AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1979

CHEMISTRY—HIGHER LEVEL

WEDNESDAY, 20 JUNE—AFTERNOON, 2 to 5

Six questions to be answered.

All questions carry the same number of marks.

Relative atomic masses: H = 1, C = 12, O = 16, Na = 23, Mg = 24, S = 32, Cl = 35·5, K = 39, Ca = 40, Br = 80

Molar volume at S.T.P. = 22·4 litres

Avogadro constant (number) = 6×10^{23}

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

(*a*) Which one of the following elements would you expect to show variable valence: K, Mg, Ne, Al, Mn ?

(*b*) What is Hund's Rule?

(*c*) What is the oxidation number of (i) Cl in $KClO_4$, (ii) Cr in $HCrO_4^-$?

(*d*) A gas occupies 190 cm^3 at 91°C and 800 mm Hg pressure. What volume will it occupy at S.T.P.?

(*e*) Write the s, p configuration of the calcium ion. Which neutral atom has the same configuration?

(*f*) Explain, by equations or otherwise, why the hydrogen sulphide ion (HS^-) can act as both an acid and a base.

(*g*) When dolomite is heated strongly it decomposes according to the equation

$$CaCO_3.MgCO_3 \rightarrow CaO.MgO + 2CO_2$$

What mass of solid product (CaO.MgO) could be obtained from 23 kg of dolomite?

(*h*) Write down the functional group of (i) carboxylic acids, (ii) secondary amines.

(*i*) What is the value of

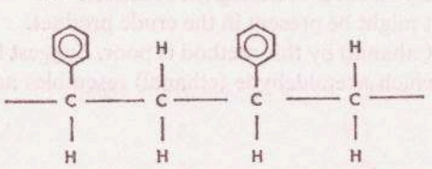
(i) the principal quantum number (*n*), (ii) the subsidiary or azimuthal quantum number (*l*),

for an electron in a 2p orbital?

(*j*) Write an equation for the reaction of calcium hydride with water.

(*k*) How many sulphite ions (SO_3^{2-}) are present in 2·1 g of anhydrous sodium sulphite (Na_2SO_3)?

(*l*) A section of a polymer molecule is represented as follows:



Give the name and structural formula of the monomer from which it is formed.

(*m*) Aluminium combines with phosphorus to form a phosphide. Which of the following:

$$AlP, \quad AlP_3, \quad Al_2P_3, \quad Al_3P, \quad Al_3P_2,$$

is the most likely formula for the phosphide?

(*n*) What volume of oxygen, measured at S.T.P., could be obtained from 8·75 g of potassium chlorate in the reaction,

$$2KClO_3 \longrightarrow 2KCl + 3O_2 \ ?$$

2. What general properties (i.e. appearance, melting-point, electrical conductivity, solubility) do you associate with covalent compounds of low relative molecular mass (molecular weight)?

Show the electronic structure of the phosphorus trichloride molecule.

Indicate the shape of the phosphorus trichloride molecule and suggest why the Cl—P—Cl bond angle of approximately 100° is different from the tetrahedral angle. Explain why the phosphorus trichloride molecule has a dipole moment.

Show the shape of the ethylene (ethene) molecule, C_2H_4, and show what type of hybridisation would give bond angles in accordance with those observed experimentally.

3. Define (*a*) heat of formation, (*b*) heat of combustion.

Given the following data:

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H = -\ 393\ kJ\ mol^{-1}$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\quad \Delta H = -\ 286\ kJ\ mol^{-1}$

$C_2H_{6(g)} + 3\frac{1}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\quad \Delta H = -\ 1560\ kJ\ mol^{-1}$

$C_2H_{2(g)} + 2\frac{1}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(l)}$ $\quad \Delta H = -\ 1295\ kJ\ mol^{-1}$

calculate (i) the heat of formation of ethane, (ii) the heat change for the reaction:

$$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$$

Using the following bond energies:

$E(C \equiv C) = 837\ kJ\ mol^{-1}$

$E(C - H) = 412\ kJ\ mol^{-1}$

$E(H - H) = 436\ kJ\ mol^{-1}$

$E(C - C) = 348\ kJ\ mol^{-1}$

calculate again the heat change for the reaction: $C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$

Assuming that the experimental error is not significant, suggest one reason why the value obtained is not identical with the value in (ii) above.

