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AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1992

CHEMISTRY — HIGHER LEVEL

MONDAY, 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.

All questions carry the same number of marks.

Relative atomic masses: H = 1, C = 12, N = 14, O = 16, Ne = 20, Na = 23, Al = 27, S = 32, Cr = 52, Ag = 108, I = 127.

Gas constant (R) = 8.3 N m K^{-1} 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*) How many (i) neutrons, (ii) electrons, are there in the ion $^{45}_{21}Sc^{3+}$?

(*b*) State any *two* factors that can affect the rate of a chemical reaction.

(*c*) What is the volume occupied by 0.35 grams of ethene gas at S.T.P.?

(*d*) Write the full structural formula for 2-chlorobutan-2-ol.

(*e*) In what ratio by volume do the gases sulphur dioxide and oxygen combine?

(*f*) Give *two* properties usually associated with transition elements or their compounds.

(*g*) When 200 cm^3 of a 1 mol dm^{-3} hydrochloric acid solution were neutralised by a solution of sodium hydroxide, 11.4 kJ of heat were produced. Calculate the heat of neutralisation of hydrochloric acid by sodium hydroxide.

(*h*) What are the two main stages in the industrial production of oxygen from air?

(*i*) Complete and balance the equation:

$$C_2H_5OH + Na \longrightarrow$$

(*j*) State *two* differences between Mendeleef's form and the modern form of the Periodic Table (Mathematics Tables, page 44).

(*k*) Identify the two species acting as acids in the following system.

$$H_2SO_4 + H_2F_2 \rightleftharpoons H_3SO_4^+ + HF_2^-$$

(*l*) Give an example of homogeneous catalysis, stating the reactant (or reactants) and the catalyst involved.

(*m*) What is the oxidation number of hydrogen in sodium hydride?

(*n*) Which one of the following represents the energy change known as the second ionisation energy of element X?

$$X^{2+} \longrightarrow X^{3+} + e^- \qquad X \longrightarrow X^+ + e^- \qquad X^+ \longrightarrow X^{2+} + e^-$$

(*o*) On reduction, 0.58 grams of an oxide of silver yielded 0.54 grams of the pure metal. What is the empirical formula of the oxide?

(11 × 6)

2. A number of groups of students carried out the following experiment to find the percentage purity of a sample of crystalline sodium thiosulphate ($Na_2S_2O_3.5H_2O$). A mass of 10.0 grams of the crystals was dissolved in deionised water and the solution was made up accurately to 500 cm^3 in a volumetric flask. A burette was then filled with this solution. A 25.0 cm^3 portion of a 0.050 mol dm^{-3} solution of iodine (previously standardised) was pipetted into a conical flask and the sodium thiosulphate solution was titrated against it. Three titrations were carried out and the titration results were 31.6 cm^3, 31.2 cm^3 and 31.3 cm^3. The equation for the titration reaction is

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

(i) In making up the iodine solution in the experiment, iodine, water and potassium iodide were used. What was the function of the potassium iodide? (6)

(ii) Which of the three pieces of titration apparatus, the pipette, the burette or the conical flask, should *not* be rinsed with the solution it is to contain? Give the reason for your answer. (9)

(iii) Due to a shortage of apparatus, one group used a 500 cm^3 graduated cylinder in place of a volumetric flask, and another group used a beaker instead of a conical flask, in carrying out the titration. Give (*a*) *one* reason why a volumetric flask is preferable to a graduated cylinder, (*b*) *one* reason why a conical flask is preferable to a beaker. (6)

