Contents

Chapter 1. Definitions and Basic Concepts

1.1 The scope and methods of thermodynamics	
1.2 Systems and units of measurement. Fundamental units	3
1.2.1 Fundamental antis	3
1.2.2 Systems of units	5
	5
1.3 Derived units. Dimensions	9
$1.3.1 Derived units \ldots \ldots$	9
1.3.2 Defining equation; measure equation	11
1.3.5 Units of force, mass, energy, power, and pressure	12
1.3.4 Number of junaumental units	15
1.3.5 Conversion equations, quantity equations	20
1.3.7 Units of pressure	20
1 A The system and its surroundings. Onen and aloged systems	
1.4 The system and its surroundings. Open and closed systems .	22
1.5 Macroscopic description of the state of a system. Classical thermodynamics	25
1.6 Microscopic description of thermodynamic systems. Statistical	
thermodynamics: classical and quantum mechanics	27
1.7 On massing to the limit $\Lambda V > 0$	20
1.7 On passing to the limit $\Delta V \rightarrow 0$	32
1.8 Extensive, intensive, and specific properties	34
List of Symbols for Chapter 1	35
Chapter 2. Temperature and Temperature Scales. Equilibrium	37
2.1. Company removing Adjoint and distinguishing wells	- 77
2.1 General remarks. Adiabatic and diathermal walls	37
2.2 Thermal equilibrium between systems	38
2.3 The Zeroth Law of thermodynamics	40
2.4 Temperature	41
2.5 Empirical temperature scales	43
2.6 The perfect-gas temperature scale	48

Contents

2.7 Relations between the different scales. The unit of temperature	53
2.8 The International, Practical Temperature Scale	56
2.9 Practical temperature measurement	62
2.9.1 Liquid-expansion thermometers	62
2.9.2 Resistance thermometers	65
2.9.3 Thermocouples	69
2.9.4 Radiation inermometers of pyrometers	72
2.10 Additional femarks concerning equinoritant.	74
List of Symbols for Chapter 2	/4
Chapter 3. The Equation of State	76
3.1 General remarks. Criteria for properties	76
3.2 Thermal equations of state	77
3.3 Geometrical representation as a surface	78
3.4 Notation	81
3.5 Geometrical representation of partial derivatives	83
3.6 Equation of state interpreted as a scalar field	86
3.7 Relations between partial derivatives	89
3.7.1 Condition of integrability	90
3.7.2 Change in the role of the variables	95
3.7.3 Change in independent variables. Jacobians.	102
3.8 Fundamental equations of state	102
3.9 The mol. \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots	104
3.10 The universal gas constant. Avogadro's hypothesis	106
3.11 Molar quantities	108
List of Symbols for Chapter 3	108
Chapter 4. Work. Reversible, Irreversible, and Quasistatic Processes	110
4.1 The concept of work in mechanics	110
4.2 Further criteria for properties	114
4.3 The theorems of Stokes and Gauss	116
4.4 The definition of work in thermodynamics	119
4.5 The calculation of work	122
4.5.1 Simple substance expanding behind a piston	122
4.5.2 General compression or expansion	126
4.6 Reversible, irreversible, and quasistatic processes	127
4.7 Quasistatic reversible and irreversible compression and expansion	134

Contents	xiii
4.8 General form of expressions for work in other reversible	
and quasistatic processes	138
4.8.1 Work of a galvanic cell	139
4.8.2 Further remarks concerning reversible work	143
4.9 General remarks about the flow of work	144
4.9.1 Work associated with the deformation of a boundary	144
4.9.2 Shaft work	145
4.9.3 Electrical work	146
List of Symbols for Chapter 4	147
Chapter 5. The First Law of Thermodynamics	
5.1 General and historical remarks	149
5.2 Joule's experiment	150
5.2 Definition of the \mathbf{P}' of \mathbf{I} and \mathbf{I}	150
5.3 Primary formulation of the First Law of thermodynamics	151
	131
5.4 Mathematical formulation of the First Law of thermodynamics for closed systems. Energy of a system	152
5.5 The nature of energy	157
5.6 Justification for the use of the term "energy." Internal energy	107
5.0 Justification for the use of the term energy. Internal energy.	160
5.7 The First Law for nonadiabatic processes in closed systems. The concept of heat	
5.8 Justification of the use of the term "heat"; equivalence	
with intuitive concept of heat	164
5.9 Principle of energy conservation. Isolated system	166
5.10 Conservation of energy in a cycle. Perpetual-motion	
engine of the first kind	169
5.11 Units of heat and energy. Mechanical equivalent of heat	172
5.12 Distinction between the flow of heat and work	175
5.12.1 Solid friction	177
5.13 The reversible transfer of heat. Heat reservoirs	181
5.14 Analysis of some elementary processes. Definition of	
specific heats and enthalpy	183
5.14.1 Constant-volume process. Specific heat at constant volume	184
5.14.2 Constant-pressure process. Enthalpy. Specific	190
neal al constant pressure	189
5.14.4 Processes at constant temperature	191
5.14.5 Adiabatic processes	196
5.14.6 Alternative forms of First Law	200
5.14.7 Quasistatic, irreversible processes	202

