TDC Odd Semester Exam., 2020
held in July, 2021

CHEMISTRY

(Honours)

(3rd Semester)

Course No. : CHMH–303

(Physical Chemistry—III)

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)* Prove the equivalence of Clausius statement and Kelvin-Planck statement of the second law of thermodynamics. 4

(b) One mole of an ideal gas at 1 atm and 300 K undergoes free expansion adiabatically to double its initial volume. Find S of the gas and comment on your result. 2+1=3

2. *(a)* Derive Clapeyron equation and integrate it to obtain the following relationship, for solid liquid transformation :

$$P \quad \frac{H_{fus}}{V_{fus}} \quad \frac{T}{T_m}$$

T is the increase in melting point corresponding to the increase in pressure, P (point out the assumptions and approximations involved). 3+2=5

(b) What is meant by 'thermodynamic temperature scale'? 2

UNIT—II

3. *(a)* What is 'law of mass action'? Derive an expression for the law of mass action from thermodynamic consideration. 1+3=4

(b) Consider the following equilibrium :

$$A \quad 3B \rightleftharpoons 2C \quad H \quad (\ )\text{ve}$$

Do you think that the following factors will change the equilibrium constant of the reaction? 1×3=3

(i) Increase of concentration of A

(ii) Decrease of temperature

(iii) Presence of a catalyst

4. *(a)* Derive the integrated form of van't Hoff equation

$$\ln K_p \quad \frac{H}{R}\frac{1}{T} \quad \text{constant}$$

and graphically show the variation of K_p with temperature. 3+1=4

(b) At 2000 K, for the reaction, $N_2 \quad O_2 \rightleftharpoons 2NO$ is given by $G^\circ \quad 22000 \quad 2 \quad 5\,T$. Estimate K_p at 2000 K. 3

UNIT—III

5. *(a)* Clearly stating the assumptions and approximations involved, derive thermodynamically a relation between the depression of freezing point and the molal concentration of the solute. 1+4=5

(b) The freezing point of pure benzene is 5·44 °C and that of a solution containing 2·092 gm benzaldehyde in 100 gm benzene is 4·44 °C. Calculate the molecular weight of benzaldehyde, when R_f of benzene is 5·1. 2

6. *(a)* Prove that equimolar quantities of different solutes dissolved in the same volume of solvent exert equal osmotic pressure at the same temperature. 3

(b) *(i)* When benzoic acid is dissolved in benzene, it shows abnormal colligative properties. Comment. 2

(ii) Calculate the van't Hoff factor of a 0·2 molal aqueous solution of $NaNO_3$ which freezes at –0·675 °C. [Given : $R_f \quad 1 \quad 86$ K kg mol ^{1}] 2

UNIT—IV

7. *(a)* The equivalent conductance of an electrolyte at infinite dilution is inversely proportional to the coefficient of viscosity of the medium. Explain. 3

(b) *(i)* State the Debye-Hückel limiting law. Why is it called a limiting law? 1+1=2

(ii) Calculate the mean ionic activity coefficient of NaCl in a solution which is 0·01 *M* with respect to NaCl and 0·02 *M* with respect to $CaCl_2$ ($A \quad 0 \quad 51$). 2

8. *(a)* Explain the idea of ion atmosphere in relation to Debye-Hückel theory of strong electrolytes. 3

(b) *(i)* Magnesium hydroxide is soluble in a solution of ammonium chloride but not in sodium chloride. Comment. 2

(ii) The equivalent conductance of 0·01 N $CaCl_2$ is given as 120·36 ohm ^{1} cm^{2} g eq ^{1}. What will be the value of molar conductance in SI unit? 2

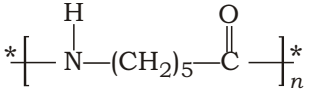
UNIT—V

9. *(a)* Explain addition and condensation polymerization reactions. Discuss the effect of cross-linking and branching on the polymer properties. 2+2=4

(b) Calculate $\overline{M}_n$ when 50% by weight of solute contains a species with molar mass 10^5 and the rest 50% contains species with molar mass 10^6. 3

10. *(a)* What are polymers? Classify them on the basis of suitable examples. 1+2=3

(b) *(i)* What is the average degree of polymerization of the following polymer with M_n 254000? 2



(ii) What is meant by 'Donnan membrane equilibrium'? 2

★ ★ ★