

Index

Note: Page numbers that are underlined refer to definitions, laws, and theorems; those that are *italicized* refer to figures and marginal notes; those that are **boldfaced** refer to (gray) boxes.

- Absolute entropy, 79, 92, 111
 Absolute temperature scale, 20
 Absolute zero temperature, 29, 39, 100, 110, 111
 Activity, 127
 absolute, 127
 Additive constant, 87, 87, 92, 93, 111
 Adiabatic, 108, 108, 133
 Adiabatic coefficient, xvii, 70, 108.
 See also Heat capacity ratio
 Air, 4, 27, 27, 45, 68, 131
 Air conditioner, 1, 56, 109
 Amount of information, 81, 80–83
 definition of, 81
 examples of (dice), 81, 82
 Amount of substance, 18, 19
 as a variable, 123
 number of moles, xvii, 18
 number of particles, xvii, 17, 18
 Argon, 37, 37, 40
 Atmosphere, atm (unit), 29
 Availability, 115. *See also* Exergy
 Available states, 42, 43, 45, 100
 number of, *see* Number of available states
 Avogadro's number, xvii, 12, 13, 18, 84, 103
 Bit, 83, 85
 Boltzmann brain paradox, 103
 Boltzmann constant, xvii, 30
 Boltzmann distribution, 42, 41–42, 111
 definition of, 42
 Boltzmann entropy formula, 84, 153. *See also* Entropy, statistical definition of
 Boltzmann factor, 42
 Boltzmann, Ludwig (bio), 143
 Bomb calorimetry, 66
 Bose-Einstein condensation, 127, 139
 Bulk matter, 1, 12, 18
 Byte, 83
 Calorie, cal (unit), 78
 Calorimetry, 66
 bomb, 66
 Carnot cycle, 80, 109, 109, 110, 108–111
 efficiency of, 109, 110
 Carnot, Sadi (bio), 143
 Celsius scale, 20
 Centigrade scale, 20
 Change, thermodynamic, *see* Thermodynamic change
 Charles's Law, 136
 Chemical potential, xvii, 19, 124, 125, 125–126
 definition of, 125
 Gibbs free energy and, 125
 ideal gas, 126
 pressure and, 126
 Chemical reaction, 28, 36, 118, 124, 139
 Classical mechanics, 14
 Classical thermodynamics, 1, 12, 14
 Clausius inequality, 104, 104–105, 105, 117
 derivation of, 105
 Clausius, Rudolf (bio), 144
 Closed system, 23, 88
 Collision, 41
 Compressibility factor, xvii, 30, 127, 127
 definition of, 30
 Compressibility, isothermal, *see* Isothermal compressibility
 Condensed phase, 29, 57
 Conjugate pair, 116, 116, 117, 124
 Conjugate variable, 85, 116, 116–117, 124. *See also* Natural variable
 Control volume, 123. *See also* Open system
 Coordinate
 molecular, *see* Molecular coordinate
 Cubic meter, m³ (unit), 20
 Cycle(s), 56, 56, 97, 97–98
 Carnot, *see* Carnot cycle
 clockwise and counterclockwise, 98, 109
 heat and work around (nonzero), 56, 97, 109, 110
 of empirical science, 13, 13
 stages of, 97, 98, 109, 109, 110
 Dead state, 121
 Definition, 3, 4, 5, 7, 78
 definition of, 4, 5, 78

