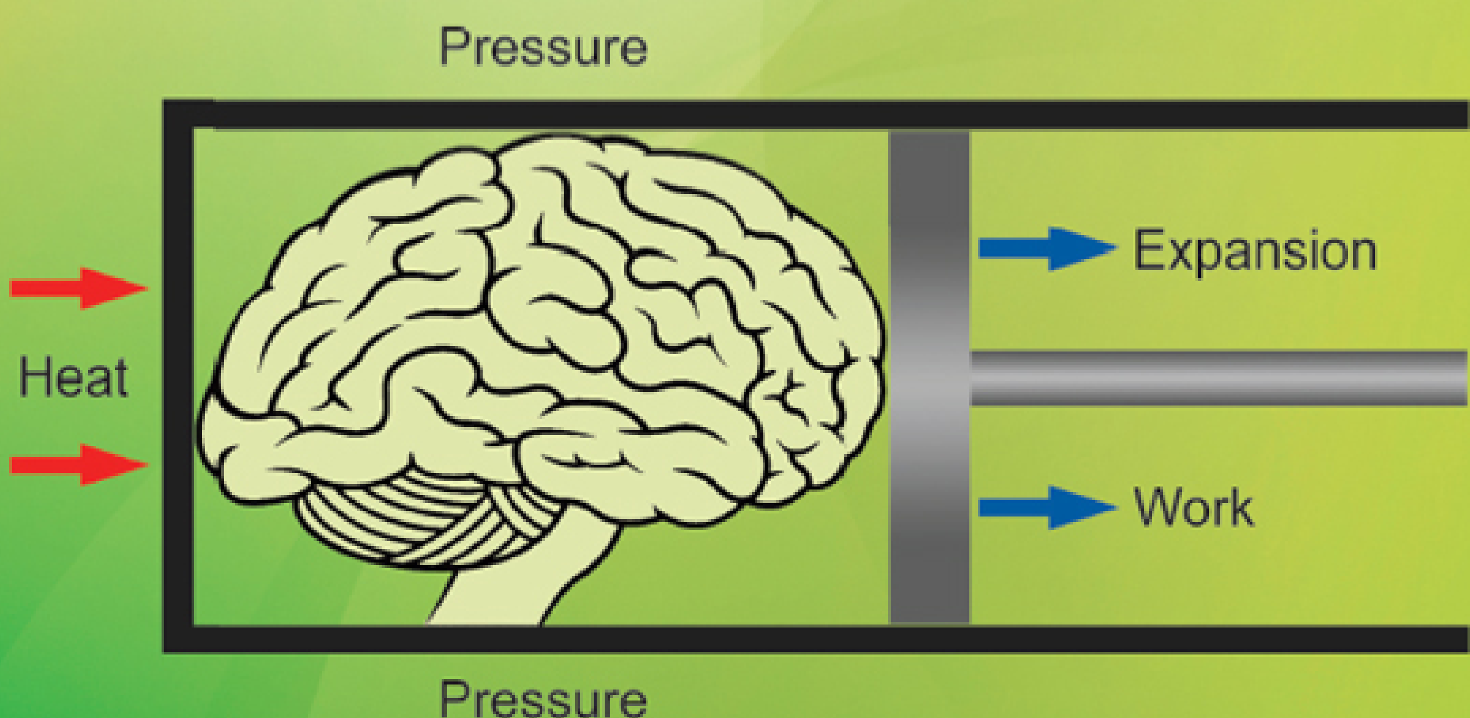
Bill Poirier

A Conceptual Guide to THERMODYNAMICS



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A Conceptual Guide to Thermodynamics

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To students everywhere

Contents

List of Illustrations

Helmholtz equation); phase transitions and mixtures (phase rule, Gibbs-Duhem equation).

James Prescott Joule: Brewer. Father of heat and the First Law. Absolute temperature; internal pressure (Joule experiment); isenthalpic expansion (Joule-Thomson effect). SI unit of energy.

