

Total No. of Printed Pages—12

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(November)

CHEMISTRY

(Major)

Course : 501

(Physical Chemistry—II)

(New Course)

Full Marks : 48

Pass Marks : 14

Time : 2 hours

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

1. Choose the correct answer : 1×5=5

(a) Half-life of a chemical reaction is inversely proportional to square root of the initial concentration of the reactant. The order of the reaction is

(i) 0

(ii) 1

(iii) $\frac{1}{2}$

(iv) $\frac{3}{2}$

- (b) For the validity of Nernst distribution law
- (i) the two solvents should be mutually immiscible
 - (ii) the solute must have the same molecular state in both the solvents
 - (iii) the solute should be soluble in both the solvents in same extent
 - (iv) the temperature must remain constant
- (c) Partial molar quantities are applicable only for
- (i) extensive variables
 - (ii) intensive variables
 - (iii) both for extensive and intensive variables
 - (iv) state variables
- (d) Which of the following statements is not true for chemisorption?
- (i) Heat of adsorption is high
 - (ii) The process is reversible
 - (iii) Only monolayer is formed
 - (iv) It occurs at high temperature

(e) The power of an ion to cause coagulation is

(i) directly proportional to its valency

(ii) inversely proportional to its valency

(iii) independent of its valency

(iv) independent of charge on the ion

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

(a) Explain how order of a reaction can be obtained from half-life of the reaction. 2

(b) State Henry's law and give one application of it. 1+1=2

(c) State and explain Le Chatelier principle. 2

(d) How does adsorption of gases in solids depend upon surface area of the adsorbent? What do you mean by activated charcoal? 1+1=2

(e) Describe the isolation method for determining the order of a reaction. 2

(f) $MgCl_2$ is a better coagulant than KCl for As_2S_3 sol. Explain. 2

3. Answer any two questions from the following : 6×2=12

(a) Derive the integrated rate expression for a first-order reaction $A \rightarrow \text{product}$. Write any one characteristic of a first-order reaction. Explain with an example how a first-order reaction in solution can be studied in the laboratory. $2\frac{1}{2}+1+2\frac{1}{2}=6$

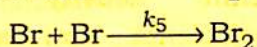
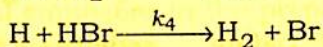
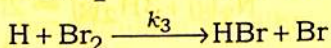
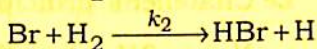
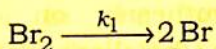
(b) (i) For the consecutive reaction $A \rightarrow B \rightarrow C$, derive an expression for concentration of B. Give the condition for maximum concentration of B. $3+1=4$

(ii) Show that the half-life period of a zero-order reaction is directly proportional to the initial concentration of the reactant. 2

(c) Discuss Lindemann's theory for unimolecular reactions. Show that at high pressure the reaction follows first-order kinetics while at low pressure the reaction follows second-order kinetics. $3+3=6$

(d) What is steady-state approximation? Derive an expression for rate constant

of the following chain reaction using steady-state approximation : 1+5=6



4. Answer any *one* question from the following : 5

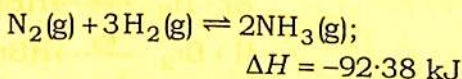
(a) What are colligative properties? Derive a relationship between osmotic pressure and amount of solute thermodynamically. 1+4=5

(b) Define osmotic pressure. Explain how molecular weight of a solute can be determined from osmotic pressure measurement. 1+4=5

5. Answer any *one* question from the following : 7

(a) Define chemical potential. Derive Gibbs-Duhem equation for a two-component system. Discuss the variation of chemical potential with temperature. 1+3+3=7

- (b) (i) Give the condition for maximum yield of ammonia for the following synthesis on the basis of Le Chatelier's principle : 3



- (ii) Define activity and activity coefficients. How is it related to fugacity? 1+1+1=3

- (iii) Write the van't Hoff isotherm showing the variation of equilibrium constant with temperature. 1

6. Answer any one question from the following : 4

- (a) What are adsorption isotherms? Show that Freundlich isotherm is a special case of Langmuir isotherm. 1+3=4

- (b) Derive Gibbs' adsorption equation for adsorption of a solute on the surface of a liquid. 4

7. Answer any one question from the following : 5

- (a) (i) What is zeta potential? How does it explain the stability of colloidal particles? 1+2=3

- (ii) A colloidal solution is not precipitated on the addition of an electrolyte in the presence of gelatin. Explain. 2
- (b) (i) What are emulsions? What is the role of emulsifier in the preparation of an emulsion? $1+1\frac{1}{2}=2\frac{1}{2}$
- (ii) How can cleansing action of soap be explained? $2\frac{1}{2}$

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer : $1 \times 5 = 5$
- (a) According to Lindemann theory a unimolecular reaction is of second-order at
- (i) low pressure
 - (ii) high pressure
 - (iii) low temperature
 - (iv) high temperature

(Turn Over)

(b) Which of the following solutes give maximum lowering of vapour pressure?

