CONTENTS

KINETIC THEORY OF GAS 1

1.1	Postulates (Assumption) of kinetic theory; Delete	002
1.2	Consequences of assumptions;	002
1.3	Justification of elastic collision;	003
1.4	Concept of pressure & temperature;	003
1.5	Velocity of molecules;	003
1.6	Derivation of pressure from kinetic theory;	005
1.7	Concept of temperature from kinetic theory;	006
1.8	Pressure from kinetic equation;	007
1.9	Gas laws from kinetic theory;	007
1.10	Pattern of distribution of molecular speed;	008
1.11	Assumptions of molecular speed distribution law;	008
1.12	Maxwell's law of molecular speed distribution;	009
1.13	Characteristic features of speed distribution law (3-dimension);	011
1.14	Average properties;	014
1.15	Wall collision frequency;	017
1.16	Application of Wall collision frequency;	018
1.17	Binary collision frequency(similar gas molecules);	019
1.18	Binary collision frequency(different gas molecules);	020
1.19	Mean free path;	021
1.20	Effect of pressure;	022
1.21	Effect of temperature;	022
1.22	Kinetic energy distribution law(3-dimension);	022
1.23	Fraction of molecules with kinetic energye $\geq E'$;	024

1.24	Average kinetic energy(3-dimension);	025
1.25	Energy distribution function in two dimension;	025
1.26	Fraction of molecules with kinetic energye $\geq E'$ in two dimension;	026
1.27	Degrees of freedom;	026
1.28	Equipartition principle;	028
1.29	Heat capacity from equipartition principle.	029

REAL GAS 2

2.1	Deviation from ideal behaviour;	045
2.2	Causes of deviation;	048
2.3-	van der Waals equation of state;	048
2.4-A)	Volume Correction;	049
2.4-(B)	Pressure Correction;	049
2.5	Validity of van der Waals equation;	050
2.5.1	Andrews curve;	050
2.5.2	PV-isotherm of van der Waals equation;	051
2.6	Critical state of van der Waals equation;	052
2.6.1	Amagat's curve from van der Waals equation;	053
2.7	Compressibility factor;	054
2.8	Reduced equation of state.	056

THERMODYNAMICS 3

3.1	Introduction;	061
3.2	Fundamental terms;	062
3.3	Thermodynamic equilibrium state;	065
3.4	State function;	065
3.5	Mathematical aspect of state function;	066
3.6	Work;	068
3.7	Heat;	070
3.8	Internal energy;	070
3.9	dq and dW are not exact differential;	071
3.10	Zeroth law of thermodynamics;	071
3.11	1^{st} law of thermodynamics;	072

3.12	Importance of thermostat;	074
3.13	Ways of transformation of state;	074
3.14	In isothermal expansion $\|W_{rev}\| > \|W_{irrev}\|$;	078
3.15	Joule's Experiment;	079
3.16	Enthalpy(H); 3.16.1-Enthalpy for an ideal gas;	079
3.17	Heat Capacity(C);	080
3.18.1	Relation between C_p and C_v;	081
3.18.2	$C_p - C_v$ for different cases;	082
3.19	Adiabatic Change.	083

THERMOCHEMISTRY 4

4.1	Introduction;	091
4.2	Laws of thermochemistry;	092
4.3	Hess's law from 1st law;	094
4.4	Heat of formation;	094
4.5	Heat of combustion;	095
4.6	Temperature dependence of Heat of reaction;	095
4.7	Heat of solution;	096
4.8	Heat of neutralisation.	097

THERMODYNAMICS 5

5.1	Need for Second law;	109
5.2	Conversion of heat into work;	110
5.3	Carnot Cycle; 5.4-Conclusion from Carnot Cycle;	112
5.4.1	Refrigerator;	115
5.5	Kelvin-Planck and Clausius statements are equal;	116
5.6	Carnot Theorem;	117
5.7	Clausius Inequality;	118
5.8	Entropy;	119
5.9	Calculation of ΔS For Reversible Processes;	123
5.10	Entropy Change for Irreversible Processes;	127
5.10.1	Entropy and unavailable work;	132
5.10.2	T-S Diagram of Carnot Cycle;	133

