AN ROINN OIDEACHAIS AGUS EOLAÍOCHTA

LEAVING CERTIFICATE EXAMINATION, 1998

CHEMISTRY — HIGHER LEVEL

WEDNESDAY, 24 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, S = 32, Cl = 35.5, K = 39, Mn = 55, Fe = 56, Cu = 63.5.

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

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

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 molecular mass (M_r).

(*b*) Select the two molecular crystals from the following list:

diamond dry ice sodium chloride iodine

(*c*) An oxide of copper contains 88.8% by mass of the metal. What is the empirical formula of the oxide?

(*d*) Name and state the law which relates the volume and the temperature of a gas at constant pressure.

(*e*) Give the common name and the structural formula for phenylethene.

(*f*) An acid-base indicator changes colour in the pH range 8.3-10. For which two types of acid-base titration would it be suitable?

(*g*) How many (i) bond pairs of electrons, (ii) lone pairs of electrons, are there in the valence shell of the phosphorus atom in the phosphine molecule (PH_3)?

(*h*) In the electrolysis of dilute sulphuric acid using inert (e.g. platinum) electrodes a mass of 0.04 g of oxygen was liberated at the anode. What mass of hydrogen was liberated at the cathode?

(*i*) Arrange the following gases in order of *increasing* rate of diffusion: hydrogen chloride, carbon dioxide, methane, nitrogen, sulphur dioxide.

(*j*) In which stage of sewage treatment may compounds of nitrogen and phosphorus be removed? Why is it important to remove them?

(*k*) Explain (i) why chemical reactions are usually faster at higher temperatures, (ii) why chemical reactions between gases are usually faster at higher pressures.

(*l*) The alkaline hydrolysis of a fat or vegetable oil produces an alcohol and a salt. Identify the alcohol. What common term is often used for the salt obtained in this reaction?

(*m*) Complete and balance the equation:

$$AsCl_3 + H_2O \longrightarrow$$

(*n*) What term is used for a separation technique in which a solvent moves along an adsorbent material such as paper or alumina?

(*o*) Use the following data (where E stands for the molar bond energy) to work out the total energy required to convert one mole of pentane (C_5H_{12}) into separate neutral atoms.

E(C–C) = 348 kJ mol^{-1} E(C–H) = 412 kJ mol^{-1}

(11 x 6)

2. A mass of 6.25 g of impure sodium thiosulphate crystals was dissolved in deionised water in a beaker. The solution was transferred to a 250 cm^3 volumetric flask and made up carefully to the mark with deionised water. The concentration of this solution was found by titrating it against 25.0 cm^3 portions of a 0.040 mol dm^{-3} solution of iodine which had been previously standardised. The mean titre was 20.0 cm^3. A 50 cm^3 volume of the sodium thiosulphate solution was then accurately diluted to 500 cm^3 with deionised water.

The equation for the reaction involved in the titration is

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

(i) What is meant by a primary standard in volumetric analysis? Why is iodine not used as a primary standard? (9)

(ii) Name the indicator used when a solution of iodine is titrated against a solution of sodium thiosulphate. 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)

(iii) Describe how you would dilute the sodium thiosulphate solution accurately from 50 cm^3 to 500 cm^3. (12)

