

## Contents

<b>List of Contributors</b>	<i>XIII</i>
<b>Preface</b>	<i>XV</i>
<b>List of Frequently Used Symbols</b>	<i>XVII</i>
<b>Glossary</b>	<i>XIX</i>

<b>1</b>	<b>Thermodynamics and Thermoelectricity</b>	<i>1</i>
	<i>Christophe Goupil, Henni Ouerdane, Knud Zabrocki, Wolfgang Seifert, Nicki F. Hinsche, and Eckhard Müller</i>	
1.1	Milestones of Thermoelectricity	<i>1</i>
1.1.1	Discovery of the Seebeck Effect	<i>2</i>
1.1.2	Discovery of the Peltier Effect	<i>8</i>
1.1.3	Discovery of the Thomson Effect	<i>9</i>
1.1.4	Magnus' Law	<i>10</i>
1.1.5	Early Performance Calculation of Thermoelectric Devices	<i>11</i>
1.1.6	First Evaluation of the Performance of a Thermoelectric Device by E. Altenkirch	<i>11</i>
1.1.7	Benedicks' Effect	<i>12</i>
1.1.8	The Bridgman Effect	<i>13</i>
1.1.9	Semiconductors as Thermoelectric Materials	<i>14</i>
1.1.10	Thermoelectric Applications – Excitement and Disappointment 1920–1970	<i>15</i>
1.1.10.1	Construction of the First Thermoelectric Generator	<i>15</i>
1.1.11	Thermoelectric Industry – Niche Applications 1970–2000	<i>16</i>
1.1.11.1	Thermoelectric Generators for Space	<i>16</i>
1.1.12	New Concepts in Thermoelectricity 2000-Present	<i>17</i>
1.2	Galvanomagnetic and Thermomagnetic Effects	<i>17</i>
1.2.1	The Hall Coefficient	<i>21</i>
1.2.2	The Nernst Coefficient	<i>21</i>
1.2.3	The Ettingshausen Coefficient	<i>21</i>
1.2.4	The Righi–Leduc Coefficient	<i>22</i>
1.2.5	Devices Using Galvano- and Thermomagnetic Effects and the Corresponding Figure of Merit	<i>22</i>
1.3	Historical Notes on Thermodynamic Aspects	<i>25</i>

1.4	Basic Thermodynamic Engine	27
1.5	Thermodynamics of the Ideal Fermi Gas	28
1.5.1	The Ideal Fermi Gas	28
1.5.2	Electron Gas in a Thermoelectric Cell	29
1.5.3	Entropy Per Carrier	30
1.5.4	Equation of State of the Ideal Electron Gas	32
1.5.5	Temperature Dependence of the Chemical Potential $\mu_c(T)$	34
1.6	Linear Nonequilibrium Thermodynamics	35
1.6.1	Forces and Fluxes	35
1.6.2	Linear Response and Reciprocal Relations	36
1.7	Forces and Fluxes in Thermoelectric Systems	37
1.7.1	Thermoelectric Effects	37
1.7.2	Forces, Fluxes, and Kinetic Coefficients	38
1.7.3	Energy Flux and Heat Flux	39
1.7.4	Thermoelectric Coefficients	40
1.7.4.1	Decoupled Processes	40
1.7.4.2	Coupled Processes	41
1.7.5	The Entropy Per Carrier	41
1.7.6	Kinetic Coefficients and Transport Parameters	42
1.7.7	The Dimensionless Figure of Merit $zT$	43
1.8	Heat and Entropy	44
1.8.1	Volumetric Heat Production	45
1.8.2	Entropy Production Density	45
1.8.3	Heat Flux and the Peltier – Thomson Coefficient	46
1.8.4	The Peltier – Thomson Term	46
1.8.5	Local Energy Balance	47
1.9	The Thermoelectric Engine and Its Applications	48
1.10	Thermodynamics and Thermoelectric Potential	50
1.10.1	Relative Current, Dissipation Ratio, and Thermoelectric Potential	51
1.10.2	Local Reduced Efficiency and Thermoelectric Potential of TEG, TEC, and TEH	53
1.10.3	Thermoelectric Potential and Nonequilibrium Thermodynamics	56
	References	59
<b>2</b>	<b>Continuum Theory of TE Elements</b>	<b>75</b>
	<i>Knud Zabrocki, Christophe Goupil, Henni Ouerdane, Yann Apertet, Wolfgang Seifert, and Eckhard Müller</i>	
2.1	Domenicali’s Heat Balance Equation	75
2.1.1	Tensorial Character of Material Properties	75
2.1.2	Heat Balance and Source Terms	76
2.1.3	Spatial and Temperature Averaging of the Material Properties	79
2.2	Transferred Heat Balance	80
2.3	Ioffe’s Description and Performance Parameters of CPM Devices	81
2.3.1	Single-Element Device	82

