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5 SEM TDC CHM M 1 (N/O)

2018

(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. Select the correct answer of the following : 1×5=5

(a) For the reaction, $N_2(g)+3H_2(g)\rightarrow 2NH_3(g)$; $\frac{d[NH_3]}{dt}=4\times10^{-4}$ mol dm^{-3} s^{-1}. The rate of decomposition of N_2 is

(i) 6×10^{-4} mol dm^{-3} s^{-1}

(ii) 8×10^{-4} mol dm^{-3} s^{-1}

(iii) 2×10^{-4} mol dm^{-3} s^{-1}

(iv) 10^{-4} mol dm^{-3} s^{-1}

(b) Which of the following 0·01 m aqueous solutions will have the lowest freezing point?

(i) KNO_3

(ii) $Al(NO_3)_3$

(iii) $C_6H_{12}O_6$

(iv) $Ba(NO_3)_2$

(c) The exothermic formation of ClF_3 is represented by the reaction

$$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g); \quad \Delta_r H = -329 \text{ kJ}$$

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3?

(i) Increasing the temperature

(ii) Removing Cl_2

(iii) Increasing volume of the container

(iv) Adding F_2

(d) Adsorption is accompanied by

(i) decrease in enthalpy and increase in entropy

(ii) increase in enthalpy and increase in entropy

(iii) decrease in enthalpy and decrease in entropy

(iv) increase in enthalpy and decrease in entropy

(Continued)

(e) The gold numbers of A, B, C and D are 0·04, 0·002, 10 and 25 respectively. The protecting powers of A, B, C and D are in the order

(i) $A > B > C > D$

(ii) $B > A > C > D$

(iii) $D > C > B > A$

(iv) $C > A > B > D$

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

(a) Show that a first-order reaction can be studied even when the initial concentration of the reactant is unknown.

(b) A solution contains 6 g urea and 18 g glucose in 1000 cc of water at 27 °C. Calculate the osmotic pressure of the solution.

(c) Show that

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T, n_1, n_2, \cdots} = \overline{V}_i$$

(d) Heat of adsorption is greater for chemisorption than physisorption. Why?

(e) State and explain Hardy-Schulze rule.

(f) Describe how the activation energy of a reaction may be determined.

(g) What is fugacity? Write its physical significance.

UNIT—I

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

(a) Using a suitable mechanism for the reaction $H_2 + Br_2 \rightarrow 2HBr$; and assuming steady-state approximation for H and Br, derive the following rate expression for the formation of HBr

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k' \frac{[HBr]}{[Br_2]}}$$

where k and k' are constants. 6

(b) (i) Show that for a first-order reaction, the time required for 99·9% completion of the reaction is 10 times that required for 50% completion. 2

(ii) Discuss the limitations of the bimolecular collision theory of gaseous reaction. 2

(iii) Give one example of pseudo-unimolecular reaction. 1

(iv) What is steady-state approximation? 1

(Continued)

(c) The following mechanism has been suggested for the decomposition of O_3 :

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

Assuming $k_{-1}[O_2] > k_2[O_3]$, show that the rate of the overall reaction is

$$-\frac{d[O_3]}{dt} = \frac{k[O_3]^2}{[O_2]}$$

What could be concluded from the appearance of $\frac{1}{[O_2]}$ in the rate equation? 5+1=6

UNIT—II

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

(a) (i) State Nernst distribution law. How is the law modified when the solute undergoes association in one of the solvents? 1+3=4

(ii) State Henry's law. 1

(b) Explain the term 'molal elevation constant'. Derive the relation between the boiling point elevation of a solution and the mole fraction of the dissolved solute. How is the expression utilized for determining molar mass of non-volatile solute? 1+3+1=5