4. Acetaldehyde (ethanal) was prepared by the controlled oxidation of ethanol as follows:

60 cm^3 of a 40% solution of sulphuric acid were heated to boiling in a flask to which silica granules had also been added. The heating was then stopped. 30 g of sodium dichromate were dissolved in 50 cm^3 water and the solution, mixed with 30 cm^3 ethanol, was placed in a dropping funnel. The mixture was added, one drop at a time, to the hot sulphuric acid solution. The acetaldehyde (ethanal) vapour formed was condensed and collected in a flask cooled with ice and water.

The acetaldehyde (ethanal) was purified by the formation, separation and subsequent decomposition of its addition product with sodium hydrogen sulphite ($NaHSO_3$). It was finally obtained by fractional distillation.

(i) Mention two points in the procedure which would help to ensure that the main product was acetaldehyde (ethanal).
(ii) What is the purpose of the silica granules?
(iii) Give the name and structural formula of the main product you would expect if the conditions of the experiment allowed the oxidation to proceed further.
(iv) Why is it necessary to cool the receiver with iced water?
(v) What colour change would you observe during the reaction?
(vi) Name three impurities that might be present in the crude product.
(vii) The yield of acetaldehyde (ethanal) by this method is poor. Suggest two reasons for this.
(viii) Mention one reaction in which acetaldehyde (ethanal) resembles acetone (propanone) and one reaction in which they differ.

5. (*a*) 5·25 g of a weak dibasic (diprotic) organic acid of relative molecular mass (molecular weight) 150 were dissolved in water and the solution made up to 500 cm^3. If 25 cm^3 of this solution required 28 cm^3 of a potassium hydroxide solution for neutralisation, using phenolphthalein as indicator, calculate the concentration of the potassium hydroxide solution

(i) in terms of molarity,

(ii) in grams per litre.

If phenolphthalein is considered as a weak acid, HIn, explain how it works as an indicator in this case.

(*b*) "Most optically active compounds contain an asymmetric carbon atom". Explain the underlined terms. Write down the structures of two optical isomers of the same compound.

(*c*) Two salts were labelled potassium iodide and potassium sulphate respectively. For each salt describe one positive chemical test, which would help confirm that the labelling of the anion was correct.

6. Below are listed some oxides of elements in the third period, together with their melting-points. By reference to this list answer the questions which follow.

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_2
m.p.(K)	1465	3075	2300	1983	297	198

(i) Name one basic oxide and show by an equation how it would react with dilute hydrochloric acid.

(ii) Name one acidic oxide and show by an equation how it would react with *either* water *or* sodium hydroxide solution.

(iii) Name an amphoteric oxide and show by an equation how it would react with dilute hydrochloric acid..

(iv) Give the name and formula of the compound this amphoteric oxide would form with sodium hydroxide.

(v) Sugest why the melting-points of the first two oxides listed are high while the melting-points of the last two oxides listed are relatively low.

(vi) Explain, by reference to its structure, why silicon dioxide has a high melting-point.

(vii) Silicon dioxide can be precipitated by adding water to silicon tetrachloride. Write an equation for this reaction and explain why it is termed "hydrolysis".

7. Hydrogen peroxide decomposes rapidly at room temperature in the presence of certain catalysts, according to the equation,

$$2H_2O_{2(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$

In one such experiment 2 g of manganese dioxide were added to 20 cm^3 of a solution of hydrogen peroxide. The volume of oxygen liberated was measured at intervals, with the following results:

Time (seconds)	0	15	30	45	60	90	120	150	180	210	240
Vol. of O_2 (cm^3)	0	60	110	134	150	170	184	193	197	200	200

(i) Using graph paper plot the volume of oxygen liberated against time.

(ii) After what time could the reaction be said to be complete?

(iii) What fraction of the hydrogen peroxide decomposed in the first minute?