Lord Kelvin (William Thomson): Member of the UK House of Lords. First, Second, *and* Third Laws. Absolute temperature; isenthalpic expansion (Joule-Thomson effect); thermoelectricity (Thomson effect). SI unit of temperature.

James Clerk Maxwell: *Huge* name in physics. Statistical mechanics (Maxwell and Maxwell-Boltzmann distributions); entropy and Second Law (Maxwell's demon); free energy (Maxwell relations); phase transitions (Maxwell construction).

Walther Nernst: Father of the Third Law. Chemical reactions (chemical affinity); electrochemistry (Nernst equation). Inventor of the Nernst electric lamp, and the electric piano. Ran afoul of the Nazis in Germany, prior to his death in 1941.

William Rankine: First, Second, *and* Third Laws. Heat engines (Rankine cycle, similar to Carnot cycle); phase transitions (enthalpy of vaporization). Inventor of the term, "potential energy." Rankine unit of temperature.

Steampunk Gallery

Goggles, top hat, ray gun, check.

Stanley Steamer with boiler.

Gorgeous, painstaking craftsmanship is a hallmark of steampunk.

around its time-averaged value, $\langle E(t) \rangle$ —indicated by the horizontal dashed line. This constant value is (essentially) the *internal energy*, U.

Figure 5.2 Intermolecular interaction potential. Typical intermolecular interaction potential energy, $E_{P,i}$, for a single point particle, i, as a function of distance, r, from another point particle. At close range, the particle feels the very steep “repulsive wall.” At intermediate ranges, there is an intermolecular attraction. At very long ranges, the particles do not interact at all, and are effectively “free.”

Chapter 6

Figure 6.1 Maxwell-Boltzmann distribution. Maxwell-Boltzmann distribution for a single velocity component, v_x, for a single particle (the v_y and v_z distributions are the same, as are those for all other system particles with the same mass). The two solid curves correspond to different values of the temperature, T. As T increases, the distributions become broader, thereby encompassing a greater effective range of available velocity states (represented by the dashed line segments).

Figure 6.2 Maxwell distribution of speeds. Maxwell distribution of speeds v, for a single particle. This is obtained by integrating the three-dimensional Maxwell-Boltzmann distribution over the two angles. The two solid curves correspond to different values of the temperature, T. The mean speed, $\langle v \rangle$ (vertical dotted lines), is nonzero, and increases with T. The RMS speed, $v_{rms} = \langle v^2 \rangle^{1/2}$ (vertical dashed lines), is larger than $\langle v \rangle$, but behaves similarly.

insulate, slowly expand. Stage 3: isothermal; insert apparatus in low T = T_c bath, slowly compress. Stage 4: adiabatic; remove apparatus from bath, insulate, slowly compress.

Chapter 14

Figure 14.1 The path less traveled. Three travellers follow three different isothermal paths from A to B: A. Lincoln (boots) takes the lower, irreversible path; M. Ghandi (bare feet) takes the middle, reversible path; E. Bunny (paw prints) takes the upper, irreversible path. The last path is not spontaneous and therefore forbidden by the Second Law—the Easter Bunny doesn’t exist!

Preface

Thank you for your interest in *A Conceptual Guide to Thermodynamics*. This book is itself a new concept of sorts, which merits some explanation.

First, a description of what this book is *not*. It is *not* a textbook; the discussion is insufficiently complete to serve as the primary text for an undergraduate thermodynamics course, and there are no problems or exercises. Neither is it a popular science or lay person's introduction; the primary intended audience is science and engineering students. Nor is it a history of thermodynamics; though that is itself a fascinating subject, you will find little such discussion here. It is definitely not a book written to impress academic colleagues; they will not be impressed.