160 Index

- Degeneracy, ground state, [111](#)
- Derivative, [65](#), [71](#)
 ordinary, [65](#)
 partial, *see* Partial derivative
- Diathermic wall, [28](#), [59](#)
- Diatomic molecule, *see* Linear molecule
- Differential, [57](#), [71–74](#)
 exact, [72](#)
 inexact, [73](#)
 total, [70](#), [72](#)
- Differential form, [57](#), [66](#)
- Diffusion, [124](#), [125](#)
- Diffusive contact, [28](#), [124](#)
- Diffusive equilibrium, [125](#)
 fugacity criterion for, [127](#)
- Diffusive wall, [124](#)
- Disorder, [4](#), [78](#)
- Dividing wall, *see* Wall
- Duhem, Pierre (bio), [144](#)
- Efficiency, heat engine, xvii, [109](#), [110](#)
- Einstein, Albert, quote, [15](#)
- Electrostatic interaction, [38](#)
- Energy, [3](#), [4](#)
 chemical, [34](#)
 free, *see* Free energy
 internal, *see* Internal energy
 internal state, *see* Internal state energy
 kinetic, *see* Kinetic energy
 molecular state, *see* Molecular state energy
 potential, *see* Potential energy
- Energy conservation, [4](#), [13](#), [34](#), [42](#), [49](#), [53](#)
- Energy transfer, [41](#). *See also* Internal energy change
- Enthalpy, xvii, [68](#), [67–69](#)
 comparison with internal energy, [69](#)
 definition of, [68](#)
 highlights, [69](#)
 ideal gas, [69](#), [134](#)
 natural variables for, [68](#), [117](#)
 total differential, [117](#), [124](#)
- Enthalpy change, [69](#)
 heat and, [68](#)
 ideal gas, [134](#)
- Entropy, xvii, [3](#), [4](#), [21](#), [79](#), [84](#), [77–85](#)
 absolute, [79](#), [92](#), [111](#)
 differential form, [78](#), [95](#), [95](#)
 fundamental, [84](#)
 ideal gas, [87–96](#), [133](#)
 information definition of, [79](#), [79–80](#), [84](#), [84–85](#), [111](#)
 natural variables for, [88](#)
 state function property of, [80](#), [87](#)
 statistical definition of, [79](#), [80](#), [84](#)
 thermodynamic definition of, [78](#), [78](#), [80](#), [95](#), [111](#)
 Third-Law, [111](#). *See also* Entropy, absolute
 total differential, [95](#)
- Entropy change, [110](#), [109–111](#)
 heat and, [95](#), [94–96](#)
 ideal gas, [92–94](#), [95](#)
 isochoric, [91–92](#)
 isothermal, [89](#), [90](#), [88–91](#)
 reversible adiabatic, [95–96](#), [107–109](#)
 surroundings, [108](#)
 total system, [101](#), [107–108](#)
- Equation of state, [23](#), [23–24](#), [108](#), [108](#)
 ideal gas, [29](#), [29](#), [37](#)
 non-ideal, [37](#)
 pizza “system” example of, [24](#), [25](#)
- Equilibrium, [4](#), [26–27](#)
 mechanical, [28](#), [104](#)
 out of, [26](#), [27](#), [27](#)
 thermal, [28](#), [104](#)
 thermodynamic, *see* Thermodynamic equilibrium
 tire system example of, [26](#), [27](#), [101](#)
- Equipartition theorem, [39](#), [38–40](#)
 derivation of, [44](#)
 statement of, [39](#)
- Euler constant, [83](#), [93](#)
- Exergy, xvii, [4](#), [121–122](#)
 derivation of, [122](#)
 Gibbs free energy and, [121](#)
- Expansion coefficient, xvii, [71](#)
- Expansion work, *see* Work
- Expansion, Gas, *see* Gas expansion
- Extensive quantity, [19](#)
 definition of, [19](#)
 examples of, [19](#), [90](#)
- External change, [50](#)
 slow, [60](#)
 sudden, [27](#), [60](#), [101](#), [101](#)
- External pressure, *see* Pressure, surroundings
- First Law, [52](#), [53](#), [52–53](#), [57](#)
 differential form, [57](#)
 statement of, [53](#)
 total system form, [52](#)
- Fluctuation, statistical, [35](#), [35](#), [101](#), [125](#)
- Force, xvii, [28](#), [37](#), [57](#)
- Free energy, [2](#), [4](#), [115](#), [117](#). *See also* Helmholtz free energy; Gibbs free energy
 negative, [4](#), [117](#)
- Free expansion, [58](#), [134](#), [134](#)
 adiabatic, [134](#)
 ideal gas, [134](#)
 isothermal, [134](#)
- Free particle, [37](#)
- Fugacity, xvii, [2](#), [126](#), [127](#), [126–127](#)
 absolute, [127](#)
 chemical potential and, [127](#)
 definition of, [126](#)
 pressure and, [127](#)
- Fugacity coefficient, [127](#)
- Fundamental entropy, [84](#)
- Fundamental temperature, [20](#), [85](#)
- Gas, [28](#)
 ideal, *see* Ideal gas
 monoatomic, *see* Point particle
 non-ideal, [29](#)
- Gas blog, [135](#)
- Gas compression, [51](#), [120](#). *See also* Gas expansion
- Gas constant, xvii, [30](#)
- Gas expansion, [51](#), [52](#), [53](#), [62–63](#), [131–135](#)
 adiabatic, [62](#), [133](#)
 comprehensive compendium, [135–137](#)
 free, *see* Free expansion
 ideal, *see* Ideal gas change
 irreversible, [62](#), [103](#)
 isobaric (constant pressure), [52](#), [53](#), [62](#), [134](#)

