2019

CHEMISTRY

(Honours)

Paper : CHE-HC-1026

(Physical Chemistry—I)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following as directed : 1×7=7

(a) From kinetic gas equation, show that PV = constant for an ideal gas at constant temperature.

(b) A gas can be liquefied, when

(i) $T > T_c$; $P = P_c$

(ii) $T < T_c$; $P < P_c$

(iii) $T < T_c$; $P > P_c$

(iv) $T = T_c$; $P < P_c$

(Choose the correct option)

(c) Define vapour pressure of a liquid.

(d) In a cubic crystal, there are ____ C_4 axes of symmetry, ____ C_3 axes of symmetry and six C_2 axes of symmetry.

(Fill in the blanks)

(e) Explain why non-stoichiometric form of NaCl is yellow in colour.

(f) Explain why pH of 1×10^{-8} mol dm^{-3} hydrochloric acid solution is not 8.

(g) An aqueous solution of Na_2CO_3 is basic. Explain.

2. Answer the following questions : 2×4=8

(a) Define mean free path of a gas. How does mean free path of a gas vary with temperature and pressure?

(b) Give a qualitative idea about the structure of water.

(c) State the symmetry elements present in the following molecules :

H_2O; C_6H_6

(Continued)

(d) The pH value of a solution containing equimolar concentrations of a weak acid and its salt is 5·0. Calculate the K_a value of the weak acid.

3. Answer any *three* of the following questions : 5×3=15

(a) Derive the van der Waals' equation for a gas. Explain why van der Waals' equation cannot be considered as a generalized equation of state for real gases.

(b) What is critical state of a gas? Derive the expressions for critical constants in terms of the van der Waals' constants.

(c) Derive the Bragg's equation. In an experiment on a crystal using X-rays of wavelength 10^{-10} m, the value of angle of incidence for the first-order reflection was found to be 30°. Calculate the interplanar distance of the crystal.

(d) For a weak monobasic acid, show that the degree of ionization at a given temperature is inversely proportional to the square root of the initial concentration of the acid. Give the expressions for dissociation constants of carbonic acid.

(Turn Over)

(e) Define solubility product of a sparingly soluble salt solution. Give the conditions for precipitation in terms of solubility product. 50 mL of 0·01 mol dm^{-3} $AgNO_3$ solution is mixed with 50 mL of 0·001 mol dm^{-3} aqueous NaCl solution. Predict whether AgCl will be precipitated or not. Given $K_{sp}(AgCl) = 1·7 \times 10^{-10}$.

4. (a) Answer *either* [(i) and (ii)] *or* [(iii), (iv) and (v)] :

(i) Give the postulates of kinetic molecular model of a gas. On the basis of these postulates, derive the kinetic gas equation. 3+4=7

(ii) Two flasks *A* and *B* have equal volumes. Flask *A* contain H_2 gas at 300 K, while flask *B* contains equal mass of C_2H_6 gas at 900 K. If both the gases behave ideally, answer the following : 3

In which flask the molecules will have higher average speed and how many times than the average speed of the other?

(Continued)

(iii) Derive an expression for root-mean-square speed of gas molecules from the expression for Maxwell distribution of molecular speeds of the gas. 3

(iv) Show that root-mean-square speed of hydrogen gas is four times that of oxygen gas at the same temperature. 3

(v) Derive an expression for reduced equation of state for any substance. State the law of corresponding states. 3+1=4

(b) Answer *either* [(i), (ii) and (iii)] *or* [(iv), (v) and (vi)] :

(i) How does viscosity of gas differ from that of liquid? 2

(ii) Describe a method with theory commonly used for the measurement of viscosity of a liquid. 4

(iii) What are liquid crystals? Give the structural difference between smectic and nematic liquid crystals. Give two applications of liquid crystals. 1+2+1=4

(iv) Define the terms—symmetry element, plane of symmetry and centre of symmetry. 3

(Turn Over)

(v) What are Bravais lattices? How can the following crystal systems be characterized?

Cubic; orthorhombic

Give one example each of these two crystal systems. 4

(vi) What are Schottky and Frenkel defects? Give example of each of these two defects. 3

(c) Answer *either* [(i), (ii) and (iii)] *or* [(iv), (v) and (vi)] :

(i) Define pH of a solution. Give the limitations of pH scale. Calculate pH of a solution obtained by mixing 50 mL 0·1 mol dm^{-3} HCl solution with 50 mL 0·2 mol dm^{-3} NaOH solution at 298 K. 1+1+3=5

(ii) Discuss briefly about the following : 2

Applications of buffers in qualitative analysis of salt sample.

(iii) Obtain an expression for hydrolysis constant for the hydrolysis of CH_3COONH_4 salt. 3

(iv) What are acid-base indicators? Give examples. Discuss briefly the Ostwald's theory of acid-base indicators. 1+1+3=5

(v) State with reasons, what indicators you would choose for the following titrations : 3

NaOH vs. CH_3COOH;

Na_2CO_3 vs. HCl

(vi) Calculate the solubility of $Mg(OH)_2$ in pure water at 298 K. Given K_{sp} for $Mg(OH)_2$ at 298 K is $1{\cdot}20\times10^{-11}$. 2

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