AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1982

CHEMISTRY—HIGHER LEVEL

WEDNESDAY, 23 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, N = 14, O = 16, Na = 23, Cl = 35·5, K = 39, Ca = 40, Cr = 52, Ag = 108, Pb = 207.
Molar volume at S.T.P. = 22·4 litres (dm^3)
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*) What mass of chromium will contain the same number of atoms as 8 g calcium?

(*b*) Write the formula of (i) one neutral oxide, (ii) one amphoteric oxide.

(*c*) Complete and balance the equation

$$C_2H_5OH + Na \rightarrow$$

(*d*) Which two of the following gases will diffuse through the same porous plug at the same rate:

$$N_2,\ CH_4,\ O_2,\ C_2H_4,\ NO\ ?$$

(*e*) How many atoms are there in 1·12 litres (dm^3) of butene gas (C_4H_8) at S.T.P.?

(*f*) Mention one use for each of any two of the following radioisotopes:

$$^{14}_{6}C,\ ^{32}_{15}P,\ ^{60}_{27}Co$$

(*g*) What is the oxidation number of

(i) the sulphur atom in $Na_2S_2O_3$, (ii) the chromium atom in $Cr_2O_7^{2-}$?

(*h*) Which two of the following will *not* react with aqueous sodium hydroxide:

$$CH_3COOC_2H_5,\ C_2H_5NH_2,\ C_2H_5OH,\ C_2H_5COOH,\ CH_3NH_3^+ ?$$

(*i*) Define the hydration energy of an ion.

(*j*) Write down the conjugate acids of the bases

(i) SO_3^{2-}, (ii) CH_3CONH^-

(*k*) State Dalton's law of partial pressures.

(*l*) Draw a simple sketch graph to indicate the relationship between pV and p for a constant amount of an ideal gas at constant temperature.

(*m*) What name is normally given to the energy change represented by

$$X_{(g)} + e^- \rightarrow X^-_{(g)}$$

where X is any isolated atom?

(*n*) What mass of silver ions (Ag^+) will be discharged by the same quantity of electricity as will discharge 2·3 g of lead ions (Pb^{2+})?

2. (i) What is meant by saying that the hydrogen chloride molecule is polar? Explain how the polarity arises.

(ii) Hydrogen chloride is completely hydrolysed by water. Show by an equation what is meant by this statement.

(iii) Indicate the electronic structure of sodium hydride and show by an equation how it reacts with water.

(iv) Indicate the electronic structure of hydrogen peroxide. Describe briefly how a solution containing hydrogen peroxide could be obtained in the laboratory.

(v) Write the structural formulae of one saturated and one unsaturated hydride of carbon. How do these hydrides differ in their reactions with chlorine?

(vi) Discuss the shape of the beryllium hydride molecule in terms of bonds formed by hybrid orbitals.

(vii) When silane (silicon tetrahydride) reacts with water one of the products is hydrogen gas. When hydrogen sulphide reacts with water hydroxonium ions (H_3O^+) are formed. Suggest a reason for the different behaviour of these two hydrides with water.

(See Table of Electronegativities, Mathematics Tables, p. 46)

3. (*a*) What is meant by a metallic bond?
Mention and explain two characteristic properties of metals which arise from metallic bonding.
The melting-points of potassium and calcium are respectively 337 K and 1123 K. Suggest a reason for the large difference between these melting-points.

(*b*) State Pauli's Exclusion Principle.
Name the species represented by each of the following structures:

(i) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^8\,4s^2$,

(ii) $[1s^2\,2s^2\,2p^6\,3s^2\,3p^6]^{2-}$

Copy the following table and complete it by filling in possible values for the missing quantum numbers which refer to the three p electrons in a nitrogen atom.

Orbital	p_x	p_y	p_z
Principal Quantum Number	2		
Azimuthal Quantum Number (Subsidiary)			1
Magnetic Quantum Number		0	
Spin Quantum Number	$-\frac{1}{2}$		

4. Identify each of the organic compounds **A** to **D** below by giving its name *or* its correct formula. Write balanced equations for all the reactions mentioned.