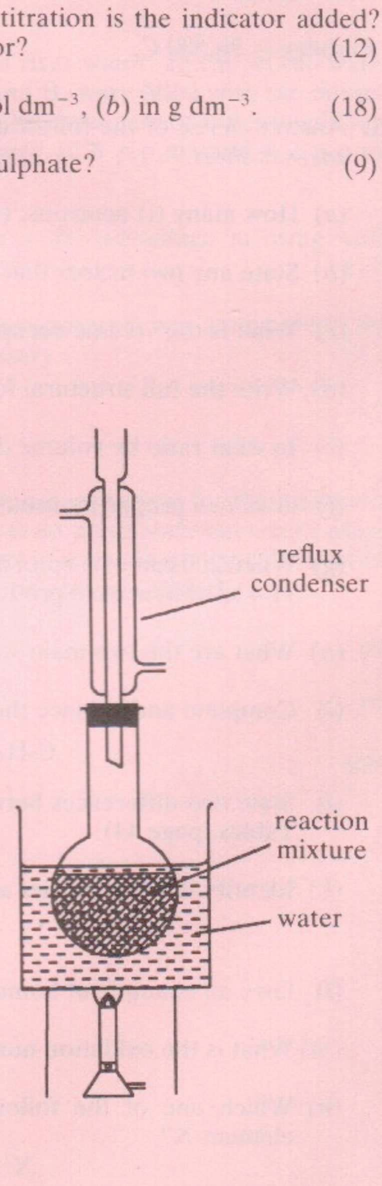
(iv) What colour change would have been observed in the conical flask as the sodium thiosulphate solution was added from the burette? (6)

(v) Name the indicator usually used in this titration. At what stage in the titration is the indicator added? What is the colour change at the end-point in the presence of the indicator? (12)

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

(vii) What was the percentage purity of the sample of crystalline sodium thiosulphate? (9)

3. To prepare a sample of ethanoic acid, 40 cm^3 of water were measured into a flask and 20 cm^3 of concentrated sulphuric acid were added. A mass of 29.8 grams of sodium dichromate (VI), (formula $Na_2Cr_2O_7.2H_2O$), was dissolved in the acid solution and the flask was fitted with a reflux condenser. A solution of 6.9 cm^3 of ethanol (density = 0.80 g cm^{-3}) in 15 cm^3 of water was added to the flask through the condenser. The apparatus was then arranged as shown in the diagram and the reaction mixture was heated under reflux for about 30 minutes. Finally the ethanoic acid was recovered from the reaction mixture by distillation. The yield of ethanoic acid was 5.4 cm^3.



The reaction may be represented by the following equation:

$$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$$

(i) What precautions would you have taken in adding the concentrated sulphuric acid to the water at the start of the experiment? Why are these precautions necessary? (9)

(ii) What is the function of the reflux condenser? State the correct way of connecting the condenser to the cold water tap. (12)

(iii) What procedure should be followed when adding the ethanol solution through the condenser to the mixture in the flask? Why is this procedure used? (12)

(iv) Describe and explain any colour change that takes place during the reaction. (9)

(v) Show that there is more than enough sodium dichromate (VI) to oxidise all the ethanol. (12)

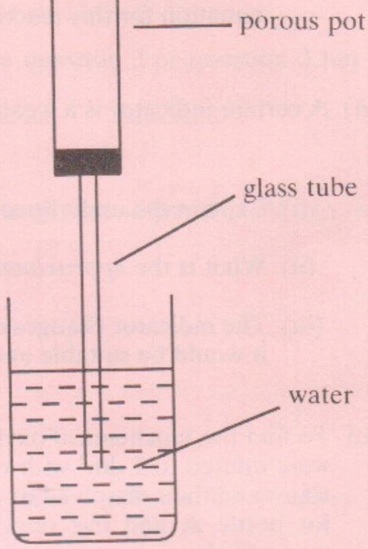
(vi) Calculate the percentage yield of ethanoic acid.
(density = 1.06 g cm^{-3}) (12)

4. Write down (*a*) Graham's Law of Diffusion of Gases, (*b*) the equation of state for an ideal gas. (9)

Give *two* reasons why real gases depart from ideal behaviour. Under what conditions of temperature and pressure do real gases come closest to ideal behaviour? (12)

List the gases SO_2, Ne, N_2O in order of increasing rate of diffusion. State which of the three gases you would expect to come closest to ideal behaviour and give a reason for the choice you have made. (12)

When the apparatus shown in the diagram was set up with the porous pot full of hydrogen, the level of the water in the glass tube was seen to rise. What is the explanation for this? State what you would observe if butane (C_4H_{10}) were used in place of hydrogen. (12)



In an experiment to measure the relative molecular mass of a volatile liquid a mass of 0.18 grams of the liquid was vapourised by heating it at 100 °C in a suitable apparatus. If the volume of the vapour was 94 cm^3 and the pressure was 1.02×10^5 N m^{-2}, use the equation of state to find the relative molecular mass of the volatile liquid. (12)

Show by means of a labelled diagram the apparatus you would have used to vapourise the volatile liquid and explain how you would have found the volume of the vapour. (9)

5. 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) Explain why, in the Periodic Table, there is (*a*) an increase in electronegativity values across a period, (*b*) a decrease in electronegativity values down a group. (12)

(ii) What is an orbital?

