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**M. Scott Shell** is an Associate Professor in the Chemical Engineering Department at the University of California, Santa Barbara. He earned his PhD in Chemical Engineering from Princeton in 2005 and is well known for his ability to communicate complex ideas and teach in an engaging manner. He is the recipient of a Dreyfus Foundation New Faculty Award, an NSF CAREER Award, a Hellman Family Faculty Fellowship, a Northrop-Grumman Teaching Award, a Sloan Research Fellowship, and a UCSB Distinguished Teaching Award.

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*Princeton University*

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*University of Texas, Austin*

"This text provides a long-awaited and modern approach that integrates statistical mechanics with classical thermodynamics, rather than the traditional sequential approach, in which teaching of the molecular origins of thermodynamic laws and models only follows later, after classical thermodynamics. The author clearly shows how classical thermodynamic concepts result from the underlying behavior of the molecules themselves."

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**To Janet, Mike, Rox, and the entire Southern Circus**

# Thermodynamics and Statistical Mechanics

## An Integrated Approach

M. SCOTT SHELL
University of California, Santa Barbara

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# Preface

Like so many texts, this book grew out of lecture notes and problems that I developed through teaching, specifically, graduate thermodynamics over the past seven years. These notes were originally motivated by my difficulty in finding a satisfactory introductory text to both classical thermodynamics and statistical mechanics that could be used for a quarter-long course for first-year chemical engineering graduate students. However, as the years pressed forward, it became apparent that there was a greater opportunity to construct a new presentation of these classic subjects that addressed the needs of the modern student. Namely, few existing books seem to provide an integrated view of both classical and molecular perspectives on thermodynamics, at a sufficient level of rigor to address graduate-level problems.

It has become clear to me that first-year graduate students respond best to a molecular-level "explanation" of the classic laws, at least upon initial discussion. For them this imparts a more intuitive understanding of thermodynamic potentials and, in particular, entropy and the second law. Moreover, students' most frequent hurdles are conceptual in nature, not mathematical, and I sense that many older presentations are inaccessible to them because concepts are buried deep under patinas of unnecessarily complex notation and equations.

With this book, therefore, I aim for a different kind of storytelling than the conventional *classical first, statistical second* approach. Namely, I have endeavored to organize the material in a way that presents classical thermodynamics and statistical mechanics side-by-side throughout. In a manner of speaking, I have thus eschewed the venerable *postulatory approach* that is so central to the development of the classical theory, instead providing a bottom-up, molecular rationale for the three laws. This is not to say that I reject the former and its impressive elegance, or that I view it as an unnecessary component of a graduate-level education in thermodynamics. It is merely a pedagogical choice, as I strongly believe one can only truly appreciate the postulatory perspective once one has a "gut feel" and a solid foundation for thermodynamics, and this is best served by a molecular introduction. Moreover, the topics of modern graduate research are increasingly focused on the nanoscale, and therefore it is essential that all students understand exactly how macroscopic and microscopic thermodynamic ideas interweave.

At the same time, this book seeks to provide a contemporary exposure to these topics that is complementary to classic and more detailed texts in the chemical thermodynamics canon. Here, I place heavy emphasis on *concepts* rather than formalisms, mathematics, or applications. My experience has been that complex notation and long analyses of intricate models at the outset get in the way of students' understanding of the basic conceptual foundations and physical behaviors. Therefore, I have tried to streamline notation and focus on simple qualitative models (e.g., lattice models) for building basic physical intuition and student confidence in model development and refinement. By the same token, this narrative does not try to be comprehensive in covering many applied

thermodynamic property models, which I feel are best left in existing and specialist texts. I also deliberately use a straightforward, casual voice for clarity.

I have included a number of problems at the end of each chapter, most of which are entirely original. Many of these are guided and multi-step problems that walk students through the analysis of different kinds of systems, including modern problems in biophysics and materials, for example. These are divided into three categories: *conceptual and thought problems* that address the basic origins, behaviors, and trends in various thermodynamic quantities; *fundamentals problems* that develop classic and general thermodynamic relations and equations; and, finally, *applied problems* that develop and analyze simple models of specific systems.

I owe tremendous thanks to the many students over the years in my group and course who have provided great amounts of feedback on my notes. Perhaps unbeknownst to them, it has been their questions, discussions, and epiphanies that have shaped this text more than anything else – inspiring a seemingly unending but happy circumstance of repeated revisions and improvements. I am also deeply indebted to my mentors Pablo, Thanos, Frank, and Ken, who not only chaperoned my own appreciation for thermodynamics, but also provided immaculate examples of clear and concise communication. Finally, I am profoundly fortunate to have the love and support of my family, and it is returned to them many times over.

As with any first edition, I am under no illusion that this book will be entirely free of errors, typographical or otherwise, despite the repeated edits it has received from many different eyes. I am grateful to future readers for pointing these out to me, and I welcome any form of feedback, positive or negative.

