PHYSICAL CHEMISTRY SYLLABUS

CHEMISTRY HONS.

DEPARTMENT OF CHEMISTRY
ST. XAVIER'S COLLEGE (AUTONOMOUS)
KOLKATA-700 016

Semester – I

UNIT I : Kinetic Molecular Theory of gases
(10-12 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), its 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

UNIT II : Chemical Kinetics I
(10-12 lectures)

o. Rate of a reaction
p. Rate laws and rate constants
q. Order and molecularity
r. Integrated rate laws
s. Half life and its significance
t. Determination of order of a reaction
u. Unimolecular reaction and reaction mechanism
v. Multi step reactions
w. Rate determining step
x. Zero and fractional order reactions
y. Opposing, parallel and consecutive reactions
z. Steady state approximation and Equilibrium approximation
aa. Rate expression for complex reactions
bb. Temperature dependence of rate constant and activation energy

UNIT III : Solids
(8-10 lectures)

cc. Types of solids: crystalline state and it's properties
dd. Types of crystals
ee. Lattice points
ff. Lattice planes
gg. Unit lattice
hh. Basis
ii. Bravais lattice and it's 14 lattice types
jj. Miller indices
kk. X-ray diffraction
ll. Bragg's law
mm. Calculation of basis per unit crystal, volume, density per unit cell
nn. Diffraction techniques (Qualitative treatment only): single crystal and powder
oo. Structure elucidation of NaCl, KCl and CsCl

UNIT IV : Thermodynamics I
(12-14 lectures)

pp. Basic concepts and definitions – Applicability of thermodynamics, thermodynamic systems and their classification, different types of boundary.
qq. Zeroth law and temperature
rr. Thermometry
ss. Processes, reversible and irreversible process, thermodynamic equilibrium and steady state.
tt. Work and heat involved in a thermodynamic process.
uu. First law and Concept of internal energy
vv. Application to various kinds of processes
ww. State and path functions, exact and inexact differentials
xx. Change in Internal energy
yy. Joule's experiment and consequences
zz. Enthalpy
aaa. Specific heat at constant volume and pressure, relationship between them and their differences
bbb. Standard states
ccc. Kirchoff's equations
ddd. Thermo chemistry

CEMA
Semester – II

UNIT I : Real gases
(8-10 lectures)

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

UNIT II : Liquid state
(8-10 lectures)

a. Vapour pressure
b. Young and Laplace equation
c. Surface tension
d. Surface energy
e. Excess pressure
f. Capillary rise
g. Work of adhesion and cohesion
h. Contact angle
i. Spreading of liquids
j. Dupre equation
k. Temperature dependence of surface tension
l. Viscosity of liquids
m. Temperature dependence of viscosity of liquids
n. Measurement of surface tension and viscosity
o. Comparison of viscosity of liquids and gases
p. Poiseuille's equation

UNIT III : Catalysis
(8-10 lectures)

q. Catalysts and inhibitors
r. Homogeneous catalysis
s. Arrhenious and van't Hoff complexes
t. Generalized acid- base catalysis
u. Identification of homogeneous and heterogeneous catalysis
v. Enzyme kinetics: Mechanism, pH and temperature dependence, Michaelis-Menten Equation
w. Activation energy diagrams
x. Reaction on surfaces- Physisorption and chemisorption
y. Adsorption isotherms
z. Mechanism of surface reactions
aa. Unimolecular and bimolecular reactions
bb. Derivation of Langmuir adsorption isotherm and Langmuir-Hinshelwood mechanism

UNIT IV : Thermodynamics II
(14-16 lectures)

cc. Need for the Second Law
dd. Carnot's heat engine and refrigerator
ee. Statements of the second law and their equivalence
ff. Thermodynamic temperature scale
gg. Carnot's theorem
hh. Entropy as a state function
ii. Entropy change of various processes (reversible and irreversible)
jj. Clausius inequality
kk. Combined first and second law
ll. Thermodynamic equation of state
mm. Auxiliary state functions – Gibbs and Helmholtz energies
nn. Maxwell relations
oo. Joule-Thomson experiment
pp. Temperature dependence of Gibbs free energy (Gibbs-Helmholtz equations)
qq. Gibbs free energy of real gases and fugacity
rr. Spontaneity and equilibrium
ss. Gibbs-Helmholtz equation
tt. Concept of chemical potential of pure substances
uu. Partial molar quantities
vv. Gibbs-Duhem equation

