
Contents

Glossary	xiii
I Introduction	1
II Mathematical Modeling of Thermodynamic Systems	5
2.1 Reversible Thermodynamic Systems	5
2.1.1 Thermodynamic Potentials	6
2.1.2 Conditions of Equilibrium	10
2.1.3 Ideal Gas	11
2.2 Transient Processes in Thermodynamic Systems	17
2.2.1 Closed Systems	18
2.2.2 Open Systems	19
2.3 Mass, Energy and Entropy Balances, and Efficiency Estimates of Thermodynamic Systems	21
2.3.1 A Heat Engine with Two Reservoirs of Infinite Capacity (the Carnot Engine)	25
2.3.2 Stationary Heat Exchange	26
2.3.3 Heat-Driven Separation of a Two-Component Mixture	27
2.3.4 Diffusive-Mechanical and Thermo-Mechanical Cycle	30
2.3.5 Using the Balance Equation to Find the Feasible Set of Parameters	31
2.3.6 Schema for the Solution of Finite-Time Thermodynamic Problems	32
III Optimization Methods	33
3.1 The Structure of Extremal Problems and Existence of Solutions	33
3.1.1 Problems to which Solutions do not Exist	33
3.2 Formulation of the Extremal Problem and General Approaches to its Solution	37
3.2.1 Carnot Problem	38
3.2.2 Optimality Conditions	40

3.2.3	Equivalent Transformation of Extremal Problems	43
3.2.4	Extensions of Extremal Problems	44
3.3	The Nonlinear Programming Problem	47
3.3.1	Convex Sets	48
3.3.2	Convex Envelopes of Sets and Functions	50
3.3.3	A Convex Problem of Nonlinear Programming	52
3.3.4	Necessary Conditions of Optimality for the Problem of Nonlinear Programming	52
3.3.5	Degenerate Solution of the Nonlinear Programming Problem	53
3.3.6	Optimality Conditions for a Nonlinear Programming Problem as Conditions for Maximizing a Lagrange Function	55
3.4	The Attainability Function and Extensions of Nonlinear Programming Problems	55
3.4.1	Extensions of the Nonlinear Programming Problem	60
3.4.2	Averaged Extensions	65
3.5	Optimality Conditions and Methods of Solution for the Averaged Problem of Nonlinear Programming	68
3.5.1	Canonical Form of the \overline{NP} Problem	69
3.5.2	Optimality Conditions for the \overline{NP} Problem	71
3.5.3	Equivalence of the \overline{NP} Problem to the Lagrange Extension of the NP Problem	72
3.5.4	The Attainability Function of the \overline{NP} Problem	74
3.5.5	Methods of Estimating the Value of the \overline{NP} Problem	75
3.5.6	Number of Basic Solutions in the \overline{NP} Problem	78
3.5.7	Different Types of Averaged NP Problem and Their Optimality Condition	79
IV	Optimal Control Methods	83
4.1	Necessary Conditions of Optimality for Variational Control Problems: the Pontryagin Maximum Principle	83
4.2	Singular Solutions and Sliding Regimes	86
4.3	Optimal Control Problems with Integral Constraints and Parameters	91
4.4	Simplification of Optimal Control Problems	92
4.4.1	Using a State Variable as a New Independent Variable	92
4.4.2	Reduction of the Problem's Dimension by Transformation of Some of its State Variables into Control Variables	94
4.4.3	Transformation of the State Space for a Problem Linear in the Unrestricted Control	96
4.4.4	Parametrization of the Optimal Control Problem	98

4.5	Optimal Control of Cyclic Processes and of Processes with a Fixed Difference between Initial and Final States	100
4.5.1	Formulation of the Optimal Cyclic Regime Problem: Maximum Principle	100
4.5.2	The Special Feature of Optimal Cyclic Regimes	102
4.5.3	Quasi Static and Sliding Regimes	103
4.5.4	Estimating the Utility of the Static Regime as a Replacement for the Cyclic, based on the Lagrange Function of the Static Problem	106
4.5.5	Estimating the Value of the Problem in which the difference between Initial and Final States is Fixed	108
4.6	Non-Autonomous Problems of Averaged Optimization	109
4.7	The Main Features of Optimal Control Problems of Thermodynamic Systems	111
4.8	The Conditions of Minimal Dissipation in the Thermodynamic Process	114
4.8.1	Formulation of the Problem	114
4.8.2	Scalar Flux	115
4.8.3	Vector Flux	116
4.9	Dynamic Programming and Finite-Time Potentials	117
4.9.1	Continuous Processes and the Hamilton–Jacobi–Bellman Equation	117
4.9.2	Discrete Processes—Traditional Description	133
4.9.3	Discrete Processes—Non-Traditional Description	136
4.10	Discrete Algorithm with Constant Hamiltonian	140
4.10.1	Preliminaries Associated with the Weak and Strong Maximum Principle	140
4.10.2	Dynamic Programming Evaluation of Necessary Optimality Conditions	142
4.10.3	Link between the Higher-order Derivatives of A^n and H^{n-1}	144
4.10.4	Enhanced Conditions for Optimal Control	147
4.11	State Variables Bounded by Conservation Equations or Other Constraints	150
4.11.1	Modification of Stage Criterion \mathcal{A}^n by Local Constraints	150
4.11.2	Adjoining Constraints in Original Form	152
4.11.3	Adjoining Constraints in Transformed Form	154
4.12	An Application to Onsagerian Thermodynamics	157
4.12.1	Performance Criteria for Exchange Processes Between Two Subsystems	157
4.12.2	Adjoining State Constraints in the Rate Form	165

