WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 3rd Semester Examination, 2019

CEMACOR05T-CHEMISTRY (CC5)

PHYSICAL CHEMISTRY-II

Time Allotted: 2 Hours Full Marks: 40

The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

Answer any *three* questions taking *one* from each unit

UNIT-I

1. (a) Define flux. How does the flux depend on the spatial gradient of the corresponding property in transport phenomena? Is there any limitation of such relation? 3

(b) Molecular explanation for dependence of viscosity coefficient on the temperature for gases is different to that for liquids. Explain. 2

(c) Define ionic mobility and ion's molar conductivity. Find the general relation between them. 1+3

(d) Calculate the terminal speed of fall in water at 25°C of a spherical steel ball of diameter 1.00 mm and density 7.8 g cm^{-3}. [Given: Viscosity coefficient of water and its density at 25°C are 0.89 cP and 1 g cm^{-3} respectively] 3

2. (a) The simple kinetic theory of gas predicts that the viscosity of a gas should be independent of pressure. Rationalize this prediction. Do you expect this prediction to hold when the pressure is very low or very large? 3

(b) The ratio of the slopes of the linear portions in the plot of $-\ln f_{\pm}$ versus $c^{1/2}$ for $BaCl_2$(aq) and KCl (aq) at 30°C is approximately 7:2. Justify or contradict. 3
[c = molar concentration, $f_{\pm}$ = mean ionic activity coefficient].

(c) The molar conductance of a solution of calcium phosphate is denoted as λ_m. Express the equivalent conductance of the solution in terms of λ_m. 2

(d) Sketch schematically the conductometric titration curves of conductance versus volume of titrant for (i) NH_4Cl (aq) versus NaOH (aq), (ii) oxalic acid (aq) versus NH_4OH (aq). 2+2

UNIT-II

3. (a) Show that $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}}$ (μ is chemical potential, A is Helmholtz free energy). 3

(b) How does the chemical potential of an ideal gas change when the standard pressure is chosen to be 2 bar instead of 1 bar? 2

(c) Find an expression for fugacity of a gas obeying the equation of state $p(V_m - b) = RT$, where b is constant and V_m is molar volume. Using your result show that the behavior of the gas approaches ideality in the limit of low pressure or high temperature. 3+1

(d) $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3(g) - 195\ \text{kJ mol}^{-1}$ 3+1

Graphically show the variation of equilibrium constant (K) with temperature for the above reaction using van't Hoff reaction isotherm. Mention the underlying assumptions, if any. Verify whether your graph is in accord with the Le Chatelier's principle.

(e) The relation between K_p and K_c is given as $K_p = K_c(RT)^{\Delta n}$. 2+1

For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the value of Δn is = 1. Hence the unit of K_p/K_c is equal to the unit of RT. Justify or contradict. What do you mean by $P°$?

4. (a) The extent of reaction at equilibrium (ξ_e) increases with increase in pressure (P) for the association reaction of potassium atoms in the vapour phase to form dimers as 3

$2K(g) \rightleftharpoons K_2(g)$. Derive the quantitative relation between ξ_e and P and hence justify the above statement.

(b) Given that the standard enthalpy change, $\Delta_r H^\circ$, has an average value of $-69.8\ \text{kJmol}^{-1}$ over the temperature range 500 K to 700 K for the reaction described as: 4

$PCl_3(g) + Cl_2\,(g) \rightleftharpoons PCl_5\,(g)$.

Find K_p at 700 K, given that $K_p = 0.0408$ at 500 K.

(c) For a binary open system at constant temperature and pressure chemical potential of a component cannot change independently. Justify. 3

(d) Thermodynamic entropy of mixing of water and diethyl-amine at constant T and P is negative. Explain. 3

(e) The change of Gibbs energy per mole of reaction, $\Delta_r G$ at 960 K for the reaction described as, 3

$2SO_2(g)(1.0\times10^{-3}\ \text{bar}) + O_2(g)(0.20\ \text{bar}) \rightleftharpoons 2SO_3(g)(1.0\times10^{-4}\ \text{bar})$ is $-13.0\ \text{kJ mol}^{-1}$. Find the value of equilibrium constant.

UNIT-III

5. (a) What is a black-body? Show that the Planck's distribution law for black-body radiation reduces to the classical Rayleigh-Jeans law in the limit of long wavelength. 3

(b) Explain why the first derivative $\frac{d\psi(x)}{dx}$ of the wavefunction $\psi(x)$ has to be continuous within the concerned interval in order for $\psi(x)$ to be a well-behaved function. 2

(c) Verify whether the operators $\hat{x}$ and $\hat{p}_x$ can have simultaneous eigenfunctions. Comment on the significance of your result. 3+1

(d) The minimum possible energy of a particle in a one-dimensional box problem is not zero. This result is in accord with the Heisenberg uncertainty principle and the de Bröglie hypothesis. Justify or contradict. 3

6. (a) Show that the members of the set of the functions $\phi_n(\theta) = e^{in\phi}, 0 \le \theta \le 2\pi$, are orthogonal if n is an integer. 3

(b) The third-lowest energy level of a free particle in a cube is threefold degenerate. Justify/Criticize. 3

(c) $\psi(x) = Ae^{ikx} + Be^{-ikx}$ is an eigenfunction of the operator d^2/dx^2. Justify/Criticise. [k is constant] 2

(d) Find the normalization constant of the function, $f = a(a-x)$ over the interval $0 \le x \le a$. Why an acceptable wavefunction is to normalizable? 4

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