

# Contents

## 1 Fundamental concepts

1-1	Scope of thermodynamics . . . . .	2
1-2	Thermodynamic systems . . . . .	3
1-3	State of a system. Properties . . . . .	3
1-4	Pressure . . . . .	4
1-5	Thermal equilibrium and temperature. The Zeroth law . . . . .	5
1-6	Empirical and thermodynamic temperature . . . . .	7
1-7	The International Practical Temperature Scale . . . . .	15
1-8	Thermodynamic equilibrium . . . . .	16
1-9	Processes . . . . .	17

## 2 Equations of state

2-1	Equations of state . . . . .	24
2-2	Equation of state of an ideal gas . . . . .	24
2-3	$P$ - $v$ - $T$ surface for an ideal gas . . . . .	26
2-4	Equations of state of real gases . . . . .	28
2-5	$P$ - $v$ - $T$ surfaces for real substances . . . . .	30
2-6	Equations of state of other than $P$ - $v$ - $T$ systems . . . . .	40
2-7	Partial derivatives. Expansivity and compressibility . . . . .	42
2-8	Critical constants of a van der Waals gas . . . . .	49
2-9	Relations between partial derivatives . . . . .	51
2-10	Exact differentials . . . . .	53

## 3 The first law of thermodynamics

3-1	Introduction . . . . .	62
3-2	Work in a volumechange . . . . .	62
3-3	Other forms of work . . . . .	65
3-4	Work depends on the path . . . . .	69
3-5	Configuration work and dissipative work . . . . .	70
3-6	The first law of thermodynamics . . . . .	72
3-7	Internal energy . . . . .	73
3-8	Heat flow . . . . .	74
3-9	Heat flow depends on the path . . . . .	77
3-10	The mechanical equivalent of heat . . . . .	77
3-11	Heat capacity . . . . .	80
3-12	Heats of transformation. Enthalpy . . . . .	83
3-13	General form of the first law . . . . .	86
3-14	Energy equation of steady flow . . . . .	87

<b>4 Some consequences of the first law</b>	
4-1 The energy equation . . . . .	98
4-2 $T$ and $v$ independent . . . . .	98
4-3 $T$ and $P$ independent . . . . .	100
4-4 $P$ and $v$ independent . . . . .	101
4-5 The Gay-Lussac-Joule experiment and the Joule-Thomson <b>experiment</b> . . . . .	102
4-6 Reversible adiabatic processes . . . . .	108
4-7 The Carnot cycle . . . . .	111
4-8 The heat engine and the refrigerator . . . . .	113
<b>5 Entropy and the second law of thermodynamics</b>	
5-1 The second law of thermodynamics . . . . .	122
5-2 Thermodynamic temperature. . . . .	
5-3 Entropy . . . . .	124 127
5-4 Calculations of entropy changes in reversible processes . . . . .	130
5-5 Temperature-entropy diagrams . . . . .	132
5-6 Entropy changes in irreversible processes . . . . .	133
5-7 The principle of increase of entropy . . . . .	135
5-8 The Clausius and Kelvin-Planck statements <b>of the</b> second law . . . . .	138
<b>6 Combined first and second laws</b>	
6-1 Introduction . . . . .	148
6-2 $T$ and $v$ independent . . . . .	
6-3 $T$ and $P$ independent . . . . .	149 153
6-4 $P$ and $v$ independent . . . . .	154
6-5 The $Tds$ equations . . . . .	155
6-6 Properties of a pure substance . . . . .	157
6-7 Properties of an ideal gas . . . . .	159
6-8 Properties of a van der Waals gas . . . . .	160
6-9 Properties of a liquid or solid under hydrostatic pressure . . . . .	163
6-10 The Joule and Joule-Thomson experiments . . . . .	164
6-11 Empirical and thermodynamic temperature . . . . .	166
6-12 Multivariable systems. <b>Carathéodory</b> principle . . . . .	168
<b>7 Thermodynamic potentials</b>	
7-1 The Helmholtz function <b>and the Gibbs function</b> . . . . .	178
7-2 Thermodynamic potentials . . . . .	
7-3 The Maxwell relations . . . . .	181
7-4 Stable and unstable equilibrium . . . . .	186
7-5 Phase transitions . . . . .	190
7-6 The Clausius-Clapeyron equation . . . . .	
7-7 The third law of thermodynamics . . . . .	196
<b>8 Applications of thermodynamics to simple systems</b>	
8-1 Chemical potential . . . . .	206
8-2 Phase equilibrium and the phase rule . . . . .	210
8-3 Dependence of vapor pressure on total pressure . . . . .	216

