AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1976

CHEMISTRY—HIGHER LEVEL

WEDNESDAY, 16 JUNE—AFTERNOON, 2 to 4.45

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, Cu = 63·5.
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*) What is meant by an atomic orbital? Indicate the shape of a *p* orbital.

   (*b*) Which species are acting as acids in the reaction:

   $$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

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

   (*d*) Which of the following is a homologue of ethene (ethylene):

   $$C_2H_6,\ C_3H_6,\ C_3H_4,\ C_2H_4Cl_2,\ C_6H_5CH_2CH_3\ ?$$

   (*e*) What is an amphoteric oxide? Give an example.

   (*f*) Write the equilibrium constant expression for the reaction:

   $$H_2 + I_2 \rightleftharpoons 2HI$$

   (*g*) Write down the s, p configuration of chlorine, and indicate briefly how the two isotopes of chlorine differ.

   (*h*) Which of the following molecules has a shape different from that of the others:

   $$H_2,\ BeH_2,\ CO_2,\ H_2O,\ C_2H_2\ ?$$

   (*i*) What type of hybrid orbital would explain the shape of the CH_4 molecule?

   (*j*) What is an asymmetric carbon atom?

   (*k*) Name two reagents you would use in a simple test for the nitrate ion in aqueous solution.

   (*l*) For what synthetic polymer is $NH_2(CH_2)_6NH_2$ one of the starting materials?

   (*m*) How many faradays of electricity are needed to deposit 95·25 g of the divalent metal copper during the electrolysis of copper sulphate solution?

   (*n*) Name two radioactive isotopes (specify their mass numbers) and state their uses.

2. Define oxidation in terms of (i) electron transfer, (ii) change in oxidation number.

   Explain clearly the reactions taking place at each electrode during the electrolysis of a dilute aqueous solution of sulphuric acid and show that this is an oxidation/reduction reaction.

   If 60 cm^3 of a colourless gas were formed at the cathode during this electrolysis what gas would be formed at the anode and what would be its volume?

   Use oxidation numbers to determine whether or not each of the following is an oxidation/reduction reaction and if so state which species is being oxidised and which is being reduced:

   $$H_2SO_3 + OH^- \rightarrow HSO_3^- + H_2O$$
   $$Cu_2O + 2H^+ \rightarrow Cu + Cu^{2+} + H_2O$$
   $$3Ag + 4H^+ + NO_3^- \rightarrow 3Ag^+ + NO + 2H_2O$$

   Using oxidation numbers, or otherwise, balance the following equation:

   $$MnO_4^- + H^+ + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$$

3. Explain what is meant by an ionic bond, taking potassium chloride as an example.

   List the general properties of ionic compounds.

   What is meant by (i) the lattice energy of an ionic solid, (ii) the hydration energy of an ion, (iii) heat of solution?

   Find the heat of solution of (i) potassium chloride, (ii) calcium chloride, in a large excess of water, given that the lattice energies of these chlorides are 701 kJ mol^{-1} and 2237 kJ mol^{-1}, respectively, and the hydration energies of the ions K^+, Ca^{2+}, Cl^- are as shown in the following table.

   Hydration Energies in kJ mol^{-1}

K^+	Ca^{2+}	Cl^-
− 322	− 1650	− 364

   Suggest why the hydration energy of the Ca^{2+} ion is much higher than that of the K^+ ion.

   Why are some ionic solids almost insoluble in water?

4. Write the structural formula for (i) acetaldehyde, (ii) acetone.
Outline briefly how acetaldehyde can be prepared from (i) ethanol, (ii) acetylene.
Acetaldehyde can be reduced to ethanol. Write the structural formula for the alcohol to which acetone can be similarly reduced.
Show by equations using structural formulae how (i) acetaldehyde, (ii) acetone, react with phenylhydrazine.
Give one chemical test to distinguish between acetaldehyde and acetone.
Acetaldehyde reacts with hydroxylamine to form a compound of formula $CH_3CH = NOH$. What type of stereoisomerism do you expect to be shown by this compound? Indicate the structure of the two isomers.

5. (*a*) 2·03 g of magnesium chloride, $MgCl_2.xH_2O$, were dissolved in distilled water and the solution made up to 250 cm³. For 25 cm³ of this solution 40 cm³ of 0·05M (0·05N) silver nitrate were required for complete precipitation of the chloride ions.
(i) Write an equation for the reaction between magnesium chloride solution and silver nitrate solution.
(ii) Find the molarity (or normality) of the magnesium chloride solution.
(iii) Find the value of x.
(*b*) An organic compound contains 48·6% carbon, 43·3% oxygen, and 8·1% hydrogen by weight. Find its simplest formula. If its vapour density is 37 what is its molecular formula?
Suggest a structural formula for the compound, which is a derivative of acetic acid.

