

# Contents

<b>1 Mathematics of Thermodynamics .....</b>	<b>1</b>
1.1 Some Properties of Special Functions .....	2
1.2 Functional Dependence .....	2
1.2.1 Concept of a Function .....	3
1.2.2 Separation of Variables .....	4
1.2.3 Power Laws .....	4
1.3 Change of the Arguments .....	4
1.4 Total Differential .....	6
1.5 Chain Rule .....	7
1.5.1 Euler's Chain Relation .....	10
1.6 Substantial Derivative .....	12
1.7 Conversion of Differentials .....	12
1.8 Legendre Transformation .....	13
1.8.1 One-Dimensional Case .....	14
1.8.2 Bijective Mapping .....	14
1.8.3 Taylor Expansion .....	15
1.8.4 Two-Dimensional Transformation .....	16
1.9 Law of Schwarz .....	17
1.10 Pfaffian Forms .....	18
1.11 Differentials of Functions .....	19
1.11.1 The First Differential – Extremes of Functions .....	19
1.11.2 The Second Differential – Type of Extremes of Functions ..	19
1.11.3 The Third Derivative – How the Function Runs Away ..	24
1.11.4 Reciprocal Extremal Problems .....	27
1.12 Euler's Theorem .....	29
1.12.1 Homogeneous Variables .....	29
1.12.2 General Form .....	30
1.12.3 Molar Energy .....	32
1.12.4 Complete Variable Sets .....	33
1.12.5 Thermodynamic Similarity of Transformed Functions ..	34
1.13 Series .....	36
1.13.1 Taylor Series .....	36
1.13.2 Series Reversion .....	37

<b>1.14</b>	<b>Analysis</b>	<b>38</b>
1.14.1	Vectors	38
1.14.2	Matrix	41
1.14.3	Tensor	42
1.14.4	Determinants	42
1.14.5	Systems of Linear Equations	43
1.14.6	Jacobian Determinant	44
1.14.7	Matrix Notation of State Functions	47
1.14.8	Shaw Tables	48
<b>1.15</b>	<b>Coordinate Systems</b>	<b>49</b>
1.15.1	Triangle Coordinates	51
	References	52
<b>2</b>	<b>Foundations of Thermodynamics</b>	<b>55</b>
2.1	Idealization	55
2.2	Energy	56
2.2.1	Extensive and Intensive Quantities	57
2.2.2	Change of Energy	59
2.2.3	Range of Energy	60
2.3	Energy Forms	60
2.3.1	Energy of Compression	61
2.3.2	Thermal Energy	63
2.3.3	Surface Energy	65
2.3.4	Gravitational Energy	66
2.3.5	Kinetic Energy	66
2.3.6	Material Energy	67
2.4	Energy Representation	68
2.5	System	70
2.5.1	Types of Systems	72
2.6	Conservation Laws	74
2.6.1	Heat of Reaction	74
2.6.2	Mass	74
2.6.3	Charge	74
2.6.4	Momentum	75
2.6.5	Volume	75
2.6.6	Surface Area	76
2.6.7	Baryon Number	76
2.6.8	Energy	76
2.6.9	Time Reversal	76
2.7	Process	76
2.8	Transformers	77
2.9	Reservoir	79
2.10	Constraint Makers	79
2.10.1	Rigid Wall	80