- isothermal (constant temperature), 62, 66
 non-free, **132**
 non-ideal, 62
 reversible, 62
 reversible adiabatic, 108
 solving problems, **133**, 132–134, 135
 true, **51**, 61, 88, 119, 134
 types of, **132**, 132–134, 135
- Gibbs free energy, xvii, **117**, 117–118
 natural variables for, **117**
 total differential, **117**, **124**
- Gibbs free energy change, **119**, 119, **126**
 maximum non-expansion work and, 120
- Gibbs, Josiah Willard (bio), 144, 147
- Ground state, *111*
- Heat, xvii, 53, 59, 59
 absorbed and released, 98, 110, **110**
 definition of, 59
 reversible, *see* Reversible heat surroundings, 53
- Heat bath, 50, 66, 66, 108
- Heat capacity at constant pressure, xvii, 68, 67–69
 definition of, 68
 ideal gas, **69**
- Heat capacity at constant volume, xvii, 67, 66–67
 definition of, 67
 ideal gas, 67, **69**
- Heat capacity ratio, xvii, 70, 133
 ideal gas, **69**, 70, 134
- Heat death, 100, 101, 148
- Heat engine, 97, 97–98, 109, 121
 efficiency of, *see* Efficiency, heat engine
- Heat pump, 109
- Heaven, equilibrium as, 9, *101*
- Helmholtz free energy, xvii, **117**, 117–118
 natural variables for, **117**
 total differential, **117**, **124**
- Helmholtz free energy change
 maximum work and, 119
- Ideal gas, 29–30, 37, 134
 equation of state, **29**, 29, 37
 internal energy of, 39, 40
 of point particles, *see* Kinetic model
 rotating, 131–134
- Ideal gas change, 62, 134
 isochoric, 91–92
 isothermal, 89, **90**, 88–91, **103**
 reversible adiabatic, 70, 107–109, *109*, 133
 reversible isothermal, 62, 66, *109*, **126**
- Ideal gas law, **13**, 29
 deviations from, 30, 70, **127**, 127
 highlights, **29**
- Independent measurement, 81.
See also Particle, noninteracting (independent)
- additivity of information for, 81, **82**, 90
- Independent variable, 23–26, 28, 51, 124, **133**
 pizza “system” example and, **24**, 25
- Indicator diagram, 52, 52
 examples of, 53, *61*, *109*, *120*
- Information theory, 79, 81, 150
- Intensive quantity, 19
 definition of, 19
 examples of, **19**
- Intensive variable, 28
- Intermediary, 121
- Intermolecular interactions, 34, 37–38, 38, 70, **127**
- Internal energy, xvii, **19**, 36, 35–36
 definition of, 36
 ideal gas, 39, 40
 molecular state energy and, 35
 natural variables for, 67, 116, **117**
 surroundings, 52
 total differential, 70, 116, **117**, **124**
 total system, 52
- Internal energy change, 52, 66–67
 ideal gas, 134
 surroundings, 52
 total system, 52
- Internal pressure, xvii, 70, **127**, 127
 definition of, 70
- Internal state energy, **34**, 36
 intramolecular interactions and, 34
- Internal structure, 20–21, 34, **34**
- Irreversible change, **60**, 60, 60–61, 78
 nonspontaneous, 100, 101, *120*
 Second Law and, 100
 spontaneous, 27, *102*, 99–103, *120*
 surroundings, 104, *104*
 total system, 104
- Isentropic path, *108*. *See also* Adiabatic
- Isolated system, 34, 49
- Isotherm, 61, 108, *108*
- Isothermal compressibility, xvii, 71
- Joule apparatus, 70
- Joule, J (unit), 19
- Joule, James Prescott (bio), 144
- Kelvin scale, 20
- Kelvin, K (unit), **29**, 85
- Kelvin, Lord (William Thomson) (bio), 145
- Kinetic energy, **34**, 36, 38
 rotational motion and, 40
 translational motion and, 34, 36
- Kinetic model, 37–38, 41–46
- Laws, 12–14
 comparison with models, **14**
 completeness of, **14**, *17*
 examples of, **13**
 of physics, 13, 14, 34
 of Thermodynamics, 4, 12, *111*
- Linear molecule, **40**
- Liquid, 28, 29
- Liter, L (unit), 19
- Log blog, **63**, **83**
- Logarithm, 82
 base of, unit of information and, 82, **83**
 common, **83**
 natural, **63**, **83**, 84
- Macroscopic completeness (of thermodynamics), 17, 28
- Macroscopic observer, 79, 88, 89, 98, *100*

