1	Intro	duction: Why Thermodynamics?	1
	1.1	Energy and Work in Our World	1
	1.2	Mechanical and Thermodynamical Forces	2
	1.3	Systems, Balance Laws, Property Relations	4
	1.4	Thermodynamics as Engineering Science	6
	1.5	Thermodynamic Analysis	7
	1.6	Applications	8
2	Syste	ems, States, and Processes	11
	2.1	The Closed System	11
	2.2	Micro and Macro	12
	2.3	Mechanical State Properties	13
	2.4	Extensive and Intensive Properties	14
	2.5	Specific Properties	14
	2.6	Molar Properties	15
	2.7	Inhomogeneous States	16
	2.8	Processes and Equilibrium States	17
	2.9	Quasi-static and Fast Processes	17
	2.10	Reversible and Irreversible Processes	18
	2.11	Temperature and the Zeroth Law	19
	2.12	Thermometers and Temperature Scale	20
	2.13	Gas Temperature Scale	21
	2.14	Thermal Equation of State	22
	2.15	Ideal Gas Law	23
	2.16	A Note on Problem Solving	24
	2.17	Example: Air in a Room	25
	2.18	Example: Air in a Refrigerator	26
	2.19	More on Pressure	27
	Probl	ems	30



X Contents

3	The	First Law of Thermodynamics	33
	3.1	Conservation of Energy	33
	3.2	Total Energy	35
	3.3	Kinetic Energy	35
	3.4	Potential Energy	35
	3.5	Internal Energy and the Caloric Equation of State	36
	3.6	Work and Power	36
	3.7	Exact and Inexact Differentials	39
	3.8	Heat Transfer	39
	3.9	The First Law for Reversible Processes	41
	3.10	The Specific Heat at Constant Volume	41
	3.11	Enthalpy	43
	3.12	Example: Equilibration of Temperature	44
	3.13	Example: Uncontrolled Expansion of a Gas	46
	3.14	Example: Friction Loss	47
	3.15	Example: Heating Problems	47
	Probl	ems	50
4	The	Second Law of Thermodynamics	55
	4.1	The Second Law	55
	4.2	Entropy and the Trend to Equilibrium	55
	4.3	Entropy Flux	57
	4.4	Entropy in Equilibrium	57
	4.5	Entropy as Property: The Gibbs Equation	59
	4.6	T-S-Diagram	60
	4.7	The Entropy Balance	61
	4.8	The Direction of Heat Transfer	63
	4.9	Internal Friction	65
	4.10	Newton's Law of Cooling	67
	4.11	Zeroth Law and Second Law	68
	4.12	Example: Equilibration of Temperature	69
	4.13	Example: Uncontrolled Expansion of a Gas	69
	4.14	What Is Entropy?	70
	4.15	Entropy and Disorder	73
	4.16	Entropy and Life	74
	4.17	The Entropy Flux Revisited	7 5
	Probl	lems	78
5	Ener	gy Conversion and the Second Law	83
	5.1	Energy Conversion	83
	5.2	Heat Engines	84
	5.3	The Kelvin-Planck Statement	86
	5.4	Refrigerators and Heat Pumps	87
	5.5	Kelvin-Planck and Clausius Statements	89
	5.6	Thermodynamic Temperature	90