2.10.2	Diathermic Border . . . . .	80
2.10.3	Porous Plug . . . . .	80
2.10.4	Semipermeable Membrane . . . . .	81
2.10.5	Electrode . . . . .	81
2.10.6	Interphase Border . . . . .	81
2.10.7	Filter Membrane . . . . .	81
2.10.8	Examples of Constraints . . . . .	81
2.11	Fundamental Equations . . . . .	83
2.12	Partial Quantities . . . . .	85
2.13	Thermodynamic Derivatives . . . . .	86
2.13.1	Potentials . . . . .	86
2.13.2	Capacities . . . . .	86
2.13.3	Susceptibilities . . . . .	88
2.13.4	Mixed Derivatives . . . . .	90
2.14	Thermodynamic Similarity . . . . .	90
2.15	Gibbs – Duhem Equations . . . . .	91
2.16	The Principle of Finite Energy . . . . .	93
2.17	The Minimum Energy Principle . . . . .	94
2.18	Energy of a Quadratic Form . . . . .	95
2.18.1	Energy . . . . .	95
2.18.2	Energy of a Spring . . . . .	95
2.18.3	Constant Energy and Length . . . . .	96
2.18.4	Minimum of Energy . . . . .	97
2.18.5	Spring Coupled with Two Gases . . . . .	99
2.19	Maximum of Entropy . . . . .	101
2.19.1	Entropy Gain in an Ideal Gas . . . . .	102
2.20	Coupled Energy Forms . . . . .	103
2.20.1	Environment Takes Up Volume Energy . . . . .	104
2.21	Dimensionless Relative Variables . . . . .	105
2.22	Stability . . . . .	106
2.23	Phases . . . . .	109
	References . . . . .	109
3	<b>The Laws of Thermodynamics</b> . . . . .	111
3.1	Zeroth Law of Thermodynamics . . . . .	111
3.2	First Law of Thermodynamics . . . . .	112
3.2.1	Conservation of Energy in Mechanical Systems . . . . .	112
3.2.2	Destructive Interference . . . . .	114
3.2.3	Pauli's Solution to Preserve Conservation of Energy . . . . .	114
3.2.4	Formulation of the First Law . . . . .	116
3.3	Second Law of Thermodynamics . . . . .	117
3.3.1	Formulation of Clausius . . . . .	117
3.3.2	Other Formulations . . . . .	118
3.3.3	Clausius' Statements in Detail . . . . .	120
3.3.4	Maximum Entropy – Minimum Energy . . . . .	131

3.4	Third Law of Thermodynamics .....	132
3.4.1	Heat Capacity .....	136
3.4.2	The Principle of Infinite Steps .....	138
3.4.3	Approaching Zero .....	141
	References .....	142
<b>4</b>	<b>Equations of State .....</b>	<b>145</b>
4.1	The Ideal Gas .....	145
4.1.1	Energy of the Ideal Gas from State Functions .....	146
4.1.2	State Functions from Fundamental Forms .....	153
4.1.3	Poisson Equation .....	156
4.2	Internal Pressure .....	159
4.3	The van der Waals Gas .....	161
4.3.1	Critical Point .....	162
4.3.2	Compressibility Factor .....	162
4.3.3	Relation to Internal Pressure .....	163
4.4	Incompressible Body .....	163
4.4.1	Isentropic Incompressible Body .....	163
4.4.2	Isothermal Incompressible Body .....	164
4.4.3	Isentropic Equation of State .....	166
4.4.4	Comparison to Ideal Gas .....	167
4.5	Corresponding States .....	168
	References .....	170
<b>5</b>	<b>Thermodynamic Processes .....</b>	<b>171</b>
5.1	Mechanical Heat Equivalent .....	171
5.1.1	On the Mechanical Equivalent of Heat .....	172
5.2	Buoyancy .....	175
5.2.1	Work in the Field of Gravity .....	175
5.2.2	Force in the Field of Gravity .....	175
5.2.3	Force Acting on a Slow-Moving Mass .....	176
5.2.4	Motion in a Medium .....	176
5.3	Processes in the Electric Field .....	177
5.3.1	Electric Plate Condenser .....	178
5.3.2	Electric Potential .....	180
5.4	Isentropic Process .....	184
5.4.1	Adiabatic Expansion of the Ideal Gas .....	184
5.5	Changes of Energy with Matter .....	185
5.6	Isothermal Process .....	187
5.7	Isodynamic Process .....	188
5.7.1	Gay – Lussac Process .....	188
5.8	Joule Thomson Process .....	189
5.8.1	Enthalpy .....	190
5.8.2	Temperature Drop .....	191
5.8.3	Entropy Gain .....	191
	References .....	193

