AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1995

CHEMISTRY — HIGHER LEVEL

MONDAY, 19 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, Na = 23, Mg = 24, Cl = 35.5, Br = 80, Pb = 207.

Avogadro constant = 6×10^{23} mol^{-1}

Molar volume at S.T.P. = 22.4 dm^3

1 Faraday = 96,500 C

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1. Answer *eleven* of the following items (*a*), (*b*), (*c*), etc. All items carry the same number of marks. *Keep your answers short.*

(*a*) Identify: (i) $1s^2 2s^2 2p^6 3s^2 3p^1$, (ii) $[1s^2 2s^2 2p^6 3s^2 3p^6]^{2+}$

(*b*) Bromine is a crystalline solid at temperatures below -7.2 °C. What type of crystal is it? What forces bind the crystal together?

(*c*) What volume of ozone would contain 2.25×10^{22} atoms of oxygen at S.T.P.?

(*d*) Define first ionisation energy of an element.

(*e*) Give *two* reasons why raising the temperature usually increases the rate of a chemical reaction.

(*f*) What is meant by nitrogen fixation?

(*g*) What mass of magnesium oxide would be produced by the complete combustion of 1.2 grams of magnesium?

(*h*) Give an example of a triad in Dobereiner's classification of the elements.

(*i*) Name *two* substances commonly used as industrial sources of hydrogen.

(*j*) Temporary hardness is found in water in limestone districts. Show, by means of an equation, how the hardness gets into the water.

(*k*) Write the structural formula of 2,3-dichloropropanoic acid.

(*l*) Give an example of autocatalysis, stating the reactants and the catalyst involved.

(*m*) What would you observe when a piece of zinc is left for some hours in an aqueous solution of copper(II) sulphate?

(*n*) The charge fed in at the top of the blast furnace consists of iron ore and two other materials. Name the two materials.

(*o*) Naturally-occurring chlorine consists of 75.5% of $^{35}_{17}Cl$ and 24.5% of $^{37}_{17}Cl$. Calculate the relative atomic mass (A_r) of chlorine.

(11 x 6)

2. A mass of 7.77 g of sodium carbonate crystals ($Na_2CO_3.xH_2O$), which had lost some of its water of crystallisation, was dissolved in deionised water and made up accurately to 500 cm^3 in a volumetric flask. The molarity of this solution was found by titrating it in 25.0 cm^3 volumes against a 0.075 mol dm^{-3} solution of sulphuric acid, the mean titre being 20.0 cm^3. The sulphuric acid, which is not a primary standard, had been previously standardised using a standard solution of a suitable base. The equation for the titration reaction between the sulphuric acid and the sodium carbonate solution is

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

(i) Explain the underlined term. (6)

(ii) What is meant by a *primary* standard in volumetric analysis? Explain why sulphuric acid is not a primary standard. Suggest a suitable base for standardising the sulphuric acid solution. (12)

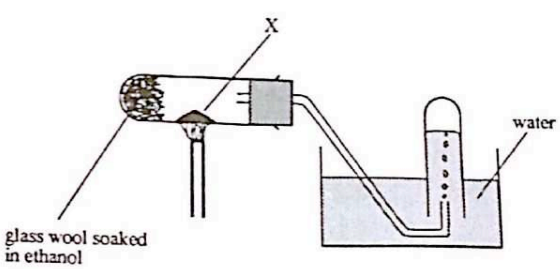
(iii) In preparing for the titration, explain (*a*) why the pipette and burette were rinsed with deionised water followed by a little of the solutions they were to contain, (*b*) why the titration flask was rinsed with deionised water only. (12)

(iv) How would you test for the presence (*a*) of carbonate ions in the sodium carbonate solution, (*b*) of sulphate ions in the solution of sulphuric acid? (12)

(v) Calculate the concentration of the sodium carbonate ($Na_2CO_3.xH_2O$) solution (*a*) in g dm^{-3}, (*b*) in mol dm^{-3}. Hence, find the percentage water in the sodium carbonate crystals and the value of x in the formula. (24)

3. (*a*) A group of students prepared ethene using the apparatus shown in the diagram. The equation for the reaction is

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$



(i) Identify X. What term is used to describe its function in the preparation of ethene? (9)

(ii) Describe *two* tests to show that ethene is an unsaturated compound. (12)

(iii) If the students had used 2.3 cm^3 of ethanol (density = 0.8 g cm^{-3}) in the above experiment and had obtained a 15% yield of ethene, what volume of ethene (measured at room temperature and pressure) would have been collected? Suggest a reason for the low yield of ethene. (Molar volume at room temperature and pressure = 24.0 dm^3). (15)

(*b*) In another organic preparation, the students oxidised ethanol to ethanoic acid. They then warmed a mixture of ethanol and ethanoic acid with concentrated sulphuric acid in a test tube.