UNIT—III

5. Answer any *two* questions of the following : $3\frac{1}{2}\times2=7$

(a) With the help of Le Chatelier's principle, work out the condition which would favour the formation of $SO_3(g)$ in the reaction

$$2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g);$$
$$\Delta_r H=-189{\cdot}4\text{ kJ} \qquad 3\frac{1}{2}$$

(b) Explain the term 'chemical potential'. Derive Gibbs-Duhem equation for two-component system. $1+2\frac{1}{2}=3\frac{1}{2}$

(c) Deduce the relationship between ΔG° and K_c of a reversible reaction. $3\frac{1}{2}$

UNIT—IV

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

(a) Derive Langmuir adsorption isotherm and show that Freundlich isotherm is a special case of this isotherm. $3+1=4$

(b) *(i)* Write four differences between physical adsorption and chemical adsorption. 2

(ii) Give reason why a finely divided substance is more effective as an adsorbent. 2

(Continued)

UNIT—V

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

(a) *(i)* Distinguish between peptization and coagulation of colloids. 2

(ii) Explain why lyophilic sols are more stable than lyophobic sols. 2

(iii) Define zeta potential. 1

(b) Write short notes on the following : $2\frac{1}{2}\times2=5$

(i) Protective action of lyophilic colloid

(ii) Donnan membrane equilibria

(Old Course)

Full Marks : 48
Pass Marks : 19

Time : 3 hours

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(b) Which of the following 0·01 m aqueous solutions will have the lowest freezing point?

(i) KNO_3

(ii) $Al(NO_3)_3$

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(iv) $Ba(NO_3)_2$

(c) A buffer solution is prepared by mixing equal concentration of acid (ionization constant K_a) and a salt. The pH of buffer is

(i) $pK_a + 7$

(ii) $14 - pK_a$

(iii) pK_a

(iv) $pK_a + 1$

(d) Adsorption is accompanied by

(i) decrease in enthalpy and increase in entropy

(ii) increase in enthalpy and increase in entropy

(iii) decrease in enthalpy and decrease in entropy

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(e) The gold numbers of *A*, *B*, *C* and *D* are 0·04, 0·002, 10 and 25 respectively. The protecting powers of *A*, *B*, *C* and *D* are in the order

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

(a) Show that half-life period ($t_{½}$) of a first-order reaction is independent of the initial concentration of the reactant.

(b) A solution contains 6 g urea and 18 g glucose in 1000 cc of water at 27 °C. Calculate the osmotic pressure.

(c) An aqueous solution of CH_3COONa is basic. Why?

(d) Heat of adsorption is greater for chemisorption than physisorption. Why?

(e) State and explain Hardy-Schulze rule.

(f) Describe how the activation energy of a reaction may be determined.

(g) Distinguish between solubility product and ionic product.

UNIT—I

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(b) *(i)* Show that for a first-order reaction, the time required for 99·9% completion of the reaction is 10 times that required for 50% completion. 2

(ii) Discuss the limitations of the bimolecular collision theory of gaseous reaction. 2

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(c) The following mechanism has been suggested for the decomposition of O_3 :

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(Continued)

(b) Explain the term 'molal elevation constant'. Derive the relation between the boiling point elevation of a solution and the mole fraction of the dissolved solute. How is the expression utilized for determining molar mass of non-volatile solute? 1+3+1=5

UNIT—III

5. Answer any *two* questions of the following : 3½×2=7

(a) Derive an expression for the pH of an aqueous solution of a salt of strong acid and weak base. 3½

(b) Define ionic product of water. Explain the effect of temperature on ionic product of water. Show that

$$pK_w = pH + pOH \qquad 1+1+1\frac{1}{2}=3\frac{1}{2}$$

(c) (i) Define buffer capacity. 1

(ii) Derive Henderson equation for a basic buffer solution. 2½

UNIT—IV

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

(a) Derive Langmuir adsorption isotherm and show that Freundlich isotherm is a special case of this isotherm. 3+1=4

(b) *(i)* Write four differences between physical adsorption and chemical adsorption. 2

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