LEAVING CERTIFICATE EXAMINATION, 1991

CHEMISTRY — HIGHER LEVEL

THURSDAY, 13 JUNE — AFTERNOON, 2 to 5

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, Mg = 24, S = 32, Fe = 56.
Avogadro constant = 6×10^{23} mol^{-1}
Molar volume at S.T.P. = 22·4 dm^3

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

(*b*) Which of the following acid/base pairs is *not* a conjugate pair?

$$H_3O^+/H_2O \qquad HSO_4^-/SO_4^{2-} \qquad H_3PO_4/HPO_4^{2-}$$

(*c*) The total number of molecules in a certain volume of nitrogen at S.T.P. is $1{\cdot}5 \times 10^{22}$. Calculate the volume.

(*d*) Identify in the following list the gas which diffuses at a rate different from that of the other two at a fixed temperature and give a reason for the choice you have made.

$$C_3H_8 \qquad SO_2 \qquad N_2O$$

(*e*) Write an equation for the reaction between a dilute acid and a sulphite.

(*f*) What type of mechanism is involved in the reaction between chlorine and an alkane?

(*g*) What term is used (i) for a bond in which the bonding electrons are not equally shared, (ii) for a bond in which there is a complete transfer of electrons?

(*h*) The kilogram calorific value of ethanol is 29,800 kJ. What is the heat of combustion?

(*i*) Name the two reagents used in the brown ring test for nitrates.

(*j*) Give a brief explanation of Newlands' Law of Octaves.

(*k*) An unsaturated gaseous hydrocarbon has a density of 2·5 g dm^{-3} at S.T.P. Identify the compound.

(*l*) The build-up of carbon dioxide in the atmosphere is causing concern at the present time. State *two* ways in which carbon dioxide is removed from the atmosphere.

(*m*) Name (i) the gas produced in the reaction between zinc and cold dilute sulphuric acid, (ii) the gas produced in the reaction between zinc and hot concentrated sulphuric acid.

(*n*) What type of catalysis is involved in the following reaction:

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

(*o*) What would be observed when manganese(II)sulphate solution and alkaline potassium iodide solution are added (i) to water containing dissolved oxygen, (ii) to water containing no dissolved oxygen?

(11 × 6)

2. An indigestion tablet, containing magnesium hydroxide as its only basic substance, was found to have a mass of 0·48 g. After crushing, the powdered tablet was carefully transferred to a beaker containing 50 cm^3 of a 1 mol dm^{-3} solution of hydrochloric acid. When the powder had dissolved the solution was transferred to a 250 cm^3 volumetric flask and made up accurately to the mark with deionised water. A burette was filled with this solution and its molarity was determined by titration against 25 cm^3 volumes of a 0·12 mol dm^{-3} solution of sodium hydroxide, using one drop of phenolphthalein solution as indicator. The first titration was used to get a rough estimate of the volume required and this was followed by two accurate titrations. The titration results are shown in the following table.

Titration	1	2	3
Volume (cm^3)	19·2	18·7	18·8

The equations for the reactions are:

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$
$$HCl + NaOH \rightarrow NaCl + H_2O$$

(i) How would you have carried out the crushing of the tablet and the transferring of the powdered tablet to the beaker of hydrochloric acid? (9)

(ii) Outline the correct procedure for bringing the solution in the volumetric flask precisely to the 250 cm^3 mark. (6)

(iii) In using a burette, why is it important (*a*) to rinse it with a little of the solution it is to contain, (*b*) to clamp it vertically, (*c*) to have the part below the tap full? (9)

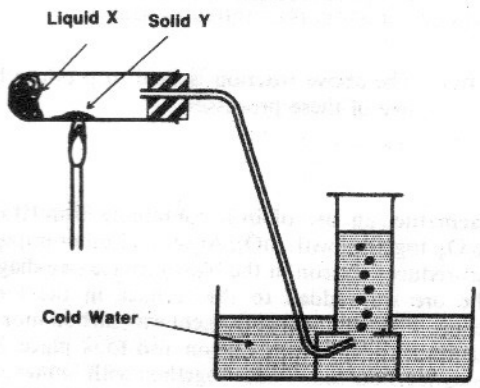
(iv) In acid-base titrations it is preferable to use as little of the indicator as possible. What is the reason for this? (6)

