AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1996

11112

CHEMISTRY — HIGHER LEVEL

MONDAY, 17 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, Al = 27, S = 32, Ca = 40, Cr = 52, Fe = 56.

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*) Give an example of (i) an ionic crystal, (ii) a covalent crystal.

(*b*) State Avogadro's Law.

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

(*d*) What mass of calcium would combine with 672 cm^3 of oxygen gas (measured at S.T.P.)?

(*e*) The molecular formula of an aromatic hydrocarbon is C_8H_8. Give the name and structural formula of the compound.

(*f*) In what ratio by volume (i) does methane gas combine with oxygen gas, (ii) does ethane gas combine with oxygen gas, under conditions of complete combustion?

(*g*) What is the conjugate acid (i) of HS^-, (ii) of SO_3^{2-} ?

(*h*) Name the two reagents used to test for the presence of nitrate ions in aqueous solution.

(*i*) The heats of formation of carbon monoxide and carbon dioxide are –110 kJ mol^{-1} and –393 kJ mol^{-1} respectively. Find the heat of combustion of carbon monoxide.

(*j*) Write a balanced equation for the reaction that takes place when zinc nitrate is heated.

(*k*) Define heat of neutralisation.

(*l*) Using a 250 cm^3 sample, the concentration of dissolved solids in water taken from a lake was found to be 600 p.p.m. What was the mass in grams of dissolved solids in the sample?

(*m*) State *two* ways in which the properties of steel may be varied.

(*n*) What term is used to describe the mechanism of the reaction between bromine and ethene?

(*o*) Draw an energy profile diagram for an endothermic reaction. Indicate on the diagram the activation energy of the forward reaction.

(11 x 6)

2. The following experiment was carried out to find the percentage purity of ammonium iron(II) sulphate crystals, $(NH_4)_2SO_4.FeSO_4.6H_2O$. A 250 cm^3 volume of solution containing exactly 8.00 g of the impure crystals was carefully made up in a volumetric flask. The molarity of this solution was found by titrating it in 25 cm^3 volumes against a 0.020 mol dm^{-3} solution of potassium manganate(VII) which had previously been standardised. The potassium manganate(VII) solution was put in the burette and a number of titrations were carried out. The average titre was 20.0 cm^3. The equation for the reaction is:

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

(i) Explain what is meant by saying that the potassium manganate(VII) solution had been standardised. Name a solution, other than a standard solution of ammonium iron(II) sulphate, that could have been used to standardise it. (9)

(ii) Outline the procedure used in preparing the burette so that it is ready for the first titration. (12)

(iii) Dilute sulphuric acid was used at two different stages of the experiment. What were these two stages? In the case of each of the two stages, explain clearly the purpose for which the dilute sulphuric acid was used. (18)

(iv) During the titration the sides of the conical flask were washed down with deionised water from a wash bottle. Explain why this procedure is necessary and why it can be carried out without affecting the result of the titration. (9)

(v) Calculate the concentration of the ammonium iron(II) sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$, solution (a) in mol dm^{-3}, (b) in g dm^{-3}. Hence find the percentage purity of the ammonium iron(II) sulphate crystals. (18)

3. A group of students prepared ethanal by the reaction between acidified sodium dichromate(VI) solution and ethanol. The masses used were 17.88 g of sodium dichromate(VI), $Na_2Cr_2O_7.2H_2O$, and 11.04 g of ethanol. The ethanal was removed from the reaction mixture as soon as it was formed and was collected in a flask surrounded by ice-water. After further purification, the yield of ethanal was found to be 2.97 g. The equation for the reaction is:

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

(i) Explain (*a*) how the ethanal was removed from the reaction mixture as soon as it was formed, (*b*) why the reaction mixture should *not* have been refluxed, (*c*) why the flask in which the ethanal was collected was surrounded by ice-water. (9)

(ii) State and explain the colour change observed during the reaction. (9)

(iii) Ethanal can also be prepared from ethyne. Outline briefly how this reaction is carried out. What term is used to describe the reaction? (12)

