2017

CHEMISTRY

(Major)

Paper : 2.1

(Physical Chemistry)

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) Find an expression for the kinetic energy of *n*-mole gas from kinetic theory equation.

   (b) State for which of the following gases the value of the compressibility factor is always greater than 1.

   (i) H_2

   (ii) N_2

   (iii) CO_2

   (iv) CH_4

(c) Find the SI unit of the van der Waals constant *a*.

(d) State when the surface tension of a liquid vanishes.

(e) The critical temperatures of NH_3 and CO_2 are 405·5 K and 304·10 K respectively. State which of these two gases will liquefy first when cooling is started from 500 K to lower temperature.

(f) Out of aluminium and silver containers, state which one will be more suitable to store 1 *M* HCl, given that

$$E^{\circ}_{Al^{3+}|Al} = -1\cdot66\text{ V and } E^{\circ}_{Ag^{+}|Ag} = 0\cdot80\text{ V}$$

(g) Find the correct answer :

The transference number of an ion

(i) is always positive

(ii) is always negative

(iii) can be positive as well as negative

(iv) is always zero

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

(a) Deduce the expression for the most probable speed from Maxwell's expression for distribution of molecular speeds.

(b) Discuss the effect of temperature on viscosity of a liquid.

(c) The molar conductances at infinite dilution of NaOH, NaCl and $BaCl_2$ are $2 \cdot 48 \times 10^{-2}$, $1 \cdot 27 \times 10^{-2}$ and $2 \cdot 8 \times 10^{-2}$ S m^2 mol^{-1} respectively. Find the molar conductance at infinite dilution of $Ba(OH)_2$.

(d) The dissociation constant of acetic acid at a certain temperature is $1 \cdot 6 \times 10^{-5}$. Find pK_a value.

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

(a) Deduce the expressions for critical constants P_c, T_c and V_c in terms of the van der Waals constants. Can a van der Waals gas be liquified for which the value of van der Waals constant a is zero? 4+1=5

(b) Define vapour pressure of a liquid. Explain a method of measurement of vapour pressure of a liquid. 1+4=5

(c) (i) What is meant by the laminar flow of liquid in a tube? 1

(ii) Explain the Ostwald's viscometer method of determination of viscosity of a liquid. 4

(d) Define transport number of ions. In a Hittorf cell, a solution of HCl is electrolyzed using Pt-electrodes. After electrolysis, the mass of HCl in the cathode compartment is found to be 0·14 g, while the initial mass of HCl in the same compartment before electrolysis was 0·155 g. During electrolysis, the mass of Ag deposited in the coulometer, connected in the same circuit is found to be 0·252 g. Find transport numbers of both the ions. 1+4=5

(e) Discuss about the Debye-Hückel theory of strong electrolyte that leads to the Debye-Hückel-Onsager equation. 5

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

(i) State and explain the principle of equipartition of energy. 2

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

(iii) The specific heat of a gas at constant volume is $0 \cdot 3138\ JK^{-1}\ g^{-1}$ and that at constant pressure is $0 \cdot 523\ JK^{-1} g^{-1}$. Calculate molecular mass of the gas. Determine the number of atoms in its molecule. 2+1=3

(iv) By considering pressure and volume correction terms, derive the van der Waals equation of state for *n* moles of real gas. 5

(v) Discuss the effect of temperature on the distribution of molecular speeds of a gas. Give graphical representations to show this effect. 3

(vi) Calculate the diameter of an oxygen molecule at 298·15 K at the pressure of 101·325 kPa. Given that van der Waals constant $b = 3 \cdot 183 \times 10^{-2}\ dm^3\ mol^{-1}$ for the gas. 2

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

(i) Explain how the van't Hoff factor will vary in case of NaCl solution in water. 2

(ii) Using the concept of chemical potential, show that the elevation of boiling point of a binary dilute solution containing non-volatile, non-electrolyte solute is proportional to the molal concentration of the solution. 5

(iii) A solution containing 3·975 g of sulphur in 100 g of CS_2 boils at 319·67 K. The boiling point of pure CS_2 is 319·30 K and $\Delta H_{vap} = 27 \cdot 78$ kJ mol^{-1}. Calculate the molar mass of sulphur in carbon disulphide. 3

(iv) State Raoult's law of ideal solutions. Give its mathematical form explaining the terms involved in it. 2

(v) 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 mole fraction of the solute. 5

(vi) The vapour pressures of pure liquids *A* and *B* at 300 K are 200 mm of Hg and 500 mm of Hg respectively. Calculate the mole fraction in the vapour and liquid phases of a solution of *A* and *B* when the equilibrium total vapour pressure of the binary solution is 350 mm of Hg at the same temperature. Assume that the solution and its vapour behave ideally. 3

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

(i) Define ion mobility. Deduce the relationship between ion mobility and molar conductance. 6

(ii) For the cell reaction

$$Zn\,(s) + Fe^{2+}\,(aq) \rightleftharpoons Zn^{2+}\,(aq) + Fe\,(s)$$

calculate the relative molar concentration of Zn^{2+} and Fe^{2+} ions at which the overall cell e.m.f. becomes zero.

Given $E^{\circ}_{Fe^{2+}, Fe} = -0 \cdot 440\ V$ and

$E^{\circ}_{Zn^{2+}, Zn} = -0 \cdot 760\ V$ 4

(iii) Deduce an expression for the e.m.f. of the concentration cell with transference. 6

(iv) The e.m.f. of cell with transference

$$Ag \mid AgCl\,(s) \mid HCl\,(a^{+} = 0 \cdot 1751)$$
$$\parallel HCl\,(a^{+} = 0 \cdot 09048) \mid AgCl\,(s) \mid Ag$$

at 298 K is 0·02802 volt. The corresponding cell without transference has an e.m.f. of 0·1696 volt. Calculate the transference number of H^{+} ion and the value of the liquid junction potential. 4

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