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LEAVING CERTIFICATE EXAMINATION, 1999

CHEMISTRY — HIGHER LEVEL

TUESDAY, 22 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.

Question 1 carries a total of 70 marks. All other questions carry a total of 66 marks each.

Relative atomic masses: H = 1, C = 12, N = 14, O = 16, Na = 23, S = 32, Cr = 52, Cu = 63.5, I = 127.

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. However, one additional mark will be given to each of the first four items for which the highest marks are obtained. *Keep your answers short.*

(*a*) Write the electronic configuration (s, p) of (i) the silicon atom, (ii) the fluoride ion.

(*b*) Name a compound from which magnesium metal is commonly extracted. State *one* common use of magnesium.

(*c*) A sealed flask is full of nitrogen gas at S.T.P. If the total number of nitrogen molecules in the flask is 2.25×10^{22}, what is the volume of the flask in cm^3?

(*d*) In the burning of gas, why is it necessary to supply heat to start the combustion reaction, but not necessary to continue the supply of heat after the reaction has started?

(*e*) Identify the *neutral* oxides in the following list:

Na_2O NO SO_2 ZnO CO

(*f*) What is the simplest whole-number ratio, by volume, in which ethyne and oxygen combine under conditions of complete combustion?

(*g*) Give the systematic (IUPAC) name *or* the structural formula of the organic compound formed when 2-chloro-2-methylpropane undergoes hydrolysis.

(*h*) Name (i) the scientist who introduced the term *triad*, (ii) the scientist who introduced the term *octave*, in the history of the classification of the elements.

(*i*) What is the pH of a 0.05 mol dm^{-3} solution of methanoic acid? ($K_a = 2.0 \times 10^{-4}$).

(*j*) State *Faraday's Second Law of Electrolysis*.

(*k*) Name (i) a major industrial source of oxygen, (ii) a major industrial source of hydrogen.

(*l*) One tonne of a compound (NPK) fertiliser contained 330 kg of ammonium sulphate as its only source of nitrogen. What was the N value of the fertiliser?

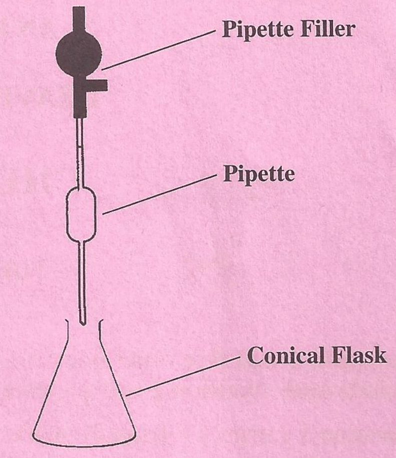
(*m*) Define *bond energy*.

(*n*) When carbon dioxide is passed through a solution of calcium hydroxide, a white precipitate is formed. State and explain what you would observe if carbon dioxide continued to be passed through the solution.

(*o*) What type of mechanism is involved in the reaction between chlorine and methane?

(70)

2. A mass of 2.52 g of ethanedioic acid crystals, $C_2H_2O_4.xH_2O$, was dissolved in deionised water and the solution was made up accurately to 500 cm^3 in a volumetric flask. Some of the solution was poured into a clean, dry beaker. A pipette, fitted with a pipette filler (see diagram), was used to transfer 25.0 cm^3 of the solution from the beaker to a conical flask and about 20 cm^3 of dilute sulphuric acid were added. A thermometer was placed in the conical flask, and the flask and contents were heated to about 70 °C. The flask was removed from the heat and the thermometer was removed from the solution. It was found by titration that the acidified solution of ethanedioic acid required 20.0 cm^3 of a 0.020 mol dm^{-3} solution of potassium manganate(VII) for complete oxidation.



The equation for the reaction involved in the titration is

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

(i) In preparing the pipette for the titration it was rinsed with deionised water and then the water was removed by rinsing the pipette with the solution to be transferred. Explain why it was important to remove the water. Why was the conical flask *not* rinsed with the solution? (12)

(ii) Pipette fillers are used for safety reasons. What property of ethanedioic acid makes the use of a pipette filler essential? (6)

(iii) What problem was encountered when removing the thermometer from the solution in the conical flask? How could this problem have been overcome? (9)

(iv) Why was it necessary to heat the contents of the conical flask immediately before carrying out the titration? Explain why it was not necessary to continue heating during the titration. (9)

(v) What colour change was observed as the potassium manganate(VII) solution reacted with the acidified ethanedioic acid solution? How was the end-point of the titration identified? (12)

(vi) Calculate the concentration of the ethanedioic acid solution in the volumetric flask (*a*) in g dm^{-3}, (*b*) in mol dm^{-3}. Hence find the percentage water in the ethanedioic acid crystals and the value of *x* in the formula. (18)

3. Ethanal and ethanoic acid were prepared in the school laboratory, in two separate experiments, by the oxidation of ethanol using an acidified solution of sodium dichromate(VI), $Na_2Cr_2O_7.2H_2O$. The two liquids were then purified by distillation. The quantities of reactants and the yields of products are given in the following table.

