St. Xavier's College

CEMA

SYLLABUS

(RESTRUCTURED)

PHYSICAL CHEMISTRY

SEMESTER - I

Thermodynamics I **12 Lectures**

a. Basic concepts and definitions – Applicability of thermodynamics, thermodynamic systems and their classification, Universe, system, surroundings and different types of boundaries
b. Zeroth law and temperature
c. Thermometry
d. Processes, reversible and irreversible process, thermodynamic equilibrium and steady state.
e. Work and heat involved in a thermodynamic process.
f. First law and Concept of internal energy
g. Application to various kinds of processes
h. State and path functions, exact and inexact differentials
i. Change in Internal energy
j. Joule's experiment and consequences
k. Enthalpy
l. Specific heat at constant volume and pressure, relationship between them and their differences
m. Standard states
n. Kirchoff's equations
o. Thermo-chemistry

Chemical Kinetics and Catalysis **12 Lectures**

a. Rate of a reaction
b. Rate laws and rate constants
c. Order and molecularity
d. Integrated rate laws
e. Half life and its significance
f. Determination of order of a reaction
g. Unimolecular reaction and reaction mechanism
h. Multi step reactions
i. Rate determining step
j. Zero and fractional order reactions
k. Steady state approximation and Equilibrium approximation
l. Rate expression for complex reactions
m. Molecular reaction dynamics and concept of reactive encounters
n. Collision theory
o. Energy and steric requirements (Basic qualitative overview)
p. Catalysts and inhibitors
q. Homogeneous catalysis
r. Arrhenius and van't Hoff complexes
s. Generalized acid- base catalysis
t. Identification of homogeneous and heterogeneous catalysis
u. Activation energy diagrams

Kinetic Molecular Theory of gases **12 Lectures**

a. Assumptions
b. Expression for average pressure

c. Arrival to other gas laws
d. Concept of temperature
e. Maxwell distribution of molecular velocity and speed (in 1, 2,and 3 dimensions), their derivation, nature and characteristics
f. Wall collision frequency
g. Calculation of average quantities
h. Most probable speed
i. Energy distribution function, average energy and most probable energy
j. Principle of equipartition of energy
k. Maxwell-Boltzmann Distribution
l. Specific heat of gases
m. Gaseous collisions
n. Mean free path
o. Viscosity of gases
p. Effect of temperature and pressure on viscosity of ideal gases

SEMESTER - II

Thermodynamics II **12 Lectures**

a. Need for the Second Law
b. Carnot's heat engine and refrigerator
c. Statements of the second law and their equivalence
d. Thermodynamic temperature scale
e. Carnot's theorem
f. Entropy as a state function
g. Entropy change of various processes (reversible and irreversible)
h. Clausius inequality
i. Combined first and second law
j. Thermodynamic equation of state
k. Auxiliary state functions – Gibbs and Helmholtz energies
l. Maxwell relations
m. Joule-Thomson experiment
n. Temperature dependence of Gibbs free energy (Gibbs-Helmholtz equations)
o. Gibbs free energy of real gases and fugacity
p. Spontaneity and equilibrium
q. Gibbs-Helmholtz equation
r. Concept of chemical potential of pure substances
s. Partial molar quantities
t. Gibbs-Duhem equation

Real gases **12 Lectures**

a. Deviation from ideal behaviour with reference to Andrew's and Amagat's experiment, Joule (qualitative idea) and Joule-Thompson experiment (qualitative idea).
b. Compressibility factor
c. Concept of attractive and repulsive forces among real gas molecules. Temperature dependence
d. van der Waal's equation of state
e. Critical state, critical pressure, volume and temperature, and their form for a van der Waal's gas.
f. Boyle temperature and their form for a van der Waal's gas.
g. Brief review of other equation of states (Dieterici).
h. Virial equation of state, first and second virial coefficient, their relation to other constants and their significance.
i. Reduced equation of state and the Law of corresponding states
j. Continuity of states
k. Nature of Intermolecular forces

Quantum Mechanics I

a. Black body radiation, Classical Theory of Rayleigh-Jean, Ultraviolet catastrophe and Planck's theory, Thermodynamic viewpoint
b. Photoelectric effect, Einstein's Quanta,
c. Compton effect,
d. Dual nature of electromagnetic radiation
e. de Broglie's hypothesis
f. Wave particle duality

g. Matter wave
h. Concept of wave packets
i. Uncertainty principle, its various mathematical forms and its justifications

SEMESTER - III

Chemical Equilibrium **12 Lectures**

a. Thermodynamics of mixing of ideal gases
b. Conditions of spontaneity and equilibrium in terms of internal energy, Enthalpy, Gibbs and Helmholtz free energy
c. Gibbs free energy change of a mixture of gases
d. Gibbs free energy change of a reaction
e. Definition of molar Gibbs free energy change of a reaction
f. Equilibrium in ideal gas mixture and heterogeneous reaction
g. Concept of Equilibrium constant, concept of activity and concentration
h. Effect of temperature and pressure on equilibrium
i. Thermodynamic derivation of vant Hoff equation
j. Temperature dependence of equilibrium constant and vant Hoff isotherm
k. Various equilibrium constants and their interrelation
l. Temperature dependence of K_c
m. Concept of standard state free energy change of a reaction in pressure and concentration scale
n. Le Chatelier principle
o. Solubility equilibria
p. Salt effect
q. Nernst distribution law and generalised Distribution equilibrium

