

NOTE: i) All the questions are compulsory.

ii) Figures to right indicate full marks.

iii) Use of non-programmable calculator / log table is allowed.

Q.1. Attempt any four:

[20]

- Discuss the different recording devices used in the actinometer.
- Give the relationship between Gibb's free energy and Helmholtz free energy.
- State Gibbs – Duhem equation. Derive the equation.
- Write a note on thermal chain reaction.
  - $A \rightarrow B$  1<sup>ST</sup> order reaction  
Rate of reaction is doubled when temperature rises from 27° C to 127° C. Find energy of activation.
- Discuss ozone depletion.
- Derive the Gibb's-Helmholtz equation.
- State : a) the Grotthus Draper law b) The Stark- Einstein law
- Explain the kinetics of complex reactions in detail.

Q.2. Attempt any four:

[20]

- Write a note on relaxation effect in Debye –Huckel theory.
- Discuss the titration of weak acid versus strong base. Explain its graph. Which indicators are suitable for such titrations?
- Explain any two applications of Kohlrausch's Law in detail.
- At 298 K the specific conductance of 0.05 M acetic acid is  $3.678 \times 10^{-2} \text{ Sm}^{-1}$ . The molar ionic conductance of  $\text{H}^+$  ions and  $\text{CH}_3\text{COO}^-$  ions are  $0.03498 \text{ Sm}^2\text{mol}^{-1}$ . Calculate the dissociation constant of acetic acid at 298 K.
- Calculate the molar conductance of  $\text{NH}_4\text{OH}$  at infinite dilution. The molar conductance at infinite dilution of  $\text{NH}_4\text{Cl}$ ,  $\text{NaOH}$  and  $\text{NaCl}$  are 0.01497, 0.02481 and  $0.01265 \text{ Sm}^2\text{mol}^{-1}$ .
  - Discuss limitations of Arrhenius Theory
- Define (i) specific conductance (ii) molar conductance (iii) equivalent conductance (iv) electrolytic conductors and state Debye Huckel Onsagar equation.
- Discuss points of Arrhenius Theory.
- Discuss the titration of weak base versus strong acid. Explain its graph. Which indicators are suitable for such titrations?

Q.3. Attempt any four:

[20]

- What is the function of Complexing agents in solvent extraction? What are the factors to be considered in selection of solvent in solvent extraction?
- State the types of EDTA titrations. Explain 'Direct titration' in detail.
- Explain the selectivity of EDTA titrations with respect to
  - pH
  - Use of masking agents
  - Use of demasking agents ; giving suitable examples.
- Write a short note on Complexones.
- Give the stepwise dissociation of EDTA.
- Derive an equation for the amount of substance unreacted  $W_n$  in solvent extraction using  $V_o \text{ cm}^3$  of organic phase in 'n' titrations.
- The distribution ratio 'D' is 10 in favour of the organic solvent for a particular system. Calculate the % extraction for a volume ratio  $V_o/V_w$  of (i) 1 (ii) 10 (iii) 0.1 (iv) 500 (v) 0.4 for a single extraction.



H). Explain the factors affecting stability of complexes.

[15]

Q.4. Attempt any three:

- A) Explain the concept of energy of activation.
- B) State: 1) Law of mass of action 2) Le- Chatelier-Braun principle.
- C) Explain Kohlrausch's Law in detail giving suitable examples
- D) Discuss neutralization of polyprotic acid with strong base. Explain its graph. Which indicators are suitable for such titrations?
- E) What do you understand by continuous extraction? How is continuous extraction carried out if the extraction is (i) heavier than water (ii) lighter than water.
- F) Define Distribution ratio. Why is Distribution law not valid for benzoic acid. Two extractions with  $20 \text{ cm}^3$  portions of ether removed 89% of solute from  $100 \text{ cm}^3$  of an aqueous solution. Calculate the Distribution ratio

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