(v) In volumetric analysis, what is the advantage in carrying out a rough titration? In this experiment, what mean titration value should be used in the calculation? (9)

(vi) Calculate the concentration of the hydrochloric acid solution in the volumetric flask in mol dm^{-3}.
How many moles of hydrogen chloride were contained (*a*) in 250 cm^3 of this solution, (*b*) in the 50 cm^3 of the 1 mol dm^{-3} hydrochloric acid solution used to dissolve the tablet?
How many moles of hydrogen chloride were used up in the reaction with the tablet? (18)

(vii) Find (*a*) the number of moles, (*b*) the mass, (*c*) the percentage, of magnesium hydroxide in the tablet. (9)

3. Ethene gas was prepared and collected using the apparatus shown in the diagram. When a mixture of ethene and hydrogen was passed over a heated catalyst, ethane (contaminated with some unreacted ethene) was produced. Another alkene, hexene, was prepared in a similar way but the method of collection used was different. The hexene produced was also converted to the corresponding alkane.



(i) Identify liquid X and solid Y. How was liquid X kept at the end of the horizontal test tube? (12)

(ii) Name the catalyst and state the temperature used in converting the two alkenes to alkanes. What term is used for reactions of this type? Give one industrial process in which this type of reaction is used. (15)

(iii) What test would you have carried out to show that the ethane produced was contaminated with unreacted ethene? Write an equation for the reaction involved in the test and give the name *and* structural formula of the product of the reaction. (18)

(iv) Why was a different method of collection used in the case of hexene? Show by means of a diagram a method of collection that would have been suitable. (9)

(v) When $1{\cdot}0 \times 10^{-2}$ moles of the alkane produced from hexene were burned completely in oxygen, 2·64 g of carbon dioxide and 1·26 g of water were produced. Show that the molecular formula of the alkane is C_6H_{14}. (12)

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) Define (*a*) mass number, (*b*) relative atomic mass.
Explain why the relative atomic masses of the naturally-occurring elements are not whole numbers. (15)

(ii) What do you understand by *energy levels* in an atom?
Explain, in terms of energy levels, why the spectra of elements consist of a series of lines of definite frequency.
Different metals impart different colours to the bunsen flame. In the case of any *two* named metals, state the colour imparted to the flame. Explain briefly why different metals produce different flame colours. (21)

(iii) What is meant by ionisation energy?
Explain why ionisation energy values generally increase across a period (e.g. from Li to Ne) and decrease down a group (e.g. group 1). (12)

(iv) The first five ionisation energies (in kJ mol^{-1}) for titanium are shown in the table. State with reference to the electronic configuration (s,p,etc.) of titanium (*a*) the sublevel from which the first electron is removed, (*b*) the reason why the increases in ionisation energy are relatively small for the first four electrons removed, (*c*) the reason for the much greater increase from the fourth to the fifth electron removed. (18)

Electron removed	Ionisation energy
1st	661
2nd	1313
3rd	2658
4th	4185
5th	9659

5. State Le Chatelier's Principle. (6)

A mixture of 6 moles of methane gas and 6 moles of steam was allowed to come to equilibrium in a closed 60 dm^3 vessel. At equilibrium 50% of the methane had reacted and the temperature in the vessel was 800 °C. The equation for the reaction is

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \quad \Delta H = 205 \text{ kJ mol}^{-1}$$

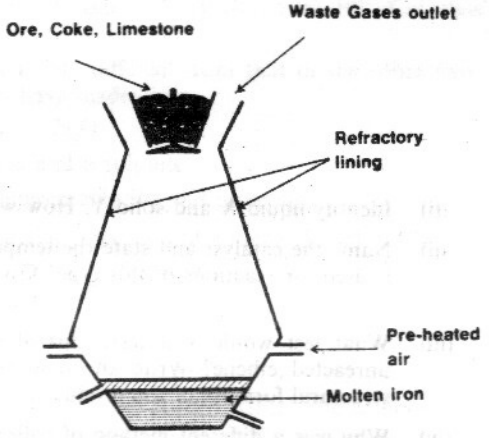
(i) Write the equilibrium constant expression (K_c) for the reaction and calculate the value of K_c at 800 °C. (18)

