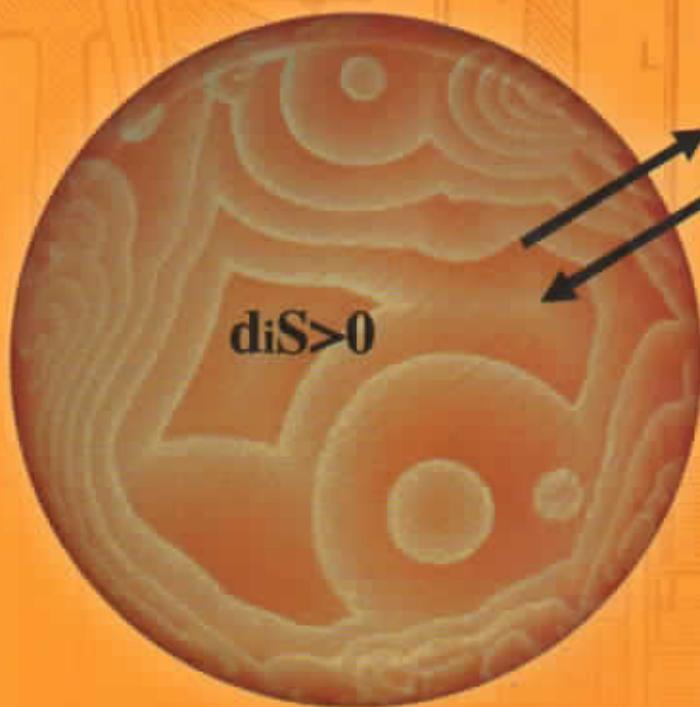


Second Edition

MODERN THERMODYNAMICS

From Heat Engines to Dissipative Structures



Dilip Kondepudi • Ilya Prigogine



WILEY

Modern Thermodynamics

From Heat Engines to Dissipative Structures

Second Edition

DILIP KONDEPUDI

Wake Forest University, USA

ILYA PRIGOGINE

Formerly Director, International Solvay Institutes, Belgium

WILEY

Contents

Preface to the Second Edition	xiii
Preface to the First Edition: Why Thermodynamics?	xv
Acknowledgments	xxi
Notes for Instructors	xxiii
List of Variables	xxv

I HISTORICAL ROOTS: FROM HEAT ENGINES TO COSMOLOGY

1 Basic Concepts and the Laws of Gases	3
Introduction	3
1.1 Thermodynamic Systems	4
1.2 Equilibrium and Nonequilibrium Systems	6
1.3 Biological and Other Open Systems	8
1.4 Temperature, Heat and Quantitative Laws of Gases	9
1.5 States of Matter and the van der Waals Equation	17
1.6 An Introduction to the Kinetic Theory of Gases	24
Appendix 1.1 Partial Derivatives	32
Appendix 1.2 Elementary Concepts in Probability Theory	33
Appendix 1.3 <i>Mathematica</i> Codes	34
References	39
Examples	39
Exercises	41
2 The First Law of Thermodynamics	45
The Idea of Energy Conservation Amidst New Discoveries	45
2.1 The Nature of Heat	46
2.2 The First Law of Thermodynamics: The Conservation of Energy	50
2.3 Elementary Applications of the First Law	57
2.4 Thermochemistry: Conservation of Energy in Chemical Reactions	61
2.5 Extent of Reaction: A State Variable for Chemical Systems	68
2.6 Conservation of Energy in Nuclear Reactions and Some General Remarks	69
2.7 Energy Flows and Organized States	71
Appendix 2.1 <i>Mathematica</i> Codes	79
Appendix 2.2 Energy Flow in the USA for the Year 2013	79
References	82
Examples	82
Exercises	85

3 The Second Law of Thermodynamics and the Arrow of Time	89
3.1 The Birth of the Second Law	89
3.2 The Absolute Scale of Temperature	96
3.3 The Second Law and the Concept of Entropy	99
3.4 Modern Formulation of the Second Law	104
3.5 Examples of Entropy Changes due to Irreversible Processes	112
3.6 Entropy Changes Associated with Phase Transformations	114
3.7 Entropy of an Ideal Gas	115
3.8 Remarks about the Second Law and Irreversible Processes	116
Appendix 3.1 The Hurricane as a Heat Engine	117
Appendix 3.2 Entropy Production in Continuous Systems	120
References	121
Examples	122
Exercises	123

4 Entropy in the Realm of Chemical Reactions	125
4.1 Chemical Potential and Affinity: The Thermodynamic Force for Chemical Reactions	125
4.2 General Properties of Affinity	132
4.3 Entropy Production Due to Diffusion	135
4.4 General Properties of Entropy	136
Appendix 4.1 Thermodynamics Description of Diffusion	138
References	139
Example	139
Exercises	140

II EQUILIBRIUM THERMODYNAMICS

5 Extremum Principles and General Thermodynamic Relations	145
Extremum Principles in Nature	145
5.1 Extremum Principles Associated with the Second Law	145
5.2 General Thermodynamic Relations	153
5.3 Gibbs Energy of Formation and Chemical Potential	156
5.4 Maxwell Relations	159
5.5 Extensivity with Respect to N and Partial Molar Quantities	160
5.6 Surface Tension	162
References	165
Examples	165
Exercises	166
6 Basic Thermodynamics of Gases, Liquids and Solids	169
Introduction	169
6.1 Thermodynamics of Ideal Gases	169
6.2 Thermodynamics of Real Gases	172
6.3 Thermodynamics Quantities for Pure Liquids and Solids	180
Reference	183
Examples	183
Exercises	184