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Semester – III

UNIT I : Quantum Mechanics I
(8-10 lectures)

m. Black body radiation, Ultraviolet catastrophe and Planck's theory
n. Particle theory of radiation (Photoelectric effect, Einstein's Quanta, Compton effect, dual nature of electromagnetic radiation)
o. de Broglie's hypothesis
p. Wave particle duality
q. Matter wave
r. Concept of wave packets
s. Uncertainty principle
t. Specific heat of solids (Dulong Petit law, Einsteins theory, Debye correction)

UNIT II : Quantum Mechanics II
(10-12 lectures)

a. Operators, Linear operators
b. Hermitian operators
c. Postulates of Quantum Mechanics, Schrödinger equation
d. Solution of Schrödinger equation as wave function and energy (eigenvalues and eigenfunctions)
e. Commutators and their implication with respect to x, p_x.
f. Expectation values
g. Properties of eigenfunctions
h. Energy quantization
i. Simple systems: 1-D, 2-D, 3-D box (eigenvalues, eigenfunctions, expectation values, quantum numbers, degeneracy, probability density)

UNIT III : Chemical Equilibrium
(12-14 lectures)

u. Thermodynamics of mixing of ideal gases
v. Conditions of spontaneity and equilibrium in terms of internal energy, enthalpy, gibbs and Helmholtz free energy
w. Gibbs free energy change of a mixture of gases
x. Gibbs free energy change of a reaction
y. Definition of molar gibbs free energy change of a reaction
z. Equilibrium in ideal gas mixture and heterogeneous reaction
aa. Concept of Equilibrium constant
bb. Effect of temperature and pressure on equilibrium
cc. Thermodynamic derivation of vant Hoff equation

dd. Temperature dependence of equilibrium constant and vant Hoff isotherm
ee. Various equilibrium constants and their interrelation
ff. Temperature dependence of K_c
gg. Concept of standard state free energy change of a reaction in p and c scale
hh. Le Chatelier principle
ii. Solubility equilibria
jj. Salt effect
kk. Distribution equilibrium and Nernst distribution law

UNIT IV : Electrochemistry and Transport phenomena
(10-12 lectures)

ll. General equation of transport
mm. Relation between flux and driving force
nn. Viscosity of gases
oo. Application to determination of viscosity of fluids and diffusion penomena (Steady and non-steady approach)
pp. Application to flow of electrical charge
qq. Type of conductors
rr. Specific and equivalent conductance
ss. Effect of dilution, dielectric constant of solvent, viscosity of solvent and temperature on molar conductance (of strong and weak electrolytes)
tt. Electrophoretic and Assymetric effect
uu. Application : Determination of acidity constant of a weak acid: Ostwald dilution law
vv. Kohlraush's law
ww. Ionic mobilities
xx. Transport number and its determination (Hittorf's and moving boundary method)
yy. Effect of concentration and temperature on transport number
zz. Abnormal transport number
aaa. Application of transport number

CEMA
Semester – IV

UNIT I : Quantum Mechanics III
(10-12 lectures)

a. Simple Harmonic Oscillator: Setting the Schrödinger equation, eigenvalues and eigenfunctions, zero point energy
b. Tunneling- Basic concepts
c. Particle on a ring and Sphere: solution
d. Concept of the effective potential
e. Convenient co-ordinate systems- introduction
f. Form of Schrodinger equation in polar coordinates
g. Form of Schrodinger equation for a two particle system in Cartesian co-ordinates and reduction to one particle system
h. The diatomic rigid rotor: solution of Theta and phi part (basic expressions only)
i. Expression of L^2,L_z in polar coordinate
j. Central force problem and formulation of the Schrodinger equation

UNIT II : Atomic structure and spectra
(10-12 lectures)

k. Appripriate treatment of Scrodinger equation for Hydrogenic system
l. Solution of radial, theta and phi part (General expression)
m. Shapes of s, p, d orbitals
n. Hydrogenic wave functions up to n=3 (expression only)
o. Atomic orbitals and their energies
p. Spectroscopic transtions and selection rules.
q. Spectra of complex atoms- singlet and triplet states
r. Spin-orbit coupling and fine structure.