How are the electrons arranged in orbitals in the s and p sublevels of the n=4 energy level of the element of atomic number 33? (9)

(iii) Write the formula of the simplest chloride you would expect the element of atomic number 33 to form. Draw a diagram showing the bonding present in this chloride and indicate, by means of an equation, how you would expect it to react with water. State the shape of this chloride molecule. (18)

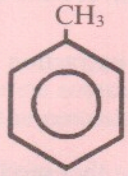
(iv) What type of bond is formed between chlorine and the element of atomic number 19? Show the formation of the bond by means of suitable diagrams. Explain why this chloride is a high melting-point solid. (15)

(v) Name the bond responsible for the forces of attraction between water molecules and comment briefly on its effects on the properties of water. (12)

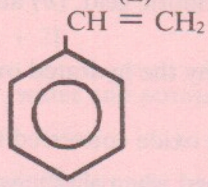
6. The formulae of five organic compounds are given as follows:

(A)	(B)	(C)
C_2H_5CHO	$CH_3COOC_2H_5$	$CF_2 = CF_2$

(D)



(E)



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

(ii) What term is used to describe compounds like **D** and **E** that have the benzene ring as part of their structure? (6)

(iii) Which one of the compounds **A** to **E** undergoes hydrolysis when heated with sodium hydroxide? Write an equation for the reaction. (9)

(iv) Which one of the compounds **A** to **E** reduces Fehling's solution? Describe what you would observe when the reduction reaction takes place, and give the name *and* structural formula of the organic product of the reaction. (18)

(v) What is a polymer? Compounds **C** and **E** both undergo addition polymerisation to form widely-used polymers. Name the two polymers and, in the case of either one of them, indicate its structure by showing two repeating units. (18)

7. What is meant by saying that a reaction system has reached a state of equilibrium? (6)

Write the equilibrium constant expression (K_c) for the reaction

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$ (6)

A mixture of 1.5 moles of hydrogen and 1.5 moles of iodine was allowed to come to equilibrium in a closed vessel at 773 K. It was found that 0.35 moles of iodine were present in the equilibrium mixture.

(i) Find the numbers of moles of hydrogen and hydrogen iodide in the equilibrium mixture, and calculate the value of the equilibrium constant (K_c) at 773 K. (12)

(ii) When a similar experiment, using the same quantities of hydrogen and iodine, was carried out at 623 K, it was found that the value of K_c had increased to 64. Calculate (*a*) the number of moles, (*b*) the mass, of iodine present in the equilibrium mixture at this temperature. (21)

(iii) Is the formation of hydrogen iodide exothermic or endothermic? Explain your reasoning. (9)

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

8. In its bauxite ore, aluminium is present as the hydrated oxide ($Al_2O_3.3H_2O$). In the extraction process, this oxide is first converted to another aluminium compound (X) and, at a later stage, X is changed back to the hydrated oxide. The hydrated oxide is then converted to alumina (Al_2O_3), from which aluminium is obtained by electrolysis. The electrolyte consists of a solution of alumina in molten cryolite.