7 Thermodynamics of Phase Change	187
Introduction	187
7.1 Phase Equilibrium and Phase Diagrams	187
7.2 The Gibbs Phase Rule and Duhem's Theorem	192
7.3 Binary and Ternary Systems	194
7.4 Maxwell's Construction and the Lever Rule	198
7.5 Phase Transitions	201
References	203
Examples	203
Exercises	204
8 Thermodynamics of Solutions	207
8.1 Ideal and Nonideal Solutions	207
8.2 Colligative Properties	211
8.3 Solubility Equilibrium	217
8.4 Thermodynamic Mixing and Excess Functions	222
8.5 Azeotropy	225
References	225
Examples	225
Exercises	227
9 Thermodynamics of Chemical Transformations	231
9.1 Transformations of Matter	231
9.2 Chemical Reaction Rates	232
9.3 Chemical Equilibrium and the Law of Mass Action	239
9.4 The Principle of Detailed Balance	243
9.5 Entropy Production due to Chemical Reactions	245
9.6 Elementary Theory of Chemical Reaction Rates	248
9.7 Coupled Reactions and Flow Reactors	251
Appendix 9.1 <i>Mathematica</i> Codes	256
References	260
Examples	260
Exercises	261
10 Fields and Internal Degrees of Freedom	265
The Many Faces of Chemical Potential	265
10.1 Chemical Potential in a Field	265
10.2 Membranes and Electrochemical Cells	270
10.3 Isothermal Diffusion	277
10.4 Chemical Potential for an Internal Degree of Freedom	281
References	284
Examples	284
Exercises	285
11 Thermodynamics of Radiation	287
Introduction	287
11.1 Energy Density and Intensity of Thermal Radiation	287
11.2 The Equation of State	291

11.3 Entropy and Adiabatic Processes	293
11.4 Wien's Theorem	295
11.5 Chemical Potential of Thermal Radiation	296
11.6 Matter–Antimatter in Equilibrium with Thermal Radiation: The State of Zero Chemical Potential	297
11.7 Chemical Potential of Radiation not in Thermal Equilibrium with Matter	299
11.8 Entropy of Nonequilibrium Radiation	300
References	302
Example	302
Exercises	302
III FLUCTUATIONS AND STABILITY	
12 The Gibbs Stability Theory	307
12.1 Classical Stability Theory	307
12.2 Thermal Stability	308
12.3 Mechanical Stability	309
12.4 Stability and Fluctuations in N_k	310
References	313
Exercises	313
13 Critical Phenomena and Configurational Heat Capacity	315
Introduction	315
13.1 Stability and Critical Phenomena	315
13.2 Stability and Critical Phenomena in Binary Solutions	315
13.3 Configurational Heat Capacity	317
Further Reading	320
Exercises	321
14 Entropy Production, Fluctuations and Small Systems	323
14.1 Stability and Entropy Production	323
14.2 Thermodynamic Theory of Fluctuations	326
14.3 Small Systems	331
14.4 Size-Dependent Properties	333
14.5 Nucleation	336
References	339
Example	339
Exercises	340
IV LINEAR NONEQUILIBRIUM THERMODYNAMICS	
15 Nonequilibrium Thermodynamics: The Foundations	343
15.1 Local Equilibrium	343
15.2 Local Entropy Production	345
15.3 Balance Equation for Concentration	346

15.4 Energy Conservation in Open Systems	348
15.5 The Entropy Balance Equation	351
Appendix 15.1 Entropy Production	354
References	356
Exercises	356
16 Nonequilibrium Thermodynamics: The Linear Regime	357
16.1 Linear Phenomenological Laws	357
16.2 Onsager Reciprocal Relations and the Symmetry Principle	359
16.3 Thermoelectric Phenomena	363
16.4 Diffusion	366
16.5 Chemical Reactions	371
16.6 Heat Conduction in Anisotropic Solids	375
16.7 Electrokinetic Phenomena and the Saxon Relations	377
16.8 Thermal Diffusion	379
References	382
Further Reading	382
Exercises	383
17 Nonequilibrium Stationary States and Their Stability: Linear Regime	385
17.1 Stationary States under Nonequilibrium Conditions	385
17.2 The Theorem of Minimum Entropy Production	391
17.3 Time Variation of Entropy Production and the Stability of Stationary States	398
References	400
Exercises	400
V ORDER THROUGH FLUCTUATIONS	
18 Nonlinear Thermodynamics	405
18.1 Far-from-Equilibrium Systems	405
18.2 General Properties of Entropy Production	405
18.3 Stability of Nonequilibrium Stationary States	407
18.4 Linear Stability Analysis	411
Appendix 18.1 A General Property of $d_F P/dt$	415
Appendix 18.2 General Expression for the Time Derivative of $\delta^2 S$	416
References	418
Exercises	418
19 Dissipative Structures	421
19.1 The Constructive Role of Irreversible Processes	421
19.2 Loss of Stability, Bifurcation and Symmetry Breaking	421
19.3 Chiral Symmetry Breaking and Life	424
19.4 Chemical Oscillations	431
19.5 Turing Structures and Propagating Waves	436
19.6 Dissipative Structures and Machines	440
19.7 Structural Instability and Biochemical Evolution	441

Appendix 19.1 <i>Mathematica</i> Codes	442
References	447
Further Reading	448
Exercises	449
20 Elements of Statistical Thermodynamics	451
Introduction	451
20.1 Fundamentals and Overview	452
20.2 Partition Function Factorization	454
20.3 The Boltzmann Probability Distribution and Average Values	456
20.4 Microstates, Entropy and the Canonical Ensemble	457
20.5 Canonical Partition Function and Thermodynamic Quantities	460
20.6 Calculating Partition Functions	461
20.7 Equilibrium Constants	467
20.8 Heat Capacities of Solids	469
20.9 Planck's Distribution Law for Thermal Radiation	472
Appendix 20.1 Approximations and Integrals	474
Reference	474
Example	475
Exercises	475
21 Self-Organization and Dissipative Structures in Nature	477
21.1 Dissipative Structures in Diverse Disciplines	477
21.2 Towards a Thermodynamic Theory of Organisms	483
References	485
Epilogue	487
Physical Constants and Data	489
Standard Thermodynamic Properties	491
Energy Units and Conversions	501
Answers to Exercises	503
Author Index	511
Subject Index	513

