TDC Even Semester Exam., 2019

CHEMISTRY

(Honours)

(4th Semester)

Course No. : CHMH–403

(Physical Chemistry)

Full Marks : 35
Pass Marks : 12

Time : 2 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, taking **one** from each Unit

UNIT—I

1. *(a)* Deduce the relation

$$A_T \qquad W_{\text{max}}$$

What is its significance? 2

(b) Show that—

(i) $\dfrac{T}{P}\,{}_S \qquad \dfrac{V}{S}\,{}_P$

(ii) $\dfrac{A}{T}\,{}_V \qquad \dfrac{G}{T}\,{}_P$ 2+2=4

(c) Give the physical significance of chemical potential. 1

2. *(a)* What is the difference between the Gibbs' and Helmholtz free energies? Explain why these are more convenient parameters for judging the spontaneity of a process. 2+2=4

(b) At –5 °C, the equilibrium vapour pressure of ice is 3·012 mm and that of supercooled liquid water is 3·163 mm. The latent heat of fusion of ice is 5·85 kJ mol ^{1} at –5 °C. Calculate G and S per mole for the transition of

$$H_2O\,(l, \quad 5\ °C) \qquad H_2O\,(s, \quad 5\ °C)$$

1½+1½=3

UNIT—II

3. *(a)* Derive an expression for rate constant for the following second-order reaction :

$$\underset{a}{A} \quad \underset{b}{B} \quad \overset{k_2}{} \quad \underset{0}{P} \quad t \quad 0$$

Show that when one of the reactants is present in large excess, the second-order rate expression becomes a first-order rate expression. Give one example of such a reaction. 3+1+1=5 *(b)* Discuss the essential features of a chain reaction taking a particular example. 2

4. *(a)* Draw a schematic diagram showing energy as a function of reaction coordinate and indicate on the plot the following : 2

(i) Energy of activation for forward and backward reactions

(ii) A thermodynamically controlled process and a kinetically controlled process

(b) "A zero-order reaction cannot be an elementary reaction." Justify or criticize. 2

(c) Derive the expression for the rate constants k_1 and $k_{\;1}$ for the reaction :

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

in which the forward as well as the reverse reactions are both first order. 3

UNIT—III

5. *(a)* Write short notes on the following : 2×2=4

(i) Electrical double layer

(ii) Zeta potential

(b) Explain the term 'critical micelle concentration'. Discuss the cleansing action of soaps and detergents on the basis of micelle formation. 3

6. *(a)* Discuss the effect of temperature and pressure on critical micelle concentration. 1½+1½=3

(b) Discuss the mechanism of flocculation of colloidal particles. 2

(c) "The surface tension of the surfactant molecules is suddenly changed at the cmc." Comment. 2

UNIT—IV

7. *(a)* Discuss the principle of determination of pH using hydrogen electrode. 3

(b) *(i)* Consider the cell

$$\text{Pt, } H_2\text{(1 atm)} \mid \text{NaOH, NaCl} \mid \text{AgCl} \mid \text{Ag}$$

Write the cell reaction and the Nernst equation. 1+1=2

(ii) Draw $\log f$ vs. $\sqrt{u}$ for 1 : 1 electrolyte stating clearly the value of the slope. How does the slope vary with temperature? 1+1=2

8. *(a)* Write a short note on liquid junction potential. 5

(b) Express mean ionic activity of $Al_2(SO_4)_3$ in terms of ionic activities. What is meant by mean ionic activity coefficient? 1+1=2

UNIT—V

9. *(a)* Estimate the mass flux in a gas with uniform density and gradient in temperature. 5

(b) State the difference between dynamic viscosity and kinematic viscosity. 2

10. *(a)* State and explain Fick's first law of diffusion. What are the factors on which diffusion coefficient depends? 2+1=3

(b) Deduce Maxwell-Boltzmann distribution law. 4

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