2016

CHEMISTRY

(Major)

Paper : 2.1

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer in brief : 1×7=7

(a) Two gases *A* and *B* have same value of van der Waals' constant *a*. If gas *A* has higher value of van der Waals' constant *b*, then state which of these two gases will be more compressible under identical condition of pressure and temperature.

(b) Of various liquid crystal phases, state which can diffract light and have colours that depend on the temperature.

(c) Applying the principle of equipartition of energy, estimate the value of C_V for helium gas at room temperature.

(d) Write the cell reaction that takes place in the cell

$Pt(s) | H_2(g) | H^+(aq) || Cl^-(aq) | Hg_2Cl_2(s) | Hg(l)$

(e) Molality of a solution of benzoic acid in benzene at the freezing point is $0 \cdot 468$ mol kg^{-1}. What will be the observed molality of the solution at the boiling point?

(f) The molar conductance at infinite dilution of KBr is $1 \cdot 5 \times 10^{-2}$ S m^2 mol^{-1} and the transport number of K^+ is $0 \cdot 48$. What will be the ion conductance of K^+ at infinite dilution?

(g) Consider two liquids *A* and *B* such that *A* has half the surface tension and twice the density of *B*. If liquid *A* rises to a height of $2 \cdot 0$ cm in a capillary tube, what will be the height to which liquid *B* will rise in the same capillary?

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

(a) For a van der Waals' gas, the value of critical pressure is $1 \cdot 01 \times 10^7$ Pa and that of the van der Waals' constant *b* is $5 \cdot 0 \times 10^{-5}$ m^3 mol^{-1}. Calculate its critical temperature.

(b) Define mean free path. How does it vary with temperature in a sample of gas at constant volume?

(c) State the principle of corresponding states.

(d) Water at 25 °C rises through a capillary of radius 0·20 mm. What is the surface tension of water at this temperature?

3. (a) Answer *either (i) or (ii)* :

(i) Discuss about the capillary rise method for determination of surface tension of liquid. 5

Or

(ii) Define refractive index. Density of ethanol is $0 \cdot 78\ g\ cm^{-3}$. If the refractive index of ethanol is 1·348, calculate the values of specific and molar refractions. 1+2+2=5

(b) Answer *either (i) or (ii)* :

(i) Define buffer solution. Deduce the Henderson-Hasselbalch equation for both acidic and basic buffers. 1+2+2=5

Or

(ii) Derive the Stokes-Einstein relation. The molar ionic conductance at infinite dilution of silver ions is

$61 \cdot 92 \times 10^{-4}$ S m^2 mol^{-1} at 25 °C.

Calculate the ionic mobility of silver ions at 25 °C at infinite dilution. 3+2=5

(c) Answer *either (i) and (ii) or (iii) and (iv)* :

(i) Calculate the equilibrium constant of the following reaction at 298 K : 3

$$FeSO_4 (aq) + Cd (s) \rightleftharpoons Fe (s) + CdCl_2 (aq)$$

Given,

$$E^\circ_{Cd^{2+}/Cd} = -0 \cdot 488 \text{ V}$$

$$E^\circ_{Fe^{2+}/Fe} = -0 \cdot 469 \text{ V}$$

(ii) Write the reactions taking place at the anode and the cathode of a Leclanché or dry cell. 2

Or

(iii) What is fuel cell? What are the advantages of a fuel cell? 1+1=2

(iv) A zinc rod is placed in 0·1 *M* solution of zinc sulphate at 25 °C. Assuming that the salt is dissociated to the extent of 95 percent at this dilution, calculate the potential of the electrode at this temperature.

Given, $E^\circ_{Zn^{2+}/Zn} = -0 \cdot 76 \text{ V}$ 3

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

(i) Using the kinetic molecular theory of gas, deduce an expression for the thermal conductivity of a gas. 4

(ii) Deduce an expression for the energy of 1 mole CO_2 (g) at T K by using the principle of equipartition of energy. 4

(iii) Show that the critical compressibility factor, Z_C, of a van der Waals' gas is 0·375. 2

Or

(iv) Deduce an expression for root-mean-square velocity by using the kinetic molecular theory of gas. 4

(v) Define collision cross-section. 2

(vi) For O_2 (g) molecules, the root-mean-square velocity at T_1, the average velocity at T_2 and the most probable velocity at T_3 are all equal to $1 \cdot 5 \times 10^3$ ms^{-1}. Calculate T_1, T_2 and T_3. 4

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

(i) Using the concept of chemical potential, show that relative lowering of vapour pressure of a dilute solution containing a non-volatile, non-electrolyte solute is equal to the mole fraction of the solute. 5

(ii) 2 g of benzoic acid dissolved in 25 g of benzene shows a depression in freezing point of 1·62 K. What is the percentage association of benzoic acid if it forms a dimer in solution? Given K_f for benzene is 4·9 K kg mol^{-1}. 5

Or

(iii) Using the concept of chemical potential, deduce the van't Hoff equation for osmotic pressure of a dilute solution. 5

(iv) The complex compound $K_4[Fe(CN)_6]$ is 45% dissociated in $M/10$ aqueous solution of the complex at 27 °C. Calculate the osmotic pressure of the solution. 3

(v) Give the molecular interpretation of lowering of vapour pressure of a solvent in presence of a solute. 2

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

(i) Explain the Hittorf's method for determination of transport number of ions. 3

(ii) Comment on the exceptionally high ionic mobility of H^+ ion in hydroxylic solvents. 2

(iii) A solution of 0·1 *M* LiCl with of $1 \cdot 06 \times 10^{-2}$ S cm^{-1} is placed in a moving boundary cell having a cross-sectional area of 1·17 cm^2. It was electrolyzed for 131 minutes with a constant current of 9·42 mA. The Li^+ ion was observed to move a distance of 2·08 cm. Calculate the transport number and mobility of Li^+ ion in this solution. 5

Or

(iv) The standard potentials of the Cu^{2+}/Cu and Cu^+/Cu couples are +0·340 V and +0·522 V respectively. Evaluate $E^\circ_{Cu^{2+}/Cu}$. 3

(v) What is the pH of 0·1 *M* CH_3COOH solution if dissociation constant of CH_3COOH is $1·6 \times 10^{-5}$? 2

(vi) Discuss the construction of a calomel electrode. Explain the reaction taking place in the electrode. 3+2=5

★★★