<b>6 Equilibrium</b>	195
6.1 Energy and Entropy Formulation	195
6.2 Mechanical and Chemical Equilibrium	196
6.3 Isodynamic and Equilibrium Processes	197
6.3.1 Constraints in Equilibrium Processes	197
6.3.2 Coupled Systems	198
6.3.3 Conditions of Equilibrium	199
6.3.4 Equilibrium of Volume Energy	201
6.3.5 Free Adjustable Parameters	202
6.3.6 Approaching Equilibrium	205
6.4 Setting Up the Equations for Equilibrium	209
6.5 Thermodynamic Functions	210
6.5.1 Isolated System	210
6.5.2 Open System	212
6.6 Diffusion Equilibria of Gases	215
6.6.1 One Kind of Gas	215
6.6.2 One Component of Two Permeating	218
6.7 A Glance on the Constraint Equations	222
6.8 Barometric Formula	224
6.8.1 Hydrostatic Derivation	224
6.8.2 Energetic Derivation	225
6.8.3 Laps Rate	227
6.8.4 Stability of Stars	230
6.9 Phase Transition Points	230
6.10 Colligative Properties	234
6.10.1 Ebullioscopy	234
6.10.2 Steam Distillation	240
6.10.3 Vapor Pressure Osmometry	241
6.10.4 Membrane Osmometry	244
6.10.5 Donnan Equilibrium	246
6.11 Isopiestic	247
6.12 Equilibrium of Distillation	247
6.12.1 Ebullioscopic Constant	249
6.13 Unlike Energy Forms	250
6.13.1 Stiff Systems	251
References	252
<b>7 The Phase Rule</b>	255
7.1 A Schematic Phase Diagram	255
7.1.1 Liquid – Gas Curve and Critical Point	256
7.1.2 Solid – Liquid Curve	256
7.1.3 Geometrical Interpretation	257
7.2 The Concept of Freedom	258
7.2.1 Set of Mathematical Equations	258

<b>7.3</b>	<b>Derivation of the Phase Rule</b>	258
7.3.1	Original Derivation	258
7.3.2	Inductive Method	259
<b>7.4</b>	<b>Maximum Number of Phases</b>	261
<b>7.5</b>	<b>Euler's Polyhedral Formula</b>	262
7.5.1	Euler – Poincaré Formula	262
7.5.2	Simplex	263
7.5.3	Inequalities	264
<b>7.6</b>	<b>Polyhedral Formula and Phase Rule</b>	265
7.6.1	Problem of Physical Interpretation of the Analogy	265
7.6.2	Thermodynamic Surfaces	267
	References	268
<b>8</b>	<b>Trouton's Rule</b>	269
8.1	Dimensionless Variables	269
<b>8.2</b>	<b>Phase Equilibrium</b>	271
8.2.1	Generalized van der Waals Equation	271
8.2.2	Maxwell's Criterion	274
8.2.3	Plank – Clausius Equation	275
8.2.4	Redlich Kwong Soave Equation	275
8.2.5	Antoine Equation	275
8.2.6	Master Curve and Trouton's Rule	276
	References	277
<b>9</b>	<b>Thermodynamic Cycles</b>	279
9.1	Thermodynamic Cycles Have Edges	279
9.1.1	The Paddle Wheel	279
9.1.2	Carnot Process	283
9.1.3	The Process of the Energy Transfer	286
9.1.4	Chemodynamic Cycles	287
9.1.5	Gluodynamic Process	290
9.1.6	The Pump	291
9.1.7	Combustion Engines	292
9.1.8	Hysteresis	292
9.1.9	Universal Reversible Cycles	292
	Reference	293
<b>10</b>	<b>Thermodynamic Paradoxes</b>	295
10.1	Gibbs' Paradox	295
10.1.1	Reasons for the Paradox	296
10.1.2	Processes Concerning the Paradox	298
10.1.3	Some Mixing Paradoxes	303
10.2	Maxwell – Boltzmann Paradox	303
10.3	Maxwell's Demon	304

