RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

M.A./M.SC. FIRST SEMESTER EXAMINATION, JANUARY 2013

FIRST YEAR

APPLIED CHEMISTRY

Date : 14/01/2013

Time : 11.00 am – 1.00 pm

Paper : III

Full Marks : 50

[Use Separate Answer Books for each group]

(*Answer <u>one question</u> from each group*)

Group – A

1. a) Show that the exact expression to compute $[H_3O^+]$ in an aqueous solution of a salt formed from a weak acid and a strong base is given by,

$$[H_3O^+]^3 + (c+K_a)[H_3O^+]^2 - K_w[H_3O^+] - K_aK_w = 0$$

Under what approximation can the following simpler form be used?

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_b + \frac{1}{2}\log C$$

b) State Le Chatelier principle and explain the principle from thermodynamic view point.

c) Show that, $\left(\partial A/\partial n_i\right)_{T,V,n_{j's},\,j\neq i} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j's},\,j\neq i}$ where, terms have their usual significance.

d) An organic compound is extracted from aqueous solution with successive quantities of 25cm^3 chloroform. The original volume of solution is 500 cm^3 and the distribution coefficient of the compound is 20 between chloroform / water. Calculate the number of extractions needed for 95% recovery of the compound after deducing the necessary equation. [(4+2)+(1+4)+3+(3+3)]

2. a) What are buffer solutions? When a small quantity of acid is added to an aqueous solution of ammonium acetate, the pH of the solution remains almost unchanged, whereas when the same acid is added to an aqueous solution of NaCl, the pH of the solution changes enormously. Explain why it is so. What do you understand by the term buffer capacity? Show that the buffer capacity is maximum when the ratio of salt to acid (or base) is one.

b) Deduce Gibbs-Duhem equation and mention its significance.

c) Derive the relation,

$$\frac{d\ln Kp}{dT} = \frac{\Delta_r H}{RT^2}$$ where the terms have their usual significance.

d) Write down the Debye-Huckel limiting law explaining the terms involved.

Explain the necessity of the concept of mean ionic activity coefficient of an electrolyte in its solution. Calculate the mean activity coefficient of a 2-1 electrolyte at a molarity of 0·001 in aqueous solution at 25°C [Given A = 0·509] [(1+2+1+3)+(3+1)+3+(2+1+3)]

Group – B

3. a) Show that adsorption is an exothermic process. Can adsorption ever be endothermic? Give reasons in support of your answer.

b) Write down the expression of the BET equation and explain the terms used. What are the main assumptions on which this equation is based?

c) What do you mean by polarizability of a molecule? How is it related with molar polarization?

d) Find out CGS and SI units of the term μ^2/kT. [(2+2)+{(1+2)+2}+(2+1)+(2+1)]

4. a) What are the different steps in the mechanism of a heterogeneously catalyzed reaction? With the help of proper energy profile diagrams, show that a heterogeneous catalyst provides an alternative path of a lower reaction activation energy.

b) Write down Gibbs adsorption equation and explain the terms used. What is meant by 'surface excess' of a solution? Give examples of positive and negative surface excess.

c) Write down the Debye equation and explain the terms used. Draw qualitatively plots of molar polarization versus 1/T for (i) a polar molecule and (ii) a non-polar molecule. Discuss what information can be obtained from these plots. [(2+3)+(2+1+1)+(2+2+2)]

Group – C

5. a) For the following two competing reactions (both 1st order) $A \xrightarrow{K_1} C$ and $A \xrightarrow{K_2} D$, show that $\frac{[C]}{[D]} = \frac{K_1}{K_2}$.

b) Using the temperature jump technique for the following reaction $A + B \underset{K_b}{\overset{K_f}{\rightleftharpoons}} C$ and considering the reaction to be elementary, show that $[A] - [A]_{eq} = \left([A]_o - [A]_{eq}\right)^{-t/\tau}$, where τ is the relaxation time.

c) Plot the concentration of Yvs. that of X for an oscillatory reaction, obeying the mechanism shown below:

i) $A + X \rightarrow X + X$

ii) $X + Y \rightarrow Y + Y$

iii) $Y \rightarrow B$

Consider each step is elementary. Also explain the plot qualitatively.

d) i) Show that for the following reaction :

$Br_2 \xrightarrow{h\gamma} 2Br$,

$$\frac{d[Br]}{dt} = 2Iabs$$

ii) Absorption of UV radiation decomposes acetone according to the reaction $(CH_3)_2CO \xrightarrow{h\gamma} CO + C_2H_6$. The quantum yield of the reaction at 280 nm is 0·2. A sample of acetone absorbs monochromatic radiation at 280 nm at the rate of $7{\cdot}5 \times 10^{-3}$ Js^{-1}. Calculate the rate of formation of CO. [4+4+3+(1+3)]

6. a) Apply the steady state approximation to the following proposed mechanism for $H_2O_2 + 2H^+ + 2I^{(-)} \rightarrow I_2 + 2H_2O$ and find the rate law :

$H^+ + I^- \rightleftharpoons HI$	rapid equilibrium
$HI + H_2O_2 \rightarrow H_2O + HOI$	slow
$HOI + I^- \rightarrow I_2 + OH^-$	fast
$OH^- + H^+ \rightarrow H_2O$	fast

b) i) Find out the order of the following reaction with respect to oxygen : $2O_3 \rightarrow 3O_2$

ii) What do you mean by 'saddle point'?

c) Discuss the principle of detailed balance.

d) Lindeman mechanism for the unimolecular reaction is given as follows :

$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$

$A^* \xrightarrow{K_2} P$

show that it leads to $\frac{d[P]}{dt} = \frac{k_2 k_1 [A]^2}{k_{-1}[A] + k_2}$ under what conditions will the order of the reaction be equal to one?

e) In a given absorption cell transmittance of 0·1 mol dm^{-3} of A is 0·75 and that of 0·1 mol dm^{-3} of B is 0·55 at a given wavelength. Calculate the optical density of the solution and hence the transmittance of a solution simultaneously with 0·1 mol dm^{-3} of A and in 0·1 mol dm^{-3} of B.

[3+(1+1)+3+4+3]