

- (ii) Mobility is the speed of the ion in a field of unit strength.
- (iii) Fraction of the total current carried by each type of ion is independent of viscosity of the solution.
- (iv) In homogeneous catalysis, doubling the catalyst concentration will not change the rate.
- (v) The desorption of a chemisorbed species is always an activated process. (1×5=5)
- (c) State reason :
- (i) Why does the first order reaction never achieve completion ?
- (ii) Why does the Beer's Law fails in case of $K_2Cr_2O_7$ solution ?
- (iii) The decomposition of NH_3 on Tungsten is 1st – order.
- (iv) The molar conductivities of the alkali metal ions increase on going from Li^+ to Cs^+ .
- (v) Molar Conductivities of strong electrolytes depends weakly on the concentration of solute ? (1×5=5)

SECTION A

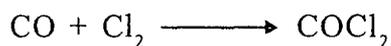
2. (a) Nitrogen pentoxide (N_2O_5) gas decomposes according to the reaction



At 328 K, the rate of reaction under certain conditions is 0.75×10^{-4} mol $dm^{-3} s^{-1}$. Neglecting the concentrations of intermediates determine the values of

$$\frac{d[N_2O_5]}{dt}, \frac{d[N_2]}{dt} \text{ and } \frac{d[O_2]}{dt} ? \quad (2)$$

- (b) Using the following data obtain the order w.r.t. each reactant and the total order and rate constant for the reaction

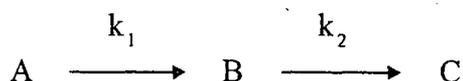


Experiment	1	2	3	4
[CO] / mol dm ⁻³	0.1	0.1	0.05	0.05
[Cl ₂]/mol dm ⁻³	0.1	0.05	0.1	0.05
Rate/mol dm ⁻³ s ⁻¹	1.2×10 ⁻²	4.26×10 ⁻³	6.0×10 ⁻³	2.13×10 ⁻³

(5)

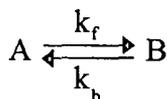
- (c) The reaction $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ has a rate constant of $2.24 \times 10^{-5} \text{ s}^{-1}$ at 320°C . Calculate the half-life of the reaction. What fraction of a sample of $\text{SO}_2\text{Cl}_2(\text{g})$ remains after being heated for 5.00 hrs at 320°C ? How long will a sample of $\text{SO}_2\text{Cl}_2(\text{g})$ need to be maintained at 320°C to decompose 92.0% of the initial amount present? (5)

3. (a) Consider two consecutive 1st-order reactions



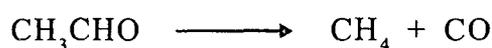
$k_1 \neq k_2$ and at time $t = 0$ only A is present. Derive expression for [A], [B] and [C] at time 't' in terms of rate constants k_1 & k_2 . Show graphically the concentration of 'A', 'B' and 'C' as function of time for the condition when $k_2 \gg k_1$. (6)

- (b) For a reversible first-order reaction

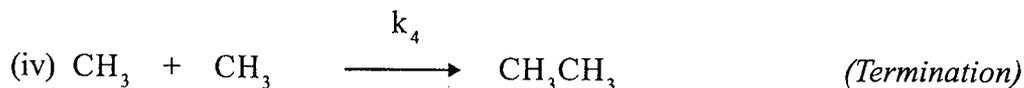
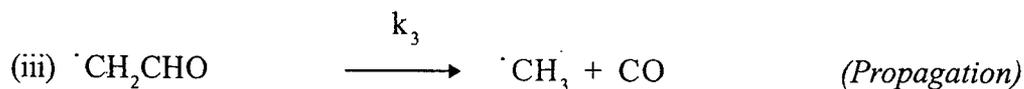
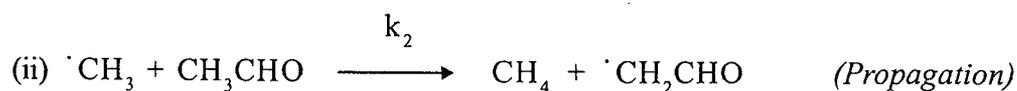
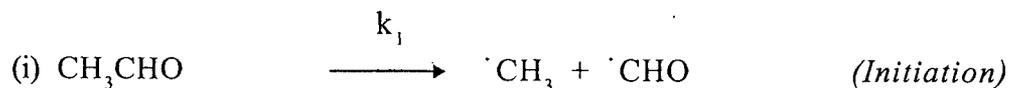