162 Index

- Macroscopic restriction, 101, 125
Macroscopic scale, 1, 11, 18, 26, 65, 135
“bulk” and, *1*
“macro” and, *1*
Macroscopic system, 12. *See also* Thermodynamic system
Macroscopic thermodynamics, 12. *See also* Classical thermodynamics
Mass
per mole (molar), xvii, 18
per particle, xvii, 18, 38
system, 18, 19
Mass trend, 39, 45
Maximum entropy, principle of, 103, 103, 103–105
Maximum work, 61, 119–120
as reversible work, 119
derivation of, 120
non-expansion, 120
Maxwell distribution of speeds, 44, 45, 44–46, 91
definition of, 44
Maxwell relation, 118
Maxwell, James Clerk (bio), 145
Maxwell-Boltzmann distribution, 42, 43, 42–44, 91
definition of, 43
Mean speed, 44, 45
Mechanical contact, 28, 53, 103, 134
Mechanical equilibrium, 28, 104
Meter, m (unit), 19
Mixture, 124, 127, 139
Model(s), 12–14
comparison with laws, 14
examples of, 13, 29
kinetic, *see* Kinetic model
Molar mass, xvii, 18
Molar quantity, xvii, 19
Molar volume, 19, 37
standard, 29
Molecular collision, 41
Molecular coordinate, 15, 20–21, 42, 88
and energy, 34
position, *see* Position
rotational, 40, 133
translational, 34, 133
velocity, *see* Velocity
Molecular scale, 1, 18, 26, 79
“micro” and, *1*
“nano” and, *1*
Molecular state, 20, 20–21, 26, 50
of the whole system, 21, 80, 88, 90
relationship to thermodynamic state, *21*, *26*
single-molecule, 20, 42, 80, 90
Molecular state energy, xvii, 34, 33–34, 35, 49
definition of, 34
Molecule, 14
comparison with dice, 82, 84
confirmation of existence of, *14*
linear (diatomic), *see* Linear molecule
nonlinear (polyatomic), *see* Nonlinear molecule
particle vs., *18*. *See also* Particle
Monoatomic gas, *see* Point particle
Movable wall, 28, 57, 58
Natural change, 101. *See also* Spontaneous change
Natural variable, 40, 52, 67.
See also Conjugate variable
Nernst theorem, 111
Nernst, Walther (bio), 145
Newton’s Laws of motion, 13, 13, 14
Nitrogen, 37, 40, 45
Non-ideal system, 29–30, 40
Non-state function, *see* Path function
Nonlinear molecule, 40
Number of available states, xvii, 80, 81, 82, 84, 101
absolute, 89
relative, 89
Number of moles, xvii, 18
Number of particles, xvii, 17, 18
Open system, 28, 123–124
Partial derivative, 65, 71–74
cross derivative “trick”, 72, 118
independent, 72
mathematical properties, 73
Partial derivative quantity, 70
Partial derivative relation, 71, 118
Particle, 14
free, 37
molecule vs., *18*. *See also* Molecule
noninteracting (independent), 29, 84, 88
point, 21, 37, 40
quantum, indistinguishability of, 93
Particle size, 38
Pascal, Pa (unit), 19
Path, 52, 53, 56, 60–61
definition via surroundings
pressure, 60
diagonal, 72, 73
irreversible, 61, 62, *104*, *120*, *134*
isothermal, 61, 62, *108*
loop, 56. *See also* Cycle(s)
reversible, 61, 62, 62, *108*, *120*
reversible adiabatic, 108.
See also Adiabatic
reversible isothermal, 108.
See also Isotherm
Path endpoint, 56
Path function, 56, 55–56, 98.
See also State function
Perfect differential, *see* Differential, exact
Perfect gas, *see* Ideal gas
Permeable wall, *see* Diffusive wall
Perpetual motion machine (of the second kind), 99, *100*
Phase, 28. *See also* Condensed phase; Gas; Liquid; Solid
Phase equilibrium, 2, 127. *See also* Mixture; Phase transition
Phase transition, 29, 57, 111, 117, 124, 127, 139
Piston-cylinder apparatus, 57, 58, 66, 108, *109*
Planck’s constant, 93
Planck, Max, 98, 111
Point particle, 21, 37, 40
Polyatomic molecule, *see* Nonlinear molecule
Polytropic path, *108*. *See also* Adiabatic
Position, xvii, 20, 34
absolute, 34
orientation, 34, 37
relative, 34