(i) What oxidising agent would you use in the oxidation of ethanol to ethanoic acid? (6)

(ii) In carrying out this experiment, how would you ensure that the main product was ethanoic acid and not ethanal? How would you obtain a reasonably pure sample of ethanoic acid from the reaction mixture? (9)

(iii) Write a balanced equation for the reaction between ethanol and ethanoic acid and name the organic product of the reaction. To which family of organic compounds does this product belong? State *two* functions of the concentrated sulphuric acid in the reaction. (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) From the third period (Na to Ar) of the Periodic Table name (*a*) a solid non-metallic element which is often trivalent in its compounds, (*b*) a solid non-metallic element which is often divalent in its compounds, (*c*) a gaseous element which is monovalent in its compounds. In what molecular form does the gaseous element exist? (12)

(ii) Define electronegativity. Of the three elements you have named in (i), explain why the electronegativity value is lowest for the solid trivalent element and highest for the gaseous element. (12)

(iii) The gaseous element combines with each of the solid elements. Write formulae for the two compounds using the valences given in (i). Also, draw diagrams showing the bonding present in the two compounds. State the shapes of the molecules of the two compounds and justify these shapes using the electron pair repulsion theory. (24)

(iv) Write an equation for the reaction between water and the compound formed from the trivalent and monovalent elements. The solution resulting from the reaction contains chloride ions. State the reagents you would use and what you would observe in a simple test to show the presence of chloride ions in aqueous solution. (18)

5. Define (i) heat of reaction, (ii) heat of formation, (iii) heat of neutralisation. (18)

Calculate the heat of reaction for

$$C_2H_{2(g)} + HCN_{(g)} \longrightarrow C_3H_3N_{(g)}$$

given that the heats of formation of $C_2H_{2(g)}$, $HCN_{(g)}$ and $C_3H_3N_{(g)}$ are 233 kJ mol^{-1}, 114.5 kJ mol^{-1} and 194.5 kJ mol^{-1} respectively. (12)

Suggest a name *and* structural formula for C_3H_3N and comment on its industrial importance. (9)

The heat of neutralisation of hydrocyanic acid ($HCN_{(aq)}$) is −12 kJ mol^{-1} whereas the heats of neutralisation of hydrochloric, nitric and sulphuric acids are all around −57 kJ mol^{-1}. Explain (i) why the value of the heat of neutralisation is about the same for the three common laboratory acids, (ii) why much less heat is evolved in the neutralisation of hydrocyanic acid. (12)

Describe how the heat of neutralisation of hydrochloric acid by sodium hydroxide may be measured in the laboratory. (15)

6. Explain what is meant by the terms *molar concentration* and *partial pressure*. (12)

Write equilibrium constant expressions in terms of molar concentrations for each of the following reactions and answer the questions that follow.

(*a*) $CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

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

(*c*) $2BrCl_{(g)} \rightleftharpoons Br_{2(g)} + Cl_{2(g)}$ (9)

(i) For which of the three reactions is it necessary to know the volume of the reaction mixture at equilibrium in order to calculate the value of K_c? Explain your answer. (6)

(ii) There is an alternative form for equation (*c*). Write down this form of the equation. What effect, if any, will the use of this alternative form of the equation have on the value of K_c? (12)

(iii) Write the equilibrium constant expression in terms of partial pressures for reaction (*a*). Explain why the values of K_c and K_p are the same for this reaction. (12)

(iv) Equal volumes of carbon dioxide and hydrogen were allowed to come to equilibrium in a closed vessel at 1000 K. Calculate the percentage by volume of carbon monoxide in the reaction mixture at equilibrium, given that the value of K_p is 0.72 at that temperature. Give your answer correct to the nearest whole number. (15)

7. Explain the terms (i) monobasic (monoprotic) acid, (ii) conjugate acid-base pair in the Bronsted-Lowry theory, (iii) acid-base indicator. (15)

Write an equation for the reaction that takes place between a strong monobasic acid (HA) and water. Write also an equation for the reaction that takes place when a weak monobasic acid (HX) accepts a proton from the strong monobasic acid (HA). Identify the conjugate pairs in the reaction between the two acids. (12)

What concentration of the strong acid (HA) will give an aqueous solution having a pH of 2.7? Give your answer correct to one significant figure.