2.3.2	Performance Parameters of a Thermoelectric Element with Constant Material Properties	84
2.3.2.1	Thermoelectric Generator (TEG)	86
2.3.2.2	Thermoelectric Cooler (TEC)	89
2.3.2.3	Thermoelectric Heater (TEH)	91
2.3.3	Inverse Performance Equations and Effective Device Figure of Merit	91
2.4	Maximum Power and Efficiency of a Thermogenerator Element	93
2.4.1	Load Resistance as Design Parameter for a Thermogenerator	96
2.4.2	Efficiency versus Power Approach	97
2.4.3	Constant Heat Input (CHI) Model	100
2.5	Temperature-Dependent Materials–Analytic Calculations	102
2.5.1	Inverse Temperature Dependence of the Thermal Conductivity	103
2.5.2	Inverse Temperature Dependence of the Thermal Conductivity and a Variable Electrical Resistivity	105
2.5.2.1	Performance Equations	106
2.5.2.2	Maximum Power Output	108
2.5.2.3	Maximum Efficiency	109
2.5.3	Constant Thomson Coefficient–Logarithmic Behavior of the Seebeck Coefficient	111
2.5.3.1	Methods of Averaged Coefficients and Geometric Optimization of a TE Couple	114
2.5.3.2	Influence of the Thomson Effect on the Performance of a TEG	116
2.5.4	Algebraic and General Temperature Dependence	119
2.5.5	Constant Thomson Coefficient Combined with Linear Temperature Dependence of Resistivity	121
2.5.6	Linear Temperature Dependence of the Resistivity	123
2.5.7	Linear Temperature Dependence of the Thermal Conductivity	125
2.6	The Influence of Contacts and Contact Resistances on the TE Performance	125
2.6.1	Thermoelectric Element with Contacting Bridge	126
2.6.2	Numerical Example for the Influence of the Electrical Contact Resistance on the Performance	130
2.7	Dissipative Coupling between the TEG and the Heat Baths	133
2.7.1	Finite-Time Thermodynamics Optimization	133
2.7.2	Thermoelectric Generator Model	133
2.7.3	Thermal Flux and Electrical Current	135
2.7.4	Calculation of the Temperature Difference across the TEG	136
2.7.5	Maximization of Power and Efficiency with Fixed $ZT_m$	137
2.7.5.1	Maximization of Power by Electrical Impedance Matching	137
2.7.5.2	Maximization of Power by Thermal Impedance Matching	137
2.7.5.3	Simultaneous Thermal and Electrical Impedance Matching	138
2.7.5.4	On the Importance of Thermal Impedance Matching	138
2.7.5.5	Maximum Efficiency	139
2.7.5.6	Analysis of Optimization and Power–Efficiency Trade-Off	139

2.8	Shaped Thermoelectric Elements	140
2.9	Other Influences on the Performance of TE Devices	144
2.9.1	Lateral Heat Losses, Convective and Radiative Heat Transfer	144
2.9.1.1	Convection Losses and Benefits	144
2.9.1.2	Radiation Losses and Benefits	146
2.9.2	Anisotropic Thermoelectric Elements	147
	References	148
<b>3</b>	<b>Segmented Devices and Networking of TE Elements</b>	<b>157</b>
	<i>Knud Zabrocki, Christophe Goupil, Henni Ouerdane, Eckhard Müller, and Wolfgang Seifert</i>	
3.1	Segmented Devices	157
3.1.1	Double-Segmented Element	160
3.1.1.1	Effective Electrical Conductivity	161
3.1.1.2	Effective Thermal Conductivity	163
3.1.2	Algorithm of Multisegmented Elements	164
3.1.2.1	Numerical Parameter Studies on Graded Elements	166
3.2	Networks	169
3.2.1	Presentation	169
3.2.2	Useful Expressions	171
3.2.3	Discretization	171
3.2.4	Solution: General Millman Theorem	172
3.2.5	Implementation	173
3.2.6	Numerical Illustration	174
	References	176
<b>4</b>	<b>Transient Response and Green's Function Technique</b>	<b>177</b>
	<i>Wolfgang Seifert, Knud Zabrocki, Steven Achilles, and Steffen Trimper</i>	
4.1	Quasi-Stationary Processes	179
4.2	Supercooling with a Transient Peltier Cooler	182
4.2.1	Steady-State Operation of a Thermoelectric Cooler	183
4.2.2	Important Parameters for the Supercooling Case	187
4.3	Transient Behavior of a Thermoelectric Generator	189
4.4	Dynamic Measurements of the Thermal Conductivity: Laser Flash Analysis	190
4.5	Dynamic Measurements of the Thermal Conductivity: Classical Ioffe Method	193
4.5.1	Theoretical Basis of Simple Ioffe Method	194
4.5.2	Laplace Transformation and Important Properties	197
4.5.3	Solution of the Classical Ioffe Method	198
4.5.3.1	LT of Original Equation	198
4.5.4	Solution of the Temperatures in the $s$ -Domain	199
4.5.5	Inverse Laplace Transformation	202
4.5.6	Inversion Theorem for the Laplace Transformation	203
4.5.7	Inversion of the Temperature Profiles	205