What this book *is* is a conceptual and practical guide—a companion to your primary thermodynamics textbook, meant to supplement and clarify the latter. The goal is to simultaneously improve both your fundamental understanding of the material (the "conceptual" part) and your homework and exam performance (the "practical" part), to better "get you through" your thermodynamics course. Culling from over a decade of experience teaching undergraduate physical chemistry thermodynamics at Texas Tech University, this book was written from top to bottom with the practical needs of *you*, the student, foremost in mind.

But why should you buy this (fairly inexpensive) supplement *in addition* to the (no doubt much more expensive) required textbook you have likely already purchased? There are several reasons. First, some textbooks (and some lecturers) may give short shrift to the explication of core thermodynamics concepts such as equilibrium and entropy. The likely reason is clear: there is much material to cover, and they do not want to get bogged down in lengthy explanations and potentially confusing subtleties. Some of the problems arising in this field are indeed profound and intractable; several of its brilliant but frustrated early founders ended their own lives (see Appendix A) … That said, I have learned over my years of teaching thermodynamics that dedicating a modest amount of time during the early stages to a careful (but not *too* rigorous) discussion of the key concepts—if done succinctly and clearly—can lead to major practical benefits for students later on.

Second, a principal advantage of this approach is that the core concepts are pretty much the same across all of the many disciplines that (with good reason!) require thermodynamics training as part of their degree plans. Thus, students of chemistry, physics, biology, geosciences, and the engineering fields, may all benefit from this book, even though the application of this fundamental science varies greatly from field to field. To this end, discipline-specific material is mostly avoided here, in favor of instruction designed to convey the general *logic* of how to solve thermodynamics problems. In this context, memorization *per se* does not really help so much, though many students are naturally inclined to fall back on this tried-and-true companion. In contrast, a conceptual understanding offers something that most students ultimately find to be far more valuable—a sense of how to approach any given problem, as opposed to that uncomfortable state of having "no clue where to begin."

Third, in its role as a true "supplement" to your primary textbook, this book provides explicit references to the latest editions of all of the major thermodynamics texts used by each of the various disciplines listed above. A comprehensive list is provided on p. xv of this book, in the Textbook Guide section. In that section, also, terminology and notation differences between your primary text and this supplement are “translated” for your convenience. Moreover, at the start of each chapter, you will find a map that directs you to the page numbers in your primary text where corresponding material is presented. You will also find the occasional textbook-specific commentary sprinkled throughout this book. All of this is to make it as beneficial and easy for you to use as possible.

Among the range of individuals who would find this book useful, then, one might encounter:

- a **premed student preparing for the MCAT**, for whom thermodynamics is the “hardest class they ever took,” but who nevertheless needs a good MCAT score to get into medical school.
- a **brilliant physics major**, who has no trouble solving problems, but is dissatisfied with vague unscientific descriptions such as “entropy is a measure of disorder.”
- a graduate or graduate-bound **engineering student**, keen on understanding what is really going on in real-world applications.
- a **geochemist** or **materials scientist**, seeking a better intuition about the role of free energy in amorphous solids, or about processes that take place far from standard temperatures and pressures.
- anyone else—student, teacher or research professional—who would benefit from a better understanding of this interesting subject.

Acknowledgments

I am extraordinarily grateful for the substantial help and encouragement I have received from various individuals, in the course of putting together this book. I must thank Texas Tech University, and especially Carol Korzeniewski, the Chair of Chemistry and Biochemistry, for supporting my faculty development leave in the fall of 2011. Much of this book was designed during this “sabbatical” period, and might not have been possible—or at least severely delayed—without it. I must also thank Gérard Parlant and the Centre national de la recherche scientifique at the Université Montpellier 2, for acting as my hosts during this period (and particularly Odile Eisenstein, for the use of her office). My wife, Anne, is also to be commended for her copious patience and understanding—particularly considering the other ways we might have spent our time in the *sud de France*. I thank David Tannor and Michael New for the LaTeX style files used to typeset the earliest versions of the manuscript, and also Peter Wilson and Piet van Oostrum—respective authors of the `changepage` and `fancyhdr` packages, used extensively for the later versions. Of course, I am grateful to the many colleagues, educators, formal reviewers, and editors who read through those preliminary drafts, and provided much useful feedback. Above all, however, I must fervently acknowledge the many students who have urged me over the years to write such a book—without their ardor and persistent arm-twisting, it never would have happened.