UNIT III : Equilibrium electrochemistry
(10-12 lectures)

s. Activity , ionic activities, mean ionic activities
t. Activity coefficient and mean ionic activity coefficient
u. Debye-Huckle Limiting law (without derivation)
v. Electrochemical cells
w. Electrode, electrolyte
x. Electrode reaction and cell reaction
y. Nernst equation
z. Standard electrode potential and application
aa. Formal potential and its application
bb. Thermodynamic functions from cell potential measurement
cc. Concentration cells (with and without transference)

dd. Liquid junction potential, it's determination and elimination
ee. Application of e.m.f. measurement (related to practical experiments

UNIT IV : Statistical Mechanics and transition state theory
(12-14 lectures)

ff. Energy states and levels
gg. Micro and macro states
hh. Thermodynamic probability
ii. Entropy and probability
jj. Maxwell-Boltzmann statistics
kk. Distribution of molecular states: Boltzmann distribution
ll. Application to Maxwell's velocity distribution and barometric distribution
mm. Partition function and it's significance
nn. Vibrational partition function and its use.
oo. Thermodynamic properties (internal energy, enthalpy, Helmholtz free energy, Gibb's free energy, chemical potential, entropy and value of beta)
pp. The Nernst heat theorem
qq. Third law of thermodynamics

CEMA
Semester – V

UNIT I : Phase equilibria
(10-12 lectures)

a. Definition of phase
b. Phase boundaries
c. Components
d. Thermodynamic condition for phase equilibrium
e. Phase rule and it's derivation
f. Phase equilibrium for one component system
g. First and second order phase transition
h. Clapeyron equation
i. Phase diagram of one component system (H_2S, S)
j. Clausius-Clapeyron equation
k. Trouton's rule
l. Liquid vapor equilibrium for two component system
m. Review of the Gibbs-Duhem and the Duhem-Margaules equation
n. Constant boiling mixture
o. Critical solution temperature
p. Completely immiscible systems
q. Thermodynamics of mixing of binary solutions
r. Simple eutectic systems

UNIT II : Colligative properties
(10-12 lectures)

s. Raoult's law
t. Henry's Law
u. Konwoloff's rule
v. Positive and negative deviation from ideal behaviour
w. Ideal solution
x. Ideally dilute solution
y. Definition and thermodynamic origin of colligative properties
z. 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)
aa. Abnormal colligative properties

UNIT III : Colloid, surface and polymer chemistry
(12-14 lectures)

bb. Colloids: Definition, general properties
cc. Optical properties of colloids
dd. Rayleigh equation and it's outcomes
ee. Qqualitative understanding of electrokinetic phenomenon: electrophoresis, electroosmosis, streaming potential and sedimentation potential
ff. Electrical double layer, Zeta potential
gg. Mechanism of coagulation
hh. Schulze-Hardy rule
ii. Gold number
jj. Surface excess and Gibbs adsorption isotherm
kk. Surfactant
ll. Critical micellar concentration, it's tensiometric and conductometric determination
mm. Micelles
nn. Thermodynamics of micellization
oo. Polymer and degree of polymerization
pp. Molecular weight of polymer (number and weight average molecular weight)
qq. Number distribution and weight distribution function
rr. Expression of number average and weight average molecular weight and their interrelation

UNIT IV : Electrical properties of molecules
(8-10 lectures)

ss. Polarizability of atoms and molecules
tt. Dielectric constant and polarization
uu. Molar polarization for polar and non-polar molecules
vv. Clausius-Mosotti and Debye equations (with derivation) and their application
ww. Determination of dipole moment