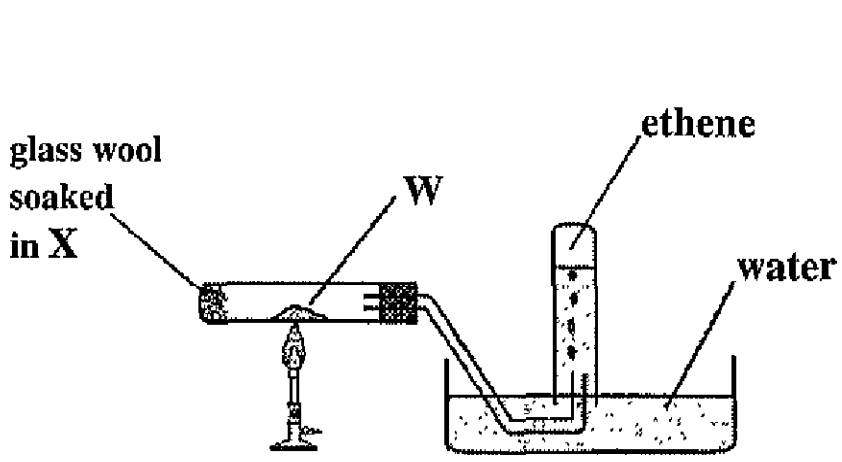
(iv) Calculate the concentration of the sodium thiosulphate solution before dilution in mol dm^{-3}. Hence find the concentration of the diluted sodium thiosulphate solution, also in mol dm^{-3}. Calculate the percentage purity of the sodium thiosulphate crystals ($Na_2S_2O_3.5H_2O$) used in making up these two solutions. (21)

(v) Acidified solutions of potassium manganate(VII) liberate iodine from iodide solutions according to the equation:

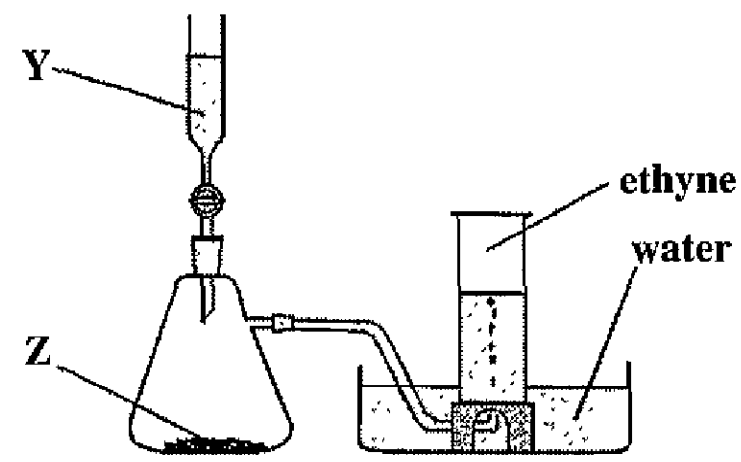
$$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

When excess potassium iodide was added to 25.0 cm^3 of an acidified potassium manganate(VII) solution, it required 37.5 cm^3 of the diluted sodium thiosulphate solution to reduce the iodine liberated. State the colour change you would have observed when the potassium iodide was added to the acidified solution of potassium manganate(VII). Find the concentration of the potassium manganate(VII) solution in mol dm^{-3}. (12)

3.



(A)



(B)

Diagram **A** shows the apparatus used by a group of students to prepare ethene in the school laboratory. Diagram **B** shows the apparatus the students used to prepare ethyne.

(i) Identify W, X, Y, Z and write balanced equations for the reactions involved in the two preparations. (18)

(ii) In preparation A, what was the purpose of the glass wool? (6)

(iii) In preparation B, what would the students have observed when Y dropped onto Z? (6)

(iv) The ethyne obtained in preparation B is likely to have contained a number of impurities. Mention *two* possible impurities other than air or water vapour. How might these impurities have been removed from the ethyne? (12)

(v) Under what conditions can ethyne be converted to ethene? What term is used in organic chemistry for the type of addition reaction involved in this conversion? (9)

(vi) Ethyne and ethene are unsaturated hydrocarbons. What is meant by the term unsaturated? (3)

When 40.5 mg (7.5×10^{-4} moles) of another unsaturated hydrocarbon were burned completely in oxygen, 67.2 cm^3 of carbon dioxide, measured at S.T.P., were produced. Find the molecular formula of this hydrocarbon. (12)

4. Answer the following questions with reference to the part of the Periodic Table shown below. Note that questions (ii) to (v) are restricted to the eight elements which are represented by their symbols in the table. (Refer where necessary to Mathematics Tables p. 44 to p. 46).

