WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 3rd Semester Examination, 2022-23

CEMACOR05T-CHEMISTRY (CC5)

Time Allotted: 2 Hours

Full Marks: 40

The figures in the margin indicate full marks.
Candidates are required to answer in their own words and adhere to the word limits as far as practicable.
All symbols carry their usual significance unless specified otherwise.

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

UNIT-I

1. (a) Define flux. What do you mean by phenomenological constant in this context? 1+1

   (b) A liquid is flowing at a rate of 1.0 $cm^3\ min^{-1}$ through a capillary of length l and radius r under a pressure p. Calculate the rate of flow of the liquid through a capillary of length $4l$ and radius $2r$ under a pressure $p/2$ at the same temperature. Argue if the formula applied in this problem is equally applicable when the capillary tube is replaced with an ordinary water supply tube. 2+1

   (c) In a solution of $\sim 0.8\ N\ CdI_2$ the cationic transport number is found to be negative. Account for the observation. 2

   (d) Qualitatively draw the conductometric titration curves for titration of (i) sulfuric acid with a strong monoacidic base, and (ii) oxalic acid with a strong monoacidic base. Do you expect any difference in the two titration curves? Explain your answer. 1+1+2

   (e) Find the SI unit of ionic mobility. 1

2. (a) (i) In the determination of viscosity coefficient of a liquid using Ostwald viscometer the liquid is made to pass through a capillary tube. Justify why it is necessary to use a capillary tube. 2+1

   (ii) Deduce the SI unit of viscosity coefficient from Newton's law, and state whether it is an extensive or intensive property.

   (b) Measurement of conductance of electrolyte solution requires the use of alternating current. Comment. 2

   (c) Qualitatively draw and explain the conductometric titration curve in aqueous medium when a KCl solution is titrated with $AgNO_3$ solution. What changes do you expect if $AgNO_3$ is replaced with $NaNO_3$? 2+1

   (d) The specific conductance of a 0.1 M NaOH solution is measured to be 0.0224 $S\ cm^{-1}$. The specific conductance is found to be lowered by four times on addition of an equal volume of 0.1 M HCl solution. Find the equivalent conductance of the salt produced in the reaction. 2

(e) Suppose you need to determine the cell constant in a conductometric experiment where the specific conductance values at various concentrations are given. Which one of the following reagents would you use for the purpose? Explain your answer. 2

(i) Acetic acid, (ii) Potassium chloride, (iii) Sodium thiosulfate.

UNIT-II

3. (a) What do you understand by the chemical potential of a substance? Does it depend on the choice of the standard state? Explain. 1+2

(b) The chemical potentials of the components in a binary mixture cannot vary independently at a given temperature and pressure. Justify or criticize. 2

(c) For the equilibrium $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$, $K_p = 8\times10^{-9}$ at 127°C. 3

Calculate the degree of dissociation of phosgene, and $\Delta H^0_{\text{reaction}}$.

Given: total pressure is 2.0 atm, and $\Delta S^0_{400K} = 30.0$ cal mol^{-1}K^{-1}.

(d) For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the equilibrium constant K_p remains unchanged if the standard pressure is changed from 1.0 bar to 2.0 bar. Justify or criticize. 2

(e) Plot the variation of $\log_{10} K$ with $1/T$ in accordance with the van't Hoff equation and indicate the slope of the plot (K is equilibrium constant at temperature T) for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $\Delta H = 177.5$ kJ 1+1+1

Clearly mention the assumption(s), if any, in your answer. Argue if your result is consistent with the Le Chatelier's principle.

(f) Prove the following relationship for a chemical reaction at equilibrium (ξ is the extent of reaction) 3

$$\left(\frac{\partial \xi}{\partial T}\right)_p = \frac{\Delta H}{TG^{(2)}}, \text{ where } G^{(2)} = \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,\,p}$$

4. (a) Explain how the standard state of carbon is different from that of iron. 2

(b) Show that the molar entropy of the i^{th} component $(S_{i,\,m})$ in an open system can be given as $S_{i,\,m} = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\,N}$. 2

(c) The entropy function is a direct consequence of the second law of thermodynamics, yet the auxiliary function G was derived. Justify why it was necessary. 2

(d) For the equilibrium $\nu_A A \rightleftharpoons \nu_B B$ the rates of the forward and backward reactions are given as $r_f = k_f[A]^\alpha$ and $r_b = k_b[B]^\beta$, respectively. Here α and β are the orders of the respective reactions. At equilibrium $r_f = r_b$, and hence the equilibrium constant is 2

$$K = k_f/k_b = [B]^\beta/[A]^\alpha.$$

As a result, K has a unit in terms of concentration if $\alpha \neq \beta$. Explicitly justify or criticize the statement.

(e) Define (i) extent of reaction, (ii) affinity of reaction, and show (with appropriate explanation) the schematic plot of variation of G, and affinity of a reaction with the extent of reaction. 1+1+3

(f) ΔH^0 and ΔG^0 for the gas phase reaction $Br_2 + Cl_2 \rightleftharpoons 2BrCl$ are $320\ \text{cal mol}^{-1}$ and $-1450\ \text{cal mol}^{-1}$, respectively at $25\,°C$. Assuming $\Delta C_p^0 = 0$ find K_p at 500 °C. 3

UNIT-III

5. (a) Verify whether the squaring operator, $(\ )^2$ is linear or not. 2

(b) Find the value of the commutator $[\hat{x}, \hat{p}_x]$. 2

(c) Calculate the de Broglie wavelength of an electron travelling at $3\times10^6\ \text{ms}^{-1}$. 3

(d) What is the zero-point energy of a particle executing simple harmonic oscillations? Calculate its value of a harmonic oscillator consisting of a particle of mass 5.16×10^{-26} kg and force constant 285 N/m. 3

(e) The kinetic energy of a particle constrained to move in a cubical box of edge-length $= a$ is found to be $38h^2/8ma^2$. How many states and levels does this energy correspond to? 2

6. (a) Sketch the energy distribution curves of the radiation emitted from a black body at two different temperatures and point out two characteristic features of the energy distribution. 3

(b) Define a Hermitian operator. Confirm whether the operator $\frac{h}{2\pi i}\frac{d}{dx}$ is Hermitian or not. 1+2

(c) "The de Broglie wavelength of the electron moving in the first orbit of the hydrogen atom (Bohr model) is equal to the circumference of the orbit". Justify. 2

(d) Find the expectation value of p_x^2 for a particle in one-dimensional box in the state with $n = 1$. 4

Given: $\psi_n = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$, where a is the length of the box.

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