

**PG EVEN SEMESTER EXAMINATION, 2023**

**CHEMISTRY**

2nd Semester

Course No. : CHM - 553

**( Physical Chemistry II )**

Full Marks : 70

Pass Marks : 28

Time : 3 hours

*The figures in the margin indicate full marks for the questions*

*(Answer five questions, selecting one from each unit)*

UNIT - I

1. (a) Discuss the postulates and obtain an expression for Debye Hückel theory. 3+6 =9
- (b) Discuss the variation of the activity coefficient with the molality of different valance types viz., KCl, CaCl<sub>2</sub>, LnCl<sub>2</sub> and ZnSO<sub>4</sub>. 2
- (c) Write short note on concentration cell. 3
2. (a) Discuss the assumption of the Born Model. Derive the free energy expression for the ion solvent interaction and comment on the importance of free energy in ion solvent interaction. 2+5+2 = 9

*( Turn Over )*

(2)

- (b) Calculate the change in the potential difference between the anode and the solution when the concentration of zinc ion in the solution is increased from  $1.00 \times 10^{-3} \text{ M}$  to  $5.00 \times 10^{-3} \text{ M}$  at  $21^\circ \text{C}$ . Given  $F = 96485 \text{ C mol}^{-1}$  2
- (c) Define kappa ( $\kappa$ ) in Debye Hückel theory and discuss its significance. 3

UNIT - II

3. (a) Discuss the different models of the electrical double layer. 6
- (b) Write short note on the  $\text{H}_2\text{-O}_2$  fuel cell. 4
- (c) What is the electronation reaction in corrosion? Discuss the factors that affect the electronation reaction. 4
4. (a) Obtain a relation between net current density to the overpotential of the cell. Discuss the two extremes of the overpotential limit.  $6 + 4 = 10$
- (b) The data below refer to the anodic current through a platinum electrode of area  $2.0 \text{ cm}^2$  in contact with  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  aqueous solution at  $298 \text{ K}$ . Calculate the exchange current density and transfer coefficient of the electrode process. 4

$\eta/\text{mV}$	50	100	150	200	250
$I/\text{mA}$	8.8	25.0	58.0	131.0	298.0

(5)

UNIT - V

9. (a) Derive the expression of the entropy production in a chemical reaction. 7
- (b) Derive Saxon's relation of the electrokinetic effect and show the interrelation between these effects.  $2+5=7$
10. (a) Derive the expression for entropy production due to heat flow. 7
- (b) What is phenomenological law? Describe Onsager's reciprocity relations.  $3+4=7$

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(4)

UNIT - IV

7. (a) Derive Gibbs-Duhem relation for chemical potentials with the composition of the system. 5
- (b) Show that decrease in Helmholtz work function in any process at constant temperature and volume is equivalent to the maximum work output that can be obtained from the system. 3
- (c) Deduce the thermodynamic equation of state 3+3=6

$$(i) \left(\frac{dE}{dV}\right)_T = T \left(\frac{dP}{dT}\right)_V - P$$

$$(ii) \left(\frac{dH}{dP}\right)_T = V - T \left(\frac{dV}{dT}\right)_P$$

8. (a) Assuming an expression for van't Hoff isotherm, derive an expression for van't Hoff isochore. 5
- (b) Derive the following from the Gibbs-Helmholtz equation. 4

$$\left[\frac{d(\Delta G|T)}{dT}\right]_P = -\frac{\Delta H}{T^2}$$

- (c) Show that the isothermal reversible work of expansion for an ideal gas is greater than that for a real gas between the same initial and final states. 5

(3)

UNIT - III

5. (a) State and prove Euler's reciprocity relation for exactness. Show that for an ideal gas, work function (W) is not an exact differential. 2 + 2 = 4
- (b) Assuming one mole ideal gas as the working substance in a Carnot cycle, arrive at a definition of entropy. 7
- (c) One mole of an ideal gas is allowed to expand isothermally from 0.02 m<sup>3</sup> to 0.2 m<sup>3</sup> at 300 K. Calculate the entropy change for the system, surrounding and universe if the expansion is (i) reversible and (ii) irreversible against a constant external pressure of 0.1 atmosphere. 3
6. (a) Show that a decrease in Gibbs free energy accompanying in a process at constant temperature and constant pressure is equivalent to the useful work obtainable from the system. 3
- (b) Calculate the work done of an expansion of a gas in an isothermally reversible process and show that it is greater than the corresponding irreversible work. 4+3=7
- (c) Evaluate  $\Delta G$  and  $\Delta H$  for the reversible isothermal expansion of a mole of the gas having an equation of state  $PV = RT(1 + B/V)$  from an initial volume  $V_1$  to a final volume  $V_2$  where  $V_1$  and  $V_2$  are the molar volume of the gas in the two states. 4

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