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 : 1×7=7

   (i) What is Eutectic Point ?

   (ii) Give *one* example of a consecutive reaction.

   (iii) What is adsorption isobar and adsorption isotherm ?

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

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(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 : 2×4=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 → 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

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ when

(a) $P_{NH_3} \neq P_{HCl}$

(b) $P_{NH_3} = P_{HCl}$

(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

$$0 = (KP)^{1/2} / \ 1 + (KP)^{1/2}$$

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

$$E + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES \xrightarrow{K_2} P$$, the rate law

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 $K_2 << K_{-1}$, 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
