2014

CHEMISTRY

(Major)

Paper : 2.1

Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions in brief : 1×7=7

(a) Find the number of vibrational degree of freedom of CO_2.

(b) State why the molar enthalpy of vaporization of a substance is larger than its molar enthalpy of fusion (at constant pressure).

(c) Which liquid crystal is generally used in applications that involve colour change with change in temperature?

(d) The value of the van der Waals' constant b for $CH_4(g)$ is $42 \cdot 8 \times 10^{-6}$ m^3 mol^{-1}. Calculate its critical volume.

(e) At infinite dilution, the molar ionic conductances of Ba^{2+} and NO_3^- ions are $127 \cdot 3 \times 10^{-4}$ S m^2 mol^{-1} and $71 \cdot 44 \times 10^{-4}$ S m^2 mol^{-1} respectively. Calculate molar conductance of $Ba(NO_3)_2$ at infinite dilution.

(f) Write cell reaction for the cell

$$Ag(s) | AgCl(s) | Cl^-(aq) \,||\, Ag^+(aq) | Ag(s)$$

(g) The molar enthalpy of vaporization of $H_2O(l)$ at 100 °C is $40 \cdot 67$ kJ mol^{-1}. What will be the enthalpy change when 1 mol steam condenses into liquid water at 100 °C?

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

(a) Find the value of the compressibility factor at the critical point for 1 mol of gas.

(b) Out of diethylether, ethanol and water, which one will have the highest vapour pressure at room temperature? Explain with justification.

(c) The ion conductances at infinite dilution of H^+ and CH_3COO^- ions are $349 \cdot 8 \times 10^{-4}$ S m^2 mol^{-1} and $40 \cdot 9 \times 10^{-4}$ S m^2 mol^{-1} respectively. Calculate the transport number of H^+ at infinite dilution.

(d) Write the reaction which takes place in each of the following half-cells :

(i) $Ca^{2+}(aq) | CaC_2O_4(s) | PbC_2O_4(s) | Pb(s)$

(ii) $H^+(aq), MnO_4^-(aq) | Mn^{2+}(aq) | Pt(s)$

3. (a) Using the *p-V* isotherms of CO_2, explain what you mean by critical point. The values of the van der Waals' constants *a* and *b* for $NH_3(g)$ are $0 \cdot 4225$ Pa m^6 mol^{-2} and $37 \cdot 1 \times 10^{-6}$ m^3 mol^{-1} respectively. Show whether $NH_3(g)$ can be liquefied at 298 K or not. 2+3=5

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

(i) Define surface tension of liquid. Discuss the stalagmometer method for determination of surface tension. 1+4=5

(ii) Explain why density of ice is less than that of water. 3

(iii) Which of octane and decane has higher viscosity at the same temperature? Explain with reason. 2

(c) Deduce the relationship between ion mobility and molar conductivity of an electrolyte in solution. 5

Or

Deduce the Nernst equation for e.m.f. of galvanic cell. Write Nernst equation for the potentials of Zn-electrode and Cu-electrode of the Daniell cell. Hence find an expression for the e.m.f. of the Daniell cell. 2+1+2=5

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

(i) Explain how the molar heat capacities at constant volume and at constant pressure can be calculated using the principle of equipartition of energy. 5

(ii) Calculate the most probable speed of gas molecules from Maxwell's speed distribution formula. 3

(iii) Calculate the mean free path of O_2 at $1 \cdot 01325 \times 10^5$ Pa and 300 K, given that its collision diameter is $2 \cdot 4 \times 10^{-10}$ m. 2

(iv) Using the postulates of the kinetic theory, deduce an expression for the pressure of the gas. 5

(v) Use the principle of equipartition of energy to deduce an expression for the molar heat capacity at constant pressure of CO(g), assuming vibration to be inactive. 3

(vi) The value of the van der Waals' constant a for H_2(g) is negligible. On the basis of this, explain what nature of Z (compressibility factor) versus p (pressure) plot you may expect at room temperature. 2

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

(i) Deduce van't Hoff's equation for osmotic pressure of a dilute solution containing non-volatile, non-electrolyte solute using the concept of chemical potential. 5

(ii) Calculate the mol fraction of O_2 in water at 298 K if the partial pressure of O_2 over the solution is $1 \cdot 0 \times 10^5$ Pa. The Henry's law constant for oxygen is $4 \cdot 40 \times 10^9$ Pa. 2

(iii) Write the characteristics of ideal solution. Explain whether an aqueous solution of NaCl can be regarded as ideal or not. 3

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

(v) The vapour pressure of a solution containing 0·012 kg of CH_3COOH in 0·100 kg water at 300 K is $3 \cdot 5 \times 10^3$ Pa. Calculate van't Hoff factor if the vapour pressure of water at the same temperature is $3 \cdot 7 \times 10^3$ Pa. 3

(vi) Explain why boiling point of solution is higher than that of the pure solvent at the same pressure. 2

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

(i) Define ion mobility. Explain why the mobility of H^+ is the highest in aqueous medium. 1+2=3

(ii) Discuss calomel electrode mentioning construction, reaction and the Nernst equation. 4

(iii) Calculate the mean ionic activity coefficient in case of 0·2 m $BaCl_2$ aqueous solution at 25 °C. 3

(iv) Write a short note on fuel cell. 4

(v) Deduce Henderson-Hasselbalch equation for buffer solution. 3

(vi) Consider a solution of an electrolyte M_xA_y with concentration m mol kg^{-1}. Deduce an expression relating activity, mean ionic activity coefficient and molality of the solution. 3

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