Mass of sodium dichromate(VI)	Volume of ethanol	Name of Product	Yield of Product
8.94 g	6.9 cm^3	ethanal	1.62 g
8.94 g	2.3 cm^3	ethanoic acid	1.73 g

The equations for the reactions involved in the above preparations are:

$$3C_2H_5OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$$
$$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$$

(i) Name the functional group (*a*) in ethanal, (*b*) in ethanoic acid. Mention a *chemical* test to distinguish between these two compounds. (12)

(ii) Apart from the different volumes of ethanol used, give *one* important difference between the procedures followed in the preparations of ethanal and ethanoic acid. What was the reason for this difference? (12)

(iii) The same final colour of the reaction mixture was observed in both preparations. What was this colour, and what species, present in the reaction mixture, gave rise to it? (6)

(iv) There was a problem involved in the collection of the distilled ethanal. What was this problem and how was it overcome? (9)

(v) The same mass of sodium dichromate(VI) was used in both preparations but the volumes of ethanol used were different. Explain clearly the reason for this. (9)

(vi) Calculate the percentage yield of (*a*) ethanal, (*b*) ethanoic acid. (The density of ethanol is 0.8 g cm^{-3}). (18)

4. The reaction between hydrogen gas and iodine vapour is <u>reversible</u>. The following experiment was carried out to find the value of the equilibrium constant (K_c) for this reaction at 350 °C. A volume of 600 cm^3 of hydrogen gas (measured at room temperature and pressure) and 6.35 g of solid iodine were sealed in a flask and heated to the required temperature. When the system had reached <u>equilibrium</u> the reaction mixture was cooled rapidly by immersing the flask in a beaker of ice-water. On analysis, the mass of iodine present was found to be 1.27 g.

The equation for the reaction is:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad \Delta H = -10 \text{ kJ}$$

(i) Explain the underlined terms. (9)

(ii) Write the equilibrium constant (K_c) expression for the reaction and calculate the value of K_c at 350 °C. In calculating K_c, why was it not necessary to know the volume of the sealed flask? (Molar volume at room temperature and pressure = 24.0 dm^3). (21)

(iii) Why was the reaction mixture cooled *rapidly*? Would the value obtained for K_c have been greater, less or unchanged if the reaction had been allowed to cool *slowly*? Explain your answer. (12)

(iv) Write the equilibrium constant (K_p) expression for the reaction. Explain why the values of K_p and K_c are the same for this reaction. (12)

(v) If equal numbers of moles of hydrogen and iodine were allowed to come to equilibrium at 500 °C, what would be the percentage of iodine by moles in the equilibrium mixture, given that the value of K_c for the reaction is 49 at 500 °C? Give your answer correct to the nearest whole number. (12)

5. (i) Define (*a*) ionic bond, (*b*) covalent bond, (*c*) polar bond, (*d*) electronegativity. (15)

State the *Valence Shell Electron Pair Repulsion Theory*. (9)

(ii) From the following compounds, sodium chloride (NaCl), aluminium chloride ($AlCl_3$), phosphorus(III) chloride (PCl_3), select (*a*) a liquid at room temperature, (*b*) a solid with a low melting point, (*c*) a solid with a high melting point. In each case, show how the bonding present may be used to explain your answer. (18)

None

(iii) Aluminium chloride and phosphorus(III) chloride both undergo hydrolysis with water. Write an equation for either one of these reactions. (6)

(iv) Show the formation of the bonds in sodium chloride and phosphorus(III) chloride by means of suitable diagrams. (9)

In the case of the chloride that exists as molecules, state the shape of these molecules, and use the Valence Shell Electron Pair Repulsion Theory to explain why the molecules have the shape you have stated. (9)

6. Copper has been used for thousands of years, and it is still very widely used today. For its most common modern use, accounting for more than forty per cent of production, the metal is needed in very pure form. This high level of purity is achieved by electrolysis.

