UNIVERSITY OF CALICUT

M.Sc. CHEMISTRY (CSS PATTERN) - SEMESTER II

CH2CO8 - ELECTROCHEMISTRY, SOLID STATE CHEMISTRY AND STATISTICAL THERMODYNAMICS (3 Credits, 54h)

Unit 1 : Ionic interaction & Equilibrium electrochemistry (9h)

The nature of electrolytes, Ion activity, Ion-ion and ion-solvent interaction, The electrical potential in the vicinity of an ion, Electrical potential and thermodynamic functions. The Debye-Hückel equation,Limiting and extended forms of the Debye-Hückel equation, Applications of the Debye-Hückel equation for the d*etermination of thermodynamic equilibrium constants* and to calculate the e*ffect of ionic strength on ion reaction rates in solution*

Origin of electrode potentials-half cell potential-standard hydrogen electrode, reference electrodes- electrochemical series, applications- cell potential, Nernst equation for electrode and cell potentials, Nernst equation for potential of hydrogen electrode and oxygen electrode- thermodynamics of electrochemical cells, efficiency of electrochemical cells and comparison with heat engines-primary cells (Zn, MnO_2) and secondary cells (lead acid, Ni-Cd and Ni-MH cells), electrode reactions, potentials and cell voltages, advantages and limitations three types of secondary cells.

-fuel cells; polymer electrolyte fuel cell (PEMFCs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), direct methanol fuel cells, electrode reactions and potentials, cell reactions and cell voltages, advantages and limitations of four types of fuel cells

Unit 2 : Dynamic electrochemistry (9h)

Electrical double layer-electrode kinetics of electrode processes, the Butler-Volmer equation-The relationship between current density and overvoltage, the Tafel equation.

Polarization - electrolytic polarization, dissolution and deposition potentials, concentration polarization; Overvoltage: hydrogen overvoltage and oxygen overvoltage: decomposition potential and overvoltage, individual electrode overvoltages and its determination-metal deposition over voltage and its determination- theories of hydrogen overvoltage, the catalytic theory, the slow discharge theory, the electrochemical theory.

Principles of polarography -dropping mercury electrode, the half wave potential.

UNIT 3: Solid State – I (9h)

Crystal symmetry: Symmetry elements and symmetry operations, mathematical proof for the non-existence of 5-fold axis of symmetry, crystal systems, Bravais lattices and crystal classes, Crystallographic point groups - Schönflies & Herman – Maguin notations, Stereographic projections of the 27 axial point groups, translational symmetry elements & symmetry operations - screw axes and glide planes, introduction to space groups.

Bragg's law and applications, lattice planes and miller indices, *d*-spacing formulae, crystal densities and unit cell contents,

Imperfections in solids - point, line and plane defects, non-stoichiometry.

UNIT 4: Solid State – II (9h)

Electronic structure of solids – free electron theory, band theory & Zone theory, Brillouin zones; Electrical properties - electrical conductivity, Hall effect, dielectric properties, piezo electricity, ferro-electricity and ionic conductivity; Superconductivity -Meisner effect, brief discussion of Cooper theory of superconductivity; Optical properties - photo conductivity, luminescence, colour centers, lasers, refraction & birefringence; Magnetic properties - diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism & ferrimagnetism; Thermal properties - thermal conductivity & specific heat

Unit 5: Statistical Thermodynamics- I (9hrs)

Fundamentals – concept of distribution, thermodynamic probability and most probable distribution, ensembles, statistical mechanics for systems of independent particles and its importance in chemistry, thermodynamic probability & entropy, idea of microstates and mac rostates, statistical weight factor (g), Sterling approximation, Maxwell - Boltzman statistics. The molecular partition function and its relation to the thermodynamic properties, derivation of third law of thermodynamics, equilibrium-constant & equi-partition principle in terms of partition functions, relation between molecular & molar partition functions, factorisation of the molecular partition function into translational, rotational, vibrational and electronic parts, the corresponding contributions to the thermodynamic properties; Evaluation of partition functions and thermodynamic properties for ideal mono -atomic and diatomic gases.

Unit 6: Statistical Thermodynamics- II (9hrs)

Heat capacities of solids - classical and quantum theories, Einstein's theo ry of atomic crystals and Debye's modification.

Quantum Statistics: Bose - Einstein distribution law, Bose-Einstein condensation, application to liquid helium; Fermi - Dirac distribution law, application to electrons in metals; Relationship between Maxwell -Boltzman, Bose-Einstein, and Fermi-Dirac statistics.

References:

For Units 1-4

1. D. R. Crow, Principles and Applications of Electrochemistry, Chapman and Hall London (1979).
2. J.O.M. Bockris and A.K.N. Reddy, *Modern Electrochemistry, Vol. I and II,* Kluwer Academic / Plenum Publishers, 2000.
3. Carl. H. Hamann, A. Hamnett, W.Vielstich, *Electrochemistry 2nd edn*., Wiley-VCH,2007.
4. Philip H Reiger, *Electrochemistry 2nd edn*., Chapman & Hall, 1994.
5. Praveen Tyagi, *Electrochemistry*, Discovery Publishing House, 2006.
6. D.A. McInnes, *The Principles of Electrochemistry,* Dover publications, 1961.
7. L.V. Azaroff, *Introduction to Solids*, McGraw Hill, NY, 1960.
8. A.R. West, *Basic Solid State Chemistry 2nd edn.*,John Wiley & Sons, 1999.
9. A.R. West, *Solid State Chemistry & its Applications,* John Wiley & Sons, 2003 (Reprint 2007).
10. Charles Kittel, *Introduction to Solid State Physics 7th edn*, John Wiley & Sons,2004 (Reprint 2009).
11. Mark Ladd, *Crystal Structures: Lattices & Solids in Stereo view,* Horwood, 1999.
12. Richard Tilley, *Crystals & Crystal Structures,* John Wiley & Sons, 2006.
13. C. Giacovazzo (ed.) *Fundamentals of Crystallography 2nd edn*., Oxford Uty. Press,2002.
14. Werner Massa, *Crystal Structure Determination 2nd edn*., Springer 2004.
15. N.B. Hanna, *Solid state Chemistry*, Prentice Hall

For Units 5 & 6

1. G.S. Rush Brooke, *Statistical mechanics,* Oxford University Press.
2. T.L. Hill, *Introduction to statistical thermodynamics,* Addison Wesley.
3. K. Huary, *Statistical mechanics, Thermodynamics and Kinetics* , John Wiley.

4. O.K.Rice, *Statistical mechanics, Thermodynamics and Kinetics* ,Freeman and Co.

5. F.C. Andrews, *Equilibrium statistical mechanics* , John Wiley and sons, 1963.

6. M.C. Guptha, *Statistical Thermodynamics* , Wiley eastern Ltd., 1993.