(i) NaCl

(ii) $MgCl_2$

(iii) Na_2CO_3

(iv) $Al_2(SO_4)_3$

(c) Phenolphthalein is not a suitable indicator for

(i) strong acid-strong base titration

(ii) weak acid-strong base titration

(iii) strong acid-weak base titration

(iv) None of the above

(d) Which of the following statements is not true for chemisorption?

(i) Heat of adsorption is high

(ii) The process is reversible

(iii) Only monolayer is formed

(iv) It occurs at high temperature

(e) For the coagulation of As_2S_3 sol, which of the following ion is much more effective?

(i) Al^{3+}

(ii) Ba^{2+}

(iii) Na^+

(iv) S^{2-}

2. Answer the following questions : $2 \times 5 = 10$

- (a) Mention the conditions for validity of Nernst distribution law.
- (b) Explain rate determining step approximation for reaction mechanism.
- (c) Explain why salt of strong acid and strong base do not undergo hydrolysis.
- (d) State any two differences between physical and chemical adsorption.
- (e) As_2S_3 sol is negatively charged but $\text{Fe}(\text{OH})_3$ sol is positively charged. Explain.

3. Answer any *two* questions from the following : $6 \times 2 = 12$

- (a) (i) Derive an expression for rate constant of a zero-order reaction. Show that half-life of such reactions is directly proportional to the initial concentration of the reactant. Give one example of zero-order reaction. $1\frac{1}{2} + 1\frac{1}{2} + 1 = 4$
- (ii) Explain how activation energy of a reaction can be determined using Arrhenius equation. 2

(b) (i) What are the drawbacks of collision theory? Write Eyring equation. Compare this equation with Arrhenius equation. $2+1+1=4$

(ii) A first-order reaction is 40% completed in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete? $1+1=2$

(c) What are chain reactions? Discuss the kinetics of a chain reaction. What do you mean by explosion limit in chain reaction? $1+3+2=6$

4. Answer any *one* question from the following : 5

(a) (i) State and explain Henry's law. Mention one of its limitations. $2+1=3$

(ii) When benzoic acid is distributed between benzene and water, benzoic acid get dimerize in benzene. Deduce the correct expression for distribution coefficient for such distribution. 2

(b) What are colligative properties? Derive an expression relating osmotic pressure and amount of solute thermodynamically. $1+4=5$

5. Answer any *one* question from the following : 7

(a) (i) Give the exact treatment for ionization of a weak monobasic acid. 4

(ii) What are buffer capacity and buffer action? Calculate the pH of a buffer solution obtained by mixing 500 ml 0.01 N CH_3COOH and 500 ml of 0.1 N CH_3COONa . ($\text{p}K_a$ of CH_3COOH is 4.774) 1+1+1=3

(b) (i) What are acid-base indicators? Mention different theories of indicators. Discuss the action of phenolphthalein on the basis of Ostwald's acid-base theory. 1+1+2=4

(ii) Define solubility product. 1

(iii) Explain why Cu^{2+} is precipitated as CuS in acidic medium while Zn^{2+} precipitated as ZnS in alkaline medium. 2

6. Answer any *one* question from the following : 4

(a) What are adsorption isotherms? Discuss the behaviour of Langmuir adsorption isotherm at very high and at very low temperatures. 1+3=4

- (b) (i) Discuss the application of adsorption in chemical analysis. 2
- (ii) Explain the effect of surface area of solid adsorbent in adsorption. 2
7. Answer any *one* question from the following : 5
- (a) (i) Write short notes on any *two* of the following : $2 \times 2 = 4$
1. Gold number
 2. Hardy-Schultz rule
 3. Electrophoresis
 4. Donnan membrane equilibrium
- (ii) Explain why lyophilic colloids are used to stabilize lyophobic colloids. 1
- (b) (i) What are emulsions? Mention different types of emulsions. $1 + 2 = 3$
- (ii) How can cleansing action of soap be explained? 2