A 0.5 mol dm^{-3} aqueous solution of the weak acid (HX) also has a pH of 2.7. Calculate the value of its acid dissociation constant (K_a), giving your answer correct to one significant figure. (18)

The weak monobasic acid (HX) can be used as an acid-base indicator with a range of 4–6. The molecules (HX) are red and the ions (X^-) are yellow. State what you understand by the range of an indicator and explain briefly how HX acts as an acid-base indicator. For which general classes of acid-base titrations would HX be suitable as an indicator? (21)

8. (i) A volatile organic liquid was found to consist of 66.67% carbon, 11.11% hydrogen and 22.22% oxygen by mass. If the relative molecular mass of the liquid is 72, show how the molecular formula C_4H_8O may be calculated from the percentage composition given above. (12)

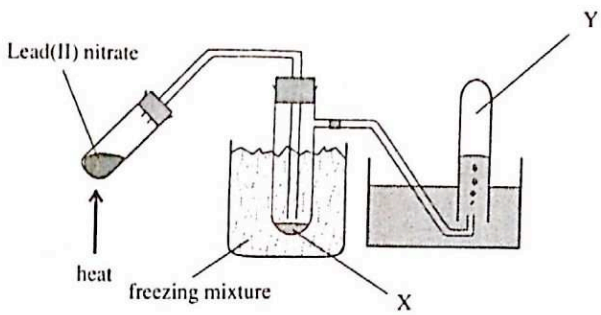
(ii) Describe a test that would allow you to distinguish between aldehydes and ketones. (9)

(iii) Give the name *and* structural formula of the liquid of molecular formula C_4H_8O (*a*) if it is a straight-chain aldehyde, (*b*) if it is a branched-chain aldehyde, (*c*) if it is a ketone. (18)

(iv) Outline briefly how you would carry out the reduction of the aldehydes in (iii) and name the products of the reactions. (15)

(v) Ketones can be reduced to secondary alcohols. What is a secondary alcohol? Write the structural formula of the secondary alcohol produced by the reduction of the ketone you have named in (iii) above. Name the organic product of the reaction between this alcohol and phosphorus(V) chloride. (12)

9. (*a*) Some lead(II) nitrate was heated using the apparatus shown in the diagram. Identify the liquid X and the gas Y and write a balanced equation for the reaction. What colour is the liquid X? State and explain what you would observe when the liquid X is heated. (21)



(*b*) Metallic lead may be obtained from lead(II) sulphide (galena) by a process including roasting as a first step. In this step the reaction of the galena with atmospheric oxygen gives lead(II) oxide and sulphur dioxide. Write a balanced equation for this reaction. (6)

Outline briefly how the sulphur dioxide, obtained as a byproduct of the roasting process, may be used in the production of sulphuric acid. (15)

(*c*) Lead(II) dibromide may be used in the school laboratory to demonstrate the electrolysis of a molten electrolyte. What property of the compound makes it particularly suitable for this purpose? (3)

Write equations for the reactions taking place at the anode and cathode in the electrolysis of molten lead(II) dibromide. (6)

When a current of 10 A was passed through molten lead(II) dibromide for t seconds, 6.21 g of lead were liberated at the cathode. Find the value of t. Find also the volume of bromine vapour liberated at the anode at 380 °C (the temperature of the molten electrolyte) and one atmosphere pressure, given that the molar volume of a gas under these conditions is 53.6 dm^3. (15)

10. Answer any *two* of the following.

(*a*) Three isomers of molecular formula C_5H_{12} belong to a homologous series of saturated aliphatic hydrocarbons.

(i) Explain the underlined terms. (9)

(ii) Give the name and the general formula of the homologous series to which the isomers belong. (6)

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

(*b*) Define (i) eutrophication, (ii) Biochemical Oxygen Demand (B.O.D.). (9)

Explain how the tertiary treatment of sewage helps to prevent eutrophication. (6)

A sample of polluted lake water was analysed to determine the concentrations of suspended and dissolved solids and also the biochemical oxygen demand. A 600 cm^3 sample of the water was found to contain 0.03 grams of suspended solids and 0.96 grams of dissolved solids. What were the concentrations of suspended and dissolved solids in parts per million? (12)

The biochemical oxygen demand of the lake water was found to be 320 p.p.m. As the maximum concentration of dissolved oxygen in fresh water at 20 °C is about 9 p.p.m., how is it possible to have a B.O.D. value of 320 p.p.m? (6)

(*c*) Define *oxidation* in terms of change in oxidation number. (6)

What is (i) the oxidation number of oxygen in SO_3, (ii) the oxidation number of hydrogen in NaH? (6)

The following equations show the reactions of sulphur trioxide and sodium hydride with water.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$NaH + H_2O \longrightarrow NaOH + H_2$$

Show, using oxidation numbers, which of the two reactions is an oxidation-reduction reaction, and indicate clearly where oxidation and reduction have taken place. (12)

Balance: $MnO_4^- + I^- + H^+ \longrightarrow Mn^{2+} + H_2O + I_2$ (9)

(*d*) State Graham's Law of Diffusion. (6)

Outline a simple experiment to show that gases diffuse at different rates. (9)

Arrange the gases hydrogen, oxygen, hydrogen chloride, ammonia in order of *increasing* rate of diffusion. (6)

The rates of diffusion of hydrogen and another gas were measured under the same conditions and were found to be 50.00 $cm^3\ s^{-1}$ and 9.28 $cm^3\ s^{-1}$ respectively. Give the molecular formula of the other gas given that it is a compound of hydrogen and carbon. (12)