4.6	Green's Function Approach in Thermoelectricity	206
4.6.1	Continuity Equations	208
4.6.2	Green's Function Approach in the Steady State	208
4.6.3	One-Dimensional Green's Functions in the Steady State	209
4.6.4	Perturbative Approach to a Full Description (1D)	210
4.7	Linear Transient Approach	212
4.7.1	Relaxation Time	212
4.7.2	Transient Field Equations	213
4.7.3	Transient Linear Response Approximation	214
4.8	Time-Dependent Green's Function Approach	215
	References	217
<b>5</b>	<b>Compatibility</b>	<b>227</b>
	<i>Wolfgang Seifert, G. Jeffrey Snyder, Eric S. Toberer, Volker Pluschke, Eckhard Müller, and Christophe Goupil</i>	
5.1	Relative Current Density and Compatibility Factors	227
5.2	Compatibility and Segmented Thermogenerators	229
5.3	Reduced Efficiencies and Self-Compatible Performance	232
5.3.1	Performance Integrals for Efficiency and COP	233
5.3.2	Local Efficiency Dependence on Current (TEG)	235
5.4	Power-Related Compatibility	238
5.5	Optimal Material Grading for Maximum Power Output	241
5.6	The Criterion " $u = s$ " and Calculus of Variations	243
5.7	Self-Compatible and Optimum Material Grading	246
5.8	Thermodynamic Aspects of Compatibility	249
5.9	Analytic Results for Self-Compatible TEG and TEC Elements	251
5.9.1	Performance of Self-Compatible TEG and TEC Elements	251
5.9.2	Self-Compatible Elements and Optimal Figure of Merit	253
5.9.3	Optimal Seebeck Coefficients for Self-Compatible Material	255
5.9.4	Temperature Profile for $u = s$ Material	256
5.10	Thermoelectric Thomson Cooler	259
5.10.1	Cooling Performance	262
5.10.2	Thomson Cooler Phase Space	265
5.10.3	Performance Limits	266
5.10.4	Further Characteristics of Self-Compatible Material for Cooling	268
5.11	Compatibility Approach versus Device Optimization	276
	References	277
<b>6</b>	<b>Numerical Simulation</b>	<b>281</b>
	<i>Knud Zabrocki and Wolfgang Seifert</i>	
6.1	Finite Difference Methods	284
6.2	Finite Volume Method	288
6.3	Finite Element Method	290
6.4	Performance Calculation of a TEG-A Case Study	291

6.4.1	Averages of the Material Properties	294
6.4.2	Processing Measured Material Properties	295
6.4.3	Different Averages and the Corresponding Performance Values	297
6.4.4	Power Factor and Figure of Merit	298
6.4.5	Optimal Performance Based on Averaged Material Properties	299
6.4.6	Comparison between CPM, FDM, and FEM Simulations	300
6.4.6.1	Finite Difference Scheme for a TE Element	300
6.4.6.2	Performance Parameters Dependent on the Current Density	305
6.4.7	Calculation for a p-n Thermocouple	309
6.4.8	Adjustment of Cross-Sectional Areas	310
6.4.9	FEM Simulation	311
6.5	Nonlinear Material Parameters	315
6.5.1	Temperature-Dependent Material Properties	315
6.5.2	Temperature-Dependent Material Properties: Mathematica Model Using the Compatibility Approach	320
A	Numerical Data and Illustrative Cases	322
A.1	Coefficients of the Polynomials of the Material Properties	322
A.2	Material Properties: p-Type Skutterudite and Averages	323
A.3	Material Properties: n-Type Skutterudite and Averages	324
A.4	Power Factor and Figure of Merit of the n-Type Material	325
A.5	Performance Parameters in dependence on the Current Density	326
A.5.1	Program code	326
A.5.2	Results	327
	References	330
	<b>Index</b>	<b>335</b>