Saint Mathieu de Tréviers, France — Bill Poirier
December, 2011

As this book nears completion, it has become clear that I must acknowledge by name those tireless volunteers who have reviewed the entire book manuscript; their copious and insightful “notes” have resulted in an immeasurably superior final product. To Joseph Ellis, Thomas Gibson, Jeremy Maddox, Jason L. McAfee, Michele S. McAfee, Corey Petty, and Caroline Taylor, you have earned my eternal gratitude. I would also be remiss not to acknowledge two specific editors at John Wiley & Sons, who bent over backwards and went the extra mile, time and again; this book *certainly* would not have happened without the many efforts taken on its behalf by Sarah Higginbotham and Sarah Keegan.

This book was fueled not so much by caffeine as by YES; may they make it into the Rock and Roll Hall of Fame.

Vienna, Austria

Bill Poirier
October, 2013

Textbook Guide

Thermodynamics is a cornerstone of many scientific disciplines. As such, there are many different textbooks that address this important subject—and a corresponding myriad of conventions, terminologies, and notations used. This section is designed to sort all of that out—at least for the specific reference textbooks considered here, listed (by discipline) below.

The list includes the latest edition of the most commonly used texts. Please do not be too discouraged if you do not see your primary text listed below; given the multiple disciplines represented, it is an inevitability that many excellent textbooks have to be omitted. That said, a *greatly expanded* list of reference texts is available on the companion website (http://www.conceptualthermo.com), which you should also consult. There, you will find customized, textbook-specific materials for the older and (as they are released) newer editions of the textbooks listed below—as well as for many other texts that are less frequently used.

If your favorite book is not listed on the website, please feel free to let me know via the website itself, or by sending an email directly to feedback@conceptualthermo.com. Please send detailed information (including ISBN) for the textbook that you are using, so that I can incorporate it into future book materials. In any case, you can still learn from the conceptual explanations provided in this book, without necessarily having to own *any* thermodynamics textbook.

Whether you wind up loving or hating this book, or somewhere in between, I certainly would appreciate your feedback—especially in the form of helpful suggestions for making it better. You can submit these via the website and email address above. If you like the book, consider spreading the word—to professors, social media friends, and even real friends, as appropriate.

0.1 List of Thermodynamics Textbooks by Discipline

In the list below, the boldfaced word at the start of each bibliographic entry is the **keyword** that will be used throughout the rest of this book to refer to that specific reference textbook. (In all but one case, the keyword is simply the first author's last name.) When looking up your primary textbook here, be sure to pay close attention to the *edition number* and publication year.

Thermodynamics Textbooks

Biological Sciences:

Atkins-life: P. Atkins and J. de Paula, *Physical Chemistry for the Life Sciences*, second edition (W. H. Freeman, 2011).

Chang: R. Chang, *Physical Chemistry for the Biosciences* (University Science Books, 2005).

Tinoco: I. Tinoco, Jr., K. Sauer, J. C. Wang, J. D. Puglisi, G. Harbison, and D. Rovnyak, *Physical Chemistry: Principles and Applications in Biological Sciences*, fifth edition (Prentice-Hall, 2013).

Chemistry:

Atkins: P. Atkins and J. de Paula, *Physical Chemistry*, ninth edition (W. H. Freeman, 2010).

Engel: T. Engel and P. Reid, *Physical Chemistry*, third edition (Pearson, 2013).

Levine: I. N. Levine, *Physical Chemistry*, sixth edition (McGraw-Hill, 2009).

McQuarrie: D. A. McQuarrie and J. D. Simon, *Physical Chemistry* (University Science Books, 1997).

