2022
B.A./B.Sc.
Second Semester
CORE – 4
CHEMISTRY
Course Code: CHC 2.21
(Physical Chemistry – II)

Total Mark: 70   *Pass Mark: 28*
Time: 3 hours

Answer <u>five</u> *questions, taking* <u>one</u> *from each unit.*

UNIT–I

1. (a) Differentiate between intensive and extensive properties. Classify the following properties in these two categories: 2+2=4
    (i) Mass   (ii) Time
    (iii) Free energy   (iv) Specific heat
   (b) State and explain the zeroth law of thermodynamics.   3
   (c) One mole of an ideal gas expands isothermally and reversibly from 1 litre to 100 litres at 27°C. Calculate w, q, ΔU and ΔH.   4
   (d) Define molar heat capacity at constant volume C_V and at constant pressure C_P for a gas. Show that $C_P - C_V = R$.   3

2. (a) Distinguish between open, closed and isolated system. Give examples.   3
   (b) Discuss the thermodynamic scale of temperature.   3
   (c) Explain entropy changes in reversible and irreversible processes. Comment on the statement "Entropy of the universe is always increasing."   4
   (d) Calculate the entropy change in the thermodynamic expansion of 2 moles of gas from: 2×2=4
    (i) a volume of 5 litres to 50 litres at 303 K.
    (ii) from a pressure of 10 atmosphere to a pressure of 2 atmosphere at 293 K.

UNIT–II

3. (a) State and explain the third law of thermodynamics.   3

   (b) The heat of combustion of ethyl alcohol is –330 kcal. If the heat of formation of CO_2 (g) and H_2O (l) be –94.3 kcal and –68.5 kcal respectively, calculate the heat of formation of ethyl alcohol.   4

   (c) The heat of combustion of carbon monoxide at constant v and at 17°C is –283.3 kJ. Calculate its heat of combustion at constant pressure. ($R = 8.314$ J degree^{-1} mol^{-1})   4

   (d) Explain the Hess's law of constant heat summation.   3

4. (a) Discuss the variation of heat of reaction with temperature.   5

   (b) Calculate the enthalpy of formation of ammonia from the following bond energy data: 5
(N–H) = 389 kJ/mol
(H–H) = 435 kJ/mol
(N≡N) = 945.36 kJ/mol

   (c) The enthalpies of combustion of C, H and sucrose are –393.5, –286.2 and –5644.2 kJ/mol respectively. Calculate the enthalpy of formation of sucrose($C_{12}H_{22}O_{11}$).   4

UNIT–III

5. (a) Derive an expression for variation of entropy with P, T, V.   5

   (b) Discuss the Maxwell's relationship.   5

   (c) What are partial molar properties? Explain.   2

   (d) Derive the Gibbs-Duhem equation.   2

6. (a) Give the expression of work function with variation in T and V.   4

   (b) Discuss the thermodynamic equation of state.   6

   (c) Write a note on change in thermodynamic functions in mixing of ideal gases.   4

UNIT–IV

7. (a) Explain the fugacity mole fraction relationship for real and ideal gases.   5

(b) The value of K_p at 20°C for the reaction

$2NO(g)+Cl_2(g) \rightleftharpoons 2NOCl(g)$ is 1.9×10^3 atm^{-1}.

Calculate the value of K_C at the same temperature.   3

(c) Write short notes on the following: 2×3=6

(i) Activity coefficient

(ii) Reaction quotient

(iii) Thermodynamic equilibrium constant

8. (a) Derive the relationship between free energy and the equilibrium constant.   5

(b) State Le Chatelier's principle and predict the effect of temperature and pressure on the following reactions: 5

(i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -22.0$ kcal

(ii) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = -43.0$ kcal

(c) Give an expression to show the relationship between K_C and K_P.   4

UNIT–V

9. (a) State and explain the Raoult's law with mathematical expressions.   4

(b) Acetone boils at 56.3°C and a solution of 1.41 grams of an organic solid in 20 grams of acetone boils at 56.86°C. If K for acetone per 100 g is 16.7, calculate the mass of one mole of the organic solid.

    3

(c) Define vapour pressure of a liquid. Give its thermodynamic derivation using chemical potential in terms of molar mass determination of solute.   7

10. (a) What do you understand by association and dissociation of solute molecules in solution? How do they affect colligative property?   5

(b) 0.440 g of a substance dissolved in 22.2 g of benzene lowered the freezing point of benzene by 0.567°C. Calculate the molecular mass of the substance. (K_f=5.12°C mol^{-1})   3

(c) Why do certain solutions show positive deviation from Raoult's law?

    3

(d) Explain how Raoult's law and Henry's law are related in ideal solution.   3