Electrochemistry I **12 Lectures**

a. Activity, ionic activities, mean ionic activities
b. Activity coefficient and mean ionic activity coefficient
c. Debye-Huckel Limiting law (without derivation)
d. Flow of electrical charge through a solution and its consequences
e. Specific and equivalent conductance
f. Effect of dilution, dielectric constant of solvent, viscosity of solvent and temperature on conductance of strong and weak electrolytes
g. Electrophoretic and Assymetric effect
h. Determination of acidity constant of a weak acid: Ostwald dilution law, ionic product of water, determination of ionic radii
i. Kohlrausch's law
j. Ionic mobilities
k. Transport number and its determination (Hittorf's and moving boundary method)
l. Effect of concentration and temperature on transport number
m. Abnormal transport number
n. Transport number in a mixture of two nonreactive electrolytes

Quantum Mechanics II **12 Lectures**

a. Operators, Linear operators
b. Hermitian operators
c. Postulates of Quantum Mechanics
d. Schrödinger equation
e. Solution of Schrödinger equation as wave function and energy (eigenvalues and eigenfunctions)

f. Commutators and their implication with respect to x, p_x.
g. Expectation values
h. Properties of eigenfunctions
i. Energy quantization
j. Simple systems: 1-D, 2-D, 3-D box (eigenvalues, eigenfunctions, expectation values, quantum numbers, degeneracy, probability density)
k. Simple Harmonic Oscillator: Setting the Schrödinger equation, derivation, eigenvalues and eigenfunctions, zero point energy
l. Tunneling- Basic concepts

SEMESTER - IV

Electrochemistry II **12 Lectures**

a. Electrochemical cells
b. Electrode, electrolyte
c. Electrode reaction and cell reaction
d. Nernst equation
e. Standard electrode potential and application
f. Formal potential and its application
g. Thermodynamic functions from cell potential measurement
h. Concentration cells (with and without transference)
i. Liquid junction potential, it's determination and elimination
j. Application of e.m.f. measurement (related to practical experiments)

Statistical Mechanics and Reaction Rate Theories **12 Lectures**

a. Energy states and levels
b. Micro and macro states
c. Thermodynamic probability
d. Entropy and probability
e. Maxwell-Boltzmann statistics
f. Distribution of molecular states: Boltzmann distribution
g. Application to Maxwell's velocity distribution and barometric distribution
h. Partition function and it's significance
i. Translational, rotational and vibrational partition function and their significance
j. Thermodynamic properties (internal energy, enthalpy, Helmholtz free energy, Gibb's free energy, chemical potential, entropy and value of beta)
k. Reaction coordinate and PES
l. Transition state theory and activated complex
m. Expression of rate constant in terms of partition function, the Eyring equation

Liquid and Solid state **12 Lectures**

a. General features of liquid state (short and long range order/disorder, hole theory)
b. Vapour pressure
c. Young and Laplace equation
d. Surface tension
e. Surface energy
f. Excess pressure
g. Capillarity phenomenon
h. Work of adhesion and cohesion
i. Contact angle
j. Spreading of liquids
k. Dupre equation
l. Temperature dependence of surface tension
m. measurement of surface tension
n. Viscosity of liquids
o. Temperature dependence of viscosity of liquids
p. Poiseuille's equation and Measurement of surface viscosity

Solid state **12 Lectures**

a. Types of solids: crystalline state and it's properties
b. Types of crystals
c. Lattice points
d. Lattice planes
e. Unit lattice
f. Basis
g. Bravais lattice and it's 14 lattice types
h. Miller indices
i. X-ray diffraction
j. Bragg's law
k. Calculation of basis per unit crystal, volume, density per unit cell
l. Diffraction techniques (Qualitative treatment only): single crystal and powder
m. Structure elucidation of NaCl, Kcl, CsCl, diamond, graphite and hcp
q. Specific heat of solids (Dulong Petit law, Einsteins theory, Debye correction qualitatively)

Quantum Mechanics III **12 Lectures**

a. Particle on a Ring
b. Concept of the effective potential
c. Particle on a sphere: coordinate system
d. Form of Schrodinger equation in polar coordinates
e. Form of Schrodinger equation for a two particle system in Cartesian co-ordinates and reduction to one particle system
f. The diatomic rigid rotor: solution of theta and phi part (basic expressions only)
g. Expression of L^2,L_z in polar coordinate, physical significance
h. Concept of effective potential
i. Central force problem and formulation of the Schrodinger equation for hydrogen atom