xiv	Contents
5.15	The principle of energy conservation and the statistical interpretation of thermal processes
List	of Symbols for Chapter 5
Chapte	er 6. Introduction to the Analysis of Continuous Systems and the First Law of Thermodynamics for Open Systems 205
6.1	Continuous systems
6.2	Examples of continuous systems 205 6.2.1 Column of gas in gravitational field 205 6.2.2 Fluid motion 207 6.2.3 The transfer of heat 209
6.3	The state of a continuous system
6.4	Principle of local state
6.5	The mass and energy of a continuous system
6.6	The First Law of thermodynamics
6.7	The First Law of thermodynamics for a closed, continuous system at rest 213
6.8	Extension of the concept of equilibrium; steady state
6.9	Reversible and irreversible processes in continuous systems
6.10	Formulation of the First Law for open systems
6.11	Steady-state open systems
6.12	Finite entrance velocity and large change in elevation2216.12.1 Perfect-fluid assumption2216.12.2 Viscous fluids and the no-slip condition224
6.13	Significance of the additive constant in the definition of energy
	and enthalpy; heat of a transformation
6.14	Remarks concerning the energy-balance equation. Eulerian and Lagrangian description
6.15	Nonsteady open systems
6.16	Summary of equations
6.17	Examples of simple, open, steady-state systems2436.17.1 Supply line2436.17.2 Heat balance for prime mover2456.17.3 The porous plug experiment. Throttling. Inversion2476.17.4 Flow of fluids. Hydraulic approximation254
6.18	The filling and discharging of rigid vessels 259 6.18.1 Discharge 260

Contents	ΧV
6.18.2 The Washburn experiment 20	61
6.18.3 Filling	64
List of Symbols for Chapter 6 20	65
Chapter 7. Thermodynamic Systems I. The Pure Substance and Simple Mixtures 20	67
7.1 A material point	67
7.2 Incompressible fluid	69
7.3 Perfect gas	73
7.4 Pure substance 2°	75
7.4.1 Phase	76
7.4.2 Evaporation	77
7.4.3 Critical point	82
7.4.4 Melting and sublimation	87
7.4.5 Triple point	89
7.4.6 Sublimation	92
7.4.7 General characteristics of phase transitions;	-
lines of constant quality	93
7.4.8 State surfaces; the P, θ diagram $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 29$	95
7.4.9 The anomalous properties of water substance	98
7.4.10 The problem of single-valuedness	08
7.4.11 Undercooling of vapor and supersaturation of liquid; metastable states	09
7.4.12 The properties of helium	14
7.4.13 Elementary, reversible processes in pure substances	17
7.4.14 The specific heats of a vapor	20
7.5 Mixtures of pure substances; diffusion	22
7.5.1 Measures of composition \ldots \ldots \ldots \ldots \ldots 32	23
7.5.2 Isothermal-isobaric mixing	25
7.5.3 Euler's theorem on homogeneous functions	26
7.5.4 Partial specific quantities of a mixture	27
7.5.5 Partial specific properties and specific properties	
of the pure components	29
756 The Bakhuis-Rooseboom rule	31
7 5 7 The Gibbs-Duhem-Margules relation	32
7.5.8 Ideal mixtures	32
7.5.9 Mixtures of inert perfect gases Dalton's law	34
	- ·
List of Symbols for Chapter 7	51
Chapter 8. Thermodynamic Systems II 3	40
8.1 Surface tension	40
8.1.1 Microscopic origin of surface tension 3	40
8.1.2 Thermal equation of state for surface film.	41

8.1.3 Mechanical equilibrium in droplets and bubbles	342 344
8.1.5 Reversible work	347
8.2 Galvanic cells	2/8
8.2 Calvance cens (,	3/8
8.2.2 Fuel cells	351
8.3 Shearing of a fluid lamina; viscosity	354
8.4 Solid rods stressed in one dimension	357
8.4.1 Stress and strain	357
8.4.2 Elastic range, inelastic behavior, and equation of state 8.4.3 Equation of state for infinitely small strains in the elastic range	362
8.4.4 Work	365
8.4.5 Strain energy in an elastic system	366
8.4.6 The inelastic range	367
8.4.7 Strain-hardening	371
8.4.8 A remark on equilibrium	375
8.4.9 Creep and relaxation	375
8.4.10 Viscoelasticity	376
8.4.11 A remark on rupture	378
8.4.12 Electrical resistance of a wire strained elastically	378
8.5 Systems interacting through fields	380
8.5.1 Criterion for the additivity of field energy	381
8.5.2 Gravitational field	384
8.5.3 Potential energy density	388
8.5.4 Electrostatic field in a vacuum	391
8.5.5 Capacitors	393
8.5.6 Electrostatic field in a dielectric	396
8.5.7 Magnetostatic field in a vacuum	399
8.5.8 Magnetostatic field in a material body	402
A. Diamagnetism	402
B . Paramagnetism	402
C. Ferromagnetism	405
List of Symbols for Chapter 8	406
Chapter 9. The Second Law of Thermodynamics. Elementary Formulation	409
9.1 Introductory remarks	409
9.2 Traditional formulation of the Second Law of thermodynamics .	410
9.3 Logical relation between alternative statements of the Second Law	413
9.4 The Carnot cycle	415
9.5 The reversed Carnot cycle	422
9.6 The efficiency of reversible Carnot engines	423
9.7 The efficiency of irreversible Carnot engines	427