8-4	Surface tension . . . . .	218
8-5	Vapor pressure of a liquid drop . . . . .	221
8-6	The reversible voltaic cell . . . . .	
8-7	Blackbody radiation . . . . .	225
8-8	Thermodynamics of magnetism . . . . .	228
8-9	Engineering applications . . . . .	233
<b>9</b>	<b>Kinetic theory</b>	
9-1	Introduction . . . . .	250
9-2	Basic assumptions . . . . .	251
9-3	Molecular flux . . . . .	254
9-4	Equation of state of an ideal gas . . . . .	
9-5	Collisions with a moving wall . . . . .	262
9-6	The principle of equipartition of energy . . . . .	
9-7	Classical theory of specific heat capacity . . . . .	267
9-8	Specific heat capacity of a solid . . . . .	271
<b>10</b>	<b>Intermolecular forces. Transport phenomena</b>	
10-1	Intermolecular forces . . . . .	276
10-2	The van der Waals equation of state . . . . .	276
10-3	Collision cross section. Mean free path . . . . .	279
10-4	Coefficient of viscosity . . . . .	286
10-5	Thermal conductivity . . . . .	292
10-6	Diffusion . . . . .	294
10-7	Summary . . . . .	296
<b>11</b>	<b>Statistical thermodynamics</b>	
11-1	Introduction . . . . .	302
11-2	Energy states and energy levels . . . . .	302
11-3	Macrostates and microstates . . . . .	307
11-4	Thermodynamic probability . . . . .	310
11-5	The Bose-Einstein statistics . . . . .	312
11-6	The Fermi-Dirac statistics . . . . .	317
11-7	The Maxwell-Boltzmann statistics . . . . .	320
11-8	The statistical interpretation of entropy . . . . .	323
11-9	The Bose-Einstein distribution function . . . . .	327
11-10	The Fermi-Dirac distribution function . . . . .	331
11-11	The classical distribution function . . . . .	333
11-12	Comparison of distribution functions for indistinguishable particles . . . . .	333
11-13	The Maxwell-Boltzmann distribution function . . . . .	334
11-14	The partition function . . . . .	336
11-15	Thermodynamic properties of a system . . . . .	337
<b>12</b>	<b>Applications of statistics to gases</b>	
12-1	The monatomic ideal gas . . . . .	350
12-2	The distribution of molecular velocities . . . . .	354
12-3	Experimental verification of the Maxwell-Boltzmann speed distribution. Molecular beams . . . . .	362
12-4	Ideal gas in a gravitational field . . . . .	366

12-5	The principle of equipartition of energy . . . . .	370
12-6	The quantized linear oscillator . . . . .	372
12-7	Specific heat capacity of a diatomic gas . . . . .	376

### **13 Applications of quantum statistics to other systems**

13-1	The Einstein theory of the specific heat capacity of a solid . . . . .	386
13-2	The Debye theory of the specific heat capacity of a solid . . . . .	387
13-3	Blackbody radiation . . . . .	395
<b>13-4</b>	Paramagnetism . . . . .	
13-5	Negative temperatures . . . . .	405
13-6	The electron gas. . . . .	407

### **APPENDIX**

<b>A Selected differentials from a condensed collection of thermodynamic formulas by P. W. Bridgman</b>	419
<b>B The Lagrange method of undetermined multipliers</b>	421
<b>C Properties of factorials</b>	424
<b>D An alternative derivation of distribution functions</b>	427
<b>E Magnetic potential energy</b>	432
<b>Answers to problems</b>	435
<b>Index</b>	445

