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GSE/M-21 **1482**

CHEMISTRY

(Physical Chemistry)

(Theory)

Paper–V (CH-105)

Time : Three Hours] [Maximum Marks : 32

Note : Attempt *five* questions in all, selecting at least *two* questions from each Section. Question No. 1 is compulsory. Use of Log-table and Non-programming calculator is allowed.

Compulsory Question

1. (a) What is the difference between Rate constant and Rate of reaction? 1

(b) Give an example of Zero order reaction. 1

(c) Write units of rate constant for Second order reaction. 1

(d) Write general expression for half-life period of a reaction of nth order. 1

(e) State Ostwald' dilution law. 1

(f) What do you mean by pH of a solution? 1

(g) Write Debye-Huckel-Onsager equation in complete form. What do different symbols signify? 2

SECTION–A

2. (a) What do you mean by second order reactions? Show that for these reactions, the half-life period is inversely proportional to the initial concentration. 2½

(b) The slope of the Arrhenius plot of log k against 1/T for a certain reaction is found to be –7610 K. Calculate the activation energy of the reaction. 2

(c) What is temperature coefficient of a reaction? Why the rate of reaction is doubled for every 10°C rise of temperature? 1½

3. (a) Explain the simple collision theory for unimolecular reactions. 3

(b) For the reaction $A \rightarrow B + C$, the following data were obtained :

Time in seconds	:	0	900	1800
Concentration of A in moles/litre	:	50.6	19.7	7.82

Find the order of the reaction. 2

(c) How is the rate constant of an ionic reaction related to the dielectric constant of the solvent? 1

4. (a) Using 'Transition state theory', derive an expression for the rate constant in terms of the free energy of activation for a reaction. What is the significance of the equation obtained? 3

(b) How does catalyst increase the speed of a reaction? What is its effect on equilibrium constant of the reversible reaction? 2

(c) What type of plot will be obtained for a zero order reaction for :

(i) Concentration versus time.

(ii) Rate of reaction versus concentration? 1

5. (a) For a third order reaction of the type $3A \rightarrow$ Products, derive an expression for the rate constant. 3

(b) Give *two* characteristics of first order reaction. 2

(c) Define 'Half-life-period' of a reaction. 1

SECTION–B

6. (a) What support do colligative properties of strong electrolytes offer in favour of Arrhenius theory of electrolytic dissociation? 2

(b) Define specific conductance, equivalent conductance and molar conductance. What are their units? 3

(c) In a conductometric titration, the solution to be added from burette should be much stronger than the solution taken in conductivity cell. Why? 1

7. (a) What is buffer solution? Explain buffer action with a suitable example for basic buffer. 3

(b) At 18°C, the saturated aqueous solution of $BaSO_4$ was found to have specific conductivity of 3.648×10^{-6} ohm^{-1} cm^{-1}, that of water being 1.250×10^{-6} ohm^{-1} cm^{-1}. Ionic conductance of Ba^{2+} and SO_4^{2-} ions are 55 and 68.3 ohm^{-1} cm^2 $equiv^{-1}$ respectively. Determine the solubility of $BaSO_4$ in water (Atomic weight of Ba = 137). 3

8. (a) How does Kohlrausch' law help in the calculation of equivalent conductance of weak electrolyte at infinite dilution? Explain by giving suitable example. 2

(b) What is the basic principle of conductometric titration? Discuss the titration curve obtained in the conductometric titration of $AgNO_3$ solution with KCl solution. 3

(c) What is the effect of dilution on specific and equivalent conductance? 1

9. (a) Derive Henderson-Hasselbalch equation for the calculation of pH of an acidic buffer mixture. 2

(b) At 293 K, the equivalent conductance at infinite dilution of HCl, CH_3COONa and NaCl solution are 383.5, 78.4 and 102.0 $ohm^{-1}cm^2$ $equiv^{-1}$ respectively. If the equivalent conductance of CH_3COOH at some other dilution is 100.0 $ohm^{-1}cm^2$ $equiv^{-1}$ at 293 K, calculate the degree of dissociation of acetic acid at that dilution. 2

(c) What are the limitations of Arrhenius theory of Ionization? 2