1 **H**																	2
3	4											5	6	7	8 **O**	9	10
11	12											13	14	15 **P**	16 **S**	17	18
19	20	21 **Sc**	22	23	24	25	26	27	28	29 **Cu**	30	31 **Ga**	32	33	34 **Se**	35	36

(i) The part of the Periodic Table shown above is based on the modern form of the Periodic Table. State *two* ways in which this form of the Periodic Table differs from that of Mendeleev. State also the contribution of Dobereiner to the classification of the elements. (9)

(ii) Hydrogen combines with oxygen, sulphur and selenium to form water, hydrogen sulphide and hydrogen selenide respectively. The boiling points of these three hydrides are 373 K for water, 212.3 K for hydrogen sulphide, and 231.3 K for hydrogen selenide. Explain (*a*) the large decrease in boiling point from water to hydrogen sulphide, (*b*) the increase in boiling point from hydrogen sulphide to hydrogen selenide. (12)

(iii) Define first ionisation energy. Explain why sulphur has a lower first ionisation energy value than oxygen and also a lower first ionisation energy value than phosphorus. (15)

(iv) Scandium has a valence of 3 in its compounds. Indicate, in terms of electron configuration, why this is so. Also illustrate the two common valences of copper by writing the electron configurations (s, p, etc.) of the copper ions. (12)

(v) Gallium normally has a valence of 3 in its compounds. Write the formula for the compound formed between gallium and oxygen. Show by means of equations how you would expect this compound to react (*a*) with hydrochloric acid, (*b*) with sodium hydroxide. What term is used for oxides that react in this way? (18)

5. Answer each of the questions below with reference to one or both of the following reactions.

(*a*) $Cr_2O^{2-}_{7(aq)} + H_2O_{(l)} \rightleftharpoons 2CrO^{2-}_{4(aq)} + 2H^{+}_{(aq)}$

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

(i) Define oxidation number. Use oxidation numbers to determine which one of the two reactions, (*a*) or (*b*), is an oxidation-reduction reaction. State clearly where oxidation and reduction have taken place. (18)

(ii) What is meant by chemical equilibrium? Write equilibrium constant expressions in terms of molar concentrations (K_c) for the two reactions. (18)

(iii) When sodium hydroxide solution is added to a solution containing dichromate ions ($Cr_2O^{2-}_7$), the colour of the solution changes from orange to yellow. Explain why this is so and state the principle you have used in your explanation. (12)

(iv) One mole of phosphorus(V) chloride was heated at 250 °C in a closed 10 dm^3 vessel. When equilibrium had been reached, some of the phosphorus(V) chloride had dissociated into phosphorus(III) chloride and chlorine according to equation (*b*). If the equilibrium constant in terms of molar concentration (K_c) for the reaction at 250 °C is 0.04 mol dm^{-3}, calculate the percentage dissociation of the phosphorus(V) chloride at equilibrium. (18)

6. Define (*a*) heat of neutralisation, (*b*) heat of combustion, (*c*) heat of formation. (18)

The heat of neutralisation of hydrochloric acid by sodium hydroxide and the heat of neutralisation of nitric acid by sodium hydroxide were measured in the laboratory and each was found to be –57.1 kJ mol^{-1}.

(i) Explain why the value of the heat of neutralisation of hydrochloric acid was the same as that of nitric acid. (6)

(ii) Outline how the heat of neutralisation of hydrochloric acid by sodium hydroxide could have been measured in the laboratory. (15)

(iii) Given that the heats of combustion of ethanoic acid, carbon and hydrogen are –876 kJ mol^{-1}, –393 kJ mol^{-1} and –286 kJ mol^{-1} respectively, calculate the heat of formation of ethanoic acid. (12)

(iv) Use the heat of combustion of ethanoic acid together with the heat of combustion of butane (–2877 kJ mol^{-1}) to calculate the heat change (ΔH) for the following reaction.

$$C_4H_{10(g)} + 2\tfrac{1}{2}O_{2(g)} \longrightarrow 2CH_3COOH_{(l)} + H_2O_{(l)}$$ (9)

This reaction occurs when ethanoic acid is manufactured by the catalytic oxidation of butane. Under what conditions is the reaction carried out? (6)

7. The following are some metals in the order of *decreasing* reactivity in which they appear in the electrochemical series:

Sodium
Magnesium
Zinc
Iron
Copper

Answer the following questions with reference to these metals.

