO_4.XH_2O$, was dissolved in deionised water to which some sulphuric acid had been added. The solution was then made up accurately to 250 cm^3. A pipette was used to measure 25 cm^3 of this solution into a conical flask and a further 10 cm^3 of dilute sulphuric acid were added. A burette was filled with a 0·02 mol dm^{-3} solution of potassium manganate (VII) and a number of titrations were carried out. The mean titration result was 22·5 cm^3. The equation for the titration reaction is

$$8H^+ + MnO_4^- + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

(i) Why was sulphuric acid added in making up the ammonium iron (II) sulphate solution? (6)

(ii) Outline the correct procedure for diluting the ammonium iron (II) sulphate solution to 250 cm^3. (12)

(iii) At what point in the potassium manganate (VII) solution are the burette readings taken? What colour change would you observe as the solution from the burette flows into the conical flask? How would you identify the end-point of the titration? (9)

(iv) During the titrations drops of the potassium manganate (VII) solution were noticed high up on the sides of the conical flask. What action would you take to deal with this problem? Why is it possible to take this action without affecting the result of the titration? (9)

(v) What would you observe if insufficient sulphuric acid were present during the titration? Explain clearly the function of the acid in the titration. (9)

(vi) Calculate the concentration of the ammonium iron (II) sulphate solution (*a*) in g dm^{-3}, (*b*) in mol dm^{-3}. Hence, find the percentage water of crystallisation in the ammonium iron (II) sulphate crystals and the value of X in the formula. (21)

3. To prepare a sample of ethanal, about 10 cm^3 of concentrated sulphuric acid were carefully added to 25 cm^3 of water. This solution was brought to boiling and then the heat was removed. Another solution containing 14·9 g of sodium dichromate (VI), $Na_2Cr_2O_7.2H_2O$, and 11·5 cm^3 of ethanol (density = 0·80 g cm^{-3}) in 20 cm^3 of water was added drop-by-drop to the hot sulphuric acid solution and the ethanal produced was immediately removed from the reaction mixture and collected. After further purification, the yield of ethanal was found to be 1·6 g. The equation for the reaction is

$$3C_2H_5OH + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$$

(i) Draw a labelled diagram of the apparatus you would use for the addition of the dichromate/ethanol solution followed by the immediate removal and collection of the ethanal. Why is it important to remove the ethanal as soon as it is formed? (12)

(ii) What colour is the dichromate/ethanol solution? What would you notice as this solution is added to the hot sulphuric acid solution? Explain your answer. (9)

(iii) One of the physical properties of ethanal makes it difficult to collect under normal laboratory conditions. What is this property and how is the difficulty overcome? (9)

(iv) What would you observe if ethanal were warmed gently (*a*) with Fehling's solution, (*b*) with ammoniacal silver nitrate solution (Tollens' reagent)? In the case of (*a*) *or* (*b*) write an equation for the reaction. (12)

(v) From the information given above, show which of the two substances, sodium dichromate (VI) or ethanol, is in excess in the reaction. Why is an excess of this substance used? (12)

(vi) Calculate (*a*) the number of moles, (*b*) the mass, of ethanal theoretically obtainable in the reaction. What was the percentage yield of ethanal? (12)

4. Define *heat of combustion*. (6)

Describe, with the aid of a diagram, how you would measure the heat of combustion of a substance. State, giving your reasons, whether or not the experiment you have described would be likely to give an accurate result. (18)

When 1·0 g of pure heptane was completely burned in a suitable apparatus the rise in temperature was 5·7°C. When 1·0 g of pure methylbenzene was burned in the same apparatus the rise in temperature was 5·0°C. Calculate the heats of combustion of heptane and methylbenzene given that the heat capacity of the apparatus is 8·5 kJ $°C^{-1}$. (18)

Methylbenzene can be produced from heptane. The reaction is: $C_7H_{16(l)} \longrightarrow C_7H_{8(l)} + 4H_{2(g)}$

Use the heats of combustion of heptane and methylbenzene to calculate the heat change for this reaction, given that the heat of combustion of hydrogen gas is −286 kJ mol^{-1}. (12)

Give the structural formula and the common name for methylbenzene. (6)

Methylbenzene is an aromatic hydrocarbon. The molecular formula of another aromatic hydrocarbon is C_8H_8. Identify this compound and state one of its uses. (6)

5. Answer this question with reference to the first thirty-six elements of the Periodic Table. (Mathematics Tables p.44 to p.46).