(ii) Write the equilibrium constant expression (K_p) for the reaction. Given that the total pressure in the reaction vessel at equilibrium is 27 atmospheres, calculate the partial pressures of the four gases in the equilibrium mixture and the value of K_p at 800 °C. (24)

(iii) How would the yield of hydrogen be affected (*a*) if the reaction were carried out at a lower temperature, (*b*) if the reaction were carried out at a lower pressure? Give a reason for your answer in each case. (12)

(iv) The above reaction is used to produce hydrogen for a number of important industrial processes. Name *one* of these processes. (6)

6. Haematite, an ore of iron containing iron(III)oxide, Fe_2O_3, together with SiO_2, Al_2O_3 and other impurities, was reduced to iron in the blast furnace (see diagram). The ore was added to the furnace in the form of pellets. The main reducing agent was carbon monoxide but some reduction by carbon also took place. Waste gases (carbon monoxide, together with some carbon dioxide) were removed from the top of the furnace.



(i) Why is it important to have the ore in the form of pellets and not in powder form? (6)

(ii) What use is made of the waste gases? (6)

(iii) In the case of *one* of the impurities mentioned above, indicate clearly how it is separated from the ore and removed from the furnace. (12)

(iv) Write balanced equations for the reduction of the iron(III)oxide (*a*) by carbon monoxide, (*b*) by carbon. (12)

(v) The pig iron from the blast furnace has a number of other elements present in it as impurities. Name *two* of these elements and describe how they are removed when iron is converted to steel. (12)

(vi) Another ore of iron (magnetite), containing 58% Fe_3O_4 as its only source of iron, was reduced to iron in the blast furnace. The equation is

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$

How many tonnes of the ore were used to produce 21 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)

7. (*a*) Define *oxidation number*. (6)

What is the oxidation number of chromium in the following:

(i) $HCrO_4^-$, (ii) Cr_2O_3, (iii) $Cr_2O_7^{2-}$? (9)

What is the oxidation number of oxygen in OF_2? Explain why the oxidation number you have given is assigned to oxygen in this case. (6)

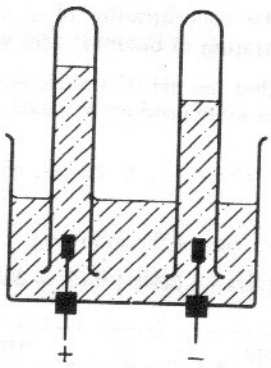
(*b*) The metals sodium, zinc and copper are found in that order in terms of decreasing reactivity. Show that the order is correct by referring to the following:

(i) the reactions, if any, of the three metals with water or steam; (9)

(ii) the effects, if any, of heat on the hydroxides of sodium and zinc; (6)

(iii) the reactions, if any, when hydrogen is passed over the heated oxides of zinc and copper. (6)

(*c*) The diagram shows the electrolysis of aqueous sodium sulphate using inert electrodes.

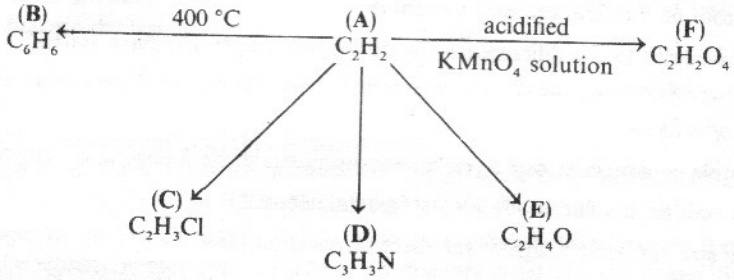


(i) Explain the underlined term. (3)

(ii) Write equations for the reactions taking place at the anode and cathode, and describe simple tests you could use to identify the products of the electrolysis. Where does oxidation take place in the process? (21)

8. Distinguish between empirical formula and molecular formula. (6)

Study the following organic reactions and answer the questions which follow.



