LEAVING CERTIFICATE EXAMINATION, 1977

CHEMISTRY—HIGHER LEVEL

THURSDAY, 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, N = 14, O = 16, Na = 23, S = 32, Fe = 56.
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*) Define the electronegativity of an element.

(*b*) What is meant by a metallic bond?

(*c*) Give an example of one molecule in each case, the shape of which can be explained by (i) sp^3, (ii) sp, hybridisation of orbitals.

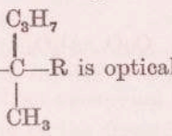
(*d*) State Dalton's law of partial pressures.

(*e*) Complete the equation: $CH_3NH_2 + HCl \rightarrow$

(*f*) Show, in terms of electron transfer, where oxidation occurs during the electrolysis of molten sodium chloride using inert electrodes.

(*g*) Give the equation for a reaction which could be used as a test for the iodide ion in aqueous solution.

(*h*) What does n represent in the general gas equation, PV = nRT?

(*i*) If the compound  is optically active and R represents an alkyl group, write down two alkyl groups that R could *not* be.

(*j*) The elements carbon, phosphorus, sodium and iodine can exist as radioactive isotopes. Mention one specific use for each of any *two* of them.

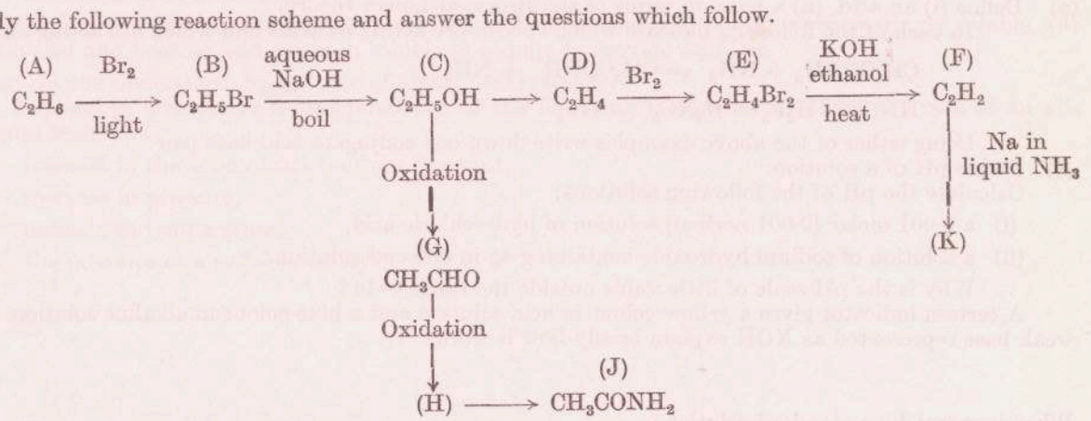
(*k*) Show the formula for the repeating unit in the polystyrene molecule.

(*l*) An insoluble compound is thought to be a carbonate. How would you confirm this?

(*m*) Anhydrous ferric chloride melts at 555K and is soluble in water, ethanol and acetone. Comment briefly on the type of bonding you expect to be present.

(*n*) How many molecules of oxygen are there in 560 cm^3 of oxygen gas at S.T.P.?

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



(i) Name the compounds B, E, F, G and J.

(ii) Name in each case the type of reaction involved in the bromination of compound A to B and of compound D to E.

(iii) Give the name and structural formula for compound H.

(iv) Give the name and structural formula for the compound that C would form if it reacted with the compound H under suitable conditions.

(v) Which one of the reactions shown can be described as "hydrolysis"?

(vi) Give the name and formula of compound K.

(vii) How could F be converted into G?

(viii) Under what conditions is C converted into D?

(ix) Explain, by equations or otherwise, how J could be obtained from H.

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3. Define (i) heat of reaction, (ii) heat of formation, (iii) heat of neutralisation.