(i) Name (*a*) a non-metal which exists as single atoms, (*b*) a non-metal which exists as giant molecules, (*c*) a non-metal which exists as a liquid at ordinary temperatures. (9)

(ii) Which common element is found in nature in the form of diatomic and triatomic molecules? Give the common name for the triatomic form of the element and indicate why this form of the element is a cause for concern among scientists at the present time. (9)

(iii) Which two elements would you expect to form the bond with the greatest ionic character? Write the electron configurations (s, p, etc.) for the ions involved. (12)

(iv) Write the formula for the compound usually formed when the elements of atomic numbers 6 and 16 combine together. What type of bond is present? Use the electron pair repulsion theory to assign a shape to the molecules of this compound. (12)

(v) Why is there a decrease (*a*) in the atomic radius, (*b*) in the first ionisation energy, in going from the element of atomic number 12 to the element of atomic number 13? (12)

(vi) The first four ionisation energies of the element of atomic number 5 are shown in the table.

Explain (*a*) why the second ionisation energy is greater than the first, (*b*) why the increase in ionisation energy is relatively small for the third electron but very large for the fourth electron. (12)

electron removed	ionisation energy (kJ mol^{-1})
1st	799
2nd	2,421
3rd	3,650
4th	24,962

6. (*a*) When concentrated hydrochloric acid is added to bismuth (III) chloride a colourless solution of $BiCl_4^-$ ions is formed. As water is slowly added to this solution a white precipitate of bismuth (III) chloride oxide (BiOCl) appears and the following dynamic equilibrium is established:

$$BiCl_4^- + H_2O \rightleftharpoons BiOCl + 2HCl + Cl^-$$

(i) State and explain what you would observe as concentrated hydrochloric acid is added to the above equilibrium system. (9)

(ii) If, having added the concentrated hydrochloric acid as described in (i), sufficient water were now added, what change, if any, would you notice in the equilibrium system? Explain your answer. (9)

(iii) Name and state in full the principle on which your explanations in (i) and (ii) are based. (9)

(*b*) A mixture of 27 g of ethanoic acid and 20·7 g of ethanol was allowed to come to equilibrium at a certain temperature. It was found by experiment that 9 g of ethanoic acid were present in the equilibrium mixture. The reaction is

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

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

(ii) State how you would experimentally determine the amount of ethanoic acid present in the equilibrium mixture. (6)

(iii) Calculate the equilibrium constant (K_c). (12)

(iv) If 13·8 g of ethanol were added to the above equilibrium mixture, what mass of ethanoic acid would be present when equilibrium was re-established at the same temperature? (15)

7. (*a*) Define (i) acid, (ii) conjugate pair, in terms of the Brönsted-Lowry theory. (6)

Sulphuric acid dissociates in water as follows: $H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$

Why is (i) sulphuric acid considered to be a strong acid, (ii) the conjugate base of sulphuric acid described as a weak base? Show by means of an equation that the conjugate base of sulphuric acid can itself act as an acid. (12)

(*b*) Explain (i) why water is a good solvent for ionic substances, (ii) why water has a higher boiling point than other compounds of comparable relative molecular mass. (12)

(*c*) What is meant by (i) pH, (ii) the ionic product of water (K_w)? (6)

The ionic product of water varies with temperature. The following table shows the values of the ionic product for pure water at three different temperatures.

Temperature (°C)	0	25	50
K_w ($mol^2\ dm^{-6}$)	$1{\cdot}13 \times 10^{-15}$	$1{\cdot}0 \times 10^{-14}$	$5{\cdot}5 \times 10^{-14}$

Is the self-ionisation of water endothermic or exothermic? Give a reason for your answer. (9)

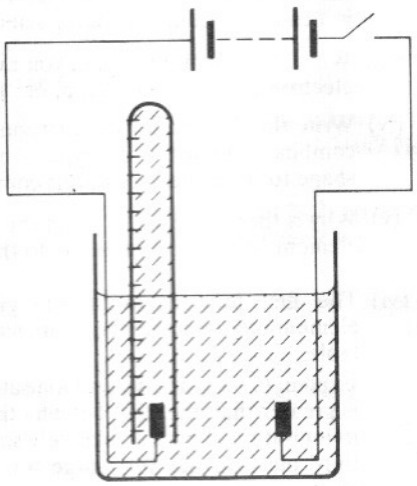
Calculate the hydrogen ion concentration at each of the three temperatures. Hence find the pH of the water at each temperature correct to the first place of decimals. (12)

Does the variation found in the three pH values mean that the acidity of pure water varies with temperature? Explain your answer. (9)

8. (*a*) State Faraday's First Law of Electrolysis. (6)

The diagram shows an apparatus for the electrolysis of aqueous copper (II) sulphate using inert (platinum) electrodes. The overall chemical change taking place may be represented by the following equation:

$$Cu^{2+}_{(aq)} + H_2O_{(l)} \longrightarrow Cu_{(s)} + \tfrac{1}{2}O_{2(g)} + 2H^{+}_{(aq)}$$



(i) Write equations for the reactions taking place at the anode and at the cathode. (9)

(ii) If 120 cm^3 of oxygen, measured at room temperature and pressure, were collected in 193 seconds, what mass of copper was produced and what constant current was used? (The molar volume of a gas at room temperature and pressure is 24·0 dm^3). (18)

(*b*) Copper may be found in nature as the free element but most copper nowadays is obtained by extraction of the metal from its ores.