(i) **A** is an inflammable colourless gas formed when ethanol is heated with excess concentrated sulphuric acid at 445 K. It decolourises a solution of bromine in carbon tetrachloride (tetrachloromethane).

(ii) **B** is a colourless liquid which is the lowest member of its homologous series. It reacts with magnesium metal to give an inflammable gas and with ethanol, in the presence of a little concentrated sulphuric acid, to give a volatile liquid with a pleasant odour.

(iii) **C** is a white crystalline solid of relative molecular mass (molecular weight) 59. It is formed by heating an ammonium salt. It can be hydrolysed by heating with aqueous sodium hydroxide, giving an alkaline gas as one of the products.

(iv) **D** is an oily liquid of relative molecular mass (molecular weight) 93 with a strong aromatic odour. It is usually yellow in colour. It is insoluble in water but dissolves easily in dilute hydrochloric acid. It will re-appear if the solution is made alkaline with potassium hydroxide solution. It reacts slowly with acetic (ethanoic) anhydride in the presence of acetic (ethanoic) acid to give a white crystalline derivative.

5. Describe how the elevation of boiling-point of a solvent by a non-volatile solute can be measured experimentally.
Explain why the solute (*a*) must be non-volatile, (*b*) must not ionise in solution, if its relative molecular mass (molecular weight) is to be found by the elevation of boiling-point method.
3·60 g glucose ($C_6H_{12}O_6$) were found to raise the boiling-point of 40 g water by 0·26 K. If 3·75 g of an unknown sugar raised the boiling-point of 50 g water by the same amount calculate the relative molecular mass (molecular weight) of this sugar.
Elevation of boiling-point is a colligative property of a solution. Explain the underlined term.
Why does a non-volatile solute

(i) lower the vapour pressure of a liquid,

(ii) raise the boiling-point of a liquid?

6. Some dried rock salt was crushed in a mortar. 5·85 g of the sample was stirred with distilled water for ten minutes and filtered to remove insoluble impurities. The residue was washed with distilled water and the washings added to the filtrate which was then made up to 500 cm^3 in a volumetric flask.
25 cm^3 of this solution required 28·0 cm^3 of 0·125 M silver nitrate solution for complete precipitation of the chloride ion.

(i) Write an equation for the reaction of sodium chloride with silver nitrate.

(ii) Mention, giving your reason, any one precaution you would take when using silver nitrate solution.

(iii) Calculate the concentration of chloride ion in the solution in moles per litre (mol dm^{-3}).

(iv) Name an indicator suitable for detecting the end-point of this titration and explain briefly how it acts as an indicator.

(v) Qualitative analysis showed that only sodium and chloride ions were present in the solution. Calculate the percentage by weight of sodium chloride in the rock salt sample.

(vi) A sample of the original salt solution was concentrated by evaporation and tests were carried out for (*a*) sulphate ions, (*b*) carbonate ions.
Describe one suitable test for each of these ions and in each case give the equation for the reaction that would occur if the ion were present.

7. Define (i) heat of formation, (ii) bond energy.
What do you understand by (i) the First Law of Thermodynamics, (ii) Hess's Law?
Calculate the heat change for the reaction,

$$C_2H_{4(g)} + HBr_{(g)} \rightarrow C_2H_5Br_{(l)}$$

given that the heats of formation of $C_2H_{4(g)}$, $HBr_{(g)}$ and $C_2H_5Br_{(l)}$ are + 52, − 36 and − 85 kJ mol^{-1} respectively.

The following are bond energies:

$$\begin{aligned} E(C - C) &= +348 \text{ kJ mol}^{-1} \\ E(C = C) &= +612 \text{ kJ mol}^{-1} \\ E(C - H) &= +412 \text{ kJ mol}^{-1} \\ E(H - Br) &= +366 \text{ kJ mol}^{-1} \\ E(C - Br) &= +276 \text{ kJ mol}^{-1} \end{aligned}$$

Use these values to calculate the heat change for the reaction, $C_2H_{4(g)} + HBr_{(g)} \longrightarrow C_2H_5Br_{(g)}$

Use the result to calculate the heat change for the reaction, $C_2H_{4(g)} + HBr_{(g)} \longrightarrow C_2H_5Br_{(l)}$

given that for the change, $C_2H_5Br_{(l)} \longrightarrow C_2H_5Br_{(g)}$, $\Delta H = +30$ kJ mol^{-1}

Suggest one reason why the result differs slightly from that obtained from heats of formation.

