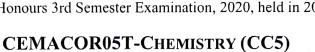


WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 3rd Semester Examination, 2020, held in 2021



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) What is a Newtonian fluid? Polymer solutions are often non-Newtonian. — Explain. 2 (b) Define ionic mobility. Does it depend on concentration? Give reasons in support of 1+1+2your answer. How is it related with conductivity of solution? (c) What is viscosity activation energy for laminar flow of a liquid? How is it related to 1+2the viscosity coefficient of the liquid? (d) The equivalent conductances at infinite dilution (Λ_0) of KNO₃ and KCl solutions are 1+2144.96 and 149.86 ohm⁻¹ cm² equiv⁻¹ at 25°C respectively. Calculate the quantity [$\Lambda_0 \, (NaCl) - \, \Lambda_0 \, (NaNO_3)].$ State the law used. 2. (a) Establish an expression for the ratio of equivalent conductance and molar conductance 3 of a given electrolytic solution. (b) The increase in equivalent conductance of a strong electrolyte with dilution is due to 2 increase in velocity of the ions in the solution. Comment on the statement. (c) At 25°C, the equivalent conductance of a 0.02 M AgNO₃ solution is 128.7 ohm⁻¹ cm² 3 equiv⁻¹, while the transport number of Ag⁺ is 0.477. Calculate (i) the ionic mobility of Ag+ in the solution and (ii) velocity of Ag+ if 6.0 volts are applied across the electrodes 4.0 cm apart. (d) Discuss the effect of temperature on the viscosity of a liquid. How does it differ from 2+2that of a gas?

UNIT-II

3. (a) If volume and density of a solution containing n_1 moles of solvent of molecular weight M_1 and 1 mole of solute of molecular weight M_2 , at a certain temperature and pressure are V litres and ρ g cm⁻³ respectively then show that

$$\overline{V}_1 = \frac{M_1}{1000 \left[\rho + V\left(\frac{d\rho}{dV}\right)\right]}$$
 (\overline{V}_1 = partial molar volume of the solvent)

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(b) Show that in a mixture of ideal gases $\left(\frac{\partial \mu_i}{\partial P}\right)_{T_{+}n_{+}} = \frac{RT}{P_i}$,

2

where the terms have their usual significances.

(c) The relation $K_P = K_C(RT)$ for the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ implies that (K_P/K_C) has the dimension of energy. — Criticize.

3

(d) Show that at constant temperature and pressure $\sum n_i d\overline{Y}_i = 0$, where \overline{Y}_i is any partial molar quantity and n_i is its mole number.

4

(e) At 25°C, the standard free energy of formation (ΔG_f^0) of gaseous C₂H₄ and C₂H₂ are 68.1 and 209.2 kJ/mol respectively. Calculate K_n at 25°C for the reaction:

3

 $C_2H_4(g) \rightleftharpoons C_2H_2(g) + H_2(g)$

4. (a) What is the degree of advancement of a reaction? Derive an expression to show its variation with temperature at a given pressure.

2+3

(b) Define fugacity coefficient of a gas. Under what condition(s) fugacity of a gas is greater than its pressure?

1+2

(c) For a gaseous reaction, $A(g) \rightarrow B(g)$ if the standard reaction Gibbs energy, $\Delta_r G^0$, is greater than 1, then reactant A(g) is favoured in the equilibrium. — Justify/ criticise.

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(d) Calculate the change in chemical potential of a gas obeying the equation of state $P(\overline{V} - b) = RT$ at 300 K due to isothermal compression from a pressure of 2 to 5 atm. Given: b = 0.043 L/mol.

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(e) Calculate the entropy of mixing when 3 mol of hydrogen is mixed with 1 mol of nitrogen. Assume ideal behaviour of the gases.

2

UNIT-III

5. (a) The Schrödinger equation for a particle of mass m free to move parallel to the x-axis with zero potential energy is $-\frac{h^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$

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The solution of this equation has the form $\psi = Ae^{ikx} + Be^{-ikx}$ (A, B and k are constants). Using the solution find E.

3

(b) Show that two eigenfunctions belonging to different eigenvalues of an Hermitian operator are orthogonal.

(c) State and explain Stefan-Boltzmann law with the help of a schematic diagram.

3

(d) The work function for metallic caesium is 2.14 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength, 300 nm.

3

[Given: $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$]

3

6. (a) If Ψ_1 and Ψ_2 are two degenerate states with an eigenvalue a_1 for a linear operator then any linear combination of Ψ_1 and Ψ_2 is also an eigenfunction of the operator with the eigenvalue a_1 . — Justify.

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- (b) If $\hat{D} = \frac{d}{dx}$, then find $(\hat{D} + \hat{x})(\hat{D} \hat{x})$.
- (c) Find the zero-point energy of a particle of mass 1×10^{-28} kg confined in a rectangular box of sides $L_x = L$ and $L_y = 2L$, where L is 10 nm.
- (d) For a free particle in a one-dimensional box with impenetrable walls when potential energy is zero inside the box, find the probability of finding the particle in the central third of the box (from a/3 to 2a/3, a = dimension of the box) in its ground state.
 - N.B.: Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.



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