

3 SEM TDC CHMH (CBCS) C 7

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(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 option : 1×5=5

(a) The unit of rate constant of a zero-order reaction is

(i) $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$

(ii) s^{-1}

(iii) $\text{dm}^{-3} \text{mol s}^{-1}$

(iv) $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

(2)

(b) For a reaction, if the plot of $\ln k$ versus $1/T$ gives a straight line, then

(i) $E_a = (\text{slope}) \times R$

(ii) $E_a = -(\text{slope}) \times R$

(iii) $E_a = (\text{slope}) \times 1/R$

(iv) $E_a = -(\text{slope}) \times 1/R$

(c) The reduced phase rule for a condensed system is

(i) $F = C - P + 2$

(ii) $F = C + 2 + P$

(iii) $F' = C + 1 - P$

(iv) $F' = C + 1 + P$

(d) The number of phases, number of components and degrees of freedom corresponding to the triple point of sulphur system are

(i) (3, 2, 1)

(ii) (3, 1, 0)

(iii) (4, 2, 0)

(iv) (2, 2, 0)

(3)

(e) The adsorption theory explains the

(i) acid-base catalysis

(ii) homogeneous catalysis

(iii) heterogeneous catalysis

(iv) enzyme catalysis

2. Answer any five questions from the following : 2×5=10

(a) What is triple point? Write its significance.

(b) Show that half-life period of a second-order reaction is inversely proportional to the initial concentration of the reactant.

(c) The reaction, $2A + B \rightarrow \text{products}$; is first-order with respect to A and second-order with respect to B. Write down its differential rate equation and rate law.

(d) Find out the number of components and degrees of freedom for the following equilibrium :



(4)

- (e) "Adsorption is exothermic in nature."
Explain.
- (f) What are catalytic promoters? Give one example.

3. Answer any *three* questions from the following : $4 \times 3 = 12$

- (a) Derive the phase rule thermodynamically.
- (b) Write the Clapeyron equations for the three-phase transition equilibria of water system. Predict the slope of the P vs. T curves of water system from the Clapeyron equations.
- (c) Construct the phase diagram for Zn-Mg from the following data :

Melting point of Zn = 420°C

Melting point of Mg = 650°C

A congruently melting stable compound Mg_xZn_y is formed at 15% by mass of Mg; the congruent melting point of which is 599°C . The lowest freezing point of zinc observed is 370°C at 4% by mass of Mg. The lowest freezing point of magnesium observed is 350°C at 50% by mass of Mg. Determine the molecular formula of the stable compound Mg_xZn_y .

$3+1=4$

(5)

- (d) Draw and discuss the phase diagram of lead-silver system.

- (e) Write short notes on any *two* of the following : $2 \times 2 = 4$

- (i) Azeotropes
(ii) Steam distillation
(iii) Eutectic point
(iv) CST

4. Answer any *three* questions from the following : $4 \times 3 = 12$

- (a) What is meant by the rate and order of a reaction?

For the reaction



the rate of formation of D is found to be

- (i) doubled when $[A]$ is doubled keeping $[B]$ and $[C]$ constant
(ii) doubled when $[C]$ is doubled keeping $[A]$ and $[B]$ constant
(iii) unchanged when $[B]$ is doubled keeping $[A]$ and $[C]$ constant

Write the rate equation for the reaction.

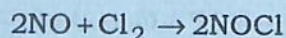
$2+2=4$

(6)

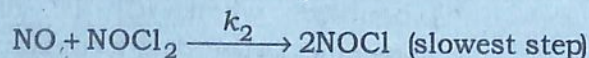
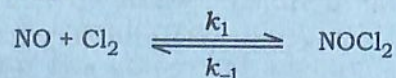
- (b) Discuss the effect of catalyst on the rate of a reaction. Draw the suitable curves showing the activation energy of uncatalyzed and catalyzed paths for (i) an exothermic and (ii) an endothermic reaction. $2+1+1=4$

- (c) Starting from the Arrhenius equation (exponential form) $k = Ae^{-E_a/RT}$, deduce its integrated form between two temperatures T_1 and T_2 . For the decomposition of acetonedicarboxylic acid $k = 2.46 \times 10^{-5}$ at 273 K and $k = 1.63 \times 10^{-3}$ at 303 K. Calculate the energy of activation of the reaction. $2+2=4$

- (d) What is meant by mechanism of a reaction? For the reaction



the following mechanism has been proposed :



Using the steady-state approximation for NOCl_2 , show that the overall rate of the reaction is given by $k[\text{NO}]^2[\text{Cl}_2]$, assuming that $k_2[\text{NO}] \ll k_{-1}$. $1+3=4$

(Continued)

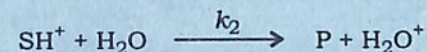
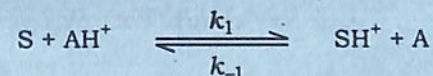
(7)

- (e) What is half-life period of a reaction? Deduce a relationship between half-life period and order of a reaction. $1+3=4$

5. Answer any three questions from the following : $3 \times 3 = 9$

- (a) What are homogeneous and heterogeneous catalysis? Give one example of each. $2+1=3$

- (b) The following mechanism is proposed for an acid-catalyzed reaction :



where S is the substrate, AH^+ is an acid and P is the product. Under what conditions, the reaction becomes (i) general acid-catalyzed and (ii) specifically hydrogen ion-catalyzed reaction? $1\frac{1}{2} + 1\frac{1}{2} = 3$

- (c) Discuss the effect of pH on enzyme catalysis.

- (d) Write a short note on any one of the following :

- (i) Nanomaterials as catalyst
(ii) Autocatalysis

6. Answer any *one* question from the following : 5

(a) Show that the Freundlich adsorption isotherm is a special case of Langmuir adsorption isotherm.

(b) (i) What are physical adsorption and chemisorption? Write four differences between physical adsorption and chemisorption. 2+2=4

(ii) Finely divided solid materials are better adsorbents than their compact solid. Why? 1

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