Silbey: R. J. Silbey, R. A. Alberty, and M. G. Bawendi, *Physical Chemistry*, fourth edition (John Wiley & Sons, Inc., 2005).

Engineering:

Cengel: Y. A. Çengel and M. A. Boles, *Thermodynamics: An Engineering Approach*, seventh edition (McGraw-Hill, 2012).

Elliot: J. R. Elliott and C. T. Lira, *Introductory Chemical Engineering Thermodynamics*, second edition (Prentice-Hall, 2012).

Moran: M. J. Moran, H. N. Shapiro, D. D. Boettner, and M. B. Bailey, *Fundamentals of Engineering Thermodynamics*, seventh edition (John Wiley & Sons, Inc., 2012).

Prausnitz: J. M. Prausnitz, R. N. Lichtenthaler, and E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, third edition (Prentice-Hall, 1999).

Sandler: S. I. Sandler, *Chemical, Biochemical, and Engineering Thermodynamics*, fourth edition (John Wiley & Sons, Inc., 2006).

Smith: J. M. Smith, H. C. Van Ness, and M. M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, seventh edition (McGraw-Hill, 2005).

Geosciences:

Anderson: G. Anderson, *Thermodynamics of Natural Systems*, second edition (Cambridge University Press, 2005).

Faure: G. Faure, *Principles and Applications of Geochemistry*, second edition (Prentice-Hall, 1998).

Physics:

Baierlein: R. Baierlein, *Thermal Physics* (Cambridge University Press, 1999).

Callen: H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, second edition (John Wiley & Sons, Inc., 1985).

Kittel: C. Kittel and H. Kroemer, *Thermal Physics*, second edition (W. H. Freeman, 1980).

Reif: F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1965; reprinted by Waveland Pr, 2008).

Schroeder: D. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley, 2000).

0.2 Terminology and Notation Used in This Book

The terminology and mathematical notation of the most important physical, chemical, and thermodynamic quantities that are employed in this book are listed in the table below. The page on which each quantity is first introduced or defined is also listed.

Terminology and Notation

Quantity	Symbol	Page Number

Quantity	**Symbol**	**Page Number**
Amount of Substance (number of moles)	n	18
Amount of Substance (number of particles)	n	18
Avogadro's Number	N_{A}	18
Boltzmann Constant	k	30
Chemical Potential	μ	125
Compressibility Factor	Z	30
Efficiency (heat engine)	η	110
Energy (molecular)	E	34
Enthalpy	H	68
Entropy	S	84
Exergy	E	121
Expansion Coefficient	α	71
Force	F	28
Fugacity	F	126
Gas Constant	R	30
Generic Thermodynamic Quantity (molar)	X_{m}	19
Generic Thermodynamic Quantity (surroundings)	X_{sur}	50
Generic Thermodynamic Quantity (system)	X	19
Generic Thermodynamic Quantity (total system)	X_{tot}	50
Gibbs Free Energy	G	117
Heat	Q	59

Quantity	Symbol	Page Number
Heat Capacity at Constant Pressure	C_P	68
Heat Capacity at Constant Volume	C_V	67
Heat Capacity Ratio (adiabat coefficient)	γ	70
Helmholtz Free Energy	A	117
Internal Energy	U	36
Internal Pressure	π_T	70
Isothermal Compressibility	κ_T	71
Mass (per mole)	M	18
Mass (per particle)	M	18
Number of Available Molecular States	Ω	81
Position	(x, y, z)	20
Pressure	P	17
Temperature	T	39
Velocity	(v_x, v_y, v_z)	20
Volume	V	17
Work	W	58

0.3 Terminology and Notation Used in Textbooks

Consult the key below to "translate" the terminology and notation of this book into that of your primary textbook (or to the **IUPAC** Gold Book standard). The key is easy to use. Textbooks are listed by keyword, in alphabetical order. Unless stated otherwise, the notation used here, and that of a given text, are presumed to be identical. Where the two notations differ, that of this book appears to the left of the arrows presented in the key, and that of the textbook to the right.

