BIRLA INSTITUTE OF TECHNOLOGY, MESRA, RANCHI
(END SEMESTER EXAMINATION)

CLASS: IMSc **SEMESTER : VII**
BRANCH: CHEMISTRY **SESSION : MO/18**

SUBJECT: SAC1001 ADVANCED PHYSICAL CHEMISTRY

TIME: 3.00 HRS **FULL MARKS: 60**

INSTRUCTIONS:
1. The question paper contains 7 questions each of 12 marks and total 84 marks.
2. Candidates may attempt any 5 questions maximum of 60 marks.
3. The missing data, if any, may be assumed suitably.
***4*. Before attempting the question paper, be sure that you have got the correct question paper.**
5. Tables/Data hand book/Graph paper etc. to be supplied to the candidates in the examination hall.

Q.1(a) Discuss the Activated Complex theory of molecular reactions. [6]
Q.1(b) Determine the concentrations of products in parallel reactions along with the half-life period. [6]

Q.2(a) Discuss briefly Langmuir's unimolecular theory of adsorption. Derive an expression for Langmuir's adsorption isotherm. Show that at normal pressures, Langmuir's adsorption isotherm becomes identical with Freundlich adsorption isotherm. What will happen at low and high pressures? [6]
Q.2(b) What are the assumptions made in the derivation of BET equation? Write down the BET equation. What are the applications of BET adsorption isotherm? [6]

Q.3(a) Give an account of the Debye-Huckel theory of strong electrolytes. How the presence of asymmetry and electrophoretic effect can be avoided? [6]
Q.3(b) Calculate the mean ionic activity coefficient $\gamma_{\pm}$ of (i) NaCl at a molality of 0.01 (ii) Na_2SO_4 at a molality of 0.001 in aqueous solutions at 25^0C. [6]

Q.4(a) Derive the equation for half-wave potential in polarography. What is its significance? [6]
Q.4(b) At 25^0C the exchange current density for the reaction H^+ (aq) + e^- → ½ H_2 (g) on the nickel surface is 1.00 x 10^{-2} mA cm^{-2}. Calculate the current density required to attain an over potential of 100 mV, using (a) the Butler-Volmer equation (b) the Tafel equation. Assume that the transfer coefficient, α = 0.50. [6]

Q.5(a) Derive the rate equation for HBr formation from the following sequence of reactions between H_2 and Br_2 [6]

$$\mathrm{Br_2} \xrightarrow{h\nu} 2\mathrm{Br}$$
$$\mathrm{Br} + \mathrm{H_2} \xrightarrow{k_2} \mathrm{HBr} + \mathrm{H}$$
$$\mathrm{H} + \mathrm{Br_2} \xrightarrow{k_3} \mathrm{HBr} + \mathrm{Br}$$
$$\mathrm{HBr} + \mathrm{H} \xrightarrow{k_4} \mathrm{Br} + \mathrm{H_2}$$
$$\mathrm{Br} + \mathrm{Br} \xrightarrow{k_5} \mathrm{Br_2}$$

Q.5(b) Derive the Stern-Volmer equation for bimolecular collisional quenching process. [6]

Q.6(a) Explain chemical potential. Show graphically the effect of temp on chemical potential. Also show how do chemical potential depend on temp? [6]
Q.6(b) Define Gibbs free energy and Helmholtz work function. Derive Gibbs-Duhem equation. [6]

Q.7(a) Define fugacity. What informations are given by Maxwell's relations. Drive the following: [6]

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Q.7(b) Explain need and limitations of first law of thermodynamics. Write different statements of IInd law of thermodynamics. 8 moles of ideal gas expand reversibly from a volume of 8 dm^3 to 80 dm^3 at a temperature of 27^0c. Calculate the change in entropy. Given $R = 8.314\, JK^{-1}\, mol^{-1}$ 1L = $1dm^3$. [6]

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