(iv) Ethanal reacts with 2,4-dinitrophenylhydrazine to give a solid product and water. Describe briefly how the solid product could be purified and how, after purification, the purity of the solid could be tested. Give the name and structural formula of the solid product. (18)

(v) Show clearly that the ethanol is in excess in the student experiment described in the introduction to the question. (9)

(vi) Calculate the percentage yield of ethanal. (9)

4. (*a*) In the treatment of water for drinking, what substance is added (i) to promote the settling of suspended particles, (ii) to prevent water-borne diseases, (iii) to raise the pH, (iv) to protect against tooth-decay? What term is used for the process involved in (i)? (15)

Is the drinking water obtained as a result of the above treatment totally pure? Give a reason for your answer. (6)

(*b*) What is hard water? Name the two ions that are mainly responsible for hardness in water. (6)

Water from limestone districts contains a dissolved compound which causes temporary hardness. Explain what is meant by temporary hardness and name the dissolved compound. Show, by writing an equation for the reaction involved, how this soluble compound is obtained from limestone. Name also a compound commonly responsible for permanent hardness in water. (12)

Give *one* advantage of hard water. (3)

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

The pH of pure water at 25 °C is 7.0 but at 0 °C it is 7.5. Does this mean that pure water becomes more basic as the temperature decreases? Explain your answer. (9)

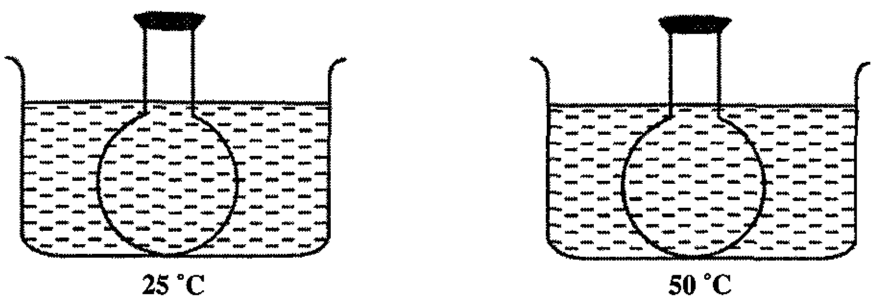
Calculate the value of the ionic product of water (K_w) at 0 °C. (9)

5. State (*a*) Dalton's Law of Partial Pressures, (*b*) Le Chatelier's Principle. (12)

Dinitrogen tetroxide dissociates into nitrogen dioxide according to the following equation:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H = 58 \text{ kJ}$$

In some laboratories, a sealed flask, containing an equilibrium mixture of the two gases, is kept for demonstration purposes. The diagrams below show the sealed flask immersed in water at two different temperatures.



(i) What difference would you expect to observe in the appearance of the contents of the sealed flask at the two different temperatures, assuming that the effect of the change in pressure was negligible? Explain clearly how the difference arises. (12)

(ii) Write the equilibrium constant expression (K_p) for the reaction taking place in the sealed flask. (6)

(iii) When a mixture of dinitrogen tetroxide and nitrogen dioxide was allowed to come to equilibrium in a closed vessel at 25 °C, the partial pressures of the two gases were found to be 0.83 atmospheres and 0.34 atmospheres, respectively. Calculate the value of K_p for the reaction at 25 °C, giving your answer correct to two decimal places. Would the value of K_p have been greater, less or unchanged if the reaction were carried out at 50 °C? Explain your answer. (15)

(iv) The pressure on the equilibrium mixture in (iii) above was lowered, without changing the temperature, and a new equilibrium was established at a pressure of X atmospheres. At this pressure, the equilibrium partial pressure of dinitrogen tetroxide was 0.73 atmospheres. Calculate the partial pressure of nitrogen dioxide at the new equilibrium and, hence, the value of X, giving your answers correct to two decimal places. (15)

Lowering the pressure resulted in an increase in the percentage of nitrogen dioxide in the equilibrium mixture. Explain, in terms of Le Chatelier's Principle, why this is so. (6)