10.4	Loschmidt's Paradox . . . . .	304
10.5	Thermodynamic Inequalities . . . . .	304
10.6	Chemical Vapor Deposition . . . . .	305
10.7	The Thermodynamics of Black Holes . . . . .	305
10.8	The Perpetuum Mobile . . . . .	306
10.9	Negative Heat Capacities . . . . .	307
10.10	Expansion of an Incompressible Body . . . . .	308
10.11	Fixing the Extensive Variables . . . . .	308
10.12	Changes in Chemical Potential and Pressure . . . . .	309
	References . . . . .	310
<b>11</b>	<b>Dimensional Analysis . . . . .</b>	<b>313</b>
11.1	Units . . . . .	313
11.1.1	The Metric System . . . . .	313
11.1.2	The Units in Detail . . . . .	314
11.1.3	The International System . . . . .	317
11.1.4	Derived Units . . . . .	318
11.2	The Minimal Set of Basic Fundamental Units . . . . .	319
11.3	The Nature of a Physical Quantity . . . . .	322
11.3.1	Conversion of Units . . . . .	322
11.3.2	Presentation of Data in Tables and Figures . . . . .	324
11.3.3	$\Pi$ -Theorem . . . . .	325
11.3.4	Basic Principles of Dimensional Analysis . . . . .	325
11.3.5	Period of a Mathematical Pendulum . . . . .	325
11.3.6	Pitch of an Organ Pipe . . . . .	326
11.3.7	Motion of Sphere in a Medium . . . . .	327
11.3.8	Dimensionless Formulation of Kinetic Equations . . . . .	329
11.3.9	Solving Differential Equations . . . . .	332
11.4	Illustrative Examples . . . . .	334
11.4.1	Melting Temperature and Coefficient of Thermal Expansion	334
11.4.2	Boiling Point of Linear Alkanes . . . . .	335
11.4.3	Kelen Tüdös Plot . . . . .	338
11.4.4	Life Expectancy and Body Weight of Mammals . . . . .	338
	References . . . . .	342
<b>12</b>	<b>Generating Functions . . . . .</b>	<b>345</b>
12.1	Computation of Probabilities . . . . .	346
12.2	Computation of the Number of Isomers . . . . .	347
12.2.1	Isomers of Propionaldehyde . . . . .	347
12.2.2	Chlorinated Isomers of Benzene . . . . .	349
12.2.3	Other Examples . . . . .	351
12.3	Calculation of Isotopic Patterns . . . . .	352
12.3.1	The Origin of Isotopic Patterns . . . . .	352
12.3.2	Isotopic Patterns of Molecules . . . . .	353

12.3.3	Average Molar Mass . . . . .	356
12.3.4	Weight Fraction of Atoms . . . . .	356
12.3.5	Mixture of Molecules . . . . .	357
12.3.6	Alternative Abundance Generating Functions . . . . .	359
12.4	Forms of Generating Functions . . . . .	359
12.4.1	Fourier Series . . . . .	361
12.4.2	Z-Transformation . . . . .	362
12.4.3	Linear Transformations . . . . .	363
12.5	Solution of Systems of Differential Equations . . . . .	364
12.6	Statistical Thermodynamics . . . . .	364
12.6.1	Thermodynamic Probabilities . . . . .	365
12.6.2	Partition Function . . . . .	369
12.7	Adsorption Isotherms . . . . .	370
12.7.1	Langmuir Isotherm . . . . .	372
12.7.2	Frumkin Isotherm . . . . .	373
12.7.3	BET Isotherm . . . . .	373
	References . . . . .	376
13	<b>Stoichiometry</b> . . . . .	379
13.1	Half-Reaction Method . . . . .	379
13.2	Balancing by Inspection . . . . .	380
13.3	A Challenging Balance . . . . .	380
13.3.1	Matrix Method . . . . .	381
13.3.2	Equating the Number of Atoms . . . . .	382
13.4	Balancing with Generating Functions . . . . .	382
13.4.1	A Fundamental Example . . . . .	382
13.4.2	System of Linear Equations . . . . .	383
13.4.3	Definition of Pseudoatoms . . . . .	385
13.4.4	Stoichiometrically Unknown Compounds . . . . .	386
13.4.5	Contradictory Equations . . . . .	387
13.4.6	Confounded Equations . . . . .	387
13.4.7	Matrix Notation . . . . .	388
13.4.8	Linear Algebra . . . . .	390
13.4.9	Ions in Equations . . . . .	392
13.4.10	Homologues . . . . .	393
13.4.11	Symbolic Computational Programs . . . . .	393
13.5	Further Examples . . . . .	393
13.5.1	Analytical Chemistry . . . . .	394
13.5.2	Fermentation . . . . .	394
13.5.3	Oxidation Numbers . . . . .	395
13.5.4	Top-down and Bottom-Up Techniques . . . . .	397
	References . . . . .	398
14	<b>Nomenclature</b> . . . . .	401
14.1	Nomenclature Systems . . . . .	401
14.1.1	Hantzsch – Widman System . . . . .	401