4.12.3	Phenomenological Equations from the Power-Type Criterion	168
4.13	Towards Finite-Time Availability of Thermal Processes	177
4.13.1	Introduction	177
4.13.2	Process in an Infinite Sequence of Infinitesimal CAN Engines	179
4.13.3	Basic Properties of the Extremal Solution	183
4.13.4	Heuristic Derivation of the Hamilton–Jacobi–Bellman Equation	184
4.13.5	Passage to the Hamilton–Jacobi Equation	187
4.13.6	Hamilton–Jacobi Equations for Extremal Work and Entropy	188
4.13.7	Principal Functions for Work and Exergy Problems	190
4.13.8	Work Optimization in Multistage Processes	191
4.13.9	Final Remarks	197
4.13.10	Appendix: Origin of the Overall Coefficient of Heat Transfer	197
V	Limiting Possibilities of Heat-Mechanical Systems with One Reservoir	199
5.1	Limiting Work in a Thermal-Mechanical System with a Constant-Temperature Heat Reservoir	199
5.1.1	Formulation of the Problem	199
5.1.2	Maximal Work	201
5.1.3	The General Law of Heat Transfer	204
5.2	The Reservoir with Finite Capacity	207
5.3	A Thermal-Mechanical System with One Reservoir with Variable Temperature	211
5.4	Heat and Mechanical Contact with the Reservoir	213
5.4.1	Maximal Work from Several Subsystems in Contact with the Reservoir and with Each Other	216
5.4.2	Estimate of Entropy Production in the Thermodynamic System	222
VI	Heat-Exchange Processes with Minimal Dissipation	225
6.1	Conditions of Thermodynamic Concordance of Heat-Exchange Processes and Control Systems which Realize them	225
6.1.1	Two-Flux Heat Exchange	225
6.1.2	Optimal Organization of the Heat Exchange in Systems with a Shared Flux	231
6.1.3	Optimal Heat Exchange in a General System	236
6.2	Optimal Distribution of the Heat-Exchange Surface	238
6.2.1	Counter-Flux Heat Exchange in a Linear Exchanger	238

6.3	Optimization of Regenerative Heat Exchange	240
6.3.1	Maximal Productivity of the Heat Exchanger	241
6.3.2	Increasing the Efficiency of the Regenerative Heat Exchange by Controlling the Rates of the Fluxes	243
6.4	Exergy-Based Constrained Temperature Control in a Horizontal Fluidized Heat Exchanger	247
6.4.1	Free Total Air Flow Rate	253
6.4.2	Fixed Total Air Flow Rate	261
6.4.3	Conclusion	266
6.5	Cascade of Fluidized Bed Exchangers	266
6.5.1	Processes without Outlet Air Exergy Recovery	268
6.5.2	Processes with Outlet Air Exergy Recovery	276
6.5.3	Conclusion	282
6.5.4	Remarks on Computational Problems	283
VII	Optimization and Estimates of the Limiting Possibilities of Heat-Mechanical Systems with a Number of Reservoirs	287
7.1	The Limits of Performance of a Heat Engine with Two Reservoirs	287
7.1.1	The Mathematical Model	287
7.1.2	Limiting Power of the Heat Engine	289
7.1.3	Limiting Efficiency of a Heat Engine with Given Power	294
7.1.4	Limiting Characteristics of Inverse Cycles	298
7.2	Optimal Distribution of the Heat-Exchange Surface	301
7.2.1	The Heat Engine Delivering Maximal Power	301
7.2.2	The Heat Engine with Maximal Efficiency and Given Power	302
7.2.3	Example	303
7.3	The Limits of Performance of a Heat Engine with Reservoirs of Finite Capacity	304
7.3.1	Solution of the Problem of Finding the Maximal Work	306
7.3.2	The Regime of Maximal Efficiency for Given Work	310
7.4	The Limits of Performance of Refrigerators and Heat Pumps with Reservoirs of Finite Capacity	311
7.4.1	Formulation of the Problem	311
7.4.2	Limiting Value of the Coefficient of Performance of a Refrigerator Required to Operate on a Given Average Power	313
7.4.3	Limiting Coefficient of Performance of a Refrigerator Required to Remove Heat from a Cold Reservoir at a Specified Rate	318

