

Roll No.

Total Pages : 6

322403

August/September 2022
B.Sc. (Chem.) IV SEMESTER
Physical Chemistry-IV (BCH-403)

Time : 3 Hours]

[Max. Marks : 75

Instructions :

- 1. It is compulsory to answer all the questions (1.5 marks each) of Part-A in short.*
- 2. Answer any four questions from Part-B in detail.*
- 3. Different sub-parts of a question are to be attempted adjacent to each other.*

PART-A

- (a) What is the EMF of a Concentration Cell consisting of Zn electrodes, one immersed in a solution of 0.01 molar concentration and the other in a solution of 0.1 molar concentration of its ions at 298 K? (If two solutions are connected by a salt bridge.)
[PO:1-4, CO:1] (1.5)

(b) A substance when dissolved in water at 0.001 M concentration absorbs 10 % of an incident radiation in a path length of 1 cm length. What should be the concentration of the solution to absorb 90% using the same radiation.
[PO:1-4, CO:4] (1.5)

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100 [P.T.O.

(c) Calculate the energy (in J) associated with (i) *one* photon and (ii) *one* Einstein of radiation of wavelength 640 nm. [PO:1-3, CO:4] (1.5)

(d) Explain 'Quantum Yield' and give any two suitable examples of high and low quantum yield reactions. [PO:1-5, CO:3] (1.5)

(e) What is the role of photochemical reactions in biochemical processes? Explain. [PO:1-3, CO:4] (1.5)

(f) The molar ionic conductivity of NH_4^+ and OH^- at infinite dilution are 72 and 198 $\text{ohm}^{-1} \text{cm}^2$ respectively. The molar conductivity of a centimolar NH_4OH solution at the same temperature is found to be 9 $\text{ohm}^{-1} \text{cm}^2$. Find the percentage dissociation of NH_4OH at this concentration?

[PO:1-4, CO:1] (1.5)

(g) A certain quantity of the electricity is passed through an aqueous solution of AgNO_3 and cupric salt solution connected in the series. The amount of Ag deposited is 1.08 g, then what will be the amount of copper deposited? [PO:1-4, CO:1] (1.5)

(h) Rewrite the below statement in corrected form (if stated 'false')

A catalyst makes the equilibrium constant of the reaction more favorable for the forward reaction compared to backward reaction.

[PO:1-4, CO:3] (1.5)

- (i) Explain the significance of Eadie Plot. Sketch the Eadie Plot and describe all measurable quantities.

[PO:1-4, CO:3] (1.5)

- (j) Rewrite the below statement in corrected form (if stated 'false')

A catalyst does not take part in the reaction mechanism but accelerate the reaction. [PO:1-4, CO:3] (1.5)

PART-B

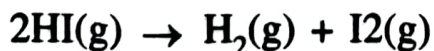
2. (a) Let the reaction $aA \rightarrow \text{product}$ have the rate law $r = k[A]^2$. Write down the equation that gives r of this reaction as a function of time. [PO:1-3, CO:2] (7)

- (b) (i) Describe Lambert's Law and derive Beer-Lambert expression. What are the limitations of Beer-Lambert law? [PO:1-5, CO:4] (4)

- (ii) What is the physical significance of absorption coefficients. Sketch 'Transmittance' versus 'Concentration' Plot and explain the nature of typical observable plot. [PO:1-4, CO:4] (4)

3. (a) Write expression for the Debye-Hückel-Onsager equation and explain the Debye-Falkenhagen effect with suitable example. [PO:1-4, CO:1] (7)

- (b) The rate constant for the reaction



is $1.22 \times 10^{-6} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ at 575 K and $2.50 \times 10^{-3} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ at 716 K. Estimate the E_a from these data. [PO:1-4, CO:2] (4)

- (c) Sketch the nature of typical plot obtained for conductometric titration using a suitable example for (i) Strong Acid-Weak Base, (ii) Weak Acid - Strong Base. [PO:1-4, CO:1] (4)
4. (a) Sketch kinetic plot for a first-order chemical reaction (i) $[A]$ is plotted as a function of time t for the values of the rate constant k of 0.0125 s^{-1} , 0.0250 s^{-1} , 0.05 s^{-1} and 0.1 s^{-1} . (ii) The same is plotted for $\ln [A]$ versus t . [PO:1-4, CO:2] (4+4=8)
- (b) Write a short note on Michaelis-Menten Catalysis. [PO:1-4, CO:3] (4)
- (c) State any *four* limitation of Arrhenius theory of electrolytic dissociation. [PO:1-4, CO:1] (3)
5. (a) Describe photosensitization and Quenching with two suitable examples. Differentiate photosensitization and Quenching by depicting a suitable reaction. [PO:1-4, CO:4] (4+3=7)
- (b) For the reversible reaction $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$, the mechanism is believed to be
- Step-1: $\text{Cl}_2 + \text{M} \rightleftharpoons 2\text{Cl} + \text{M}$
- Step-2: $\text{Cl} + \text{CO} + \text{M} \rightleftharpoons \text{COCl} + \text{M}$
- Step-3: $\text{COCl} + \text{Cl}_2 \rightarrow \text{COCl}_2 + \text{Cl}$

- (i) Identify the initiation, propagation, and termination step.
- (ii) Assume step 1 & 2 each to be in equilibrium, and find the rate law for the forward reaction?
- (iii) What is the rate law for the reverse reaction?
- [PO:1-4, CO:2] (2+3+3=8)

6. (a) For the decomposition of $(\text{CH}_3)_2\text{O}$ (species A) at 777 K, the time required for $[\text{A}]_0$ to fall $0.69[\text{A}]_0$ as a function of $[\text{A}]_0$ is

$10^3 [\text{A}]_0 / (\text{mol}/\text{dm}^3)$	8.13	6.44	3.10	1.88
0.69/s	590	665	900	1140

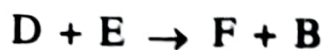
- (i) Find the order of the reaction (justify)
- (ii) Find k_A in $d[\text{A}]/dt = -k_A[\text{A}]^n$.

[PO:1-4, CO:2] (4)

- (b) Find out the rate law for



(k_1 , rate constant for forward reaction; k_2 , rate constant for backward reaction)



(k_3 , rate constant for rate determining step)

[PO:1-4, CO:2] (4)

(c) Explain Moving Boundary methods for determination of Hittorf Number with a suitable example diagrammatically. [PO:1-5, CO:2] (7)

7. Describe the following with any-one/two suitable examples :

(a) Parallel reactions and their rate law.

[PO:1-5, CO:2] (5)

(b) Catalyst Poisoning versus Enzyme inhibition.

[PO:1-4, CO:3] (5)

(c) Walden's rule.

[PO:1-4, CO:1] (5)
