2019

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 the following as directed : 1×7=7

(a) Name two gases for which the compressibility factor be never less than 1 at any temperature and pressure.

(b) State the principle of equipartition of energy.

(c) Define coefficient of viscosity.

(d) According to _____ law, relative lowering of vapour pressure is equal to mole fraction of the solute in solution.
(Fill in the blank)

(e) What is meant by abnormal colligative properties?

(f) At 298 K, the conductivity of 0·1 *M* KCl solution is $1{\cdot}286 \times 10^{-3}$ S cm^{-1} and its resistance is 337·6 ohm, when conductivity is measured with a cell. Calculate the cell constant.

(g) Define buffer action.

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

(a) Write the causes of deviations from ideal behaviour by the real gases.

(b) Define vapour pressure of a liquid. What are the highest and lowest limits of the variation of vapour pressure with temperature?

(c) State Henry's law. Give one limitation of the law.

(d) What is corrosion? Give two preventive measures of corrosion of metals.

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

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

(b) Give a general discussion on the structure of liquid water and ice.

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

(d) What is battery? What are primary and secondary batteries? Give one example of each.

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

(i) Derive van der Waals' equation of state for *n* moles of a gas. Explain how van der Waals' equation explains the behaviour of real gases. 4+2=6

(ii) The van der Waals' constants for HCl(g) are $a = 371{\cdot}843$ kPa $dm^6 mol^{-2}$ and $b = 4{\cdot}08 \times 10^{-2}$ dm^3 mol^{-1}. Find the critical constants for HCl(g). 4

(iii) Explain what is meant by distribution of molecular speed. Deduce the expression for the root-mean-square speed of gas molecules from Maxwell distribution expression. 2+3=5

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

(v) For a gas, the van der Waals' constants are $a = 0$ and $b = 0$. Explain whether the gas can be liquidified or not. 1

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

(i) Write the virial equation of state of 1 mole of a gas. Explain the terms involved in it. 2

(ii) Deduce the expressions for critical constants P_c, V_c and T_c in terms of the van der Waals' constants. 4

(iii) Using principle of equipartition of energy, calculate the energy of 1 mol CO_2(g) at 298 K. 4

(iv) On the basis of kinetic theory, obtain an expression for coefficient of viscosity of a gas. 5

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

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

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

(ii) A moving boundary experiment was carried out with 20 mol m^{-3} NaCl solution in water. In the experiment,

a current of $1{\cdot}60\times10^{-3}$ A moved the boundary through a distance 0·06 m in 34 minutes and 30 seconds. Calculate the transport number of Na^+ ion, if the radius of the tube used in the experiment is $1{\cdot}88\times10^{-3}$ m. 3

(iii) Explain the terms 'asymmetric effect' and 'electrophoretic effect' of the ions of strong electrolyte in solution. 4

(iv) Write Nernst equations for the potentials of Zn-electrode and Cu-electrode in the Daniell cell. Hence find an expression for the e.m.f. of the Daniell cell at any given temperature. 2+2=4

(v) For the reaction $Fe^{3+} + 3e^- \rightleftharpoons Fe$, standard electrode potential is –0·036 V and the standard electrode potential for the reaction $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ is 0·771 V.

Calculate the standard electrode potential for the reaction $Fe^{2+} + 2e^- \rightleftharpoons Fe$. Predict whether the reaction $Fe + 2Fe^{3+} \rightleftharpoons 3Fe^{2+}$ is spontaneous or not. 4+2=6

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