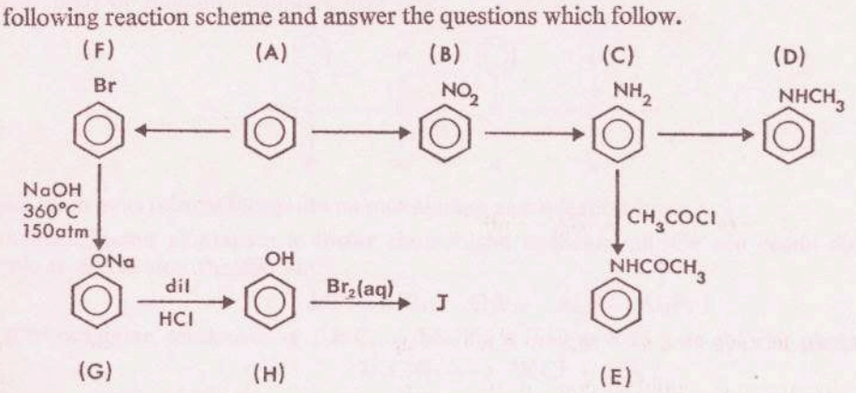
(iv) Explain why the rate of the reaction gets slower as the reaction proceeds.

(v) If this reaction were carried out at a temperature higher than room temperature, would the curve lie above or below the curve you have drawn for room temperature? Explain fully the reason for your answer.

(vi) Explain why the decomposition of hydrogen peroxide at room temperature is very slow in the absence of a catalyst.

(vii) Explain why (*a*) an increase in pressure would have no measurable effect on the rate of this reaction, (*b*) it is nevertheless necessary to maintain a constant pressure (e.g. 1 atmosphere) while the readings of volume of oxygen are being taken.

8. Study the following reaction scheme and answer the questions which follow.



(i) Name the compounds A, C, D, F and H.

(ii) Name the two reagents used to convert A to B.

(iii) Name reagents suitable for converting B to C.

(iv) Name *or* give the formula for one reagent which would convert C to D.

(v) Name and give the formula for a reagent which could be used instead of acetyl chloride (ethanoyl chloride), CH_3COCl, for converting C to E.

(vi) Write a balanced equation for the change H to J

(vii) Which of the compounds labelled A to H would you expect to be most soluble in water? Give your reason.

(viii) There is a difference in the acidic nature of the $-OH$ group in ethanol and the $-OH$ group in compound H. Suggest a reason for this difference.

9. Write the equilibrium constant expression for the reaction,

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

Explain what is happening when the above reaction reaches a state of equilibrium.

At a certain temperature the equilibrium constant for the above reaction is 4·0. If 88 g of the ester, ethyl acetate (ethyl ethanoate), and 18 g water are mixed and heated at this temperature until equilibrium is attained, how many moles of (i) ethanol, (ii) ester, will be present?

State Le Chatelier's Principle.

If less than 18 g water had been used in the above reaction, would the amount of ester present at equilibrium have been more, less or unchanged? Explain your reasoning.

Dilute hydrochloric acid can catalyse this reaction. Explain how, if at all, you would expect it to affect

(i) the time taken to reach equilibrium, (ii) the equilibrium constant.

10. Answer any *two* of the following.

(*a*) The elevation of boiling-point method for determining relative molecular mass (molecular weight) has certain limitations in that it cannot be used for all substances. Mention three such limitations, explaining why the method is unsuitable in each case.

When 2·4 g of an organic compound were dissolved in 130 g water the boiling point was raised by 0·16 K. If the boiling point constant for water is 0·52 K mol^{-1} kg^{-1} calculate the relative molecular mass (molecular weight) of the compound.

(*b*) Define (i) a strong acid, (ii) the pH of a solution.

Explain why an aqueous solution of sodium sulphide (Na_2S) has a pH greater than 7.

Assuming that both acids are fully ionised in aqueous solution, calculate the pH of

(i) a 0·03 M solution of HCl, (ii) a 0·03 M solution of H_2SO_4.

(*c*) Explain what happens (i) at the cathode, (ii) at the anode, during the electrolysis of an aqueous solution of copper (II) sulphate using copper electrodes, and show why this is a redox reaction.

Mention one practical application of this process.

The elements Na, Zn, H and Cu occur in this order in the electrochemical series, sodium being the most electropositive. Explain how these placings are justified on the basis of the following:

(i) the reactions, if any, of the metals with water and dilute hydrochloric acid,

(ii) the reactions, if any, of the heated metal oxides with hydrogen.

(*d*) Explain the terms: (i) empirical formula, (ii) molecular formula, (iii) structural formula, (iv) structural isomers.

An organic liquid contained 12·7% carbon, 2·1% hydrogen and 85·2% bromine. Find its empirical formula. If its relative vapour density is 94, what is its molecular formula? Write two structural formulae for the compound.