14.2	A Nomenclature for Simple Chemicals . . . . .	402
14.3	Machine-Readable Representations . . . . .	403
14.3.1	Wiswesser Line Notation . . . . .	404
14.3.2	SMILES and SMARTS Notation . . . . .	404
14.3.3	IUPAC International Chemical Identifier . . . . .	405
14.4	File Formats . . . . .	405
14.4.1	MOL File . . . . .	405
14.4.2	Z-Matrix . . . . .	406
14.5	Chemical Markup Language . . . . .	407
14.6	Molecules as Graphs . . . . .	407
	References . . . . .	407
<b>15</b>	<b>Symmetry . . . . .</b>	<b>409</b>
15.1	Noether's Symmetry Theorem . . . . .	409
15.2	Group Theory . . . . .	410
15.2.1	Transformation Groups . . . . .	410
15.2.2	Wallpaper Groups . . . . .	411
15.2.3	Point Groups and Symmetry Operations . . . . .	414
15.2.4	Crystallographic Point Groups . . . . .	416
15.3	Stereochemistry . . . . .	417
15.3.1	Structure of Benzene . . . . .	418
15.3.2	Tetrahedral Structure of Methane . . . . .	418
15.3.3	Optical Activity . . . . .	418
15.3.4	Separation of Racemic Compounds . . . . .	422
15.4	Woodward – Hoffmann Rules . . . . .	422
15.5	Chemical Kinetics . . . . .	422
15.6	Dipole Moments . . . . .	424
15.7	Mechanics . . . . .	424
15.7.1	Mechanical Systems . . . . .	424
15.7.2	Quantum Mechanics . . . . .	425
15.8	Thermodynamics . . . . .	425
15.8.1	Entropy . . . . .	425
15.8.2	Statistical Thermodynamics . . . . .	425
15.9	Crystallography . . . . .	426
15.9.1	Snowflakes . . . . .	426
15.10	Biosciences . . . . .	427
15.10.1	Chirality . . . . .	427
	References . . . . .	428
<b>16</b>	<b>Harmony . . . . .</b>	<b>431</b>
16.1	Tools of Harmony . . . . .	432
16.1.1	Means . . . . .	432
16.1.2	Harmonic Analysis . . . . .	432
16.2	Vibrating String . . . . .	434

16.3	Particle in a Box . . . . .	434
16.4	Fourier Transform Techniques . . . . .	435
16.4.1	Fourier Transform Infrared Spectroscopy . . . . .	435
16.4.2	Fourier Transform Mass Spectroscopy . . . . .	436
16.4.3	Diffraction . . . . .	437
16.4.4	Fourier Transform Gas Chromatography . . . . .	438
16.4.5	Time-of-Flight Mass Spectroscopy . . . . .	441
	References . . . . .	442
<b>17</b>	<b>Generating Functions in Polymer Science . . . . .</b>	<b>443</b>
17.1	Polymerization . . . . .	443
17.1.1	An Introductory Example . . . . .	444
17.1.2	Other Examples . . . . .	449
17.2	Polycondensation . . . . .	460
17.2.1	An Introductory Example . . . . .	461
17.2.2	Direct Substitution into the Kinetic Equations . . . . .	467
17.2.3	Cascade Theory and the Equivalency to Dynamic Equilibrium . . . . .	470
17.3	Degradation . . . . .	477
17.3.1	Olefins in Thermodynamic Degradation Equilibrium . . . . .	477
17.3.2	Kinetic Equation . . . . .	478
17.3.3	Generating Function . . . . .	479
17.3.4	Differential Equation for the Generating Function . . . . .	479
17.3.5	Thermodynamic Approach . . . . .	479
17.3.6	Simple Approach . . . . .	480
17.3.7	Generating Function for Free Enthalpy . . . . .	480
17.3.8	Plot of Amounts $\alpha$ -Olefins . . . . .	482
	References . . . . .	484
<b>18</b>	<b>Chemical Kinetics . . . . .</b>	<b>487</b>
18.1	Formal Kinetics . . . . .	487
18.2	Stochastic Nature of Chemical Kinetics . . . . .	491
18.2.1	Simple Reaction with First Order . . . . .	491
18.2.2	Markov Chains . . . . .	491
18.2.3	Opposing Reactions of First Order . . . . .	494
18.3	Mechanical – Chemical Analogy . . . . .	498
18.3.1	Extremal Principles in Mechanics . . . . .	498
18.3.2	The Principle of Least Action in Chemical Kinetics . . . . .	499
18.3.3	Calculation of the Energies . . . . .	500
	References . . . . .	506
<b>19</b>	<b>Transport Phenomena . . . . .</b>	<b>509</b>
19.1	The Equations of Continuity . . . . .	509
19.1.1	Energy Equation . . . . .	511

