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**3 (Sem-3/CBCS) CHE HC 3**

**2023**

**CHEMISTRY**

(Honours Core)

Paper : CHE-HC-3036

**(Physical Chemistry III)**

Full Marks : 60

Time : Three hours

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

1. Answer the following as directed:  $1 \times 7 = 7$

(i) What is Eutectic Point ?

(ii) Give one example of a consecutive reaction.

(iii) What is adsorption isobar and adsorption isotherm ?

Contd.

- (iv) How many components are present in the following equilibria ?



- (v) What is autocatalysis ?
- (vi) A radioactive substance has  $t_{1/2}$  of 6.93 min. Find its average life.
- (vii) Under what condition of pressure, would the Lindemann theory of unimolecular gaseous reaction show first-order kinetics ?
2. Answer the following questions :  $2 \times 4 = 8$
- (i) Explain why the slope of vapour pressure vs temperature plot for solid-vapour equilibrium is steeper than the slope of liquid-vapour equilibrium.
- (ii) Why are zeolites suitable as catalysts for cracking and reforming reactions ?

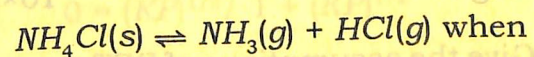
- (iii) If the reaction  $\text{A} \rightarrow \text{Products}$  follows zero-order kinetics, show with the help of a diagram, how  $[\text{A}]$  will change with time.

- (iv) The activation energy of a certain uncatalyzed reaction at 300 K is  $76 \text{ kJ mol}^{-1}$ . The activation energy is lowered to  $57 \text{ kJ mol}^{-1}$  by the use of a catalyst. By what factor is the rate of the catalysed reaction increased ?

3. Answer **any three** questions from the following :  $5 \times 3 = 15$

- (i) Derive Gibbs' Phase rule. How is the number of component  $C$  calculated for systems involving ions and having some chemical reactions equilibrium among the constituents ? Evaluate the degrees of freedom for the following equilibrium

$$2 + 1 + 2 = 5$$



(a)  $P_{\text{NH}_3} \neq P_{\text{HCl}}$

(b)  $P_{\text{NH}_3} = P_{\text{HCl}}$

(ii) Draw and explain *five* general types of isotherms that have been observed during adsorption of gas on solid surface.

(iii) Draw and interpret the phase diagram for a two-component system involving simple eutectic.

(iv) What are chain reactions? Discuss the kinetics of  $H_2 - Br_2$  chain reaction.

$$1+4=5$$

(v) Distinguish between order and molecularity of a reaction. Discuss *one* experimental method for the determination of the order of a reaction.

$$2+3=5$$

4. Answer **any three** questions from the following :

$$10 \times 3 = 30$$

(a) Give the assumptions of BET theory. On the basis of these assumptions, deduce the BET equation of adsorption.

$$3+7=10$$

(b) (i) Explain briefly the phase diagram for a two-component system with incongruent melting point. Explain the cooling curve for such a system.

$$5+2=7$$

(ii) Discuss the mutual solubility curve of a conjugate solution having upper critical solution temperature.

$$3$$

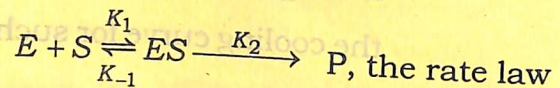
(c) What are the assumptions of Langmuir Isotherm? Derive Langmuir Adsorption Isotherm. Show that for adsorption of a gas with dissociation ( $X_2 \rightarrow 2X$ ) the Langmuir adsorption isotherm becomes

$$\theta = \frac{(KP)^{1/2}}{1 + (KP)^{1/2}}$$

Draw the Langmuir Isotherms for with and without dissociation.

$$2+4+2+2=10$$

- (d) Discuss Enzyme catalysis with an example. For the Michaelis-Menten mechanism of enzyme action



is given by

$$r = K_2 [E]_0 [S]_0 / [S]_0 + K_M$$

Where  $K_M = K_2 + K_{-1}/K_1$  is Michaelis constant.

Answer the following :

- (i) Show that enzyme reaction is of first-order and zero-order with respect to low and high initial concentration of S respectively.

- (ii) What type of graph is expected between the rate and  $[S]_0$  ?

- (iii) Show that if  $K_2 \ll K_{-1}$ ,  $K_M$  represents the dissociation constant for ES.

- (iv) What is 'Turnover number' of an enzyme catalyst ? 3+2+2+2+1=10

- (e) (i) How does the reaction rate depend on temperature ? Show how Arrhenius plot of a reaction can be obtained. What is the significance of the pre-exponential factor ?

- (ii) Write the mechanism of unimolecular reaction as proposed by Lindemann. Using this mechanism, deduce an expression for the rate of unimolecular reaction.

5+5=10

- (f) State and explain the Nernst Distribution Law. Under what conditions the law is valid ? How is the law derived from thermodynamic considerations ? Discuss the practical applications of the Nernst Distribution Law.

2+2+4+2=10