Author Index

- Andrews, Thomas 17, 20
Arrhenius, Svante August 235
Avogadro, Amedeo 13–14, 26
- Bernoulli, Daniel 24–5, 26, 451
Bertholet, Mercellin 61
Betz, Albert 78
Black, Joseph 10–11, 46, 187
Boltzmann, Ludwig 25, 27–8, 111, 287, 327, 451,
 452
Boyle, Robert 12–13, 24, 27, 46
- Carnot, Lazare 90
Carnot, Nicholas Léonard Sadi 46, 90–3
Celsius, Anders 11
Charles, Jacques 13, 14
Clapyrone, Émile 93
Clausius, Rudolf 22, 99–101, 103, 106
Cowen, Clyde 70
Crick, Francis 424
- Davy, Sir Humphrey 10
De Donder, Théophile 68, 107, 125–6, 128–9
de la Tour, Cagniard 17
Debye, Peter 182–3, 220
Duhem, Pierre 106, 153, 194
- Einstein, Albert 4
- Fahrenheit, Gabriel 11
Faraday, Michael 45
Fermat, Pierre 145
Fourier, Jean Baptiste Joesph 46, 72
Fowler 319
- Galilei, Galileo 10
Galvani, Luigi 45
Gay-Lussac, Joseph-Louis 14, 15
- Gibbs, Josiah Willard 125–6, 127, 153
Guggenheim, E.A. 266, 284, 319
- Helmholtz, Hermann von 50, 51
Henry, William 210
Hero of Alexandria 3
Hess, Germain Henri 50, 61, 62–3
Hildebrandt 319
Hill, Terrel 331, 339
Hückel, Erich 220
- Joule, James Prescott 14, 46, 47, 48
- Kelvin, Lord (William Thomson) 96
Kirchhoff, Gustav 66, 287, 288
- Landau, Lev 201–2
Laplace, Pierre-Simon de 46, 163
Lavoisier, Antoine-Laurent 46
Lewis, G.N. 178, 179, 208
- Mariotte, Edmé 12
Maxwell, James Clerk 25, 27, 159, 451
Mayer, Julius Robert von 50
- Nernst, Walter 110
Newton, Isaac 12, 46
- Oersted, Hans Christian 45
Onnes, Kamerlingh 173
Onsager, Lars 4, 359–60
Ostwald, Wilhelm 61
- Pascal, Blaise 7
Pasteur, Louis 424
Pauli, Wolfgang 70
Planck, Max 3, 50, 52, 105, 117, 290
Poisson, Siméon-Denis 46
Prigogine, Ilya 4, 107

Raoult, François-Marie 209
 Reines, Frederick 70
 Rumford, Count 47

Sackur 464
 Seebeck, Thomas 45
 Smith, Adam 3
 Stefan, Joseph 287

Tetrode 464
 Thomsen, Julius 61

Thompson, Benjamin 47
 Thompson, Benjamin (Count Rumford) 47
 Thomson, William (Lord Kelvin) 96

van der Waals, Johannes Diderik 17, 18, 22
 van Larr, J.J. 216
 van 't Hoff, Jacobus Henricus 213, 214
 Volta, Alessandro 45

Watt, James 3, 89
 Wien, Wilhelm 287, 295

Subject Index

- absolute scale of temperature 11, 96–7
 absolute zero 12
 absolute zero of chemical potential 299
 activation energy 235
 activity 220–1
 coefficient 208, 211
 reaction rates 238
 adiabatic processes
 ideal gases 170
 radiation 293–4
 real gases 176–7
 affinity 108, 129–32, 214
 general properties 132
 additivity 132–3
 coupling 133–5
 direction of reaction 132
 amino acids 424, 429
 anisotropic solids 375–7
 antimatter 297–9
 Arrhenius equation 234–5
 transition state theory 236
 Arrhenius theory of rates 249–50
 arrow of time 103
 athermal solutions 224
 atmosphere (unit of pressure) 12
 atmosphere of the Earth 7–8, 11–12, 268
 autocatalytic reactions 410
 average values 329–31, 456–7
 Avogadro number 12
 Avogadro volume 41
 azeotropes 195–6, 225
 azeotropic composition 225
 azeotropic transformation 225
 bar (unit of pressure) 11
 barometric formula 267
 Belousov–Zhabotinsky reaction 431, 433–5, 440
 Mathematica code 446–7
 Berthelot equation 173
 Betz law 78–9
 bifurcation 422–3
 general theory 423–4
 bifurcation equations 424
 bifurcation point 423
 binary systems
 azeotropes 195–6
 critical phenomena 317–20
 liquid mixtures in equilibrium with vapor 194–5
 perfect binary solutions 209
 solutions in equilibrium with pure solids 196–7
 binding energy per nucleon 232
 binomial distribution 33
 biochemical evolution 441–2
 biological systems 8–9
 energy flows 76–8
 biomolecular asymmetry 429–31
 blackbody radiation 50, 73, 289, 290
 boiling point 211–13
 Boltzmann constant 12, 27, 235
 Boltzmann principle 28
 Boltzmann probability distribution 453, 456–7
 bomb calorimeter 56
 bond enthalpy 67
 Boyle temperature 184
 Boyle's law 12, 14
 broken symmetry 422
 Brusselator reaction 410, 431
 Mathematica code 445–6
 caloric 12, 46
 calorie (unit of energy) 12, 47
 calorimeter 56
 calorimetry 56
 canonical ensemble 459–60
 canonical partition function 459, 460–1
 capillary rise 163–5
 Carnot's theorem 93, 97
 catalysis 235