19.1.2	Entropy Equation . . . . .	511
19.1.3	Diffusion Equation . . . . .	512
19.2	Capillary Flow . . . . .	513
19.2.1	Capillary Flow of Nonmixing Fluids . . . . .	513
19.3	Irreversible Thermodynamics . . . . .	515
19.3.1	Thermokinetic Potential . . . . .	516
	References . . . . .	517
<b>20</b>	<b>Separation Science . . . . .</b>	<b>519</b>
20.1	Particle Motion in a Homogeneous Field . . . . .	519
20.2	Charged Particle in a Quadrupole Field . . . . .	522
20.2.1	Mathieu's Equation . . . . .	522
20.2.2	Mathieu's Equation with a Friction Force . . . . .	523
20.3	The Filter as an Instrument in Analytical Chemistry . . . . .	524
20.3.1	The Ideal Filter . . . . .	524
20.3.2	The Leaching Filter . . . . .	525
20.3.3	Transmission . . . . .	525
20.3.4	Selectivity of the Filter . . . . .	525
20.3.5	Measurement of the Particle Size Distribution . . . . .	527
20.3.6	Continuous Filters – Separation Columns . . . . .	527
20.3.7	Elution Chromatography . . . . .	528
20.3.8	Concentration Signal in the Case of Mixtures . . . . .	529
20.3.9	Infrared Spectroscopy . . . . .	529
20.4	Alternating Regression in GC/MS . . . . .	530
20.4.1	Tung's Equation . . . . .	530
20.4.2	Convolution . . . . .	531
20.4.3	Uncertainty Relation in Analytical Chemistry . . . . .	531
	References . . . . .	532
<b>21</b>	<b>Stochastic Processes . . . . .</b>	<b>533</b>
21.1	Ludo . . . . .	534
21.2	Wiener or Brown Process . . . . .	537
21.2.1	Random Walk . . . . .	537
21.2.2	Generating Function . . . . .	537
21.2.3	Difference Equation . . . . .	538
21.2.4	Differential Equation . . . . .	538
21.3	Generalization of the Formalism . . . . .	539
21.3.1	Stochastic Differential Equations . . . . .	539
21.3.2	Fokker – Planck Equation . . . . .	539
21.4	Stochastic Motion . . . . .	540
21.4.1	The Fokker – Planck Equation for Stochastic Motion . . . . .	540
21.4.2	Further Examples . . . . .	543
21.5	Related Differential Equations . . . . .	544
	References . . . . .	545

<b>22 Structure – Property Relationships</b> .....	547
22.1 Increments .....	547
22.2 Graph Theoretical Numbers .....	548
22.2.1 Morgan Algorithm .....	548
22.2.2 Wiener Index .....	549
References .....	553
<b>23 Factorial Designs</b> .....	555
23.1 Simplex Method .....	555
23.1.1 Two-Level Factorial Experiments .....	556
23.1.2 Setup of the Model .....	558
23.1.3 Encoded Experimental Variables .....	559
23.1.4 Evaluation of a Factorial Experiment .....	562
23.1.5 Testing the Significance .....	563
23.1.6 Incomplete Designs .....	563
23.1.7 Method of Steepest Descent .....	564
23.1.8 Generating Functions .....	566
23.1.9 Relationship to Binary Numbers .....	568
23.2 Monte Carlo Methods .....	571
23.3 General Rules for Setting Up a Design .....	572
23.3.1 Interpretation of the Results .....	573
23.3.2 The Storage Example .....	573
23.4 Time Series .....	573
References .....	576
<b>Author Index</b> .....	577
<b>Subject Index</b> .....	581