8. The formulae of five organic compounds are given below. In answering the questions which follow each compound may be used once, more than once or not at all.

A. CH_3NH_2

B. $CH_3CH(OH)COOH$

C. 

D. $CH_3CH=CH_2$

E. $(CH_3)_2CHCH_3$

(i) Name the compounds A to E.

(ii) Which compound will undergo addition polymerisation? Indicate the structure of the polymer by showing two repeating units.

(iii) Which compound will burn in air giving four times its own volume of carbon dioxide? Write the structural formula of another isomer with the same molecular formula.

(iv) Which compound will decolourise bromine water forming a white precipitate? Give the structural formula for the precipitate and state whether this is an addition or a substitution reaction.

(v) Which compound will react with methyl iodide (iodomethane) under suitable conditions to form a product which is a stronger base than the compound itself? Give an equation for this reaction and explain why the organic product can act as a base.

(vi) Which compound can exist as stereoisomers? Name the type of stereoisomerism, explain how it arises and show clearly how the two isomers differ.

9. Bromine monochloride dissociates on heating according to the equation

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

In an experiment 0·9 moles of BrCl were heated in a 5 litre (dm^3) vessel at a certain temperature until equilibrium was established. The amount of free chlorine in the mixture was found to be 0·4 moles.

(i) Write the equilibrium constant expression for this reaction.

(ii) Calculate the equilibrium constant for the reaction at this temperature.

(iii) Explain why it is not necessary to know the volume of the vessel in calculating the equilibrium constant.

(iv) Is the value of the equilibrium constant for the reaction when represented by the equation $BrCl_{(g)} \rightleftharpoons \frac{1}{2} Br_{2(g)} + \frac{1}{2} Cl_{2(g)}$ the same as that calculated in (ii) above? Explain your answer.

(v) In another experiment 0·9 moles of BrCl and 0·2 moles of bromine were heated in a similar vessel to the same temperature as before until equilibrium was reached. How many moles of each of the three constituents would now be present in the vessel?

(vi) If the forward reaction as shown above is exothermic, explain, giving your reasons, whether or not the reaction would be expected to go to completion at a sufficiently high temperature.

(*a*) An organic liquid containing carbon, hydrogen and oxygen only was found on analysis to contain 62·1% carbon and 10·3% hydrogen. Its relative molecular mass (molecular weight) was found to be 58. Find the molecular formula of the compound.
Suggest two possible structural formulae for it.
Describe one chemical reaction which would distinguish between the two structures, stating clearly how each would or would not react in the test chosen.

(*b*) **V**, **W**, **X**, **Y**, and **Z** are code letters for five metals. Using the information given below place the five metals in their order in the electrochemical series, putting the most electropositive metal first. Explain briefly the general principles on which you base your reasoning.
W is the only one of the five found free in nature. Some wire of the metal **V** dipped in a solution containing Z^{2+} ions becomes coated with **Z**. The strongest reducing agent is **X**. The nitrate of **V** decomposes at a lower temperature than that of **Y**.

(*c*) Explain, by reference to the energy factors involved, why
(i) sodium chloride crystals will dissolve in water but not in carbon tetrachloride (tetrachloromethane),
(ii) iodine crystals will dissolve in carbon tetrachloride (tetrachloromethane) but hardly at all in water.

What do you understand by a saturated solution?
The solubility of potassium nitrate is 32 g per 100 g water at 293 K and 112 g per 100 g water at 333 K. What mass of potassium nitrate crystals will be deposited when 53 g of a saturated solution of the salt in water at 333 K is cooled to 293 K?

(*d*) Define the pH of a solution.
Calculate the pH of
(i) a 0·05 M aqueous solution of hydrochloric acid,
(ii) a 500 cm^3 aqueous solution containing 0·007 g of potassium hydroxide,
(iii) a solution obtained by adding 50 cm^3 of 0·1 M hydrochloric acid to 50 cm^3 of 0·01 M potassium hydroxide.