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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 ?

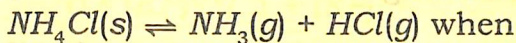
(iii) If the reaction $A \rightarrow \text{Products}$ follows zero-order kinetics, show with the help of a diagram, how $[A]$ will change with time.

(iv) The activation energy of a certain uncatalyzed reaction at 300 K is 76 kJmol^{-1} . The activation energy is lowered to 57 kJmol^{-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 : 5×3= 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

$$2+1+2 = 5$$



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

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

(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 :

10×3=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.

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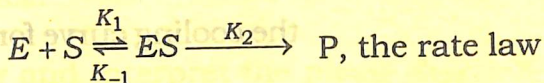
(c) What are the assumptions of Langmuir Isotherm? Derive Langmuir Adsorption Isotherm. Show that for adsorption of a gas with dissociation ($X_2 \rightarrow 2X$) the Langmuir adsorption isotherm becomes

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

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.

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