- cell diagrams 273–4
 Celsius (unit of temperature) 12
 characteristic equation 414
 Charles' law 13
 chemical affinities 180
 chemical oscillations 431–2
 Belousov–Zhabotinsky reaction 433–5, 440
 other reactions 436
 chemical potential 126–7, 156–7, 265
 entropy production in a continuous system 267–8
 entropy production in a electrical conduction 269
 gases 178–80
 ideal gases 170–1
 in a field 265–7
 internal degrees of freedom 281–3
 Debye equation 283–4
 mean chemical potential 218
 radiation 296
 not in equilibrium with matter 299–300
 two level atom 296–7
 small systems 332–3
 zero chemical potential 297–9
 chemical reaction energy changes 127–9
 chemical stability 324–5
 chemical transformations
 coupled reactions 251
 first-order reactions, consecutive 252–4
 first-order reactions, reversible 252
 steady state assumption 254–5
 zero-order reactions 251–2
 entropy production 245–6
 example 246–8
 flow reactors 255–6
 law of mass action 239–41
 perturbation from equilibrium 242–3
 relationship between equilibrium constants and rate
 constants 241–2
 van 't Hoff equation 242
 matter transformations 231–2
 principle of detailed balance 243–5
 reaction rates 232–5, 248
 activities 238
 Arrhenius theory of rates 249–50
 rate equations 236–8
 transition state theory 251
 chirality 246
 symmetry breaking 424–8
 entropy production 428–9
 nonequilibrium symmetry breaking 429–31
 Clapron equation 190–1
 classical theory of nucleation 337
 Classical Thermodynamics 4
 Clausius inequality 106
 Clausius–Clapron equation 191–2, 226
 climate periodicity 482–3
 closed systems 4
 coefficient of thermal diffusion 381
 coefficient of volume expansion 159
 coexistence curve 189
 coexistence line 20
 colligative properties 211
 boiling and freezing point changes 211–13
 osmotic pressure 213–17
 collision cross-section 249
 collision frequency 249
 compressibility factor 21–2, 178
 concentration balance equation 346–8
 concentration cells 275
 condensed phases 180
 conduction 72, 112–13
 configurational heat capacity 315, 320–1
 conservation of energy 46, 50–7
 consolute point 317
 contact angles 164–5
 continuous systems entropy 120–1
 convection 72
 correlations 329–31
 corresponding states law 21
 molecular forces 23–4
 cosmic microwave background 231
 critical constants 21
 critical molar volume 20
 critical phenomena 315
 binary solutions 317–20
 stability 315–17
 critical point 189, 201–3
 critical pressure 20
 critical radius 337
 critical solution 317
 critical temperature 17, 20, 317
 cryoscopic constant 213
 Curie and Voigt method 376
 Curie principle 362
 cycle 91
 Dalton's law of partial pressures 14
 dark energy 231
 dark matter 231
 Debye equation in electric dipole relaxation 283–4
 Debye function 471–2
 Debye T^5 law 472
 Debye temperature 471

- Debye's theory 182–3
 Debye's theory of solids 470–2
 degree of advancement 68
 degrees of freedom 27, 193
 chemical potential 281–3
 Debye equation 283–4
 density of states 28
 designed structures 440
 detailed balance principle 243–5, 362
 Dieterici equation 173
 diffusion
 energy production 135
 nonequilibrium thermodynamics 366–70
 thermodynamic description 138–9
 diffusion energy production in discrete systems 135–6
 diffusion flow 347
 diffusion reaction 278–9
 direction of reaction 132
 dissipative structures 9, 405
 chemical oscillations 431–2
 Belousov–Zhabotinsky reaction 433–5, 440
 other reactions 436
 chiral symmetry breaking 424–8
 entropy production 428–9
 nonequilibrium symmetry breaking 429–31
 constructive role of irreversible processes 421
 loss of stability 421–2
 bifurcation 422–3
 bifurcation theory 423–4
 symmetry breaking 422–3
 machines 440–1
 structural instability 441–2
 Turing structures and propagating waves 436–40
 dissipative structures in nature
 climate periodicity 482–3
 geological systems 480
 local equilibrium assumption 477
 material science 478
 multicellular systems 478–80
 social insects 482
 drift velocity 280
 Dufour coefficient 382
 Dufour effect 379
 Duhem's theorem 194
 Duhem–Jouget theorem 312
 Earth's atmosphere 7–8, 11–12, 268
 ebullioscopic constant 213
 eigenvalue equation 414
 eigenvalues 412
 eigenvectors 412
 Einstein relation 280
 Einstein's theory of solids 469–70
 electric dipole relaxation 283–4
 electrochemical affinity 270–3
 electrochemical cells 273–4
 electrochemical potential 266
 electrokinetic phenomena 377–9
 electrolytes 218
 electrolytic cells 273–5
 electromotive force (EMF) 270–3
 EMF of a cell 273
 electroneutrality 218, 266
 elementary step 234
 emissivity 289, 290
 enantiomeric excess (EE) 262
 enantiomers 246, 424
 endothermic reactions 63
 energy 3
 conservation in open systems 348–51
 conservation of energy 46, 50–7
 energy flows and organized states 71
 biological systems 76–8
 process flows 73–5
 self-organization 71–2
 solar energy flow 75–6
 USA energy flow for 2013 79–81
 wind energy and Betz law 78–9
 extensivity 116
 Gibbs energy of formation 156–7
 minimum 146
 total change 53
 total internal energy 6, 7
 energy density 7, 287–90
 enthalpy 62
 ion formation 219
 minimum 151–2
 of reaction 63
 entropy 3, 6, 7, 99–103
 continuous systems 120–1
 extensivity 116
 gases 178
 ideal gas 115, 170
 irreversible 112
 irreversible processes
 gas expansion 113–14
 heat conduction 112–13
 local production 345–6
 maximum 146
 microstates 457–9
 canonical ensemble 459–60
 minimum entropy production theorem 391–2

