

Contents

Preface	ix
Structure	xiii
Symbols	xv
1 State of Equilibrium	1
1.1 Equilibrium of a thermodynamic system	2
1.2 Helmholtz energy (Helmholtz function)	5
1.3 Gibbs energy (Gibbs function)	6
1.4 The use and significance of the Helmholtz and Gibbs energies	6
1.5 Concluding remarks	9
Problems	10
2 Availability and Exergy	13
2.1 Displacement work	13
2.2 Availability	14
2.3 Examples	15
2.4 Available and non-available energy	21
2.5 Irreversibility	21
2.6 Graphical representation of available energy and irreversibility	25
2.7 Availability balance for a closed system	27
2.8 Availability balance for an open system	34
2.9 Exergy	36
2.10 The variation of flow exergy for a perfect gas	42
2.11 Concluding remarks	43
Problems	43
3 Pinch Technology	47
3.1 A heat transfer network without a pinch problem	49
3.2 A heat transfer network with a pinch point	56
3.3 Concluding remarks	60
Problems	61

4	Rational Efficiency of a Powerplant	64
4.1	The influence of fuel properties on thermal efficiency	64
4.2	Rational efficiency	65
4.3	Rankine cycle	69
4.4	Examples	71
4.5	Concluding remarks	82
	Problems	82
5	Efficiency of Heat Engines at Maximum Power	85
5.1	Efficiency of an internally reversible heat engine when producing maximum power output	85
5.2	Efficiency of combined cycle internally reversible heat engines when producing maximum power output	92
5.3	Concluding remarks	96
	Problems	96
6	General Thermodynamic Relationships (single component systems, or systems of constant composition)	100
6.1	The Maxwell relationships	100
6.2	Uses of the thermodynamic relationships	104
6.3	Tds relationships	108
6.4	Relationships between specific heat capacities	111
6.5	The Clausius–Clapeyron equation	115
6.6	Concluding remarks	118
	Problems	118
7	Equations of State	121
7.1	Ideal gas law	121
7.2	Van der Waals' equation of state	123
7.3	Law of corresponding states	125
7.4	Isotherms or isobars in the two-phase region	129
7.5	Concluding remarks	131
	Problems	132
8	Liquefaction of Gases	135
8.1	Liquefaction by cooling – method (i)	135
8.2	Liquefaction by expansion – method (ii)	140
8.3	The Joule–Thomson effect	141
8.4	Linde liquefaction plant	148
8.5	Inversion point on p – v – T surface for water	150
8.6	Concluding remarks	155
	Problems	155
9	Thermodynamic Properties of Ideal Gases and Ideal Gas Mixtures of Constant Composition	158
9.1	Molecular weights	158

9.2	State equation for ideal gases	159
9.3	Tables of $\mu(T)$ and $h(T)$ against T	164
9.4	Mixtures of ideal gases	172
9.5	Entropy of mixtures	175
9.6	Concluding remarks	178
	Problems	178
10	Thermodynamics of Combustion	182
10.1	Simple chemistry	184
10.2	Combustion of simple hydrocarbon fuels	185
10.3	Heats of formation and heats of reaction	187
10.4	Application of the energy equation to the combustion process – a macroscopic approach	188
10.5	Combustion processes	192
10.6	Examples	195
10.7	Concluding remarks	205
	Problems	205
11	Chemistry of Combustion	208
11.1	Bond energies and heats of formation	208
11.2	Energy of formation	210
11.3	Enthalpy of reaction	216
11.4	Concluding remarks	216
12	Chemical Equilibrium and Dissociation	218
12.1	Gibbs energy	218
12.2	Chemical potential, μ	220
12.3	Stoichiometry	221
12.4	Dissociation	222
12.5	Calculation of chemical equilibrium and the law of mass action	225
12.6	Variation of Gibbs energy with composition	229
12.7	Examples of the significance of K_p	231
12.8	The Van't Hoff relationship between equilibrium constant and heat of reaction	238
12.9	The effect of pressure and temperature on degree of dissociation	239
12.10	Dissociation calculations for the evaluation of nitric oxide	242
12.11	Dissociation problems with two, or more, degrees of dissociation	245
12.12	Concluding remarks	259
	Problems	259
13	The Effect of Dissociation on Combustion Parameters	265
13.1	Calculation of combustion both with and without dissociation	267
13.2	The basic reactions	267
13.3	The effect of dissociation on peak pressure	268
13.4	The effect of dissociation on peak temperature	268
13.5	The effect of dissociation on the composition of the products	269
13.6	The effect of fuel on composition of the products	272
13.7	The formation of oxides of nitrogen	273

14	Chemical Kinetics	276
14.1	Introduction	276
14.2	Reaction rates	276
14.3	Rate constant for reaction, k	279
14.4	Chemical kinetics of NO	280
14.5	The effect of pollutants formed through chemical kinetics	286
14.6	Other methods of producing power from hydrocarbon fuels	288
14.7	Concluding remarks	289
	Problems	289
15	Combustion and Flames	291
15.1	Introduction	291
15.2	Thermodynamics of combustion	292
15.3	Explosion limits	294
15.4	Flames	296
15.5	Flammability limits	303
15.6	Ignition	304
15.7	Diffusion flames	305
15.8	Engine combustion systems	307
15.9	Concluding remarks	314
	Problems	314
16	Irreversible Thermodynamics	316
16.1	Introduction	316
16.2	Definition of irreversible or steady state thermodynamics	317
16.3	Entropy flow and entropy production	317
16.4	Thermodynamic forces and thermodynamic velocities	318
16.5	Onsager's reciprocal relation	319
16.6	The calculation of entropy production or entropy flow	321
16.7	Thermoelectricity – the application of irreversible thermodynamics to a thermocouple	322
16.8	Diffusion and heat transfer	332
16.9	Concluding remarks	342
	Problems	342
17	Fuel Cells	345
17.1	Electric cells	346
17.2	Fuel cells	351
17.3	Efficiency of a fuel cell	358
17.4	Thermodynamics of cells working in steady state	359
17.5	Concluding remarks	361
	Problems	361
	Bibliography	363
	Index (including Index of tables of properties)	369