(i) Why is it possible for copper to exist in nature as the free element? (3)

(ii) Name one of the main ores of copper. (6)

(iii) Outline the stages in the process used to extract the copper from the ore you have named in (ii). (15)

(iv) Describe briefly how very pure copper is obtained from the impure metal left at the end of the extraction process you have outlined in (iii). (9)

9. The formulae of five organic compounds are given as follows:

A

$CH_3CH = CHCH_3$

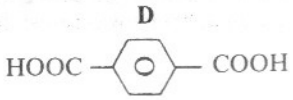
B

$CH_3CH_2CHClCH_3$

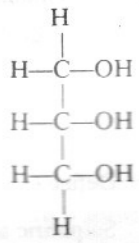
C

$CH_3COCH_2CH_3$

D



E



(i) Name each of the compounds **A** to **E**. (15)

(ii) Which one of the compounds undergoes hydrolysis when warmed with sodium hydroxide solution? Give the structural formula of the organic product. (6)

(iii) With which one of the compounds does ethane-1,2-diol react to give a condensation polymer? Name the polymer and give the formula of the repeating part. (9)

(iv) Which one of the compounds can be reduced to a secondary alcohol? Write a balanced equation for the reaction. (9)

(v) One of the compounds is derived as a byproduct from fats and oils by saponification (i.e. the soap-making reaction). Identify this compound and give a brief outline of how a sample of soap may be prepared in the laboratory. (12)

(vi) With which one of the compounds does bromine form an addition product? Name this product and describe briefly the mechanism of the addition reaction. (15)

10. Answer any *two* of the following.

(*a*) When dilute hydrochloric acid is added to a solution of sodium thiosulphate the following reaction occurs.

$$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + SO_{2(aq)} + S_{(s)}$$

A student carried out the above reaction between 100 cm^3 of 0·1 mol dm^{-3} sodium thiosulphate solution and 10 cm^3 of 1·0 mol dm^{-3} hydrochloric acid at a number of different temperatures. The time (t) taken for a mark on the bottom of the reaction vessel to be obscured by the suspended sulphur was noted for each temperature. The reciprocal (1/t) of the time was used as a measure of the initial rate of the reaction in each case. The results are shown in the following table.

temperature (°C)	time (t) (s)	rate (1/t) (s^{-1})
10	100	0·010
20	59	0·017
30	36	0·028
40	21	0·048
50	12	0·083
60	7	0·143

(i) How would you carry out the above reaction at any one of the given temperatures? (6)

(ii) Plot on graph paper the rate (1/t) against temperature. (12)

(iii) If the reaction had been carried out at 35°C what time would have elapsed before the mark became obscured? (9)

(iv) What change would you expect to see in the graph if 100 cm^3 of 0·5 mol dm^{-3} sodium thiosulphate solution had been used? (6)

(*b*) Chlorine is a very reactive element with a number of important uses. In many of its reactions it acts as an oxidising agent.

(i) Why is chlorine used in water purification? Give *one* other important use of chlorine. (6)

(ii) Chlorine exists as a solid below −103°C. State the type of crystal structure you would expect the solid to have and name the forces responsible for holding the crystal together. (9)

(iii) What would you observe when chlorine is added to a solution containing iodide ions? How does this reaction indicate the relative positions of chlorine and iodine in the electrochemical series? (9)

(iv) Complete and balance the following equations in which chlorine is acting as an oxidising agent.

$$Fe + Cl_2 \longrightarrow$$

$$SO_3^{2-} + Cl_2 + H_2O \longrightarrow$$

(9)

(*c*) Explain clearly why fertilisers can sometimes be harmful to the environment. (9)

In making a compound (NPK) fertiliser, ammonium phosphate, $(NH_4)_3PO_4$, was used as the only source of nitrogen and phosphorus. What percentage of ammonium phosphate would be needed to give an N value of 10? Calculate also the percentage phosphorus in the fertiliser. (18)

What substance could be used to supply the potassium needed for the fertiliser? (6)

(*d*) A student was given salt X for analysis in the laboratory. When dilute hydrochloric acid was added to the salt there was brisk effervescence of a colourless gas which gave a white precipitate when bubbled through limewater. Another white precipitate was observed when magnesium sulphate solution was added to an aqueous solution of the salt. Finally, it was found that salt X gave a lilac colour to the Bunsen flame.

(i) Identify X. (6)

(ii) Give the names of the colourless gas and the two white precipitates. (9)

(iii) Write a balanced equation for each reaction that took place. (18)