(i) Give the systematic (IUPAC) names *or* the structural formulae of **A, C, D, E**. (12)

(ii) What reagent is used (*a*) to convert **A** to **C**, (*b*) to convert **A** to **D**? Write an equation for the reaction involved in either (*a*) *or* (*b*) and give one use of the product of the reaction you have chosen. (12)

(iii) How would you convert **A** to **E**? What term is usually used to describe this type of reaction? (12)

(iv) What would you observe in the reaction in which **A** is converted to **F**? What does your observation indicate about the structure of **A**? Give the name *or* structural formula of **F**. (9)

(v) **B** is an aromatic compound. Another aromatic compound consists of 36·36% carbon, 3·03% hydrogen, 32·32% oxygen and 28·28% nitrogen by mass. Find its empirical formula. If its relative molecular mass is 198 and it undergoes a condensation reaction with **E**, identify the compound. (15)

9. (*a*) What is meant by hardness of water? Distinguish clearly between temporary and permanent hardness. (6)

Which calcium compound is a cause of temporary hardness? How does this compound get into the water? (9)

A whitish deposit ('fur' or 'scale') is often found on the insides of kettles in hard-water districts. Write an equation for the reaction involved in producing this deposit. (6)

(*b*) Give the names *or* formulae of the products formed when water reacts with each of the following compounds:

(i) the peroxide of a group I metal,

(ii) the chloride of a group III metal,

(iii) the chloride of a trivalent solid element from group V.

In the case of (ii) *or* (iii) write a balanced equation for the reaction. (24)

(*c*) Find the concentration of a nitric acid solution in mol dm^{-3} if the pH of the solution is 3. What concentration of butanoic acid would give the same pH? (K_a for butanoic acid = $1{\cdot}6 \times 10^{-5}$). (15)

Show that the pH of a nitric acid solution of concentration 1×10^{-8} mol dm^{-3} is less than 7. (K_w, the ionic product of water = 1×10^{-14} mol^2 dm^{-6}) (6)

10. Answer any *two* of the following.

(*a*) The following table provides data on three of the group VII elements.

Element	Atomic radius (A)	Melting point (°C)	Boiling point (°C)	Bond energy (kJ mol^{-1})
Chlorine	0·71	−103	−34·6	242
Bromine	0·99	−7·2	58·8	193
Iodine	1·14	113·5	184·4	150

(i) What common name is used for the group VII elements? (3)

(ii) In the solid state, the molecules of the group VII elements are held together by Van der Waals' forces. What evidence is there in the table that these forces become stronger down the group?

Give a reason for this increase in strength. (9)

(iii) Why do the bond energies of the group VII elements decrease down the group? (6)

(iv) State two possible shapes for molecules of general formula QX_2, where Q is a divalent element and X is an atom of chlorine, bromine or iodine.

What gives rise to the difference between the two shapes you have stated? (15)

(*b*) Define *rate of reaction.* (6)

Describe simple experiments, one in each case, to illustrate the following statements.

(i) Ionic reactions in solution are almost instantaneous. (9)

(ii) Particle size can have a significant effect on reaction rate. (9)

Excluding particle size, and the ionic or covalent nature of the reactants, list *three* factors that can affect the rate of a chemical reaction. (9)

(*c*) Define *heat of neutralisation.* In what units is it measured? (9)

When 200 cm^3 of a sodium hydroxide solution were added to 200 cm^3 of a 0·4 mol dm^{-3} solution of sulphuric acid in a plastic container, a neutral solution was produced and the temperature rose by 5·5°C. The density and specific heat capacity of the neutral solution (assumed equal to those of water) are 1·0 g cm^{-3} and 4·2 kJ kg^{-1} $°C^{-1}$ respectively.

(i) Why was a plastic container used? (3)

(ii) What steps would you have taken to ensure an accurate measurement of the temperature rise? (9)

(iii) Calculate the heat of neutralisation of one mole of sulphuric acid by sodium hydroxide. (12)

(*d*) An ester of molecular formula $C_2H_4O_2$ was hydrolysed by refluxing it with sodium hydroxide solution. At the end of the reflux period, excess hydrochloric acid was added to the reaction mixture and the carboxylic acid liberated was recovered from the reaction mixture by distillation.

(i) Identify (*a*) the ester, (*b*) the products of the hydrolysis with sodium hydroxide. (12)

(ii) Write an equation for the reaction in which the carboxylic acid was liberated. (6)

(iii) Another carboxylic acid has the same molecular formula as the ester. Give the name *and* structural formula of this acid and describe briefly a chemical test that would allow you to distinguish it from the carboxylic acid liberated above. (15)