5.11 Free energy; 134
5.12 Criteria of spontaneity and equilibrium; 135
5.13 Lowering of Gibbs Free Energy and Entropy of universe; 137
5.14 Properties of G; 137
5.15 Variation of G with Pressure; 138
5.16 Gibbs-Helmholtz Equation; 139
5.17 Application of G-H Equation; 141
5.18 Maxwell Relations; 142
5.19 Heat Capacity Relations; 144
5.20 Joule-Thomson Expansion; 146
5.21 J-T Experiment; Isenthalpic Process; 147
5.22 Derivation of $\mu_{J,T}$. 148

CHEMICAL KINETICS 6

6.1 Introduction; 165
6.2 Rate of reaction; 166
6.3 Rate law and rate constant; 167
6.4 Order and Molecularity; 168
6.5 Integrated rate law for isolated reactions; 169
6.6 Determination of order of reaction; 179
6.7 Opposing Reaction; 181
6.8 Consecutive reaction; 183
6.9 Application of steady-state approximation; 186
6.10 Concept of pre-equilibrium step; 187
6.11 Parallel reaction; 188
6.12 Temperature dependence of reaction; 189
6.13 Thermodynamically controlled and kinetically controlled reactions; 192
6.14 Catalytic reaction; 193
6.14.1 Introduction; 193
6.14.2 Catalyst increases rates of both forward and backward reactions equally; 194
6.14.3 Classification of catalytic reaction; 195
6.14.4 Mechanism of homogeneous catalysis; 195
6.14.5 Pre-equilibrium treatment; 196

6.14.6 Mechanism of acid-base catalysis; 197
6.14.7 Acid Catalysed reaction; 197
6.14.8 Protolytic Mechanism; 198
6.14.9 Prototropic Mechanism; 199
6.14.10 Enzyme Catalysis. 200

THERMODYNAMICS OF SYSTEM OF VARIABLE COMPOSITION 7

7.1 Systems with variable compositions; 215
7.2 Partial molar properties; 216
7.3 Lowering of μ_i; 219
7.4 Chemical potential(μ_i); 220
7.5 Gibbs-Duhem equation; 221
7.6 Condition of spontaneity and equilibrium; 222
7.7 Variation of μ_i with pressure; 222
7.8 Free energy change of mixing; 224
7.9 Thermodynamic criteria of ideal solution; 225
7.10 Fugacity; 226
7.11 Activity and activity coefficient. 227

CHEMICAL EQUILIBRIUM 8

8.1 Introduction; 237
8.2 Variation of Free energy with advancement of reaction; 237
8.3 Equilibrium Constant and $\Delta_r G$; 239
8.4 Different aspects of K_p, K_c, K_x; 241
8.5 Reaction Isotherm; 244
8.6 Van't Hoff Equation; 246
8.7 Effect of pressure on equilibrium composition; 247
8.8 Le Chatelier's principle of mobile equilibrium; 248
8.9 Effect of addition of a constituent; 249
8.10 Effect of addition of inert gas; 250
8.11 Distribution law; 253
8.11.1 Dimerisation of benzoic acid; 254
8.11.2 Solvent Extraction. 256

IONIC EQUILIBRIUM 9

9.1	Ionic Equilibrium;	273
9.2	Ionic Product of water;	275
9.3	True Dissociation Constant of weak acid;	276
9.4	pH;	276
9.5	Ionisation of monoprotic acid;	277
9.6	Hydrolysis of salt;	278
9.7	Buffer Solution;	282
9.8	Mechanism of buffer action;	282
9.9	pH of buffer solution;	283
9.10	Buffer Capacity;	283
9.11	Acid-Base Indicator.	285

LIQUID 10

10.1	Introduction of Surface tension;	295
10.2	Surface of a liquid;	295
10.3	Surface Free Energy;	296
10.4	Surface tension;	297
10.5	Contact angle;	298
10.6	Excess pressure within a curved membrane;	299
10.7	Temperature dependence of surface tension;	300
10.8	Variation of surface tension with concentration;	300
10.9	Determination of surface tension;	302
10.10	Introduction of Viscosity;	307
10.11	Streamline Flow;	308
10.12	Turbulent Flow;	308
10.13	Viscosity;	308
10.14	Viscosity coefficient;	308
10.15	Critical Velocity;	309
10.16	Poisueille's Equation;	310
10.17	Error in the determination of η largely depends on radius;	312
10.18	Temperature dependence of η;	312
10.19	Determination of η.	313