Colloids, Polymers and Surface Processes **12 Lectures**

a. Colloids: Definition, general properties
b. Optical properties of colloids
c. Rayleigh equation and it's outcomes
d. Qualitative understanding of electrokinetic phenomenon: electrophoresis, electroosmosis, streaming potential and sedimentation potential
e. Electrical double layer, Zeta potential
f. Mechanism of coagulation
g. Schulze-Hardy rule
h. Gold number
i. Surface excess and Gibbs adsorption isotherm
j. Surfactant
k. Critical micellar concentration, it's tensiometric and conductometric determination
l. Micelles
m. Thermodynamics of micellization
n. Liquid crystals
o. Polymer and degree of polymerization
p. Molecular weight of polymer (number and weight average molecular weight)
q. Number distribution and weight distribution function

r. Expression of number average and weight average molecular weight and their interrelation
s. Reaction on surfaces- Physisorption and chemisorption
t. Adsorption isotherms, derivation of Langmuir adsorption isotherma
u. Mechanism of surface reactions
v. Derivation of Langmuir adsorption isotherm

SEMESTER - V

Phase equilibria **12 Lectures**

a. Definition of phase
b. Phase boundaries
c. Components
d. Thermodynamic condition for phase equilibrium
e. Phase rule and its derivation
f. Phase equilibrium for one component system (for example H2O, S, CO2)
g. First and second order phase transition
h. Clapeyron equation
i. Clausius-Clapeyron equation
j. Trouton's rule
k. Liquid vapor equilibrium for two component system
l. Review of the Gibbs-Duhem and the Duhem-Margules equation
m. Constant boiling mixture
n. Critical solution temperature
o. Completely immiscible systems
p. Thermodynamics of mixing of binary solutions
q. Simple eutectic systems

Spectroscopy I **12 Lectures**

a. Spectroscopy- Nature of electromagnetic radiation, range of wavelength
b. Transition moment integral (qualitative idea) and allowed transitions
c. Separation of electronic and nuclear motion – Born-Oppenheimer approximation
d. Signal to noise ratio
e. Width and intensity of transition, line broadening

<u>Rotational spectroscopy</u>

f. Rigid rotor (diatomic only)
g. Selection rule
h. Spectrum: position and intensity of spectral lines.
i. Non-rigid rotor and it's effect on energy levels
j. Selection rule and spectrum
k. Application
l. Isotope effect

Atomic Structure and Atomic Spectra **12 Lectures**

a. Appripriate treatment of Scrodinger equation for Hydrogenic system
b. Solution of radial, theta and phi part (General expression)
c. Shapes of s, p, d orbitals
d. Hydrogenic wave functions up to n=3
e. Atomic orbitals and their energies
f. Spectroscopic transtions and selection rules.
g. Concept of electronic spin
h. Spectra of complex atoms- singlet and triplet states
i. Spin-orbit coupling and fine structure
j. Term-Symbol and LS coupling

SEMESTER -VI

Thermodynamics III **12 Lectures**

a. The Nernst heat theorem
b. Third law of thermodynamics
c. Residual entropy
d. Raoult's law
e. Henry's Law
f. Positive and negative deviation from ideal behaviour
g. Ideal solution and ideally dilute solution
h. Definition and thermodynamic origin of colligative properties
i. Thermodynamic derivation of colligative properties of solution using chemical potential and their interrelationships (lowering of vapour pressure, depression of freezing point, elevation of boiling point and osmotic pressure)
j. Abnormal colligative properties

Spectroscopy II **12 Lectures**

a. Vibration of a diatomic molecule and simple harmonic oscillator
b. Review of Solution of quantum harmonic oscillator (general expression)
c. Selection rule for harmonic oscillator
d. Spectrum
e. Anharmonicity and its effect on energy levels
f. Selection rule for anharmonic oscillator
g. Vibrational spectrum
h. Rotational – vibrational coupling in the limit of Born-Oppenheimer approximation

Raman spectroscopy (Qualitative)

i. Rayleigh and Raman scattering
j. Polarizability ellipsoids
k. Features and condition for Raman activity (for linear and non-linear AB_2 molecule)
l. Rotational and vibrational Raman spectra and its characteristics

Photochemistry **12 Lectures**

a. Potential energy curves for electronic states, Frank-Condon principle
b. Decay of excited states by radiative and non-radiative paths
c. Time scales
d. Fluorescence and phosphorescence
e. Jablonski diagram
Mechanism of relaxation through non-radiative paths (Unimolecular and bimolecular mechanism (colision, energy transfer))
f. Photophysics of the excited state
g. Laws of photochemistry
h. Quantum yield and it's measurement for photochemical processes
i. Photostationary state
j. Photosensitized reactions
k. Photochemistry of Photosynthesis

Sem I	Sem II	Sem III	Sem IV	Sem V	Sem VI
Thermodynamics I	Thermodynamics II	Chemical Equilibrium	Electrochemistry II	Phase Equilibria	Thermodynamics III
Chemical Kinetics AND Catalysis		Electrochemistry I	Statistical Mechanics AND Reaction rate theories		
Kinetic Theory of Gases	Real Gases		Liquids		
	Quantum Mechanics I	Quantum Mechanics II	Quantum Mechanics III	Spectroscopy I	Spectroscopy II
			Colloids, Surface Processes	Atomic Structure and Atomic Spectra	Photochemistry
			Solids		