AN ROINN OIDEACHAIS M. 56

LEAVING CERTIFICATE EXAMINATION, 1972

CHEMISTRY - HIGHER LEVEL

WEDNESDAY, 21st JUNE - MORNING, 9.30 to 12

Six questions to be answered

1. What is (i) an atomic orbital, (ii) a hybrid orbital ?
Show how the idea of energy levels in atoms results from a study of the emission spectrum of hydrogen.
What is Hund's rule ? Illustrate it by referring to the s, p build-up of the elements in the period, lithium to neon.
Discuss and interpret the shape of the BF_3 molecule in terms of hybrid orbitals.

(66 marks)

2. Compare (i) the structure of, (ii) the bonding in, calcium oxide, carbon dioxide, silicon dioxide, iron, (III) chloride (ferric chloride) and phosphorus trichloride.
Describe the reactions, if any, of these compounds with water and show how the behaviour towards water is related to the type of bonding or to the molecular structure.

(66 marks)

3. (a) Discuss the nature of the metallic bond and show how it accounts for some of the characteristic properties of metals.
The melting-points of sodium and magnesium are 371 K (98°C) and 923 K (650°C) respectively. Suggest a reason for the large difference between these melting-points of these metals.

(b) Suggest reasons for the general increase in first ionisation energies of the elements from lithium to neon. How may the relatively high values of the elements beryllium and nitrogen be accounted for ?
Suggest a reason for the relatively small change in the first ionisation energies of the elements from scandium to copper.
(Refer to the table of first ionisation energies, Mathematical Tables, p. 45.)

(66 marks)

4. Describe, giving essential conditions and equation, how you would prepare a dilute solution of hydrogen peroxide.
Define oxidation and reduction in terms of (i) electron transfer, (ii) change in oxidation number.
In each of the following reactions indicate clearly where the electron changes occur and state which substance is being oxidised and which is being reduced:

(a) the action of zinc on copper sulphate solution,

(b) the formation of sodium hydride from sodium and hydrogen.

Use oxidation numbers to show that hydrogen peroxide acts

(i) as an oxidising agent in the reaction

$$H_2O_2 + 2H^+ + 2Fe^{2+} \longrightarrow 2H_2O + 2Fe^{3+},$$

(ii) as a reducing agent in the reaction

$$MnO_2 + H_2O_2 + 2H^+ \longrightarrow Mn^{2+} + O_2 + 2H_2O.$$

Comment on the reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$ as an oxidation - reduction process.

(66 marks)

5. What do you understand by (i) a strong acid, (ii) a weak acid ?
Explain what is meant by the statement that the dissociation constant (Ka) of acetic acid in water is $1{\cdot}8 \times 10^{-5}$.
Use this value of Ka for acetic acid to calculate the pH of (a) 1·00 molar (1·00 normal) acetic acid, (b) 0·01 molar (0·01 normal) acetic acid. (Mathematical Tables may be had from the Superintendent.)
Explain why you would expect (i) the pH of an aqueous solution of sodium acetate to be greater than 7, (ii) the pH of an aqueous solution of ammonium acetate to be approximately 7.

(66 marks)

6. Write structural formulae for (i) acetic acid, (ii) ethyl acetate, (iii) acetamide.
Show by equations how acetic acid could be converted to (i) sodium acetate, (ii) ethyl acetate, (iii) acetamide. Draw a labelled sketch of the apparatus you would use to prepare and collect a sample of ethyl acetate.
Show by equations how (i) ethyl acetate, (ii) acetamide, react when heated with dilute sodium hydroxide solution and name the products in each case.
What type of compound is ethyl acetate ? Give the name and structural formula of one other compound of the same type.

(66 marks)

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7. (a) Define (i) heat of formation of a compound, (ii) heat of reaction.
Calculate ΔH, in kilojoules or kilocalories, for the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$, given the following bond energies (E):

E (H - H) = 436 kJ (104 kcal) per mole
E (C - H) = 412 kJ (98 kcal) per mole
E (C - C) = 348 kJ (83 kcal) per mole
E (C = C) = 612 kJ (146 kcal) per mole.

(b) Explain briefly what you understand by the lattice energy of an ionic solid. (Mathematical expressions are not required.)
Outline the main energy changes which occur when an ionic solid dissolves in water. Why is the process of solution exothermic in some cases and endothermic in other cases ? Explain why some ionic solids are almost insoluble in water.

(67 marks)

8. When 41 grams of nitrobenzene were refluxed with tin and concentrated hydrochloric acid, a solution containing phenylammonium ions, chloride ions and other ions was obtained. Excess sodium hydroxide was added and the mixture steam-distilled. Aniline was extracted from the distillate with ether and was purified by distillation. 12·4 grams of aniline were obtained.

(i) How many moles of nitrobenzene were used ?

(ii) What type of reaction did the nitrobenzene undergo ?

(iii) Suggest a metal, other than tin, which could have been used.

(iv) Show how the phenylammonium ion can be regarded as an acid. What is its conjugate base ?

(v) Why was excess sodium hydroxide solution added ?

(vi) Calculate the yield of aniline as a percentage of the theoretical yield.

(vii) Indicate how aniline may be converted to methylaniline.

(viii) Aniline reacts readily with (a) hydrochloric acid, (b) acetic anhydride. Using structural formulae, write equations for these reactions and name the products in each case.

(67 marks)

9. (a) Why does cis-trans isomerism occur in some ethylene derivatives ? Write down the structural formulae for maleic and fumaric acids and indicate which is the cis-form and which is the trans-form.
Show how maleic and fumaric acids differ in the following properties: (i) polar nature or otherwise of the molecule, (ii) the formation of an anhydride. Relate these differences as far as possible to difference in structure.
Write down the structural formulae of the three isomers of dichloroethylene ($C_2H_2Cl_2$).

(b) What do you understand by optical activity ? Show the structure of the two isomers of lactic acid.
How do you account for the fact that lactic acid isolated from sour milk is not optically active ?

(67 marks)

10. (a) A solution of barium chloride was made by dissolving 14·64 grams of hydrated barium chloride ($BaCl_2.xH_2O$) in water and diluting to one litre (1000 cm^3). Excess sodium sulphate was added to 25 cm^3 of the barium chloride solution to remove barium ions, and 30 cm^3 of 0·10 molar (0·10 normal) silver nitrate solution were then required for complete precipitation of chloride ions. Potassium chromate was the indicator.

(i) Calculate the molarity (or normality) of the barium chloride solution, using the results of the titration.

(ii) Calculate the formula weight of $BaCl_2.xH_2O$.

(iii) Find the value of x. (H = 1, O = 16, Cl = 35·5, Ba = 137).

(iv) Write an equation for the reaction of barium chloride with silver nitrate.

(v) Explain briefly how potassium chromate acts as an indicator in this case.

(vi) How does sodium sulphate solution remove the barium ions ? Suggest why it is necessary to do so.

(b) Describe one test in each case to confirm the presence of (i) the chloride ion in barium chloride, (ii) the nitrate ion in silver nitrate, (iii) the sulphate ion in sodium sulphate.

(67 marks)