ALLIED COURSE PAPER - II

THERMODYNAMICS, QUILIBRIUM IN CHEMISTRY AND ELECTROCHEMISTRY Marks: 150

It is important to understand the forces which drive the chemical reactions in forward direction and the concept of the interchange of energy in a system. This paper also discusses the use of electrical energy for initiating chemical reactions and also how chemical reactions can be utilized to produce electrical energy. The basic principle used in the formation of cells and battries would also be taken up.

THEORY

Unit 1: Thermodynamics

State of a system, state variables, intensive and extensive variables, concept of heat and work, thermodynamic equilibrium,

First Law of thermodynamics. Calculation of work (w), heat (q), changes in internal energy (ΔU) and enthalpy (ΔH) for expansion or compression of an ideal gas under isothermal conditions for both reversible and irreversible processes. Calculations of w, q, ΔU and ΔH for processes involving changes in physical states. Laws of thermochemistry, enthalpy of combustion, enthalpy of neutralization and integral enthalpies of solution. Calculation of bond energy, bond dissociation energy and resonance energy from thermochemical data. Kirchhoff's equation.

Statements of Second Law of thermodynamics, concept of entropy, Gibbs energy and Helmholtz energy, criteria of spontaneity. Gibbs–Helmholtz equation.

Statement of Third Law of thermodynamics and calculations of absolute entropies of substances.

Unit 2: Chemical Equilibrium

Free energy change in a chemical reaction. Thermodynamic derivation of the law of chemical equilibrium. Distinction between ΔG and ΔG^{o}, Qualitative treatment of Le Chatelier's principle. Relationships between K_p, K_c and K_x.

Unit 3: Ionic Equilibrium

Strong and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water, pH scale. Ionization of weak acids and bases, common ion effect, Salt hydrolysis and simple calculation of hydrolysis constant, degree of hydrolysis and pH for different salts. Buffer solutions, buffer capacity and buffer range. Solubility and solubility product of sparingly soluble salts – applications of solubility product principle.

Unit 4: Electrochemistry

Metallic and electrolytic conductance, conductivity, equivalent and molar conductivity and their variation with dilution for weak and strong electrolytes. Kohlrausch law of independent migration of ions.Concept of transference number. Ionic mobility. Applications of conductance measurements: determination of degree of ionization of weak electrolyte, conductometric titrations (acid-base).
Reversible and irreversible cells. Concept of EMF of a cell, measurement of EMF of a cell. Nernst equation and its importance. Types of electrodes, standard electrode potential, electrochemical series. Thermodynamics of a reversible cell. Calculation of equilibrium constant of a cell reaction from EMF data.

Recommended Texts:

1. Atkins, P. W. & Paula, J. de *Atkin's Physical Chemistry* , Oxford University Press IX Edition 2011.
2. Ball, D. W. *Physical Chemistry* Thomson Press, India 2007.
3. Castellan, G. W. *Physical Chemistry* , Narosa, IV Edition 2004.
4. Mortimer, R. G. *Physical Chemistry* , Elsevier: Noida, UP, III Edition 2009.

PRACTICAL

THERMOCHEMISTRY, POTENTIOMETRIC AND CONDUCTOMETRY

(I) Thermochemistry

1. Determination of heat capacity of a calorimeter for different volumes.
2. Determination of the enthalpy of neutralization of hydrochloric acid with sodium hydroxide.
3. Determination of integral enthalpy of solution of salts (endothermic and exothermic).

(II) pH and potentiometric measurements

4. Preparation of sodium acetate-acetic acid buffer solutions and measurement of their pH.
5. Potentiometric titrations of (i) strong acid *vs* strong base (ii) weak acid *vs* strong base
6. Determination of dissociation constant of a weak acid.

(III) Conductometry

7. Conductometric titrations of (i) strong acid-strong base (ii) weak acid-strong base.

Recommended Texts:

1. Khosla, B.D.; Garg, V.C.; Gulati, A. & Chand, R. *Senior Practical Physical Chemistry*, New Delhi, 1985.
2. Sindhu, P.S. *Practicals in Physical Chemistry,* Macmillan India Ltd. 2005.