6. The following are some elements in the order in which they appear in the electrochemical series:
K, Ca, Na, Mg, Al, Zn, Fe, Sn, Pb, H, Cu, Ag, Hg.
By reference to this series comment briefly on each of the following.
(i) The occurrence of the metals and the stability of their oxides.
(ii) The displacement of hydrogen from water and acids by metals.
(iii) The displacement of one metal by another from salt solutions.
(iv) The merit or otherwise of zinc and tin for preventing iron from rusting.
(v) Why is aluminium not as reactive as its position in the series would suggest?

7. Answer *three* of the following.
(*a*) State Le Chatelier's principle.
What would be the influence of (i) increasing the pressure, (ii) increasing the temperature, on the condition of equilibrium in the following exothermic reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$?
(*b*) What are colligative properties of solutions?
Outline briefly a method of measuring the relative molecular mass (molecular weight) of a non-volatile compound.
(*c*) Sulphur dioxide was prepared by heating excess dilute hydrochloric acid with 6·3 g of sodium sulphite according to the equation $Na_2SO_3 + 2HCl \rightarrow 2NaCl + SO_2 + H_2O$. Find (i) how many moles of sodium sulphite were used, (ii) the volume at S.T.P. of sulphur dioxide obtained, (iii) how many molecules of sulphur dioxide would the volume in (ii) contain.
(*d*) Discuss the principle involved in the use of indicators in acid-base titrations. Suggest suitable indicators for the following titrations: (i) strong acid-strong base, (ii) strong acid-weak base, (iii) weak acid-strong base.

8. From the following list:
Na_2O_2, LiH, H_2S, CuO, CCl_4, Fe_2O_3, $SiCl_4$, CO_2
identify *four* of the compounds *V*, *W*, *X*, *Y*, *Z* mentioned below. In the case of each of the four you select, explain as fully as you can, by equations or otherwise, the reactions given.
(i) *V* is a colourless odourless gas which is slightly soluble in water giving a weakly acid solution. *V* dissolves in sodium hydroxide solution to form a solution of a salt. When dilute hydrochloric acid is added to this salt effervescence occurs and *V* is given off.
(ii) *W* is a pale yellow solid. It reacts vigorously with water forming a colourless gas which relights a glowing splint. When the solution remaining is heated with ammonium chloride, an alkaline gas is evolved.
(iii) *X* is a black powder which is insoluble in water but dissolves in dilute sulphuric acid forming a blue solution from which blue crystals can be obtained. A solution of these crystals gives a white precipitate with barium chloride solution.
(iv) *Y* is a colourless liquid which fumes slightly in air. It reacts vigorously with water forming a white precipitate. When this precipitate is filtered off a clear solution is obtained which gives a white precipitate with a solution of silver nitrate.
(v) *Z* is a colourless solid which reacts vigorously with water leaving an alkaline solution and forming a colourless gas which burns easily. The same gas is liberated at the anode when some molten *Z* is electrolysed.

9. What is meant by (i) a weak acid, (ii) the pH of a solution?
Given that the ionic product of water at room temperature is 1×10^{-14} explain why the pH of pure water is 7.
Monochloroacetic acid ($CH_2ClCOOH$) is a weak monobasic acid, stronger than acetic acid but weaker than dichloroacetic acid ($CHCl_2COOH$).
(i) What is the pH of a 0·01 M (0·01 N) solution of monochloroacetic acid if its dissociation constant is $1·6 \times 10^{-3}$?
(ii) By reference to the structure of monochloroacetic acid explain why you expect it to be a stronger acid than acetic acid.
(iii) Explain why the following can be regarded as bases:
CH_3COO^-, CH_2ClCOO^-, $CHCl_2COO^-$
State, giving reasons, which of them is the strongest base.

10. Outline briefly, by means of an equation or a reaction scheme, how each of the following conversions could be carried out, indicating in each case the reagents used and stating the necessary conditions (heat, catalyst, etc.):

benzene to bromobenzene,
toluene to benzoic acid,
ethyl benzoate to benzoic acid,
aniline to methylaniline.

Show, with the aid of a labelled diagram, how you would prepare and collect a sample of either ethyl benzoate *or* ethyl acetate. Name two impurities other than water, which your sample might contain.

Discuss briefly the structure of the benzene molecule, mentioning some evidence on which it is based.

11. Give brief explanations, in chemical terms or in terms of the kinetic theory, for *four* of the following.

(*a*) An aqueous solution of zinc chloride is acidic.

(*b*) The freezing-point of a solution of potassium iodide in water is not altered when iodine dissolves in it according to the equation $K^+ + I^- + I_2 \rightarrow K^+ + I_3^-$

(*c*) Ammonia gas is very soluble in water but phosphine gas (PH_3) is virtually insoluble (Refer to Mathemathics Tables p. 46).

(*d*) Nitrogen does not form a pentachloride but phosphorus, which is in the same group, forms a pentachloride easily.

(*e*) The vapour pressure of a solution of sugar in water is lower than that of pure water at the same temperature.

(*f*) Beryllium and nitrogen are exceptions to the general increase in ionisation energies shown by the other elements in the period lithium to neon. (Refer to Mathematics Tables p. 44 and p. 45).