COLLIGATIVE PROPERTIES 11

11.1	Solution;	321
11.2	Ideal Solution;	322
11.3	Raoult's Law;	323
11.4	Colligative Properties;	324
11.5	Elevation of boiling point;	325
11.6	Depression of freezing point;	327
11.7	Osmosis and Osmotic pressure;	330
11.8	Relation between different colligative properties;	331
11.9	Deviation from ideal behaviour;	332
11.10	Van't Hoff factor (i);	333
11.11	Ideal dilute solution;	333
11.12	Measurement of molecular weight from colligative properties.	334

SOLID 12

12.1	Introduction;	347
12.2	Laws of Crystallography;	349
12.3	Crystal system;	354
12.4	Crystal lattice;	355
12.5	Interplanar separation;	356
12.6	X-ray diffraction by crystal;	358
12.7	Diffraction by atoms;	359
12.8	Bragg's Law.	360

CONDUCTANCE 13

13.1	Introduction;	371
13.2	Conduction of electricity by electrolytic solution;	372
13.3	Moving boundary method;	375
13.4	Conductance;	376
13.5	Equivalence conductance;	379
13.6	Measurement of conductivity;	381
13.7	Debye-Huckel-Onsager Theory;	382

13.8 Temperature dependence of ionic conductance; 384
13.9 Variation of specific conductance with dilution; 384
13.10 Variation of equivalent conductance with dilution; 384
13.11 Kohlrausch's law of independent migration of ions; 385
13.12 Ostwald Dilution Law; 386
13.13 Application of conductance measurement; 387
13.14 Ionic strength; 392
13.15 Debye-Huckel Limiting law; 393
13.16 Effect of dielectric constant on activity coefficient. 394

HETEROGENEOUS EQUILIBRIUM 14

14.1 Henry's Law; 409
14.2 Distribution law; 410
14.3 Solvent Extraction; 412
14.4 Phase Rule; 413
14.4.5 One component system; 419
14.5 Two component system; 422
14.5.1 Liquid-liquid system; 422
14.5.2 Liquid-vapour system. 425

QUANTUM CHEMISTRY 15

15.1 Waves and classical wave equation; 439
15.2 Debroglie's Hypothesis; 441
15.3 Particle in a box in the light of Debroglie's Hypothesis; 443
15.4 Matter wave-what it is? 446
15.5 Schrodinger time -independent wave equation; 447
15.6 Well behaved function; 449
15.7 Operator; 450
15.8 Operator in Quantum mechanics; 454
15.9 Postulates of Quantum mechanics; 455
15.10 Free particle moving along axis; 457
15.11 Particle in one dimensional potential box; 458
15.11.1 Wave function for the particle; 460
15.11.2 Plotting of wave function and probability density at different quantum levels. 460

MOLECULAR SPECTROSCOPY 16

16.1	Introduction;	463
16.2	Characterisation of electromagnetic radiation;	464
16.3	Interaction of radiation with molecule;	464
16.4.1	Rigid diatomic molecule and its rotation;	468
16.4.2	Selection rules for rotational spectra;	470
16.4.3	Appearance of rotational spectra;	470
16.5	Rotation-Vibration spectra;	472
16.5.1	Vibration of a diatomic molecule;	472
16.5.2	Selection rule for vibrational spectra;	474
16.5.3	Anharmonic oscillation;	474
16.5.4	Vibration-rotation transition.	477

ELECTROCHEMICAL CELL 17

17.1	Introduction;	487
17.2	Conversion of chaotic dispersal of energy to ordered dispersal;	487
17.3	Reversible cell and irreversible cell;	489
17.4	Principle of determination of E.m.f of cell;	489
17.5	Electrochemical potential;	490
17.6	Electrode potential;	491
17.7	Cell construction, its E.m.f. and Nernst equation;	492
17.8	Types of electrodes and expression of electrode potential;	494
17.9	Standard Hydrogen Electrode and standard electrode potential;	497
17.10	Secondary standard electrodes;	499
17.11	Thermodynamics of electrochemical cells;	499
17.12	Concentration cell with transference;	501
17.13	Concentration cell with transference with cation reversible electrodes;	502
17.14	Liquid junction potential;	504
17.15	Concentration cell without transference;	506
17.16	Application of E.m.f. measurement.	508