- Position state, 89, 89
 volume and, 88
- Potential energy, **34**, 36, 37
 intermolecular interactions and,
34
- Precision, perfect, 18, 19
- Pressure, xvii, 11–12, 17, **19**
 force and, 57
 internal, *see* Internal pressure
 surroundings, 58, 57–58
- Probability distribution, 42, 102
- Property, 12. *See also*
 Thermodynamic quantity
 emergent, 12, 100
- Pure substance, 18. *See also*
 Substance
 in a single phase, 28, 119, 124,
125
- Quantity, *see* Thermodynamic
 quantity
- Quantum mechanics, 5, **13**, 14, 92,
127
 discreteness of, 93
 internal structure and, 34
 particle indistinguishability, 93
- Rankine scale, 20
- Rankine, R (unit), 20
- Rankine, William (bio), 145
- Reaction, chemical, *see* Chemical
 reaction
- Reversible change, **60**, 60, 60–61,
78–79, 107–111
 surroundings, 108
 total system, 107–108
- Reversible heat, 78, 78, 94
- Reversible work, 60, 62, 94
- RMS speed, *see* Root-mean-square
 (RMS) speed
- Root-mean-square (RMS) speed,
45, 45
- Rotational coordinate, 40, 133
- Sackur-Tetrode equation, 87, 93,
111
- Second Law, 78, 99, 100, 97–103,
104
 as “arrow of time”, 100, 101
 as inequality, 99
 differential form, 104
 entropy statement of, 99, 99–100
 information statement of, 100,
100–103
 philosophy of, 100
 total system form, 99, 102
 traditional Statements of, 98–99
- SI units, *see* *Système International*
 (SI) units
- Sign convention, 53, 58, 110
- Single-molecule state, 20, 42, 80, **90**
- Solid, 28, 29
- Spiñal Tap*, *This is*
 excerpt of dialog, 157
 quote, 75, 78
- Specific heat, 67, 85
- Speed, 44
 mean, 44, 45
 nitrogen, 45
 root-mean-square (RMS), 45, 45
- Spontaneous change, 27, 102,
99–103, 120
 Gibbs criterion for, **119**, 119
- Standard deviation, 44, 45, 91
 definition of, 44
- Standard Temperature and
 Pressure (STP), **29**, 68, 121
- State, 20
 molecular, *see* Molecular state
 reference, 126–127
 standard, 121, 126, 126
 thermodynamic, *see*
 Thermodynamic state
- State function, 39, 55, 55–56
 cross derivative “trick”, 72
 mathematical properties, 56
- Statistical average, 14, 35, 39, 43,
88
 per particle, 14, 19
 time, 15, 35, 42
- Statistical mechanics, 3, 5, 14–15,
41–46, 127, 139
 description of, 14
 philosophy of, 14
 relationship to thermodynamics,
15, 15
- Statistical thermodynamics
 Albert Einstein quote regarding,
15
- Steam engine, 1, 98, 139, 149, 153
- STP, *see* Standard Temperature
 and Pressure (STP)
- Substance, 18, 24
 amount of, *see* Amount of
 substance
- Subsystem, 27, 27, **103**
 picture vs. system-plus-
 surroundings, 50, 60, 104
- Sudden external change, **27**, 60,
101, 101
- Surroundings, 34, 50, 49–50
 comparison with “externals”,
104
- Système International* (SI) units, 19
- System, *see* Thermodynamic
 system
- System mass, 18, **19**
- Talking Heads, excerpt of lyrics by,
9, 50
- Temperature, xvii, 11–12, 17, **19**,
39, 38–40
 absolute zero, *see* Absolute zero
 temperature
 definition of, 39
 fundamental, 20, 85
 negative, 110, 139
 surroundings, 66
- Temperature scale
 absolute, 20
 Celsius, 20
 centigrade, 20
 Kelvin, 20
 Rankine, 20
- Thermal contact, 28, 53, 104
- Thermal equilibrium, 28, 104
- Thermodynamic change, 50–52
 infinitesimal, 57, **69**
 irreversible, *see* Irreversible
 change
 isochoric (constant volume), 66,
66
 reversible, *see* Reversible change
- Thermodynamic constant, 92
- Thermodynamic equilibrium, 23,
26, 26–27, 34. *See also*
 Equilibrium
 definition of, 26
- Thermodynamic potential, **117**,
117, 118, **124**. *See also*
 Internal energy; Enthalpy;
 Gibbs free energy; Helmholtz
 free energy

