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GSE/M-20 **1482**

CHEMISTRY

(Physical Chemistry)

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. Answer the following in short :

(a) What do you understand by 'Order of reaction? (1)

(b) Write Arrhenius equation giving the effect of temperature on the rate constant of a reaction. What do different symbols signify? (1)

(c) Give an example of Zero ordrer reaction. (1)

(d) What are the units of rate constant for reactions of third order. (1)

(e) Define specific conductance and equivalent conductance. (2)

(f) In conductometric titrations, the solution to be added from burette should be much stronger than the solution taken in titration flask. Why? (2)

SECTION–A

2. (a) How is the rate of the reaction :

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

expressed in terms of different reactants and products? What do +ve and –ve singns signify? (1½)

(b) The rate constant of a reaction increases two-fold with increase in temperature by 10°C. Why? (1½)

(c) 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)

3. (a) What is rate constant? Derive an expression for the rate constant for a second order reaction of the type $2A \rightarrow$ Products. (3)

(b) A first order reaction is 15% complete in 20 minutes. In what time will the reaction be 60% complete? (2)

(c) Show diagrammatically how the rate of zero order reaction varies with concentration of the reactants. (1)

4. (a) What is 'Half-life period' of a reaction ? Show that half-life period of a first-order reaction is independent of the initial concentration. (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) Does the rate of reaction remain constant throughout the reaction? Why or why not? (1)

5. (a) Explain the simple collision theory for unimolecular reactions. (2)

(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) Briefly explain the effect of solvent on the rate of the reaction. (2)

SECTION–B

6. (a) State and explain Ostwald's dilution law. (2)

(b) The equivalent conductivity at infinite dilution of HCl and CH_3COONa are 396 and 78 $ohm^{-1}cm^2$ $equiv^{-1}$ respectively. If the equivalent conductivity of NaCl at infinite dilution is 109 ohm^{-1} cm^2 $equiv^{-1}$, calculate the equivalent conductivity of acetic acid at infinite dilution. (2)

(c) How do specific conductivity and equivalent conductivity vary with dilution and why? (2)

7. (a) Derive Henderson-Hasselbalch equation for the calculation of pH of an acidic buffer mixture. (2½)

(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). (2½)

(c) State Kohlrausch's law. (1)

8. (a) What is the basic principle underyling conductometric titrations? Discuss the titration curve obtained in the conductometric titration of an aqueous solution of HCl with an aqueous solution of NaOH. (3)

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

(c) Solutions A and B have pH equal to 2 and 4 respectively. Which solution is more concentrated and how many times that of the other? (1)

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

(b) What are the limitations of Arrhenius theory of electrolytic dissociation? (2)

(c) Why does the pH of the buffer consisting of acetic acid and sodium acetate not change when a few drops of HCl are added to it? (2)