Subject Code : RCCSCH7

Core Course IX : Physical Chemistry I

UNIT 1: TERMODYNAMICS I :

System and surrounding – isolated, closed and open systems - state of the system - Intensive and extensive variables. Thermodynamic processes - reversible and irreversible, isothermal and adiabatic processes - state and path functions - exact and inexact differentials. work of expansion at constant pressure and free expansion.

First law of thermodynamics - statement - definition of internal energy (E), enthalpy (H) and heat capactiiy. Relation between Cp and Cv. calculation of w, q, dE and dH for expansion of ideal and real gases under isothermal and adiabatic conditions of reversible and irreversible processes. Definition of joule - thomson coefficient ($\mu_{J.J}$) - calculation of ($\mu_{J.J}$) for ideal and real gases - Inversion temperature.

Thermochemistry - relation between enthalpy of reaction at constant volume (q_v) and at constant pressure (q_p) - temperature dependence of heat of reaction - Kirchoffs equation - bond energy and its calculation from thermochemical data - Integral and differential heats of solution and dilution.

UNIT 2: THERMODYNAMICS II

Second law of thermo dynamics - need for the law - different statements of the law - Carnot's cycle and efficiency of heat engine - Carnot's theorem - thermodynamic scale of temperature - concept of entropy - definition and physical significance of entropy - entropy as a function of P, V and T - entropy changes during phase changes - entropy of mixing - entropy criterion for spontaneous and equilibrium processes in isolated system - Gibb's free energy (G) and Helmholtz free energy (A) - variation of A and G with P, V and T- Gibb's - Helmholtz equation and its applications - thermodynamic equation of state - Maxwell's relations - ΔA and ΔG as criteria for spontaneity and equilibrium - advantage of ΔG over entropy change.

UNIT 3: THERMODYNAMICS III

Equilibrium constant and free energy change - thermodynamic derivation of law of mass action - equilibrium constants in terms of pressure and concentration - NH_3, PCl_5, $CaCO_3$ - thermodynamic interpretation of Lechatelier's principle (Concentration, temperature, pressure and addition of inert gases.) systems variable composition - partial molar quantities - chemical potential - variation of chemical potential with T, P and X (mole fraction) - Gibb's Duhem equation. van't Hoff's reaction isotherm - van't Hoff's isochore - Clapeyron equation and Clausius –

Clapeyron equation-applications-third law of thermodynamics –Nernst heat theorem-

statement of III law and concept of residual entropy - evaluation of absolute entropy from heat capacity data. Exception to III law (ortho and para hydrogen, CO, N_2O and ice).

UNIT 4: SOLUTIONS

Ideal and non-ideal soultions, methods of expressing concentrations of solutions - mass percentage, volume percentage, normality, molarity, molality, mole fraction. concept of activity and activity coefficients - completely miscible liquid systems - benzene and toluene. Raoult's law and Henry's law. deviation from Raoult's law and Henry's law. Duhem - Margules equation, theory of fractional distillation. azeotropes - HCl - water and ethanol - water systems - partially miscibe liquid systems - phenol - water, triethanolamine - water and nicotine - water systems. lower and upper CSTs - effect of impunities on CST - completely immiscible liquids - principle and applications of steam distillation. Nernst distribution law – derivation.

applications –determination of formula of a complex ($KI + I_2 = KI_3$).solvent extraction-principle and derivation of a general formula of the amount unextracted - dilute solutions: colligative properties, relative lowering of vapour pressure, osmosis, law of osmotic pressure, thermodynamic derivation of elevation of boiling point and depression in freezing point. determination of molecular masses using the above properties. abnormal molecular masses, molecular dissociation - degree of dissociation - molecular association.

UNIT 5: THERMODYNAMICS OF PHASE CHANGES

Definition of terms in the phase rule - derivation and application to one component systems - water and sulphur - super cooling, sublimation. two component systems - solid liquid equilibria, simple eutectic (lead-silver, Bi-Cd), desilverisation of lead - compound formation with congruent melting point. (Mg-Zn) and incongruent melting point (Na-K). solid solutions - (Ag-Au) - fractional crystallisation. freezing mixtures - $FeCl_3$ - H_2O systems, $CuSO_4$-H_2O system.

Book for Reference :

1. Puri B.R., Sharma L.R., Pathania M.S., Principles Of Physical Chemistry, (23rd edition), New Delhi, Shoban Lal, Nagin Chand & Co., (1993)
2. Maron and Prutton,Physical Chemistry, London, Mac Millan.
3. Atkins P.W.,Physical Chemistry, (5th edition) Oxford Uiversity Press. (1994)
4. Castellan G.V., Physical Chemistry, New Delhi, Orient Longmans.