	5.7	Perpetual Motion Engines	91
	5.8	Reversible and Irreversible Processes	91
	5.9	Internally and Externally Reversible Processes	93
	5.10	Irreversibility and Work Loss	93
	5.11	Examples	94
	Proble	cms	100
6	Prop	erties and Property Relations	103
	6.1	State Properties and Their Relations	103
	6.2	Phases	104
	6.3	Phase Changes	105
	6.4	p-v- and T-s-Diagrams	110
	6.5	Saturated Liquid-Vapor Mixtures	111
	6.6	Identifying States	113
	6.7	Example: Condensation of Saturated Steam	115
	6.8	Superheated Vapor	117
	6.9	Compressed Liquid	120
	6.10	The Ideal Gas	123
	6.11	Monatomic Gases (Noble Gases)	125
	6.12	Specific Heats and Cold Gas Approximation	126
	6.13	Real Gases	127
	6.14	Fully Incompressible Solids and Liquids	128
	Probl	ems	128
7	Reve	ersible Processes in Closed Systems	131
	7.1	Standard Processes	131
	7.2	Basic Equations	131
	7.3	Isochoric Process: $v = const.$, $dv = 0 \dots$	133
	7.4	Isobaric Process: $p = const.$, $dp = 0 \dots \dots$	134
	7.5	Isentropic Process: $q_{12} = \delta q = ds = 0$	135
	7.6	Isothermal Process: $T = const$, $dT = 0$	137
	7.7	Polytropic Process (Ideal Gas): $pv^n = const$	138
	7.8	Summary	139
	7.9	Examples	139
	Probl	eins	147
8	Close	ed System Cycles	153
	8.1	Thermodynamic Cycles	153
	8.2	Carnot Cycle	155
	8.3	Carnot Refrigeration Cycle	158
	8.4	Internal Combustion Engines	159
	8.5	Otto Cycle	162
	8.6	Example: Otto Cycle	164
	8.7	Diesel Cycle	165
	8.8	Example: Diesel Cycle	167

XII Contents

	8.9	Dual Cycle	168
	8.10	Atkinson Cycle	169
		ems	172
9	Open	Systems	177
	9.1	Flows in Open Systems	177
	9.2	Conservation of Mass	178
	9.3	Flow Work and Energy Transfer	179
	9.4	Entropy Transfer	181
	9.5	Open Systems in Steady State Processes	181
	9.6	One Inlet, One Exit Systems	182
	9.7	Entropy Generation in Mass Transfer	184
	9.8	Adiabatic Compressors, Turbines and Pumps	186
	9.9	Heating and Cooling of a Pipe Flow	187
	9.10	Throttling Devices	188
	9.11	Adiabatic Nozzles and Diffusers	188
	9.12	Isentropic Efficiencies	190
	9.13	Summary: Open System Devices	192
	9.14	Examples: Open System Devices	192
	9.15	Closed Heat Exchangers	200
	9.16	Open Heat Exchangers: Adiabatic Mixing	201
	9.17	Examples: Heat Exchangers	202
	Proble	ms	203
10	Basic	Open System Cycles	209
	10.1	Steam Turbine: Rankine Cycle	209
	10.2	Example: Rankine Cycle	212
	10.3	Vapor Refrigeration/Heat Pump Cycle	216
	10.4	Example: Vapor Compression Refrigerator	218
	10.5	Gas Turbine: Brayton Cycle	221
	10.6	Example: Brayton Cycle	225
	10.7	Gas Refrigeration System: Inverse Brayton Cycle	226
	Proble	ms	228
11		encies and Irreversible Losses	235
	11.1	Irreversibility and Work Loss	235
	11.2	Reversible Work and Second Law Efficiency	237
	11.3	Example: Carnot Engine with External Irreversibility	239
	11.4	Example: Space Heating	241
	11.5	Example: Entropy Generation in Heat Transfer	244
	11.6	Work Potential of a Flow (Exhaust Losses)	245
	11.7	Heat Engine Driven by Hot Combustion Gas	246
	11.8	Exergy	251
	Proble	ms	252