Contents	xvii
9.8 The thermodynamic temperature scale	429
9.9 Evaluation of the efficiency of a reversible Carnot cycle	433
9.10 The Clausius integral. Entropy	437
9.11 The second part of the mathematical formulation of the Second Law.	
The principle of entropy increase	445
9.12 Isentropics of various systems. Entropy diagrams	450
List of Symbols for Chapter 9	456
Chapter 10. The Second Law of Thermodynamics. The Born-Carathéodory Formulation	
10.1 Verbal statement of the Second Law	. 457
10.2 Properties of Pfaffians associated with rotational vector fields	. 460 . 461 . 466 . 469
10.2.4 Ergomedic lines and potential surfaces	. 472
10.2.5 Vector fields associated with nonintegrable Pfaffians	. 4/3
10.2.0 Curatheodory's converse theorem	. 470
10.3 Carnot's theorem	. 4/9
10.3.2 Thermodynamic temperature scale	. 484
10.3.3 Entropy	. 485
10.3.4 Concluding remarks	. 486
10.4 The second part of the Second Law. Principle of entropy increase .	. 487
10.5 Concluding remarks on the Born-Carathéodory formulation of the Second Law	
 10.6 Review of previous verbal statements of the Second Law. Carnot and other reversible cycles. 10.6.1 Clausius' statement of the Second Law of thermodynamics. 	
	491
10.6.2 The Planck-Kelvin statement of the Second Law	492
$10.0.5 Ine Carnoi cycle \dots \dots \dots \dots \dots \dots \dots \dots \dots $	493
10.6.5 Regenerative cycle	498
List of Symbols for Chapter 10	501

Chapter 11. The Calculation of Entropy and Entropy Diagrams

11.1 Incompressible fluids and perfect gases	505
11.1.1 One of Maxwell's reciprocal relations.	506
11.1.2 Dependence of internal energy and enthalpy on pressure	507
11.1.3 Entropy	509

xviii Contents	
11.2 Entropy and Mollier charts	compressible
fluid and a perfect gas	513
11.2.2 The temperature-entropy diagram for a pure	e substance
11.2.3 The Mollier chart for a pure substance	
List of Symbols for Chapter 11	
Chapter 12. Some Consequences of the First Part of the Sec Thermodynamics (Relations between Properties	ond Law of) 531
12.1 Maxwell's relations	531
12.2 The thermal equation of state	
12.3 Relation between the perfect-gas and the	540
thermodynamic temperature scales	
12.4 The use of Jacobians in thermodynamics	544
12.5 The specific heats \ldots \ldots \ldots \ldots \ldots \ldots	
12.6 Internal energy and enthalpy	551
12.7 Isentropic processes	553
12.8 The Joule-Thomson coefficient	555
12.9 The Joule coefficient.	
12.10 Condition for internal energy and enthalpy to be	557
functions of temperature only	
12.11 Simple examples of fundamental equations	
List of Symbols for Chapter 12	
Chapter 13. Some Consequences of the Second Part of the S	econd Law
of Thermodynamics. Entropy Production	563
13.1 General remarks	563
13.2 Engine efficiencies	
13.3 Calorimetric mixing	
13.4 Adiabatic throttling	
13.5 Mixing and diffusion	570
13.5.1 Semipermeable membranes	
13.5.2 Equilibrium across a semipermeable membr	rane 572
13.5.3 Reversible separation	
13.5.4 Entropy of mixing	
13.5.5 Work of reversible separation	578
$13.5.0 Gibbs' paradox. \dots \dots$	
13.5.8 Nonideal mixtures: fugacity and activity	580

Cart

Contents	xix
13.6 Open system	582
13.7 Entropy production during quasistatic irreversible processes	585
13.8 Systems exchanging heat with a single reservoir	590
13.8.1 Maximum work in constant-volume processes	591
13.8.2 Maximum work in a constant-pressure process	595
List of Symbols for Chapter 13	599
INDEX .	603