

Total No. of Printed Pages—8

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(November)

CHEMISTRY

(Major)

Course : 501

(Physical Chemistry—II)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

1. Select the correct answer : 1×5=5

(a) For the reaction $A \rightarrow B$, the rate of the reaction increases by a factor of 1.857 when the concentration of A is increased by 1.5 times. The order of the reaction with respect to A is

(i) 1

(ii) 1.5

(iii) 2

(iv) 2.5

(b) The osmotic pressure of equimolar solution of glucose, sodium chloride and barium chloride will be in the order

(i) $\text{BaCl}_2 > \text{NaCl} > \text{glucose}$

(ii) $\text{BaCl}_2 > \text{glucose} > \text{NaCl}$

(iii) $\text{glucose} > \text{BaCl}_2 > \text{NaCl}$

(iv) $\text{NaCl} > \text{BaCl}_2 > \text{glucose}$

(c) A plot of $\log \frac{x}{m}$ versus $\log p$ for the adsorption of a gas on a solid gives a straight line with slope equal to

(i) n

(ii) $\frac{1}{n}$

(iii) $\log k$

(iv) $-\log k$

(d) The electrolyte which requires maximum concentration to cause coagulation of As_2S_3 sol is

(i) AlCl_3

(ii) MgSO_4

(iii) $\text{K}_3[\text{Fe}(\text{CN})_6]$

(iv) KCl

(e) When solid lead iodide is added to water, the equilibrium concentration of I^- becomes $2.6 \times 10^{-3} M$, the value of K_{sp} for PbI_2 is

(i) 2.2×10^{-9}

(ii) 8.8×10^{-9}

(iii) 1.8×10^{-8}

(iv) 3.5×10^{-8}

2. Answer any *five* questions : 2×5=10

(a) Prove that the half-life period of a first-order reaction is independent of the initial concentration of the reaction.

(b) A buffer solution of pH 9 is to be prepared by mixing NH_4Cl and NH_4OH . Find out the number of moles of NH_4Cl that should be added to one litre of 1.0 M NH_4OH .

(c) How are osmotic pressure measurements utilized for determining molar mass of a non-volatile solute?

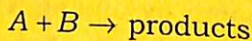
(d) For the decomposition of acetone dicarboxylic acid, $k = 4.92 \times 10^{-5}$ at 273 K and 3.26×10^{-3} at 303 K. Calculate the energy of activation for the reaction.

- (e) Describe the cleansing action of soaps on the basis of micelle formation.
- (f) When a gas is adsorbed by a solid sample, then both the enthalpy and entropy of the system decrease. Explain.
- (g) Mention four important uses of adsorption phenomenon.

UNIT—I

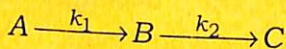
3. Answer any *two* questions : 6×2=12

- (a) Deduce the integrated rate expression of the following second-order reaction :



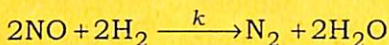
Prove that when either *A* and *B* is taken in excess, then this second-order reaction shows first-order kinetics. 4+2=6

- (b) Give one example of consecutive reaction. Discuss the kinetics of first-order consecutive reaction

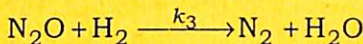
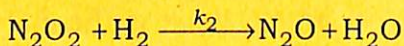
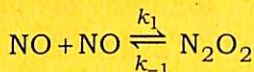


Depict graphically the concentrations of *A*, *B* and *C* with time. 1+4+1=6

(c) (i) For the reaction



the following mechanism is proposed :



Show that the overall rate equation is given by $k[\text{NO}]^2[\text{H}_2]$.

3

(ii) Describe one method for determining the order of a reaction.

2

(iii) Give one example of pseudo-unimolecular reaction.

1

UNIT—II

4. Answer any one question :

5

(a) What is solvent extraction? Show that multistep extraction is more economical than single-step extraction.

1+4=5

- (b) (i) Deduce the relation between osmotic pressure and vapour pressure lowering when a non-volatile solute is dissolved in a solvent. 3
- (ii) A solution of glycol containing 1.821 g per litre has an osmotic pressure of 51.8 cm of mercury at 10 °C. What is the molecular mass of glycol? 2

UNIT—III

5. Answer any *one* question : 7

- (a) (i) What is salt hydrolysis? Prove that the aqueous solution of a salt formed by a strong base and a weak acid is alkaline in nature. 1+3=4
- (ii) Calculate the hydrolytic constant, the degree of hydrolysis and pH of an aqueous 0.01 M sodium acetate solution. (K_a is 1.85×10^{-5} at 298 K) 3
- (b) (i) Establish the relation between solubility and solubility product of calcium phosphate. 2
- (ii) Explain why NiS is precipitated in alkaline medium whereas CdS is precipitated in acidic medium. 2

- (iii) Explain why methyl orange indicator is not used as indicator in the titration between a strong acid with a strong base. 1½
- (iv) Find out the pH of a 0.002 M acetic acid solution if it is 2.3% ionized at this dilution. 1½

UNIT—IV

6. Answer any *one* question : 4
- (a) Derive Langmuir adsorption isotherm and show that Freundlich isotherm is a special case of this isotherm. 3+1=4
- (b) Derive Gibbs' adsorption equation for the adsorption of a solute on the surface of a liquid. 4

UNIT—V

7. Answer any *one* question : 5
- (a) (i) Explain why lyophilic sols are more stable than lyophobic sols. 2
- (ii) For the coagulation of a certain amount of a sol $\text{Al}(\text{NO}_3)_3$ was found to be more effective than NaNO_3 . How would you account for this observation? Also state the rule associated with it. 1½+1½=3

- (b) (i) Write the differences between electrophoresis and electro-osmosis. 2
- (ii) Ferric hydroxide sol is positively charged while arsenious sulphide sol is negatively charged. Explain. 2
- (iii) Define zeta potential. 1

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