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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

1. (a) What is the EMF of a Concentration Cell consisting of Zn electrodes, one immense 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)

(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 ohm^{-1} cm^2 respectively. The molar conductivity of a centimolar NH_4OH solution at the same temperature is found to be 9 ohm^{-1} 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** $\rightarrow$ **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

$$2HI(g) \rightarrow H_2(g) + I2(g)$$

is 1.22×10^{-6} $dm^3mol^{-1}s^{-1}$ at 575 K and 2.50×10^{-3} $dm^3mol^{-1}s^{-1}$ at 716 K. Estimate the Ea 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 $CO + Cl_2 \rightarrow COCl_2$, the mechanism is believed to be

Step-1: $Cl_2 + M \rightleftharpoons 2Cl + M$

Step-2: $Cl + CO + M \rightleftharpoons COCl + M$

Step-3: $COCl + Cl_2 \rightarrow COCl_2 + Cl$

(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 $(CH_3)_2O$ (species A) at 777 K, the time required for $[A]_0$ to fall $0.69[A]_0$ as a function of $[A]_0$ is

10^3 $[A]_0$ /(mol/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 $d[A]/dt = -k_A[A]^n$.

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

(b) Find out the rate law for

$$A + B \rightleftharpoons C + D$$

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

$$D + E \rightarrow F + B$$

(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)