Contents XIII

12	Vapor	Engines	257
	12.1	Boiler Exhaust Regeneration	257
	12.2	Regenerative Rankine Cycle	25 9
	12.3	Example: Steam Cycles with Feedwater Heaters	266
	12.4	Cogeneration Plants	27 3
	12.5	Refrigeration Systems	275
	12.6	Linde Method for Gas Liquefaction	278
	Proble	ms	27 9
13	Gas E	Engines	289
	13.1	Stirling Cycle	289
	13.2	Ericsson Cycle	296
	13.3	Compression with Intercooling	297
	13.4	Gas Turbine Cycles with Regeneration and Reheat	300
	13.5	Brayton Cycle with Intercooling and Reheat	303
	13.6	Combined Cycle	305
	13.7	The Solar Tower	306
	13.8	Simple Chimney	309
	13.9	Aircraft Engines	310
		ms	322
			022
14	Comp	pressible Flow: Nozzles and Diffusers	327
	14.1	Sub- and Supersonic Flows	327
	14.2	Speed of Sound	327
	14.3	Speed of Sound in an Ideal Gas	329
	14.4	Area-Velocity Relation	330
	14.5	Nozzle Flows	333
	14.6	Converging Nozzle	334
	14.7	Example: Safety Valve	336
	14.8	Laval Nozzle	337
	14.9	Rockets, Ramjet and Scramjet	338
	14.10	Example: Ramjet	340
	Proble	ms	342
15	Trans	ient and Inhomogeneous Processes	
		en Systems	345
	15.1	Introduction	345
	15.2	Heat Exchangers	345
	15.3	Heating of a House	352
	15.4	Reversible Filling of an Adiabatic Container	355
	15.5	Reversible Discharge from an Adiabatic Container	357
	15.6	Reversible Discharge after Cooling	357
	15.7	Reversible Filling of a Gas Container with Heat	501
		Exchange	360
	15.8	CAES: Compressed Air Energy Storage	362
		ms	368
			_

XIV Contents

16	More	on Property Relations	371
	16.1	Measurability of Properties	371
	16.2	Thermodynamic Potentials and Maxwell Relations	371
	16.3	Two Useful Relations	374
	16.4	Relation between Specific Heats	376
	16.5	Measurement of Properties	377
	16.6	Example: Gibbs Free Energy as Potential	380
	16.7	Compressibility, Thermal Expansion	381
	16.8	Example: Van der Waals Gas	383
	16.9	Joule-Thomson Coefficient	387
	16.10	Example: Inversion Curve for the Van der Waals Gas	388
		ems	389
17	Ther	nodynamic Equilibrium	393
	17.1	Equilibrium Conditions	393
	17.2	Equilibrium in Isolated Systems	394
	17.3	Barometric and Hydrostatic Formulas	397
	17.4	Thermodynamic Stability	397
	17.5	Equilibrium in Non-isolated Systems	398
	17.6	Interpretation of the Barometric Formula	401
	17.7	Equilibrium in Heterogeneous Systems	402
	17.8	Phase Equilibrium	404
	17.9	Example: Phase Equilibrium for the Van der Waals	101
	11.0	Gas	406
	17.10	Clapeyron Equation	407
	17.11	Example: Estimate of Heat of Evaporation	408
	17.12	Example: Ice Skating	409
		ems	410
18	Mixt		415
	18.1	Introduction	415
	18.2	Mixture Composition	415
	18.3	Example: Composition and Molar Mass of Air	416
	18.4	Mixture Properties	417
	18.5	Mixing Volume, Heat of Mixing and Entropy of Mixing	418
	18.6	Ideal Gas Mixtures	42 0
	18.7	Energy, Enthalpy and Specific Heats for Ideal Gases	42 1
	18.8	Entropy of Mixing for Ideal Gas	421
	18.9	Gibbs Paradox	422
	18.10	Example: Isentropic Expansion through a Nozzle	423
	18.11	Example: Isochoric Mixing of Two Gases at	
		Different $p, T \dots$	424
	18.12	Ideal Mixtures	425
	18.13	Entropy of Mixing and Separation Work	428
	18.14	Non-ideal Mixtures	429
	Proble	mis	430