For example, after the **Atkins** keyword below, the string "$P \to p$" appears. This means that this book uses '*P*' to denote the pressure, whereas *Physical Chemistry* by P. Atkins and J. de Paula uses '*P*'. Likewise, since *W* in this book is the work done *on* the system *by* the surroundings, the "$W \to -W$" that appears after **Cengel** below implies that '*W*' in that textbook is the work done *on* the surroundings *by* the system (a typical engineering convention).

Sometimes, more than one expression appears to the right or left of a given arrow. When found to the right of the arrow, separated by "or," it means that the textbook uses more than one notation to denote the same mathematical quantity. Likewise, multiple expressions to the left of an arrow, separated by "and," correspond to distinct quantities that the textbook represents using the same notation. When "(sometimes)" appears, it means that the textbook sometimes uses the phrase indicated, and other times uses the terminology of this book.

Note that the Terminology and Notation Key can be downloaded in tabular form, just for your specific textbook, from the website (`http://www.conceptualthermo.com`). For reference purposes, it is recommended that you download and print a copy of this key—together with various other textbook-specific materials that are also available online, for free.

Terminology and Notation Key

Anderson: molar mass $M \to$ gram formula weight gfw; $P_{\mathrm{sur}} \to P_{\mathrm{ext}}$; $Q \to q$; $dQ \to \delta q$; $W \to w$; $dW \to \delta w$; $X \to Z$; $X_{\mathrm{m}} \to Z$; $\Omega \to W$;

molecular state → microstate; state function → property or state variable

Atkins: M and $nM \to m$; $P \to p$; $P_{\rm sur} \to p_{\rm ex}$; $Q \to q$; $W \to w$; $\Omega \to W$; compressibility factor → compression factor; ideal gas → perfect gas; quantity → property (sometimes)

Atkins-life: $nM \to m$; $P \to p$; $P_{\rm sur} \to p_{\rm ex}$; $Q \to q$; $W \to w$; ideal gas → perfect gas; quantity → property (sometimes)

Baierlein: $A \to F$; E and $U \to E$; $dQ \to q$; $U \to E$ or $\langle E \rangle$; $dW \to w$; $X_{\rm sur} \to X_{\rm environment}$; $X_{\rm tot} \to X_{\rm total}$; $\Omega \to$ multiplicity; ideal gas law → empirical gas law (sometimes); quantity → attribute or property

Callen: $A \to F$; $E \to \varepsilon$ or E; $f \to (\xi/\xi^\circ)P^\circ$; $k \to k_B$; $n \to N$; $N \to \tilde{N}$; $dQ \to dQ$; $W \to W_M$; $dW \to dW_M$; $\eta \to \varepsilon_e$; diathermic → diathermal; exact differential → perfect differential; quantity → parameter; spontaneous → irreversible

Cengel: $C_P \to mc_p$; $C_V \to mc_{\mathcal{V}}$; exergy E → total exergy X; k and $\gamma \to k$; $nM \to m$; $n \to N$; $dQ \to \delta Q$; $R \to R_{\rm u}$; $(v_x, v_y, v_z) \to (V_x, V_y, V_z)$; $V \to \mathcal{V}$; $W \to -W$; $dW \to -\delta W$; $\alpha \to \beta$; $\kappa_T \to \alpha$; number of available molecular states Ω → thermodynamic probability P; closed system → control mass (sometimes); expansion coefficient → volume expansivity; open system → control volume (sometimes); Second Law → increase of entropy principle (sometimes); state function → property; work (expansion) → (moving) boundary work