(i) Use the reactions, if any, of the metals on the list with water or steam to show that sodium is the most reactive and that copper is the least reactive of the five metals. (9)

(ii) Write a balanced equation for (*a*) the reaction that takes place when sodium nitrate is heated, (*b*) the reaction that takes place when magnesium nitrate is heated. (12)

(iii) Which one of the five metals corrodes most easily? What method is used, in the school laboratory, to protect this metal from corrosion? The resistance to corrosion of a metal, not included in the above list, is often improved by anodising. Identify this metal. State the electrolyte normally used in the anodising process and show the anode reaction by means of a balanced equation. (15)

(iv) What would you observe when a piece of zinc is left in an aqueous solution of copper(II) sulphate? Explain, in terms of electrons, what has taken place. (12)

(v) An iron ore, containing 64% iron(III) oxide as its only source of iron, was reduced to iron in the blast furnace. The equation for the main reduction reaction is:

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

How many tonnes of the ore were used to produce 5.6 tonnes of iron? What volume of carbon monoxide (measured at S.T.P.) was required, assuming it was the only reducing agent? (1 tonne = 1000 kg). (18)

8. (*a*) Define (i) acid, (ii) conjugate pair, in the Bronsted-Lowry theory of acids and bases. (9)

Identify the species acting as acids and also the conjugate pairs in the following acid-base reaction.

$$H_2O + CH_3NH_2 \rightleftharpoons CH_3NH_3^+ + OH^-$$ (6)

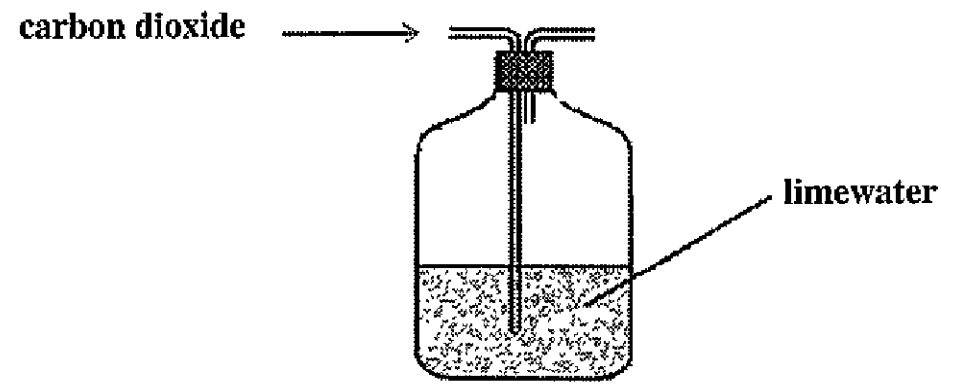
(*b*) In an experiment to measure the acid dissociation constant of a <u>weak</u> <u>monobasic</u> (monoprotic) acid (HA), a 0.1 mol dm^{-3} solution of the acid was prepared. The pH of this solution was found to be 3.1.

(i) Explain the underlined terms. (9)

(ii) Define pH. What was the hydrogen ion concentration of the acid solution? (9)

(iii) What do you understand by the acid dissociation constant (K_a)? Calculate the value of the acid dissociation constant for the weak acid (HA). (12)

(*c*) To prepare a sample of water having temporary hardness, carbon dioxide was bubbled through limewater using the apparatus shown in the diagram. Initially the limewater became cloudy due to the formation of a white insoluble solid. However, as the carbon dioxide continued to bubble through the limewater, the cloudiness gradually disappeared and a clear solution, with temporary hardness, was formed.