(i) Suggest why copper was one of the earliest metals to be widely used. (6)

(ii) What is the most common use of copper in the modern world? On what property of copper does this use depend? (6)

(iii) What is the difference between the material used for the anode and the material used for the cathode in the purification of copper by electrolysis? What electrolyte is used in the process? Write an equation for the reaction at each electrode. (15)

If the anode and cathode were replaced by inert (platinum) electrodes, state a difference you would observe as the electrolysis took place? Write an equation for the reaction at the anode in this case. (9)

(iv) When crystalline copper(II) nitrate is heated the following reaction takes place.

$$2Cu(NO_3)_2.3H_2O \longrightarrow 2CuO + 4NO_2 + O_2 + 6H_2O$$

Give the colour *or* state of (*a*) copper(II) oxide, (*b*) nitrogen dioxide. (12)

If 4.83 g of crystalline copper(II) nitrate were heated, calculate (*a*) the mass of copper(II) oxide, (*b*) the volume of nitrogen dioxide (at S.T.P.), (*c*) the number of molecules of oxygen, that would be produced according to the above equation. (18)

7. (i) Explain the terms (*a*) exothermic reaction, (*b*) heat of formation. (9)

State *Hess's Law.* (6)

(ii) The heats of formation of water, $H_2O_{(l)}$, and sulphur dioxide, $SO_{2(g)}$, are –286 kJ mol^{-1} and –297 kJ mol^{-1} respectively. Use these values, together with the values of the heats of reaction given below, to calculate the heat of formation of sulphuric acid, $H_2SO_{4(l)}$.

$$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)} \qquad \Delta H = -196 \text{ kJ}$$

$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(l)} \qquad \Delta H = -133 \text{ kJ}$$ (12)

(iii) State the conditions used for the conversion of sulphur dioxide to sulphur trioxide in the manufacture of sulphuric acid by the Contact Process. Outline briefly how the sulphur trioxide is converted to sulphuric acid, and explain why it is necessary to use the procedure you have outlined. (15)

(iv) Sulphuric acid acts as a dehydrating agent. Describe what you would observe when the concentrated acid is added (*a*) to crystalline copper sulphate, (*b*) to sugar. (12)

(v) Sodium sulphite reacts with dilute sulphuric acid to produce a colourless gas.

Name the gas and write an equation for the reaction. Why is the release of this gas into the atmosphere a cause of serious environmental concern? (12)

8. Two experiments were carried out to find the <u>molecular formula</u> of a volatile organic liquid. In the first experiment, the percentage composition, by mass, of the liquid was found to be 62.07% carbon, 10.34% hydrogen and 27.59% oxygen. From this information the <u>empirical formula</u> of the liquid was calculated. In the second experiment, the relative molecular mass of the liquid was found to be 58.

(i) Explain the underlined terms. (6)

(ii) Show how the empirical formula (C_3H_6O) of the liquid may be calculated from the percentage composition given above. What is the molecular formula of the liquid? (15)

(iii) When the liquid was reacted with 2,4-dinitrophenylhydrazine, a yellow solid and water were formed. However, when the liquid was heated with Fehling's solution, no change was observed. Give the name *and* structural formula of the liquid. To which homologous series does it belong? What is the *name* of the functional group in this homologous series? (15)

(iv) What term is used in organic chemistry for the type of reaction that took place between the liquid and 2,4-dinitrophenylhydrazine? Write an equation for the reaction and name the solid product. What method could be used to purify the solid, and what simple test could be used to find out if the purification was successful? (18)

(v) When the vapour of the liquid was passed, with hydrogen, over a heated nickel catalyst, an alcohol was produced. Give the systematic (IUPAC) name *and* structural formula of the alcohol. To which *class* of alcohols does it belong? (12)

9. (*a*) Phenolphthalein is an acid-base indicator which changes from colourless to red/violet in the pH range 8.3 - 10. When put in deionised water at 25 °C, the following equilibrium is established, where HIn represents the indicator molecules.

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

(i) State and explain the appearance of the solution of the indicator in deionised water. (6)

(ii) What would be the appearance of the indicator when dissolved in a 0.001 mol dm^{-3} solution of sodium hydroxide at 25 °C? Explain your answer. (9)

(iii) Explain why phenolphthalein is a suitable indicator for a weak acid-strong base titration. (6)

(*b*) (i) What do you understand by *hardness* in water? Give the name *and* formula of a compound that could be responsible for causing *temporary hardness* in water. (9)

(ii) The total hardness in water can be determined by titration with standard EDTA solution.