Calculate the heat change ($\triangle H$) for the reaction

$$SO_{2(g)} + 2H_2S_{(g)} \rightarrow 3S_{(s)} + 2H_2O_{(l)}$$

from the following data:

$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$ $\quad \triangle H = -297$ kJ mol^{-1}

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

$H_{2(g)} + S_{(s)} \rightarrow H_2S_{(g)}$ $\quad \triangle H = -20$ kJ mol^{-1}

The heats of neutralisation of $HCl_{(aq)}$, $HNO_{3(aq)}$, $H_2S_{(aq)}$ by $KOH_{(aq)}$ are respectively $-57{\cdot}3$, $-57{\cdot}3$ and $-16{\cdot}0$ kJ mol^{-1}. ($_{aq}$ = in dilute aqueous solution.)

Explain why (i) the heats of neutralisation of $HCl_{(aq)}$ and $HNO_{3(aq)}$ are the same, (ii) the heat of neutralisation of $H_2S_{(aq)}$ is different from the other two.

4. Answer this question by referring to the first thirty six elements in the Periodic Table. (Mathematics Tables, p. 44).

(i) State the number of electrons, protons and neutrons in an atom of the isotope $^{26}_{12}Mg$.

(ii) Write the formula for the compound that the element of atomic number 15 would form with hydrogen and indicate, showing outer electrons only, the type of bonding present.

(iii) Write the formula for a hydride in which the bonding is completely different from that present in (ii) and indicate clearly how the binding forces arise.

(iv) Explain, mentioning the factors involved, how you expect the atomic radius to change (*a*) across a typical period (e.g. Na to Ar), (*b*) down a group.

(v) Write the s, p, d configurations for (*a*) the Fe^{2+} ion, (*b*) the Fe^{3+} ion. Which of the two structures do you expect to be the more stable? Give your reason.

(vi) The atomic number of $^{14}_{7}N$ atoms is sometimes changed from 7 to 6 in the atmosphere, without any change in mass number. What do the nitrogen atoms become as a result?

5. Describe briefly how either hydrogen chloride *or* sulphur dioxide could be prepared and collected in the laboratory. Give an equation for the reaction you select.

From the following list:

$$CO_2 \quad P_2O_5 \quad Li_2O \quad NO_2 \quad NO \quad SiO_2 \quad CuO \quad Al_2O_3$$

select (i) a basic oxide which is soluble in water,

(ii) a highly coloured acidic oxide,

(iii) a neutral oxide.

In each case state whether the oxide you have selected reacts with water and if so give an equation for the reaction.

Mention the different type of crystal structure represented by each of the following:

solid CO_2 SiO_2 Li_2O

Mention in *each* case (*a*) the basic particle units present, (*b*) the type of bonding between them, (*c*) the general solubility of this type of crystal.

6. (*a*) Define (i) an acid, (ii) a base, in terms of the Bronsted-Lowry theory.

In each of the following indicate which species are acting as acids and which are acting as bases:

$$CH_3CONH_2 + NH_2^- \rightleftharpoons CH_3CONH^- + NH_3$$

$$HNO_3 + H_2F_2 \rightleftharpoons H_2NO_3^+ + HF_2^-$$

Using either of the above examples write down one conjugate acid-base pair.

(*b*) Define pH of a solution.

Calculate the pH of the following solutions:

(i) a 0·001 molar (0·001 normal) solution of hydrochloric acid,

(ii) a solution of sodium hydroxide containing 4g in 500 cm^3 solution.

Why is the pH scale of little value outside the range 0–14?

A certain indicator gives a yellow colour in acid solution and a blue colour in alkaline solution. If it is a weak base represented as XOH explain briefly how it works.

7. What is meant by a standard solution?

A standard solution of ammonium iron (II) sulphate ($Fe\,SO_4\,(NH_4)_2\,SO_4\,.\,6H_2O$) was prepared by dissolving 11·76 g of the crystals in dilute sulphuric acid and making up the solution to 250 cm^3 with distilled water.

