

2016

CHEMISTRY

(Major)

Paper : 2.1

Full Marks : 60

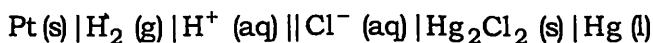
Time : 3 hours

*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



(e) Molality of a solution of benzoic acid in benzene at the freezing point is $0.468 \text{ mol kg}^{-1}$. What will be the observed molality of the solution at the boiling point?

(f) The molar conductance at infinite dilution of KBr is $1.5 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$ and the transport number of K^+ is 0.48. 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 2.0 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 $1.01 \times 10^7 \text{ Pa}$ and that of the van der Waals' constant b is $5.0 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. 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 0.78 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

(4)

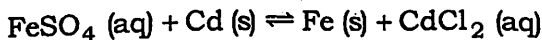
$61.92 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ at 25°C .

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



Given,

$$E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.488 \text{ V}$$

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.469 \text{ V}$$

(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, $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$

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 $1.5 \times 10^3 \text{ ms}^{-1}$. 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.

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(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 $4.9 \text{ K kg mol}^{-1}$.

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 $1.06 \times 10^{-2} \text{ S cm}^{-1}$ 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 1.6×10^{-5} ? 2

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