(i) Explain the term *hydrated*. Show that alumina is an amphoteric oxide by writing (*a*) an equation for its reaction with hydrochloric acid, (*b*) an equation for its reaction with sodium hydroxide. (18)

(ii) Name X. Explain why the hydrated oxide is converted to X in the extraction process. (9)

(iii) How is the hydrated oxide converted to alumina?
Alumina is also formed when aluminium nitrate is heated. Give one other product of this reaction. (12)

(iv) Show, by means of equations, the reactions taking place at the anode and cathode during the electrolytic stage of the extraction process. (12)

(v) A current of 1.93×10^4 amperes was passed through a molten mixture of alumina and cryolite. Calculate the time in hours required to produce 16.2 kilograms of aluminium. (15)

9. Define (i) heat of combustion, (ii) heat of formation, (iii) bond energy. (18)

Heats of formation cannot usually be found directly by experiment. They are calculated either from heats of combustion or from bond energy values. Which of the two methods would be likely to give the more accurate result? Give a reason for your answer. (6)

When 1.5 grams of methanol (CH_3OH) were burned completely in a suitable apparatus the rise in temperature was 4.5 K. If the heat capacity of the apparatus is 7.45 kJ K^{-1}, show that the heat of combustion of methanol is -715.2 kJ mol^{-1}, and then find the heat of formation of methanol given that the heats of combustion of carbon and hydrogen are -393 kJ mol^{-1} and -286 kJ mol^{-1} respectively. (18)

Use the heat of formation, together with the following thermochemical data (where E stands for the molar bond energy) to work out the molar bond energy value for the bond between carbon and oxygen in methanol.

$$E(H-H) = 436 \text{ kJ mol}^{-1}$$
$$E(C-H) = 412 \text{ kJ mol}^{-1}$$
$$E(O=O) = 496 \text{ kJ mol}^{-1}$$
$$E(O-H) = 463 \text{ kJ mol}^{-1}$$

$$C_{(s)} \longrightarrow C_{(g)} \quad \Delta H = 715 \text{ kJ mol}^{-1}$$ (18)

In methanal (HCHO), the molar bond energy of the bond between carbon and oxygen was found to be 693 kJ mol^{-1}. Explain why this is considerably different from the result obtained above. (6)

10. Answer any *two* of the following.

(*a*) The artificial fixation of nitrogen can be carried out by combining it with hydrogen to form ammonia. Nitrogen fixation also takes place by natural means.

(i) What is the importance of nitrogen fixation? (6)

(ii) State *two* natural nitrogen fixation methods. (12)

(iii) Some of the ammonia produced by artificial nitrogen fixation is converted to nitric acid. The first stage in this process is the catalytic oxidation of ammonia to nitrogen monoxide (NO) and water. Write an equation for this reaction and state the conditions under which it is carried out. (15)

(*b*) A certain <u>indicator</u> is a <u>weak</u> acid ($K_a = 2 \times 10^{-5}$ at 25 °C). Its dissociation in water may be represented

$$HIn_{(aq)} \rightleftharpoons H^+_{(aq)} + In^-_{(aq)}$$

(i) Explain the underlined terms. (12)

(ii) What is the *approximate* pH of a 0.01 mol dm^{-3} solution of the indicator at 25 °C? (9)

(iii) The indicator changes colour in the pH range 3.7 — 5.7. State the types of acid-base titration for which it would be suitable and explain why it can be used in these titrations. (12)

(*c*) To find the biochemical oxygen demand (B.O.D.) of a sample of polluted river water, 25 cm^3 of the water were diluted to 1 dm^3 with well-oxygenated pure water. Two bottles, A and B, were filled with the diluted water and their dissolved oxygen concentrations were determined. The analysis was carried out immediately for bottle A and five days later for bottle B. The results obtained were 12.8 p.p.m. and 8.2 p.p.m. respectively.

(i) Why was it necessary to dilute the polluted river water? What was the advantage in using well-oxygenated water for this purpose? (12)

(ii) Under what conditions should bottle B have been kept for the five days before it was analysed? In the case of one of the conditions you have stated, explain why it is necessary. (12)

(iii) What is the B.O.D. of the polluted river water? (9)

(*d*) A sodium salt, which was a sulphate, a sulphite or a thiosulphate, was given to a student for identification. When dilute hydrochloric acid was added to a solution of the salt, there was no precipitate but a colourless, pungent gas was produced. When barium chloride solution was added to a solution of the salt, a white precipitate was observed. The precipitate dissolved when dilute hydrochloric acid was added.

(i) Identify the salt. (6)

(ii) Give the names of the gas and the white precipitate. (9)

(iii) Write balanced equations for the three reactions that took place. (18)