- entropy (*Continued*)
 chemical systems 392–4
 coupled chemical reactions 395–6
 electrical circuit elements 397–8
 sequence of chemical reactions 394–5
 thermal conduction 396–7
 mixing 171–2
 nonequilibrium balance 351–3
 nonequilibrium production
 alternative forms 355
 invariant 354–5
 nonequilibrium radiation 300–1
 phase transformations 114–15
 production from chemical reactions 245–6
 example 246–8
 production from chiral-symmetry-breaking transitions 428–9
 production from stability 323–4
 chemical stability 324–5
 thermal stability 325–6
 production in a continuous system 267–8
 production in a electrical conduction 269
 radiation 293–4
 statistical interpretation 110–11
 time variation of entropy production 398–400
 entropy density 7
 entropy in chemical reactions 125–6
 affinity 129–32
 affinity, general properties 132
 additivity 132–3
 coupling 133–5
 direction of reaction 132
 chemical potential 126–7
 chemical reactions 127–9
 diffusion energy production 135
 discrete systems 135–6
 general properties 136–8
 equilibrium 239–41
 Le Chatelier–Braun principle 242–3
 equilibrium constants 220, 240, 241, 467–8
 relationship with rate constants 241–2
 equilibrium state stability 152
 equilibrium systems 6–7
 equipartition theorem 27
 Euler's theorem 137
 eutectic composition 197
 eutectic point 197
 eutectic temperature 197
 eutectics 196–7
 excess entropy production 409
 excess functions 223–4
 exothermic reaction 63
 extended thermodynamics 345
 extensive functions 116
 extensive variables 5
 extensivity 116, 160–1
 extent of reaction 68–9, 236–8
 extremum principles 145
 extensivity 160–1
 general thermodynamic relations 153
 chemical potential 156–7
 Gibbs energy of formation 156–7
 Gibbs energy of formation tabulation 157–8
 Gibbs–Duhem equation 153–4
 Gibbs–Helmholtz equation 155–6
 Helmholtz equation 154–5
 Maxwell relations 159–60
 partial molar quantities 160–1
 Second Law of Thermodynamics 145–6
 equilibrium state stability 152
 Legendre transforms 153
 maximum entropy 146
 minimum energy 146
 minimum enthalpy 151–2
 minimum Gibbs energy 149–51
 minimum Helmholtz energy 146–9
 surface tension 162
 capillary rise 163–5
 excess pressure in a liquid drop 163
 Fahrenheit (unit of temperature) 12
 Fick's law 269, 278, 358
 Field–Köros–Noyes (FKN) model 433, 434
 First Law of Thermodynamics 45–6
 conservation of energy 50–7
 conservation of energy in chemical reactions 61–5
 computation of ΔH_f using bond enthalpies 67
 enthalpy variation with temperature 65–6
 conservation of energy in nuclear reactions 69–71
 elementary applications
 adiabatic processes in an ideal gas 58–9
 molar heat capacities 57–8
 sound propagation 59–60
 energy flows and organized states 71
 biological systems 76–8
 process flows 73–5
 self-organization 71–2
 solar energy flow 75–6
 wind energy and Betz law 78–9
 extent of reaction 68–9
 heat, nature of 46–50

- first-order phase transitions 201
 first-order reactions 237
 consecutive 252–4
 reversible 252
 flow reactors 255–6
 fluctuations
 average values and correlations 329–31
 probability distribution 326–9
 forward rates 233
 Fourier's law 358, 386
 freezing point 211–13
 fugacity 178
 functions of state variables 5
 galvanic cells 273–5
 gas constant 12
 gas laws 11–17
 ideal gas law 14
 gases
 see also ideal gases
 thermodynamics 172–4
 adiabatic processes 176–7
 chemical affinities 180
 chemical potential 178–80
 entropy 178
 Helmholtz and Gibbs energies 177–8
 molar heat capacities 175
 total internal energy 174–5
 gases, kinetic theory *see* kinetic theory of gases
 Gauss divergence theorem 388
 Gaussian curve 29
 Gaussian distribution 34
 geological systems 480
 Gibbs–Duhem equation 153–4, 182, 190
 Gibbs energy of formation 156–7
 tabulation 157–8
 Gibbs energy of reaction 240
 Gibbs free energy 131, 202
 excess Gibbs energy 223–4
 gases 177–8
 ion formation 219
 minimum 149–51
 partial 161
 Gibbs–Helmholtz equation 155–6, 217
 Gibbs–Konovalov theorem 196
 Gibbs paradox 172
 Gibbs phase rule 192–4
 Gibbs stability theory 307
 fluctuations in molar amounts 310
 chemical stability 310–11
 diffusion fluctuations 311–13
 mechanical stability 309–10
 thermal stability 308–9
 Gibbs–Thompson equation 334
 Graham's law of diffusion 43
 Haber process 41
 half-life 237
 half-reactions 271
 heat 12
 definition 47
 nature of 46–50
 heat capacity 47, 170
 bases 175
 liquids and solids 182–3
 solids 469
 Debye theory of solids 470–2
 Einstein theory of solids 469–70
 heat conduction in anisotropic solids 375–7
 heat engines 90, 91
 heat flow 349
 heat flow laws 72
 heat of combustion 83
 Helmholtz energy
 gases 177–8
 minimum 146–9
 partial 161
 Helmholtz equation 154–5
 Henry's constant 210
 Henry's law 210, 225–6
 Hess's law 50, 61–3
 heterogeneous nucleation 339
 heterogeneous systems 189
 historical background 3–4, 9–10
 First Law of Thermodynamics 45–6
 gas laws 11–17
 homochirality 429
 homogeneous nucleation 339
 hurricanes 98–9, 117–20
 ideal gas law 14, 169
 ideal gases 169
 see also gases
 adiabatic processes in an ideal gas 58–9
 chemical potential 170–1
 entropy 115
 entropy and thermodynamic processes 170
 entropy of mixing and Gibbs paradox 171–2
 equation of state 169
 heat capacities and adiabatic processes 170
 total internal energy 169–70
 ideal mixtures 151