Contents XV

19	Psych	rometrics	433
-	19.1	Characterization of Moist Air	433
	19.2	Dewpoint	435
	19.3	Adiabatic Saturation and Wet-Bulb Temperature	436
	19.4	Psychrometric Chart	437
	19.5	Dehumidification	440
	19.6	Humidification with Steam	442
	19.7	Evaporative Cooling	443
	19.8	Adiabatic Mixing	445
	19.9	Cooling Towers	446
	19.10	Example: Cooling Tower	447
		ems	449
2 0		Chemical Potential	455
	20.1	Definition and Interpretation	455
	20.2	Properties of the Chemical Potential	456
	20.3	Gibbs and Gibbs-Dulicm Equations	458
	20.4	Mass Based Chemical Potential	459
	20.5	The Chemical Potential for an Ideal Mixture	460
	20.6	The Chemical Potential for an Ideal Gas Mixture	460
	20.7	The Chemical Potential as Driving Force for Mass	
		Transfer	461
	Proble	ems	463
21	Mixir	ng and Separation	467
	21.1	Osmosis and Osmotic Pressure	467
	21.2	Osmotic Pressure for Dilute Solutions	468
	21.3	Example: Pfeffer Tube	469
	21.4	Desalination in a Continuous Process	471
	21.5	Reversible Mixing: Osmotic Power Generation	474
	21.6	Example: Desalination in Piston-Cylinder Device	477
	21.7	Example: Removal of CO ₂	479
		ems	484
	D.		400
22		Equilibrium in Mixtures	493
	22.1	Phase Mixtures	493
	22.2	Gibbs' Phase Rule	493
	22.3	Liquid-Vapor-Mixtures: Idealized Raoult's Law	494
	22.4	Phase Diagrams for Binary Mixtures	495
	22.5	Distillation	498
	22.6	Saturation Pressure and Temperature of a Solvent	498
	22.7	Freezing of a Liquid Solution	501
	22.8	Non-ideal Mixtures: Activity and Fugacity	502
	22.9	A Simple Model for Heat of Mixing and Activity	504
	22.10	Gas Solubility: Henry's Law	505

XVI Contents

	22.11	Phase Diagrams with Azeotropes	506 509
	Proble	ems	JUS
23	React	ing Mixtures	517
	23.1	Stoichiometric Coefficients	517
	23.2	Mass and Mole Balances	518
	23.3	Heat of Reaction	519
	23.4	Heating Value	520
	23.5	Enthalpy of Formation	520
	23.6	The Third Law of Thermodynamics	522
	23.7	The Third Law and Absolute Zero	523
	23.8	Law of Mass Action	524
	23.9	Law of Mass Action for Ideal Mixtures and Ideal Gases	524
			526
	23.10	Example: NH ₃ Production (Haber-Bosch Process)	
	23.11	Le Chatelier Principle	528
	23.12	Multiple Reactions	529
	Proble	ems	530
24	Activ	ation of Reactions	535
	24.1	Approaching Chemical Equilibrium	535
	24.2	Reaction Rates and the Chemical Constant	536
	24.3	Gibbs Free Energy of Activation	537
	24.4	Entropy Generation	539
		ems	540
25	Comb	oustion	541
	25.1	Fuels	541
	25.2	Combustion Air	542
	25.3	Example: Mole and Mass Flow Balances	542
	25.4	Example: Exhaust Water	544
	25.5	First and Second Law for Combustion Systems	545
	25.6	Adiabatic Flame Temperature	546
	25.7	Example: Adiabatic Flame Temperature	546
	25.8	Closed System Combustion	547
	25.9	Example: Closed System Combustion	548
	25.10	Entropy Generation in Closed System Combustion	548
	25.11	Work Potential of a Fuel	549
	25.12	Example: Work Losses in a CH ₄ Fired Steam	
		Power Plant	552
	Proble	ems	558
			<u>.</u>
26		modynamics of Fuel Cells	563
	26.1	Fuel Cells	563
	26.2	Fuel Cell Potential	564
	26.3	Fuel Cell Efficiency	567
	26.4	Nerust Equation	571

Contents	XVII
9-	

26.5	Mass Transfer Losses	
26.6	Resistance Losses	
26.7	Activation Overpotential	
26.8	Voltage/Current and Power/Current Diagrams	
26.9	Crossover Losses	
26.10	Electrolyzers	
26.11	Hydrogen	
Proble	ems	
ex		