3 SEM TDC CHMH (CBCS) C 7

2023

(Nov/Dec)

CHEMISTRY

(Core)

Paper: C-7

(Physical Chemistry)

Full Marks: 53
Pass Marks: 21

Time: 3 hours

The figures in the margin indicate full marks for the questions

- 1. Choose the correct answer from the following: 1×5=5
 - (a) For a reaction $A+B \rightarrow C+D$, doubling the concentration of both the reactants increases the reaction rate by 8 times and doubling the concentration of only B simply doubles the reaction rate. The rate law is given as

(i)
$$r = k[A]^{\frac{1}{2}}[B]^{\frac{1}{2}}$$

(ii)
$$r = k[A][B]^2$$

- (iii) $r = k[A]^2[B]$
- (iv) r = k[A][B]
- (b) Sulphur can exist as sulphur rhombic, sulphur monoclinic, liquid sulphur (l) and sulphur vapour (g). The maximum number of phases which can coexist in equilibrium can be
 - (i) 3
 - (ii) 4
 - (iii) 1
 - (iv) 2
- (c) A solute undergoes complete association in solvent 2 out of the two solvents 1 and 2. The distribution law equation that will be applicable is
 - (i) $\frac{c_1}{c_2}$ = constant
 - (ii) $\frac{c_1}{\sqrt[n]{c_2}}$ = constant
 - (iii) Depends upon the temperature
 - (iv) $\frac{c_2}{\sqrt[n]{c_1}}$ = constant

- (d) A plot of $\log \frac{x}{m}$ versus $\log p$ for the adsorption of a gas on a solid gives a straight line with slope equal to
 - (i) n
 - (ii) $\frac{1}{n}$
 - (iii) $\log x$
 - $(iv) \log k$
- (e) The E_a for the forward reaction is 40 kJ mol^{-1} and that for the reverse reaction is 60 kJ mol^{-1} . The reaction is
 - (i) exothermic
 - (ii) endothermic
 - (iii) chain reaction
 - (iv) spontaneous
- **2.** Answer any *five* questions from the following: $2 \times 5 = 10$
 - (a) Show that the half-life period of a firstorder reaction is independent of the initial concentration of the reactant.

- (b) Explain why the fusion curve of ice has a negative slope whereas the sublimation curve has a positive slope in the phase diagram of water.
- (c) A eutectic mixture has a definite composition and a sharp melting point, yet it is not a component. Give reason.
- (d) Distinguish between physical adsorption and chemical adsorption.
- (e) What are pseudounimolecular reactions? Give one example.
- (f) Explain the term 'autocatalysis' giving one example.
- **3.** Answer any *two* questions from the following: $6\times2=12$
 - (a) (i) Draw and explain the phase diagram of water system.
 - (ii) What is triple point? Distinguish between the triple point and the freezing point of a pure substance.

1+1=2

(b) (i) Explain the terms 'phase', 'component' and 'degrees of freedom' with one example of each. 3+1½=4½

(ii) Write down the number of components, number of phases and degrees of freedom for the following equilibrium: 1½

 $NH_4Cl(s) \Rightarrow NH_3(g) + HCl(g), P_{NH_3} \neq P_{HCl}$

- (c) (i) Derive Gibbs-Duhem-Margules equation.
 - (ii) What is CST? What happens to critical solution temperature on adding NaCl to phenol-water system? Write the effect of increasing pressure on a system having UCST as well as LCST.

1+1+1=3

3

- **4.** Answer any *two* questions from the following: $6 \times 2 = 12$
 - (a) Deduce the integrated rate expression for the following second-order reaction:

 $A + B \rightarrow Product$

Prove that when either A or B is taken in excess, then this second-order reaction shows first-order kinetics. 4+2=6

(b) (i) For the pyrolysis of acetaldehyde $CH_3CHO \xrightarrow{\Delta} CH_4 + CO \,, \qquad \text{the}$ following mechanism is suggested :

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$
 $CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$

 $CH_3CO \xrightarrow{k_3} CH_3 + CO$ $2CH_3 \xrightarrow{k_4} C_2H_6$

Show that the overall rate equation is given by rate = $k[CH_3CHO]^{\frac{3}{2}}$.

2

- (ii) Describe the half-life period method for determining the order of a reaction.
- (c) Give one example of consecutive reaction. Discuss the kinetics of first-order consecutive reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Depict graphically the concentrations of A, B and C with time. 1+4+1=6

- **5.** Answer any *two* questions from the following: $4\frac{1}{2} \times 2 = 9$
 - (a) Discuss the mechanism of enzyme catalysis with the help of Michaelis-Menten equation. Define Michaelis constant.

 3½+1=4½
 - (b) What is acid-base catalysis? Explain the theories of acid-base catalysis with suitable examples. 1+3½=4½
 - (c) (i) Explain the action of catalytic promoter with one example. 2
 - (ii) Write a brief note on nano-catalyst. 21/2

(Continued)

- **6.** Answer any *one* question from the following:
 - (a) What are adsorption isotherms? Derive Freundlich adsorption isotherm equation and graphically represent the equation. Discuss the limitations of Freundlich adsorption isotherm. 1+2+2=5

5

- (b) (i) Write the main assumptions of Langmuir adsorption isotherm. 2
 - (ii) Discuss the effect of pressure and temperature on the adsorption of gases on solids. $1\frac{1}{2}+1\frac{1}{2}=3$

* * *