CEMA
Semester – VI

UNIT I : Spectroscopy I
(10-12 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
i. Non-rigid rotor and it's effect on energy levels
j. Selection rule and spectrum
k. Application
l. Isotope effect on rotational energies

UNIT II : Spectroscopy II
(10-12 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 it's effect on energy levels
f. Selection rule for anharmonic oscillator
g. Vibrational spectrum
h. Vibronic spectroscopy : Rotational – vibronic coupling

<u>Raman spectroscopy (Qualitative)</u>

i. SHO-PR model under Born Oppenheimer limit
j. Rayleigh and Raman scattering
k. Polarizability ellipsoids
l. Features and condition for Raman activity (for linear and non-linear AB_2 molecule)
m. Rotational and vibrational Raman spectra and its characteristics

UNIT III : Photochemistry
(8-10 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. Actinometry
j. Photostationary state
k. Photosensitized reactions

UNIT IV : Chemical Kinetics II
(8-10 lectures)

a. Molecular reaction dynamics and concept of reactive encounters
b. Collision theory
c. Energy and steric requirements
d. Reaction coordinate
e. Ionic reaction and kinetic salt effect
f. Transition state theory and activated complex
g. Expression of rate constant in terms of partition function, the Eyring equation

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CHEMISTRY GENERAL

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GROUP: A (20 marks, each semester)

SEMESTER – I

UNIT I : Kinetic Molecular Theory of Gases

(8-10 lectures)

Kinetic theory of gas - assumptions, derivation of gas pressure, derivation of gas laws from kinetic theory. Maxwell's distribution law of molecular speeds, determination of average quantities. Mean free path and collision frequencies. Heat capacity of gases.

UNIT II : Real Gases & Liquids

(8-10 lectures)

Real gases, deviation from ideality, compressibility factor, van der Waals equation of state, Critical phenomena, intermolecular forces, liquefaction of gases. Physical properties of liquids-vapour pressure, surface tension, viscosity, refractive index and dipole moment.

SEMESTER – II

UNIT III : Chemical Kinetics and Catalysis

(8-10 lectures)

Order and molecularity of reactions, rate laws and rate equations for zero, first and second order reactions: Determination of order of reactions. Arrhenius equation and energy of activation. Homogeneous and heterogeneous catalytic reactions, autocatalytic reactions.

UNIT IV : Photochemistry

(3-4 lectures)

Laws of photochemistry, Lambert – Beer's law, quantum yield, Photosensitised reactions.

UNIT V : Electrolytic conductance

(3-4 lectures)

Specific conductance, equivalent conductance of electrolytic solutions. Influence of temperature, dilution and solvent on conductance of both strong and weak electrolytes.

SEMESTER – III

UNIT I : Thermodynamics I

(10-12 lectures)

Definition of terms, isolated, closed and open systems, intensive and extensive variables, zeroth law, concept of heat and work. First law, internal energy and enthalpy, heat capacities, isothermal and adiabatic processes involving ideal gases, Joule's experiment. Thermochemistry, Kirchoff's equation.

UNIT II : Thermodynamics II

(10-12 lectures)

Heat engine, Carnot's cycle, efficiency. The different statements of the second law, concept of entropy, entropy changes in simple transformations concept of Gibbs free energy, its temperature dependence, criteria for equilibrium and spontaneity of a process.

SEMESTER – IV

UNIT I : Chemical equilibrium

(4-6 lectures)

Derivation of expression of equilibrium constants, temperature dependence of equilibrium constants, effect of inert gases on equilibrium. Some examples from homogeneous and heterogeneous systems.

UNIT II : Ionic equilibrium

(4-6 lectures)

Ionisation of weak acids and bases in aqueous solution, Ostwald's dilution law, ionization constants, ionic product of water, pH, buffers, salt hydrolysis.

UNIT III : Colligative properties

(8-10 lectures)

Raoult's law, relative lowering of vapour pressure, osmosis and osmotic pressure, elevation of boiling point and depression of freezing point of solvents.