Total number of printed pages–8

3 (Sem–3 / CBCS) CHE HC 3

2022

CHEMISTRY

(Honours)

Paper : CHE–HC–3036

(Physical Chemistry III)

Full Marks : 60

Time : Three hours

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

(Symbols used signify their usual meaning)

1. Answer ***any seven*** of the following as directed : 1×7=7

   (a) Define phase of a system.

   (b) For a one-component system, maximum number of phases that can exist in equilibrium is three.

   *(State true **or** false)*

Contd.

(c) The order of a chemical reaction at $300K$ is 1. The order of the reaction at $600K$ will be

(i) 0
(ii) 1
(iii) 1·5
(iv) 2 *(Choose the correct option)*

(d) For a *nth* order reaction which of the following relations is correct ?

(i) $t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}$
(ii) $t_{\frac{1}{2}} \propto \frac{1}{a^{1-n}}$
(iii) $t_{\frac{1}{2}} \propto \frac{1}{a^{n+1}}$
(iv) $t_{\frac{1}{2}} \propto \frac{1}{a^{1+n}}$ *(Choose the correct option)*

(e) Give one example of parallel reaction.

(f) What is a negative catalyst ?

(g) Explain how physical adsorption is influenced by temperature.

(h) An iceberg is floating in a lake. Considering the lake, iceberg and atmosphere as a single system, determine the number of phases.

(i) Consider a heterogeneous system of p phases at equilibrium containing three components. Express degrees of freedom F of the system.

(j) Give one example of a reaction where order and molecularity are the same.

(k) Give *one* example of chemical adsorption process.

(l) What is meant by selectivity of a catalyst ?

2. Answer ***any four*** of the following questions : 2×4=8

(a) Can there be a 'quadruple point' on a phase diagram for a one-component system ? Give reason.

(b) Explain why solid-liquid equilibrium line has a negative slope.

(c) State and explain the steady state approximation.

(d) What is temperature coefficient of a reaction ?

(e) Describe the characteristics of a catalytic reaction.

(f) Discuss the factors on which adsorption of gas on solid depends.

(g) What are Zeolites ? Give one example of a reaction catalysed by a Zeolite catalyst.

(h) Explain pseudo-order reaction. Give example.

3. Answer ***any three*** of the following questions : 5×3=15

(a) Draw and interpret the phase diagram of water system.

(b) Derive Gibbs-Duhem-Margules equation.

(c) Deduce BET equation of adsorption.

(d) Consider the following Lindemann mechanism for the decomposition of a molecule A, in presence of a species M :

$A + M \xrightarrow{k_1} A^* + M$ (activation)

$A^* + M \xrightarrow{k_{-1}} A + M$ (deactivation)

$A^* \xrightarrow{k_2} P$ (decomposition)

Using the steady state approximation, derive the rate law for formation of products.

(e) What is chain reaction. Give the Rice-Herzfeld mechanism for the reaction

$$H_2 + Br_2 \longrightarrow 2HBr$$

Based on this mechanism derive the rate law for the formation of product.

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

(g) For adsorption of gases on solid surfaces, five general types of isotherms have been observed. Draw these isotherms.

(h) Explain a suitable method of experimental determination of order of a reaction.

4. Answer ***any three*** of the following questions : 10×3=30

(a) (i) Derive the integrated form of the Clausius-Clapeyron equation to show the variation of vapour pressure of a liquid with temperature. Give the graphical variation of log P with $\frac{1}{T}$. 5+1=6

(ii) At $300K$ and $350K$ the vapour pressure of a liquid are $1{\cdot}5\times10^5\ Nm^{-2}$ and $2{\cdot}0\times10^5\ Nm^{-2}$ respectively. Calculate the enthalpy of vaporization of the liquid. 4

(b) (i) State and explain the Nernst distribution law. Give the essential preconditions for the validity of the distribution law. With the help of suitable example, explain the limitations of the distribution law. 2+2+2=6

(ii) Thermodynamically derive the Nernst distribution law. 4

(c) (i) On the basis of hard sphere collision theory of reaction for elementary bimolecular gaseous reaction $A + B \rightarrow$ Products, find out an expression for Arrhenius pre-exponential factor, A. 6

(ii) Why the steric factor, p, had to be introduced into the expression for the rate constant using the collision theory? Discuss the physical significance of the steric factor. 4

(d) Give the assumptions of Langmuir adsorption theory. On the basis of these assumptions, deduce the Langmuir isotherm. Under what condition does the Langmuir isotherm reduce to the Freundlich isotherm? 3+5+2=10

(e) (i) Derive the integrated rate law for the reaction $A + B \rightarrow$ Products. 5

(ii) From the integrated rate law for the reaction $A + A \rightarrow$ Products, show that half-life time of the reaction is inversely proportional to the initial concentration of the reaction. 2

(iii) In a particular reaction the time required to complete half of the reaction was found to increase nine times when the initial concentration of the reactant was reduced to one-third. Determine order of the reaction. 3

(f) Give one example of enzyme catalysed reaction. Mention three characteristic features of enzyme catalysed reaction. Derive an expression for the rate of formation of product of an enzyme catalysed reaction using the Michaelis-Menten mechanism. How is the rate influenced by high substrate concentration? 1+3+5+1=10

(g) (i) What are solid solutions? Discuss briefly three types of solid solutions. Give examples. 1+3+3=7

(ii) How is the phase rule applied in the preparation of freezing mixture? 3

(h) (i) What are consecutive reactions? Give one example. 3

(ii) Discuss the kinetics of a consecutive reaction to obtain the concentration of product. Show how the concentrations of different species involved in a consecutive reaction vary with time. 5+2=7
