

INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR

End Semester examination: 2012-13 Subject: Physical Chemistry: CY20101
Duration: 3 h

DATA: $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$, $h = 6.625 \times 10^{-34} \text{ Js}$ Total Marks 60

Instructions: Answer all the questions.

[1] (a) Draw phase diagram of phenol-water system and explain it in terms of P, C and F.

(b) Determine the number of components, number of phases and the degree of freedom in the following equilibria: (i) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ (ii) $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$, when $P_{\text{NH}_3} = P_{\text{HCl}}$ (iii) $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$, when $P_{\text{NH}_3} \neq P_{\text{HCl}}$. (iv) A liquid at its critical point

(c) C_v for a metal is $3.04 \text{ JK}^{-1} \text{ mol}^{-1}$ at 20 K. Calculate the absolute entropy of the metal in JK^{-1} at 20 K.

(4+4+4=12)

[2] (a) Explain the collision theory of unimolecular reaction rates. What is its limitation?

(b) Comment on the effect of pressure role of volume of activation on the constant. of a reaction in terms of volume of activation of activated complex.

(6+6=12)

[3] (a) Describe the double sphere model for a reaction between two ions $Z_A e$ and $Z_B e$ in a medium of dielectric constant. Show that the logarithm of the rate constant of the reaction varies nearly with the reciprocal of the dielectric constant. Give explanations in terms of $\Delta^* S^0$ electrostriction of the solvent of solvent molecules when two ions are of the same some sign and opposite sign.

(b) Explain the third law of thermodynamics proposed by different workers. How is absolute entropies of solids, liquids and gases determined? What is Debye Power law and its importance in the calculation of absolute entropy.

(6+6=12)

[4] (a) How is the kinetics of the fast reaction determined by relaxation method.

(b) What are the exceptions to the third law of thermodynamics?

(c) The pre-exponential factor for a first order gas phase reaction is $2.75 \times 10^{15} \text{ sec}^{-1}$ at 220°C . Calculate the entropy of activation.

(4+4+4=12)

[5] Deduce the following expressions:

(6+6=12)

$$(a) \ln\left(\frac{f}{P}\right) = \frac{1}{RT} \int_0^P \alpha \cdot dP \quad (b) d\mu_1 = -\left(\frac{n_2}{n_1}\right) d\mu_2$$