6. Explain the terms (i) energy level, (ii) atomic orbital, (iii) first ionisation energy, (iv) d-block element. (18)

Describe briefly how the emission spectra of elements (e.g. hydrogen) can be explained by the presence of energy levels in atoms. (12)

Phosphorus and sulphur have atomic numbers of 15 and 16, respectively. How many electrons occupy the third main (n = 3) energy level (*a*) in an atom of phosphorus in its ground state, (*b*) in an atom of sulphur in its ground state? Write the electronic configuration (s,p) for these electrons in the case of phosphorus, and draw a labelled diagram to show the shapes and arrangement of the orbitals involved. Explain, in terms of their electronic configurations, why there is a drop in the value of the first ionisation energy from phosphorus to sulphur. (18)

The values of the first four ionisation energies (in kJ mol^{-1}) for scandium and titanium (atomic numbers 21 and 22 respectively) are shown in the table at right. From which electron sublevel (i) is the *first* electron lost, (ii) is the *third* electron lost? Suggest (*a*) why the values of the first three ionisation energies are greater in the case of titanium than they are in the case of scandium, (*b*) why the value of the fourth ionisation energy is much greater in the case of scandium than it is in the case of titanium.

	Sc	Ti
1st	633	661
2nd	1239	1313
3rd	2395	2658
4th	7152	4185

(18)

7. (i) Show the structure of the functional group (*a*) in alcohols, (*b*) in carboxylic acids. What is an ester? (9)

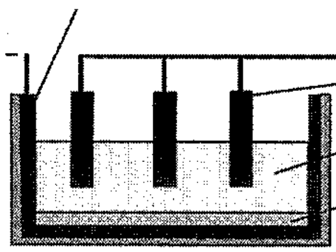
(ii) (*a*) The weakly acidic nature of alcohols may be shown by their reaction with very electropositive metals such as sodium. Write an equation for the reaction between sodium and an alcohol of your choice and name the organic product of the reaction. (9)

(*b*) Show, by means of an equation, the reaction of phosphorus(V) chloride with the alcohol you have chosen in (*a*) and name the phosphorus compound produced. What use is made of this reaction in organic chemistry? (12)

(iii) An ester, containing two carbon atoms in the molecule, was prepared by the reaction between an alcohol and a carboxylic acid. Give the name *and* structural formula of the ester, and write an equation for the reaction involved in its preparation. The ester is a structural isomer of another carboxylic acid. Identify this other acid. (15)

(iv) The polyester, terylene, is formed from two simpler compounds by a condensation reaction. What is meant by condensation? Identify the *two* simpler compounds and write the structural formula for the repeating part of terylene. State *one* use of terylene. (21)

8. Aluminium is obtained from alumina (Al_2O_3), an amphoteric oxide, by an electrolytic process carried out in cells similar to the one shown in the diagram.



(i) Explain the underlined term and name the ore from which the alumina for the electrolytic process is obtained. Write an equation for the reaction between alumina and sodium hydroxide. (12)

(ii) The electrolyte used is a solution of alumina in another substance. Name the other substance and explain why this mixture is used. How is the molten aluminium removed from the cell? (12)

(iii) The same material is used for the anode and cathode. What is this material? Assuming that the electrode reactions only involve ions from the alumina, write equations for the reactions taking place at the anode and cathode, and also for the overall reaction taking place in the cell. (15)

(iv) The anode material has to be replaced from time to time. What reaction is responsible for this? Explain why this reaction is of benefit to the extraction process. (9)

(v) How long would it take for the electrolytic process to produce 4.5 kg of aluminium if a constant current of 3.86×10^4 amperes were used? (12)

(vi) Alumina is produced in Ireland but it is shipped abroad for the electrolytic stage of the process. Suggest a reason for this. (6)

9. In a reaction rates experiment carried out at room temperature and pressure, a group of students added 0.25 g of calcium carbonate to 50 cm^3 of a 1.0 mol dm^{-3} solution of hydrochloric acid, the acid being in excess. The volume of carbon dioxide liberated was measured at ten second intervals of time and the results are shown in the following table.