What indicator is used in this titration? What colour change is observed at the end-point? (9)

A buffer solution is used in this titration. What is the purpose of the buffer solution? (6)

(*c*) An experiment was carried out to measure the biochemical oxygen demand (B.O.D.) of a water sample taken from a polluted lake. A volume of 10 cm^3 of the sample was pipetted into a 1 dm^3 volumetric flask, which was then made up accurately to the mark using well-oxygenated distilled water. The diluted lake water was divided into two portions. The dissolved oxygen concentration of one of the portions was measured immediately and was found to be 7.5 p.p.m. After storing the other portion for a period of time and under the conditions required for the determination of B.O.D., its dissolved oxygen concentration was found to be 5.4 p.p.m.

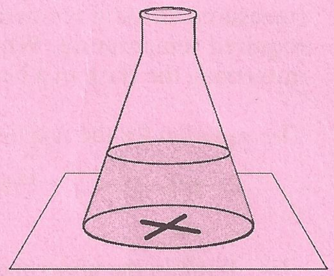
(i) How might the distilled water used to dilute the lake water have been oxygenated? Why was it important to do so? (6)

(ii) For what period of time and under what conditions was the second portion stored? (9)

(iii) What was the B.O.D. of the lake water? (6)

10. Answer any *two* of the following.

(*a*) To investigate the effect of concentration on reaction rate, a student measured 100 cm^3 of a 0.02 mol dm^{-3} solution of sodium thiosulphate into a conical flask, added 10 cm^3 of a 1.0 mol dm^{-3} solution of hydrochloric acid, and then placed the flask on top of a cross on a sheet of white paper as shown in the diagram. The student noted the time required for the cross to become obscured by the precipitate that formed in the solution. The procedure was repeated a number of times using thiosulphate solutions of the same volume (100 cm^3) but different concentrations, adding 10 cm^3 of a 1.0 mol dm^{-3} solution of hydrochloric acid each time. The reciprocal of the time ($^1/_{time}$) was used as a measure of the initial rate of the reaction in each case. The results obtained are shown in the following table.



Conc. of thiosulphate solution (mol dm^{-3})	Time (minutes)	Rate i.e. $^1/_{time}$ (min^{-1})
0.02	8.27	0.12
0.04	4.13	0.24
0.06	2.76	0.36
0.08	2.07	0.48
0.10	1.66	0.60

(i) Identify the precipitate and give *one* other product of the reaction between sodium thiosulphate and hydrochloric acid. (9)

(ii) Plot on graph paper the rate of the reaction ($^1/_{time}$) against the concentration of sodium thiosulphate. What conclusion can you draw from the graph about the relationship between the rate of the reaction and the concentration of sodium thiosulphate? (15)

(iii) If the student had used a 0.03 mol dm^{-3} solution of sodium thiosulphate, how long would it have taken before the cross became obscured? (9)

(*b*) (i) What is meant by *energy levels* in an atom? How many sublevels are there in the fourth (n = 4) main energy level? (6)

(ii) If you were given samples of the nitrates of sodium and potassium, describe how you could distinguish between them using flame tests. Explain, in terms of energy levels, why flame tests can be used to distinguish between different metals. (18)

(iii) Outline a test you could carry out to show that the salts mentioned in (ii) contain the nitrate ion. (9)

(*c*) Define *reduction* in terms of (i) electron transfer, (ii) change in oxidation number. (6)

What is the oxidation number of (i) oxygen in O_2^{2-}, (ii) iodine in I_2O_5? (12)

Use oxidation numbers in the following reaction (i) to show where oxidation and reduction have taken place, (ii) to balance the equation for the reaction.

$$IO_3^- + S^{2-} + H^+ \rightarrow I_2 + S + H_2O$$ (15)

(*d*) An unsaturated hydrocarbon of molecular formula C_5H_{10} has five different structural isomers. Two of these, pent-1-ene and pent-2-ene, are straight-chain compounds. The other three have branched chains.

(i) To which homologous series do the five isomers belong? Why are the members (homologues) of this series described as mono-unsaturated? What is the characteristic type of chemical reaction for unsaturated compounds? (9)

(ii) What is the structural difference between pent-1-ene and pent-2-ene? (6)

(iii) Give the systematic (IUPAC) names *and* the structural formulae of any *two* of the branched isomers. (18)