

5 SEM TDC CHM M 1

2014

(November)

CHEMISTRY

(Major)

Course: 501

(Physical Chemistry—II)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

Chem = 501, 503, 504

G = 501

Math = 501, 503, 505, 507

G = 501

Math = 501, 502, 503, 507

G = 501

Zoo = 501, 503, 505, 507

Geo = 501, 503, 505, 507

G = 501

Phy = 501, 502, 505

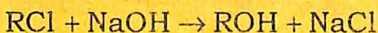
G = 501

The figures in the margin indicate full marks for the questions

Select the correct answer :

1×5=5

(a) The rate law for the reaction



is given by, Rate = $k[\text{RCl}]$. The rate of the reaction will be

- (i) doubled on doubling the concentration of sodium hydroxide
- (ii) halved on reducing the concentration of alkyl halide to one half
- (iii) decreased on increasing the temperature of reaction
- (iv) unaffected by increasing the temperature of the reaction

(b) The depressions in freezing point of 0.1 M aqueous solutions of HCl, CuSO₄ and K₂SO₄ are in the ratio

(i) 1 : 1 : 1

(ii) 1 : 2 : 3

(iii) 1 : 1 : 1.5

(iv) 2 : 4 : 3

(c) Which of the following is true about chemisorption?

(i) It is reversible in nature

(ii) It usually occurs at low temperature

(iii) It is highly specific in nature

(iv) The attractive forces between adsorbate and adsorbent are van der Waals' forces

(d) In the preparation of AgI sol, excess of AgNO₃ is added to potassium iodide solution. The particles of the sol will acquire

(i) negative charge

(ii) positive charge

(iii) no charge

(iv) Unpredictable

(e) The pH of pure water at 50 °C ($K_w = 13 \cdot 26$ at 50 °C) is

(i) 7.0

(ii) 7.13

(iii) 6.0

(iv) 6.63

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

(a) Explain the effect of temperature on the rate of a reaction.

(b) pK_a of acetic acid is 4.74. Find the pH of 0.01 M aqueous solution of sodium acetate.

(c) When a non-volatile solute is dissolved in a solvent, then the vapour pressure of the solution becomes less than the pure solvent. Explain why.

(d) The rate constant of a second-order reaction



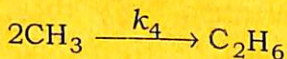
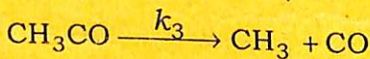
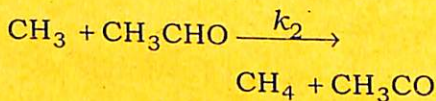
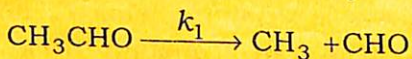
is $10^{-4} \text{ L mol}^{-1} \text{ min}^{-1}$. If the initial concentration of the reactant is $10^{-2} \text{ mol L}^{-1}$, then find the half-life period in minute.

- (e) What are emulsions? What is the role of an emulsifier in the preparation of an emulsion?
- (f) Write four differences between physical adsorption and chemical adsorption.
- (g) 0.5 molar aqueous solution of a weak acid (HX) is 20% ionized. If K_f for water is $1.86 \text{ K kg mol}^{-1}$, then find the lowering in freezing point of the solution.

UNIT—I

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

- (a) (i) The mechanism for the thermal decomposition of acetaldehyde is



Derive an expression for the rate of this decomposition.

4

- (ii) Discuss the limitations of the bimolecular collision theory of gaseous reaction. 2
- (b) (i) Discuss how Lindemann explained mathematically the variation of the order of a unimolecular gas-phase reaction with pressure. 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) (i) What are chain reactions? Give one example of this type of reaction. Explain the occurrence of different explosion limits in a chain reaction. 1+1+2=4
- (ii) Show mathematically how the knowledge of half-life period of a reaction helps in determining the order of a reaction. 2

UNIT—II

4. Answer any one question : 5

- (a) Define molal depression constant. Derive an expression relating the freezing point depression of a solution with the mole fraction of the dissolved

solute. Discuss the utility of the expression in determining the molar mass of a non-volatile solute. $1+3+1=5$

- (b) (i) Explain how the degree of dissociation of an electrolyte may be determined from the measurement of colligative properties of an aqueous solution of the electrolyte. 2
- (ii) KI and sucrose solutions with 0.1 M concentration have osmotic pressures of 0.465 atm and 0.245 atm respectively. Find the van't Hoff factor and degree of dissociation of KI. 3

UNIT—III

5. Answer any *one* question : 7

- (a) (i) Derive an expression for the pH of an aqueous solution of salt of a strong acid and a weak base. 3
- (ii) Explain the acidic or basic nature of aqueous solutions of FeCl_3 and NH_4NO_3 . 2
- (iii) The dissociation constant of a weak acid HA is 1×10^{-4} . Find the value of equilibrium constant for its reaction with strong base BOH. 2

- (b) (i) Derive an expression relating the pH of a buffer solution with the concentration of its components. 3
- (ii) How many moles of sodium acetate must be added to 2 L of 0.1 M acetic acid to give a solution that has a pH equal to 5? Ignore volume change due to the addition of sodium acetate. (pK_a of CH_3COOH is 4.744) 2
- (iii) Write the application of solubility product principle in qualitative analysis by giving one example. 2

UNIT—IV

6. Answer any one question : 4
- (a) (i) When a gas is adsorbed by a solid sample, then both the enthalpy and entropy of the system decrease. Explain. 2
- (ii) Show different types of adsorption isotherms diagrammatically. 2
- (b) (i) Discuss various factors which affect the adsorption of a gas on a solid adsorbent. $2\frac{1}{2}$
- (ii) Discuss the limitations of Langmuir's adsorption isotherm. $1\frac{1}{2}$

UNIT—V

7. Answer any *one* question : 5
- (a) (i) Discuss the origin of charges on colloidal particles. 2
- (ii) Define zeta-potential. 1
- (iii) Discuss the mechanism of coagulation. 2
- (b) (i) State and explain Hardy-Schulze rule. 2
- (ii) What is cmc? Mention two properties of the ionic surfactant solution which undergo abrupt change at cmc. 1+1=2
- (iii) Explain the term 'gold number'. 1

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