(i) Why was the salt dissolved in dilute sulphuric acid?

(ii) Calculate the molarity (or normality) of the solution.

25cm^3 of this solution was taken and further acidified with dilute sulphuric acid. It required 33·3 cm^3 of a potassium permanganate solution for complete oxidation according to the equation

$$10Fe^{2+} + 2MnO_4^- + 16H^+ \rightarrow 10Fe^{3+} + 2Mn^{2+} + 8H_2O$$

(iii) Why is it necessary to ensure that the solution is strongly acidic?

(iv) Show clearly, using oxidation numbers, where oxidation and reduction occur in this reaction.

(v) Calculate the molarity (or normality) of the potassium permanganate solution.

8. What do you mean by saying that a system has reached a state of equilibrium?
Write the equilibrium constant expression for the reaction,

$$SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$$

When 7·68 g of sulphur dioxide and 4·6 g of nitrogen dioxide were heated together in a closed vessel at a certain high temperature it was found that at equilibrium 4·8 g of sulphur trioxide were present. Calculate the equilibrium constant for the reaction at that temperature.

Then 0·17 moles of nitrogen dioxide were added to this reaction mixture and when equilibrium was re-established it was found that an additional 0·03 moles of sulphur trioxide had been formed. Find (i) the number of moles of each of the four gases in the final equilibrium mixture, (ii) the value of the equilibrium constant.

How do you know that the temperature has not changed when this final equilibrium has been reached?

9. Some phenol was prepared as follows: 30 g of sodium hydroxide was dissolved in the minimum amount of water in a nickel basin. 18 g of sodium benzenesulphonate ($C_6H_5SO_3Na$) were added and the mixture heated gently for two hours to allow the reaction

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$

to take place. The mixture was cooled, dissolved in water and acidified with concentrated hydrochloric acid in a fume-cupboard. The phenol was extracted with ether, dried overnight and the ether was distilled off. The phenol was then distilled at 453–458 K (180–185°C) using an air condenser. 2·35 g of phenol were obtained.

(i) How many moles of sodium benzenesulphonate does 18 g represent?

(ii) Name the compound C_6H_5ONa

(iii) Why do you expect this compound to be soluble in water?

(iv) Write an equation for the action of hydrochloric acid on C_6H_5ONa

(v) Why is it possible to extract the phenol with ether?

(vi) Why is it not advisable to use a water-cooled condenser for the distillation of the phenol?

(vii) What is the percentage yield of phenol?

(viii) Write an equation for the reaction of phenol with bromine water.

(ix) The – OH group in phenol is slightly more acidic than the – OH group in ethanol. Suggest a reason for this.

10 Answer any *two* of the following:

(*a*) Give a brief account of the significance of the four quantum numbers used to characterise electrons in an atom. Explain why an orbital is defined by three quantum numbers but it takes four quantum numbers to define an electron occupying an orbital.

(*b*) Describe how the lowering of the freezing-point of a pure solvent by a dissolved solute can be found experimentally.

When 2·3 g of a certain alcohol were dissolved in 75 g of pure water the freezing-point was lowered by 0·62 K. If the freezing-point constant for water is 1·86 K mol^{-1} kg^{-1} find the relative molecular mass (molecular weight) of the alcohol.

(*c*) Outline 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:

(i) benzene to nitrobenzene,

(ii) aniline to acetanilide,

(iii) benzoic acid to benzamide.

Suggest why (i) acetic acid is soluble in cold water but benzoic acid is only very sparingly soluble, (ii) acetic acid and benzoic acid are both soluble in sodium hydroxide solution.

(*d*) What do you understand by the rate of a chemical reaction?

Explain, in qualitative terms, how each of the following factors would affect the rate of an all-gaseous reaction:

(i) increase in the concentration of one reactant,

(ii) increase in pressure,

(iii) increase in temperature,

(iv) the presence of a suitable catalyst.