$k_f = 10^{-2} \text{ s}^{-1}$ and $[\text{B}]_{\text{eq}}/[\text{A}]_{\text{eq}} = 4$. If $[\text{A}]_0 = 0.01 \text{ mol L}^{-1}$ and $[\text{B}]_0 = 0$, what will be concentration of B after 30s? (6)

4. (a) Considering the following mechanism for the thermal decomposition of acetaldehyde:



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Derive the differential rate law for the formation of CH_4 using steady state approximation and also determine the chain length for the same reaction. (6)

- (b) The rate constant for the 1st-order decomposition of ethylene oxide into CH_4 and CO follows the equation :

$$\log k \text{ (in s}^{-1}\text{)} = 14.34 - (1.25 \times 10^4)/T.$$

Calculate (i) the activation energy of the reaction (ii) the rate constant at 700 K and (iii) the frequency factor, A. (3)

- (c) What conclusion can be reached about adsorption on the surface from the following facts ?

(i) On gold, the rate of decomposition of HI is independent of the pressure of HI .

(ii) The decomposition rate of NH_3 on Pt is proportional to $\frac{P_{\text{NH}_3}}{P_{\text{H}_2}}$. (3)

SECTION B

5. (a) Discuss the determination of hydrolysis constant of salts from conductometric measurements. (4)

- (b) A dilute solution of potassium chloride was placed between two Pt electrodes 10.0 cm apart, across which a potential of 6.0 volts was applied. How far would the K^+ ion move in 2 hours at $25^\circ C$? Molar ionic conductance of K^+ ion at infinite dilution at $25^\circ C$ is known to be $73.52 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$. (4)
- (c) At $25^\circ C$, the specific conductance of distilled water is $58.0 \times 10^{-7} \text{ S m}^{-1}$ and the λ_m° values for H^+ and OH^- ions are 349.8×10^{-4} and $198.5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$, respectively. Assuming that A_m differs very little from Λ_m° , calculate the ionic product of water at $25^\circ C$. (4)
6. (a) Define Transport Number. How will you determine it by using Hittorf's method? (6)
- (b) Calculate the transport numbers of H^+ ions and Cl^- ions from the following data obtained by the moving boundary method using cadmium chloride as the indicator electrolyte : [Given : $A_g = 108 \text{ g mol}^{-1}$]
- | | | |
|--|-----------------------|-----|
| Concentration of HCl solution | = 0.100 N | |
| Mass of silver deposited in the coulometer | = 0.1209 g | |
| Movement of boundary | = 7.50 cm | |
| Cross-section of the tube | = 1.24 cm^2 | (6) |
7. (a) Discuss the asymmetric effect and electrophoretic effect. How these effect can be minimized? (6)
- (b) A cell contains 0.10 mol dm^{-3} aqueous KCl, which at that concentration has a molar conductivity of $129 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The measured resistance was 28.44Ω . When the same cell was filled with 0.05 mol dm^{-3} NaOH aqueous solution the resistance was 31.6Ω . Find the molar conductivity of aqueous NaOH at that concentration. (4)
- (c) The molar conductance of sodium acetate, hydrochloric acid and sodium chloride at infinite dilution are 91.0×10^{-4} , 426.16×10^{-4} and $126.45 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$, respectively at $25^\circ C$. Calculate Λ_m° at infinite dilution for acetic acid. (2)

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SECTION C

8. (a) State and derive Lambert-Beer's Law for light absorption by solutions. Also, plot the graph for (i) Absorbance ~ concentration and (ii) Transmittance ~ concentration. (6)
- (b) Radiation of wavelength 2500 \AA was passed through a cell containing 10 ml of a solution which was 0.05 M in oxalic acid and 0.01 M in uranyl sulphate. After absorption of 80 joules of radiation energy, the concentration of oxalic acid was reduced to 0.04 M. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength. (4)
- (c) In a given absorption cell transmittance of 0.1 mol dm^{-3} of A is 0.75 and that of 0.1 mol dm^{-3} of B is 0.55 at a given wavelength. Calculate the transmittance of a solution that is simultaneous 0.1 mol dm^{-3} in A and 0.1 mol dm^{-3} in B. (2)
9. Write short note on any three :
- (i) Ostwald's Dilution Law
 - (ii) Mechanism of Acid-Base catalyzed reactions
 - (iii) Chemical Actinometer
 - (iv) Langmuir Adsorption Theory
 - (v) Collision theory of bimolecular gaseous reactions (3×4=12)