164 Index

- Thermodynamic process, 55.
See also Thermodynamic change
- Thermodynamic quantity, xvii, 18, 17–20
as statistical average, 36, 126
extensive, *see* Extensive quantity
intensive, *see* Intensive quantity
molar, xvii, 19
partial derivative, 70
relative, 127
surroundings, xvii
total system, xvii
well-defined, 18, 26, 27
- Thermodynamic state, 20, 20–21, 26, 28, 50
change of, *see* Thermodynamic change
final, 51, 134, 135
initial, 51, 134, 135
relationship to molecular state, 21, 26
- Thermodynamic system, 18, 50, 49–50
closed, 23, 88
isolated, 34, 49
non-ideal, 29–30, 40
open, 28, 123–124
- Thermodynamic variable, 12, 17–18, 23, 26
conjugate, *see* Conjugate variable
extensive, *see* Extensive variable
independent, *see* Independent variable
intensive, *see* Intensive variable
natural, *see* Natural variable
- Thermodynamics, 11–12
applications of, 1, 28, 123, 139–140
classical, 1, 12, 14
core concepts of, xi, 3–4, 139
description of, 11
Laws of, 4, 12, *111*
philosophy of, 12
relationship to statistical mechanics, 15, 15
- Thermometer, 28
- Third Law, 79, 100, 111
statement of, 111
- Thomson, William (Lord Kelvin) (bio), 145
- Time average, 15, 35, 42
- Total differential, 70, 72
- Total system, 50, 50, 53, 99
- Translational coordinate, 34, 133
- Tufnel, Nigel, 80, 152
excerpt of dialog, 157
quote, 75, 78
- Uncertainty principle
quantum mechanics, 93
thermodynamics, 96
- Unnatural change, 101. *See also* Irreversible change, nonspontaneous
- Variable, *see* Thermodynamic variable
- Velocity, xvii, 20, 38–39
- Velocity state, 42, 43, 45, 91
temperature and, 88, 92
- Volume, xvii, 17, **19**
molar, *see* Molar volume
total differential, 70
- Volume change, **51**, 58, 89, **90**
infinitesimal, 57
- Wall, 28
diathermic, 28, 59
diffusive, 124
fixed, 28, 101
movable, 28, 57, 58
thermally insulating, 108
- Water, **40**, 78
- Work, xvii, 28, 53, 58, 58, 57–59
chemical, 53, 122
definition of, 58
electrical, 53, 122
infinitesimal, 57
maximum, *see* Maximum work
reversible, *see* Reversible work
surroundings, 53
total system, 121
useful (non-expansion), 121, 121–122
- Zeroth Law, 28, 27–29
statement of, 28