Chang: $k \to k_B$; M and $nM \to m$; $M \to \mathcal{M}$; $P_{\rm sur} \to P_{\rm ex}$ or $P_{\rm ext}$; $Q \to q$; $dQ \to dq$; $W \to w$; $dW \to dw$; $X \to X_{\rm sys}$ or X; $X_{\rm m} \to \overline{X}$; $X_{\rm sur} \to X_{\rm surr}$; $X_{\rm tot} \to X_{\rm univ}$; $\Omega \to W$; Faraday constant → F; quantity → property

Elliott: $\mathrm{E} \to \underline{B}$; M and $nM \to m$; $(v_x, v_y, v_z) \to (u_x, u_y, u_z)$; $X \to \underline{X}$; $X_{\rm m} \to X$; $X_{\rm sur} \to \underline{X}_{surr}$; $X_{\rm tot} \to \underline{X}_{univ}$; $\alpha \to \alpha_P$ or α; $\eta \to \eta_\theta$; $\Omega \to W$ or p_i; diathermic → diathermal; exergy → availability (sometimes); molar quantity → intensive quantity; spontaneous → irreversible; state function → property; work (expansion) → expansion/contraction work

Engel: E and $\eta \to \varepsilon$; $k \to k_B$; $P_{\mathrm{sur}} \to P_{external}$; $Q \to q$; $dQ \to đq$; $W \to w$; $dW \to đw$; compressibility factor Z → compression factor Z; $\alpha \to \beta$; $\kappa_T \to \kappa$; $\Omega \to W$; diathermic → diathermal; quantity → function; spontaneous → natural

Faure: $Q \to q$; $U \to E$; $W \to -w$

IUPAC: $C_P \to C_p$; $f \to \overline{p}$ (sometimes); mass (per mole) M → relative molecular mass M_{r}; $N_{\mathrm{A}} \to L$ (sometimes); $P \to p$; $Q \to q$ (sometimes); $W \to w$ (sometimes); $\Omega \to W$; compressibility factor → compression factor

Kittel: $A \to F$; $C_P \to k_B C_p$; $C_V \to k_B C_V$; $E \to \varepsilon$; $F \to f$; $k \to k_B$; $m \to M$; $N_{\mathrm{A}} \to N_0$; $N/V \to n$; $P \to p$; $dQ \to đQ$; entropy S → conventional entropy $k_B \sigma$ or S; kT → fundamental temperature τ or kT; $dW \to dW$; $\mu \to N_0 \mu$; $\Omega \to g$; electron rest mass → M; heat capacity → conventional heat capacity; internal energy → energy; molecular state → microstate; Second Law → law of increase of entropy (sometimes); spontaneous → irreversible; surroundings → reservoir; thermodynamic state → macrostate

Levine: M and $nM \to m$; $Q \to q$; $W \to w$; $X \to X_{\mathrm{syst}}$ or X; $X_{\mathrm{sur}} \to X_{\mathrm{surr}}$; $X_{\mathrm{tot}} \to X_{\mathrm{univ}}$; $\eta \to e$; $\Omega \to W$; diathermic → thermally conducting; movable wall → nonrigid wall; diffusive equilibrium → material equilibrium; work (expansion) → P–V work; expansion coefficient → thermal expansivity

McQuarrie: $nM \to M$; F and $F \to F$; $k \to k_{\mathrm{B}}$; $Q \to q$; $(v_x, v_y, v_z) \to (u_x, u_y, u_z)$; $W \to w$; $X_{\mathrm{m}} \to \overline{X}$; $X_{\mathrm{sur}} \to X_{\mathrm{surr}}$; $X_{\mathrm{tot}} \to X_{\mathrm{total}}$; $\Omega \to W$

Moran: $A \to \Psi$; $C_P \to mc_p$; $C_V \to mc_v$; $k \to \mathrm{k}$; $nM \to m$; $P \to p$; $dQ \to \delta Q$; $R \to \overline{R}$; $(v_x, v_y, v_z) \to (\mathrm{V}_x, \mathrm{V}_y, \mathrm{V}_z)$; $W \to -W$; $dW \to -\delta W$;