- ideal solutions 207, 223
 independent state of polarization 287
 intensive variables 5
 interfacial energy 332
 ion formation enthalpy and Gibbs free energy 219
 ion numbers 218
 ionic mobility 280, 281
 ionic strength 221
 irradiance 287
 irreversible processes 6
 entropy changes 112
 gas expansion 113–14
 heat conduction 112–13
 Second Law of Thermodynamics 116–17
 isolated systems 4
 isolated systems 109
 heat conduction 112
 isothermal calorimeter 56
 isothermal compressibility 159
 isothermal diffusion 277
 diffusion in a continuous system 277–8
 diffusion reaction 278–9
 Stokes–Einstein relation 279–81
 isothermal expansion 83
 Mathematica code 79
 isothermal volume change 55
 Jacobian matrix 412, 413
 joule (unit of energy) 12
 kelvin (unit of temperature) 12
 kinetic energy 82
 kinetic energy of diffusion 348
 kinetic potential 407
 kinetic theory of gases 24–5
 Maxwell speed distribution 29–31
 Maxwell–Boltzmann velocity distribution 27–9
 pressure 25–7
 Kirchhoff's law 66, 289, 290
 Landau theory 201–3
 Laplace equation 163
 latent heat 17
 law of mass action 239–41
 perturbation from equilibrium 242–3
 relationship between equilibrium constants and rate
 constants 241–2
 van 't Hoff equation 242
 Le Chatelier–Braun principle 242–3
 Legendre transforms 153
 Lennard–Jones energy 23–4
 lever rule 200
 linear phenomenological coefficient 269
 linear regime 232
 chemical reactions 371
 alternative forms of entropy productions 373–4
 linearity in coupled reactions 374–5
 many reactions 372–3
 single reaction 372
 diffusion 366–70
 Onsager reciprocal relations 359–62
 phenomenological laws 357–9
 symmetry principle 362–3
 thermoelectric phenomena 363–4
 Peltier effect 366
 Seebeck effect 364–5
 linear stability analysis 411–14
 liquid junction potential 273
 liquid junctions 273
 liquids
 thermodynamics
 equation of state 180–1
 heat capacities 182–3
 thermodynamic quantities 181–2
 local equilibrium 107, 343–5
 local equilibrium assumption 477
 Lotka–Volterra 'prey–predator' interaction 407, 449
 Lyapunov function 409
 Lyapunov functional 409
 second variation of entropy 409–10
 Lyapunov's theory of stability 407–9
 machines 440–1
 macrostate 111
 material science 478
Mathematica codes
 Belousov–Zhabotinsky reaction 446–7
 Brusselator 445–6
 chiral symmetry breaking 442–4
 corresponding states law 38
 equation of state 35–7
 linear kinetics 256–7
 Maxwell–Boltzmann speed distribution 38–9
 racemization reaction 259–60
 reversible reaction 258
 van der Waals equation 37
 work done in isothermal expansion 79
 matter transformations 231–2
 temperature ranges 232
 matter–antimatter equilibrium 297–9
 maximum entropy 146
 Maxwell–Boltzmann velocity distribution 27–9, 249

- Maxwell construction 198–200
 Maxwell distribution of velocities 344
 Maxwell relations 159–60
 Maxwell speed distribution 29–31
 Maxwell velocity distribution 29
 mean chemical potential 218
 mean ionic activity coefficient 219
 mechanical stability 309–10
 mechanical work 54–5
 melting point size-dependency 334–6
 membrane potentials 270
 metastable states 317
 Michaelis–Menten mechanism 254
 Michaelis–Menten rate law 375
 microscopic reversibility 362
 microstates 111, 452
 entropy 457–9
 - canonical ensemble 459–60
 minimum energy 146
 minimum enthalpy 151–2
 minimum Gibbs energy 149–51
 minimum Helmholtz energy 146–9
 mixing, entropy of 171–2
Modern Thermodynamics 4
 modes of motion 451
 molality 212, 219
 molar energy 15
 - partial 156
 molar enthalpy
 - of fusion 114
 - of vaporization 114
 - partial 161
 molar entropy
 - of fusion 114
 - of vaporization 114
 molar Gibbs energy 157–8
 molar heat capacities 47
 - gases 175
 motion energy levels 455
 multicellular systems 478–80
 nanothermodynamics 331
 near-equilibrium linear regime 364
 Nernst equation 273, 275
 Nernst heat theorem 110
 nonequilibrium stationary states 385
 - entropy production in electrical circuit elements 389–91
 - minimum entropy production theorem 391–2
 - chemical systems 392–4
 - coupled chemical reactions 395–6
 electrical circuit elements 397–8
 sequence of chemical reactions 394–5
 thermal conduction 396–7
 open chemical systems 387–9
 thermal gradients 385–7
 time variation of entropy production 398–400
 nonequilibrium systems 6–7, 9
 nonequilibrium thermodynamics
 - chemical reactions 371
 - alternative forms of entropy productions 373–4
 - linearity in coupled reactions 374–5
 - many reactions 372–3
 - single reaction 372
 - concentration balance equation 346–8
 - diffusion 366–70
 - electrokinetic phenomena 377–9
 - energy conservation in open systems 348–51
 - entropy balance equation 351–3
 - heat conduction in anisotropic solids 375–7
 - linear phenomenological laws 357–9
 - local entropy production 345–6
 - local equilibrium 343–5
 - extended thermodynamics 345
 - Onsager reciprocal relations 359–62
 - symmetry principle 362–3
 - thermal diffusion 379–82
 - thermoelectric phenomena 363–4
 - Peltier effect 366
 - Seebeck effect 364–5
 - nonideal behavior 211
 - nonideal solutions 208
 - nonionic solutions 217–18
 - nonlinear thermodynamics
 - far-from-equilibrium systems 405
 - general properties of entropy production 405–7
 - linear stability analysis 411–14
 - stability of stationary states 407
 - Lyapunov's theory of stability 407–9
 - second variation of entropy 409–10
 - stability criterion 410–11
 - normalization constant 453
 - normalization factor 28–9
 - nuclear chemistry 69–71
 - nucleation 336–9
 - nucleation sites 339
 - occupation number 456
 - ohmic heat 269
 - Ohm's law 56, 269, 358
 - Onsager reciprocal relations 365, 329, 359–62