(i) Write an equation for the reaction involved in the formation of the white insoluble solid. (6)

(ii) Name the compound responsible for the temporary hardness in the clear solution. Show by means of an equation how this compound was formed from the white insoluble solid. (9)

(iii) The level of hardness in the water could be estimated by titration with standard EDTA solution using Eriochrome Black T (Solochrome Black) as indicator. It is necessary to add another solution to the water before carrying out the titration. What term is used to describe this solution? Why is the solution added to the water? (6)

9. Explain the terms (i) homologous series, (ii) functional group, (iii) structural isomerism. (18)

Answer the questions below with reference to the following reaction scheme in which three organic compounds (**A**, **B**, **C**) are represented by their molecular formulae.

$$\underset{\mathbf{A}}{C_3H_8O} \longrightarrow \underset{\mathbf{B}}{C_3H_6O} \longrightarrow \underset{\mathbf{C}}{C_3H_6O_2}$$

(i) Distinguish clearly between primary and secondary alcohols. Compound **A** is a primary alcohol which can be formed from the chloroalkane, $CH_3CH_2CH_2Cl$, by reaction with sodium hydroxide. What term is used for this type of substitution reaction? (9)

(ii) Compound **A** can be oxidised to compound **B** which can then be easily oxidised to compound **C**. Compound **B** can also be reduced to compound **A**. What is the structure of the functional group in compound **B**? Describe briefly how compound **B** can be reduced to compound **A**. There is another compound which is a structural isomer of compound **B** but which is not easily oxidised. Identify this compound and outline a simple chemical test that would allow you to distinguish between it and compound **B**. (18)

(iii) To which homologous series does compound **C** belong? Show the structure of the functional group in this homologous series. Two esters exist which are structural isomers of compound **C**. Give the names *and* structural formulae of these esters and, in the case of either *one* of them, write an equation for the reaction involved in its preparation. (21)

10. Answer any *two* of the following.

(*a*) (i) Define *catalyst.* (6)

(ii) Describe a simple laboratory experiment to show the effect of a catalyst on a chemical reaction. (9)

(iii) Distinguish clearly between homogeneous and heterogeneous catalysis. Which of these two types of catalysis was involved in the experiment you described in (ii)? (9)

(iv) Give a brief outline of the intermediate formation theory of catalysis. (9)

(*b*) Chlorine gas was prepared by reacting 3.95 g of potassium manganate(VII) with excess concentrated hydrochloric acid. The equation for the reaction is

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

(i) How many moles of hydrogen chloride were used? (6)

(ii) What was the total mass of chlorides produced? (9)

(iii) How many water molecules were produced? (6)

(iv) What volume of chlorine, measured at S.T.P., was obtained? How many atoms of chlorine were present in this volume? (12)

(*c*) Nitric acid is manufactured from ammonia and then some of the nitric acid is combined with more ammonia to produce ammonium nitrate, which is widely used as a fertiliser.

(i) Outline the main stages involved in the manufacture of nitric acid from ammonia. (12)

(ii) Write an equation for the reaction between ammonia and nitric acid. In what way can the use of ammonium nitrate as a fertiliser be harmful to the environment? (9)

(iii) A compound (NPK) fertiliser was produced containing 10.5% nitrogen by mass. If ammonium nitrate was the only compound of nitrogen used, what mass of it was required to make one tonne of the fertiliser? (12)

(*d*) Two sulphur-containing salts, (X and Y), were given to a group of students for analysis in the school laboratory. When dilute hydrochloric acid was added to a solution of salt X, a colourless, pungent gas was produced and an insoluble solid was formed in the solution. When dilute hydrochloric acid was added to a solution of salt Y, the same gas was produced, but there was no insoluble solid. When barium chloride solution was added to another portion of the solution of salt Y, a white precipitate was immediately observed. Both salts were found to give a yellow colour to the Bunsen flame.

(i) Identify the two salts. (12)

(ii) Give the names *or* formulae of the colourless, pungent gas, the insoluble solid and the white precipitate. (9)

(iii) Write (*a*) an equation for the reaction between salt X and dilute hydrochloric acid, (*b*) an equation for the reaction between salt Y and barium chloride solution. (12)