7.5	A Heat Engine with a Non-Stationary Reservoir	322
7.6	A Thermal-Mechanical System with One Working Body and a Number of Reservoirs	325
7.6.1	Formulation of the Problem	325
7.6.2	The Method of Solution	327
7.6.3	Computation of the Distribution of the Rates of Entropy Production	330
7.6.4	Computational Algorithm	331
7.6.5	The System with a Continuum of the Stationary Reservoirs	333
7.6.6	Non-Stationarity of the Reservoirs	336

VIII Limiting Possibilities of Complex Systems with a Number of Heat-Mechanical Systems **339**

8.1	The Limits of Performance of Heat Transformers	339
8.1.1	Formulation of the Problem	339
8.1.2	Formulation of the Problems and Characteristics of Optimal Irreversible Cycles	341
8.1.3	Limiting Heat Transformation Coefficients in Irreversible Thermodynamic Processes	344
8.1.4	Limiting Productivity of Heat Transformers	345
8.2	Dependence of Exergy on Power	345
8.2.1	Power-Determined Exergy	345
8.2.2	Distribution of Power Among Thermodynamic Cycles	347
8.2.3	Computation of the Poweral Exergy	348
8.3	Active Heat Insulation	349
8.3.1	Formulation of the Problem	350
8.3.2	Active Potentiostatting with One Intermediate Chamber	350
8.3.3	Active Potentiostatting with n Intermediate Chambers	354
8.3.4	Irreversibilities of Refrigerator Cycles	356

IX Mass Transfer Processes with Minimal Irreversibility **359**

9.1	Gas Throttling with Minimal Irreversibility	359
9.1.1	Formulation of the Problem	359
9.1.2	Optimality Conditions	360
9.2	The Conditions of Minimal Irreversibility for Mass Transfer Processes	363
9.2.1	One-Way Isothermal Mass Transfer	363
9.2.2	Taking into Account the Interrelation of Temperature and Concentrations	368
9.2.3	Estimating the Extent of Approach to Thermodynamic Perfection	369

9.2.4	Two-Way Isothermal Equimolar Mass Transfer	370
9.2.5	Mass Transfer with Time-Variable Concentration in a Reservoir	371
9.3	Minimal Work of Separation in Finite Time	375
9.3.1	Introduction	375
9.3.2	Minimal Irreversible Work of Separation	376
9.3.3	Ideal Gas	378
9.4	Crystallization with Minimal Irreversibility	379
9.4.1	Formulation of the Problem	379
9.4.2	Optimality Conditions	381
9.4.3	Optimal Solution	381
X	Thermodynamic Analysis of Separation Processes and Chemical Reactions	383
10.1	Thermodynamic Analysis of the Processes for Separating a Gas Mixture	383
10.2	Membrane Gas Separation	387
10.2.1	Periodic Process	387
10.2.2	Scalar Case	389
10.2.3	Continuous Processes	389
10.3	Thermodynamic Analysis of the Adsorption–Desorption Process	390
10.4	Absorption–Desorption Cycle with Infinite-Capacity Reservoirs	393
10.4.1	Estimating the Efficiency of the Thermo-Diffusion Cycle	393
10.4.2	A Mathematical Model of the Absorption–Desorption Cycle and Reversible Estimates of its Efficiency	394
10.4.3	The Limiting Productivity of an ADC	397
10.4.4	Limiting Effectiveness of the ADC with a Given Productivity	400
10.4.5	Taking into Account Finite Capacities of the Reservoirs	403
10.5	Estimating the Efficiency of Irreversible Distillation	408
10.5.1	Thermodynamic Balance Equations	408
10.5.2	Estimate of the Reversible Efficiency	409
10.5.3	Entropy Production in Irreversible Distillation	410
10.5.4	Example of Computation of the Optimal Profile of Concentrations in Distillation	412
10.6	Minimum Exergy Cost in Multistage Cross-Current Drying Exchangers	414
10.6.1	Free Total Air Flow Rate	416
10.6.2	Fixed Total Air Flow Rate	426

10.7 Optimal Control of Continuous Fluidized Drying with Variable Temperature and Humidity of Inlet Gas	429
10.7.1 Problem Formulation	429
10.7.2 Results and Discussion	431
XI Commodity Exchange in Economic Systems	435
11.1 Introduction	435
11.2 Equilibrium Exchange	436
11.2.1 Equilibrium Description of an Economic System	436
11.2.2 Direct Contact of Economic Subsystems	437
11.2.3 Kinetics of Commodity Exchange	443
11.2.4 Optimal Organization of the Commodity Exchange	446
Bibliography	457
Index	465