Time(s)	0	10	20	30	40	50	60	70	80	90	100
Volume (cm^3)	0	23	37	46	52	56	58	59	60	60	60

(i) Draw a labelled diagram of an apparatus that could have been used in the above experiment. If an apparatus for measuring gaseous volumes were not available, what alternative method could have been used to follow the production of carbon dioxide? (12)

(ii) Write a balanced equation for the reaction between calcium carbonate and hydrochloric acid and calculate the maximum volume of carbon dioxide (at S.T.P.) that could have been obtained in the experiment. Why do you think the calculated value differs from that shown in the table above? (18)

(iii) Draw a graph of volume against time using the results obtained by the group of students. (12)

(iv) Use the graph to find (*a*) the time required to liberate 1.5×10^{-3} moles of carbon dioxide, (*b*) the number of moles of carbon dioxide liberated after 25 seconds, (*c*) the instantaneous rate of the reaction after 40 seconds. (Molar volume at room temperature and pressure = 24 dm^3). (24)

10. Answer any *two* of the following.

(*a*) How many (i) neutrons, (ii) electrons, are in the chloride ion $^{37}_{17}Cl^-$? (6)

In the chloride ion and in many compounds in which chlorine is combined with one other element, the oxidation number of chlorine is −1. State the oxidation number of chlorine in chlorine monoxide, Cl_2O, and explain why it differs from the more usual value. (9)

Chlorine monoxide and beryllium chloride, $BeCl_2$, both consist of planar molecules, but their shapes are not the same. State the shapes of the two molecules and give the reason for the difference between them. (12)

The chloride of arsenic, $AsCl_3$, reacts with water. Give the names *or* formulae of the two products of the reaction. (6)

(*b*) Define *bond energy.* (6)

Chloroethane and bromoethane can be produced from ethene by the following reactions:

$$C_2H_{4(g)} + HCl_{(g)} \longrightarrow C_2H_5Cl_{(g)} \qquad \Delta H = -55 \text{ kJ}$$

$$C_2H_{4(g)} + HBr_{(g)} \longrightarrow C_2H_5Br_{(g)} \qquad \Delta H = -58 \text{ kJ}$$

Use the following data (where E stands for the molar bond energy), to work out a value for E(C–Cl) in chloroethane, and a value for E(C–Br) in bromoethane.

E(C–C) = 348 kJ mol^{-1} E(H–Cl) = 431 kJ mol^{-1}

E(C=C) = 612 kJ mol^{-1} E(H–Br) = 366 kJ mol^{-1}

E(C–H) = 412 kJ mol^{-1} (21)

Suggest why the value of E(C–Br) is less than that of E(C–Cl). (6)

(*c*) Explain (i) empirical formula, (ii) molecular formula. (9)

A mass of 11.6 mg (2 x 10^{-4} moles) of a saturated organic liquid, containing the elements carbon, hydrogen and oxygen, gave 26.4 mg of carbon dioxide and 10.8 mg of water on complete combustion. Find the molecular formula of the liquid. (15)

Suggest a name and structural formula for the liquid, given that it is not easily oxidised. (9)

(*d*) What is meant by nitrogen fixation? (6)

Nitrogen is fixed artificially by combination with hydrogen in the Haber process. The plants in which the process is carried out also produce large amounts of carbon dioxide, and this can be combined with ammonia to produce an important compound of formula $CO(NH_2)_2$.

(i) State the usual conditions used in the combination of nitrogen and hydrogen in the Haber process. (9)

(ii) Name the compound of formula $CO(NH_2)_2$ and write an equation for the reaction by which it is formed from ammonia and carbon dioxide. (9)

(iii) The compound of formula $CO(NH_2)_2$ could be used to supply the nitrogen for an NPK fertiliser. What percentage by mass of the compound would give the fertiliser an N value of 7? (9)