- open systems 4, 8–9, 109
 - energy conservation 348–51
- order of reactions 234
- order through fluctuations 421
- organized states 71
 - process flows 73–5
 - self-organization 71–2
 - solar energy flow 75–6
- osmosis 213
 - osmotic coefficient 211
 - osmotic pressure 213–17
- Ostwald–Freundlich equation 334
- Ostwald ripening 334, 335

- p*–*V* isotherm 20, 188
- partial derivatives
 - basic identities 32
 - many variables 32
- partial molar energy 156
- partial molar Gibbs energy 161
- partial molar Helmholtz energy 161
- partial molar quantities 160–1
- partition function 453, 461
 - rotational partition function 465
 - thermodynamic quantities 463–4
 - translational partitions function 461–3
 - vibrational partition function 466
- pascal (unit of pressure) 11
- Peltier effect 358, 366
- perfect binary solutions 209
- perfect solutions 207, 222–3
- phase change 187
 - binary systems 194
 - azeotropes 195–6
 - binary liquid mixtures 194–5
 - solutions in equilibrium with pure solids 196–7
 - Duhem's theorem 194
 - Gibbs phase rule 192–3, 194
 - lever rule 200
 - Maxwell's construction 198–200
 - phase equilibrium 187–90
 - Clapryon equation 190–1
 - Clausius–Clapryon equation 191–2
 - phase transitions 201
 - behavior near critical point 201–3
 - general classification 201
 - tertiary systems 197–8
- phase diagrams 187–90
- phase transition 20
 - entropy changes 114–15
- phases 17

- phenomenological coefficients 357
- photon gas pressure 292
- photosynthesis 76–7
- Planck's constant 235
- Planck distribution 472
 - Planck's distribution law for thermal radiation 472–4
- plasma 232
- Poisson distribution 33–4
- positive definitive matrices 359
- pre-exponential factor 235, 249
- pressure
 - definition 11
 - kinetic theory 25–7
- pressure coefficient 159
- principle of detailed balance 243–5, 362
- probability density 27
- probability distribution 326–9
- probability distribution of molecular velocity 27
- probability theory 33
 - average values 33
 - common probability distributions
 - binomial distribution 33
 - Gaussian distribution 34
 - Poisson distribution 33–4
 - useful integrals 34
- proteins 424

- racemization 246, 425
- radiance 287
- radiant flux density 287
- radiation 73, 287
 - chemical potential 296
 - two level atom 296–7
 - energy density 287–90
 - entropy and adiabatic processes 293–4
 - entropy of nonequilibrium radiation 300–1
 - equation of state 291–3
 - matter–antimatter equilibrium 297–9
 - not in thermal equilibrium 299–300
 - Wien's theorem 295–6
- radiation intensity 287
- rate constants 234
 - relationship with equilibrium constants 241–2
- rate equations 236–8
- rate of conversion 68, 130
- rate of net conversion 233, 234
- rate-determining step 374
- reaction rates 232–5
 - elementary theory 248
 - Arrhenius theory of rates 249–50
 - transition state theory 251
 - rate equations 236–8

- reaction velocity 233, 234
 reactive collisions 344
 Redlich-Kwong equation 22, 173
 reduced heat flow 380
 reduced mass 250
 reduced variables 21
 regular solutions 224
 renormalization group 203
 residence time 255
 reverse rates 233
 reversible engine efficiency 93–6
 reversible processes 91
 Raoult's law 209
 rotational partition function 465
- Sackur-Tetrode equation 464
 salt bridges 273, 274
 saturated vapor pressure 189
 Saxen relations 377–9
Second Law of Thermodynamics
 absolute scale of temperature 96–7
 efficiency of a reversible engine 93–6
 entropy 99–103
 statements about the Second Law 103–4
 entropy changes in irreversible processes 112
 gas expansion 113–14
 heat conduction 112–13
 entropy changes with phase transformations 114–15
 entropy of an ideal gas 115
 entropy production in continuous systems 120–1
 extremum principles 145–6
 equilibrium state stability 152
 Legendre transforms 153
 maximum entropy 146
 minimum energy 146
 minimum enthalpy 151–2
 minimum Gibbs energy 149–51
 minimum Helmholtz energy 146–9
 historical background 89–93
 irreversible processes 116–17
 modern formulation 104–10
 second-order phase transitions 201
 second-order reactions 237
 Seebeck effect 358, 364–5
 self-organization 71–2, 117
 self-organization in nature 477–85
 Shomate equation 65
 size-dependent properties 333
 melting point 334–6
 solubility 333–4
 small systems 331–2
 chemical potential 332–3
- social insects 482
 solar energy flow 75–6
 solar radiant flux 77
 solids
 heat capacity 469
 Debye theory of solids 470–2
 Einstein theory of solids 469–70
thermodynamics
 equation of state 180–1
 heat capacities 182–3
 thermodynamic quantities 181–2
 solubility 217, 221
 size-dependency 333–4
 solubility product 220
 solutions
 azeotropy 225
 colligative properties 211
 boiling and freezing point changes 211–13
 osmotic pressure 213–17
 excess functions 223–4
 regular and athermal solutions 224
 ideal and nonideal solutions 207–11
 solubility equilibrium 217
 activity 220–1
 ionic solutions 218–20
 ionic strength 220–1
 nonionic solutions 217–18
 solubility 220–1
 thermodynamic mixing
 ideal solutions 223
 perfect solutions 222–3
 Soret coefficient 381
 Soret effect 379
 sound propagation 59–60
 spatial dissipative structure 436
 spatial structures 438
 specific enthalpy 74
 specific heat 11, 47
 specific intensity 287
 specific spectral entropy intensity 294
 spectral absorptivity 289
 spectral energy density 287
 spectral intensity 288
 spectral irradiance 288
 spectral radiance 288
 stability
 entropy production 323–4
 chemical stability 324–5
 thermal stability 325–6
 stability condition 325
 stability criterion 410–11
 standard electrode potentials 276

- standard molar enthalpy of formation 63, 64
 standard reaction enthalpy 64
 standard states 63–4, 158, 219
 state functions 5
 state of systems 4
 state variables 4–5
 states of matter 17–21
 corresponding states law 21
 molecular forces 23–4
 stationary states 385
 entropy production in electrical circuit elements 389–91
 minimum entropy production theorem 391–2
 chemical systems 392–4
 coupled chemical reactions 395–6
 electrical circuit elements 397–8
 sequence of chemical reactions 394–5
 thermal conduction 396–7
 open chemical systems 387–9
 stability 407
 linear stability analysis 411–14
 Lyapunov's theory of stability 407–9
 second variation of entropy 409–10
 stability criterion 410–11
 thermal gradients 385–7
 time variation of entropy production 398–400
 statistical interpretation of entropy 110–11
 statistical thermodynamics 451
 approximations and integrals 474
 Boltzmann probability distribution and average values 456–7
 canonical partition function 460–1
 equilibrium constants 467–8
 fundamentals and overview 452–4
 heat capacity of solids 469
 Debye theory of solids 470–2
 Einstein theory of solids 469–70
 microstates and entropy 457–9
 canonical ensemble 459–60
 partition function calculation 461
 rotational partition function 465
 thermodynamic quantities 463–4
 translational partitions function 461–3
 vibrational partition function 466
 partition function factorization 454–6
 Planck's distribution law for thermal radiation 472–4
 steady state assumption 254–5
 steam turbines 87
 Stefan–Boltzmann constant 73, 292
 Stefan–Boltzmann law 291–2
 Stirling approximation 172, 458, 474
 Stokes–Einstein relation 279–81
 strictly regular solutions 319
 structural instability 441–2
 surface tension 162, 332
 capillary rise 163–5
 excess pressure in a liquid drop 163
 symmetry breaking 422–3
 chiral 424–8
 entropy production 428–9
 nonequilibrium symmetry breaking 429–31
 symmetry number 465
 symmetry principle 362–3

 temperature 12
 terminal velocity 280
 tertiary systems 197–8
 thermal coefficients 69
 thermal conduction 396–7
 thermal diffusion 379–82
 thermal equilibrium 5–6
 thermal radiation 50, 287
 Planck's distribution law 472–4
 thermal stability 308–9, 325–6
 thermodynamic branch 411
 thermodynamic equilibrium 6
 thermodynamic flow 107
 thermodynamic forces 107
 thermodynamic mixing
 ideal solutions 223
 perfect solutions 222–3
 thermodynamic potential 145, 146
 ideal gases 170
 thermodynamic probability 327, 452
 thermodynamic quantities 463–4
 thermodynamics systems 4–6
 closed systems 4
 extensive variables 5
 functions of state variables 5
 intensive variables 5
 isolated systems 4
 open systems 4
 state functions 5
 state of systems 4
 state variables 4–5
 thermal equilibrium 5–6
 thermodynamics, historical origins 3
 Classical Thermodynamics 4
 Modern Thermodynamics 4
 thermodynamics theory of organisms 483–5
 thermoelectric effect 45
 thermoelectric phenomena 363–4
 Peltier effect 366
 Seebeck effect 364–5

24/2/14

- thermoelectric power 365
theta temperature 217
Third Law of Thermodynamics 110
torr (unit of pressure) 12
total internal energy of gases 174–5
total solar radiance 75
transition state theory 251
transition states 235
Arrhenius equation 236
translational partitions function 461–3
transport properties 451
triple point 193
Turing structures 436–40
unstable modes 412
upper critical temperature 317
USA energy flow for 2013 79–81
- van der Waals constants 16
van der Waals equation 16, 17–21
- corresponding states law 21
molecular forces 23–4
van der Waals forces 23
van der Waals isotherms 20
van 't Hoff equation 215–16, 242
velocity of reaction 130
vibrational partition function 466
virial coefficients 173–4
virial equation 173
- water
phase diagram 190
triple point 188, 193
wave propagation 436–40
Wien's theorem 295–6
wind energy 78–9, 87–8
work, definition of 47
- zero chemical potential 297–9
zero-order reactions 251–2
zeroth law of thermodynamics 6