**M.S.S.**
Santa Barbara, CA

# Reference tables

**Table A** Counting and combinatorics formulae

| Description | Example | Formula |
|---|---|---|
| Number of ways to pick $k$ ordered objects from $n$ without replacement | How many ways are there to put $k$ distinctly colored marbles in $n$ separate buckets, with at most one marble per bucket? | ${}_nP_k = \frac{n!}{(n-k)!}$ |
| Number of ways to pick $k$ unordered objects from $n$ without replacement | How many ways are there to put $k$ identical blue marbles in $n$ separate buckets, with at most one marble per bucket? | ${}_nC_k = \frac{n!}{k!(n-k)!}$ |
| Number of ways to pick $k$ ordered objects from $n$ with replacement | How many ways are there to put $k$ distinctly-colored marbles in $n$ separate buckets, with any number of marbles per bucket? | $n^k$ |
| Number of ways to pick $k$ unordered objects from $n$ with replacement | How many ways are there to put $k$ identical orange marbles in $n$ separate buckets, with any number of marbles per bucket? | $\frac{(k+n-1)!}{k!(n-1)!}$ |
| Number of ways to pick $k_1$ objects of type 1, $k_2$ of type 2, etc., out of $n = k_1 + k_2 + \cdots$ in an unordered manner and without replacement | How many ways are there to put $k_1$ blue, $k_2$ orange, and $k_3$ red marbles in $k_1 + k_2 + k_3$ buckets, with at most one marble per bucket? | $\frac{n!}{\prod_i k_i!} = \frac{\left(\sum_i k_i\right)!}{\prod_i k_i!}$ |

**Table B** Useful integrals, expansions, and approximations

| | |
|---|---|
| $\ln n! \approx n \ln n - n$<br>$n! \approx (n/e)^n$ | $\int_0^\infty e^{-cx^2}\,dx = \frac{\pi^{1/2}}{2c^{1/2}}$ |
| $e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$ | $\int_0^\infty xe^{-cx^2}\,dx = \frac{1}{2c}$ |
| $(1+x)^n = \sum_{k=0}^{n} \frac{n!}{k!(n-k)!} x^k$ | $\int_0^\infty x^2e^{-cx^2}\,dx = \frac{\pi^{1/2}}{4c^{3/2}}$ |
| $\int_0^\infty x^n e^{-x}\,dx = n! = \Gamma(n+1)$ | $\int_0^\infty x^3e^{-cx^2}\,dx = \frac{1}{2c^2}$ |
| $\ln(1+x) \approx x$ for small $x$ | $\int_0^\infty x^4e^{-cx^2}\,dx = \frac{3\pi^{1/2}}{8c^{5/2}}$ |
| $(1+x)^{-1} \approx 1 - x$ for small $x$ | $\int_0^\infty x^n e^{-cx^2}\,dx = \frac{\pi^{1/2}(n-1)!!}{2^{n/2+1}c^{(n+1)/2}}$ ($n$ even) |

**Table C** Extensive thermodynamic potentials

| Name | Independent variables | Differential form | Integrated form |
|---|---|---|---|
| Entropy | $S(E, V, \{N\})$ | $dS = \frac{1}{T}\,dE + \frac{P}{T}\,dV - \sum_i \frac{\mu_i}{T}\,dN_i$ | $S = \frac{E}{T} + \frac{PV}{T} - \sum_i \frac{\mu_i N_i}{T}$ |
| Energy | $E(S, V, \{N\})$ | $dE = T\,dS - P\,dV + \sum_i \mu_i\,dN_i$ | $E = TS - PV + \sum_i \mu_i N_i$ |
| Enthalpy | $H(S, P, \{N\})$ | $dH = T\,dS + V\,dP + \sum_i \mu_i\,dN_i$ | $H = E + PV = TS + \sum_i \mu_i N_i$ |
| Helmholtz free energy | $A(T, V, \{N\})$ | $dA = -S\,dT - P\,dV + \sum_i \mu_i\,dN_i$ | $A = E - TS = -PV + \sum_i \mu_i N_i$ |
| Gibbs free energy | $G(T, P, \{N\})$ | $dG = -S\,dT + V\,dP + \sum_i \mu_i\,dN_i$ | $G = E + PV - TS = A + PV$ $= H - TS = \sum_i \mu_i N_i$ |

**Table D** Intensive per-particle thermodynamic potentials for single-component systems

| Name | Independent variables | Differential form | Integrated relations |
|---|---|---|---|
| Entropy per particle | $s(e, v)$ | $ds = \frac{1}{T}\,de + \frac{P}{T}\,dv$ | $\frac{\mu}{T} = -s + \frac{e}{T} + \frac{Pv}{T}$ |
| Energy per particle | $e(s, v)$ | $de = T\,ds - P\,dv$ | $\mu = e - Ts + Pv$ |
| Enthalpy per particle | $h(s, P)$ | $dh = T\,ds + v\,dP$ | $h = e + Pv$ $\mu = h - Ts$ |
| Helmholtz free energy per particle | $a(T, v)$ | $da = -s\,dT - P\,dv$ | $a = e - Ts$ $\mu = a + Pv$ |
| Gibbs free energy per particle | $g(T, P)$ | $dg = -s\,dT + v\,dP$ | $g = e + Pv - Ts = a + Pv$ $= h - Ts$ $\mu = g$ |

**Table E** Thermodynamic calculus manipulations

| Name | Applies to | Functional form | Example |
|---|---|---|---|
| Inversion | Anything | $\left(\frac{\partial X}{\partial Y}\right)_Z = 1 \Big/ \left(\frac{\partial Y}{\partial X}\right)_Z$ | $\left(\frac{\partial P}{\partial S}\right)_T = 1 \Big/ \left(\frac{\partial S}{\partial P}\right)_T$ |
| Triple product rule | Anything | $\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial Y}{\partial Z}\right)_X = -1$ | $\left(\frac{\partial P}{\partial T}\right)_S = -\left(\frac{\partial S}{\partial T}\right)_P \Big/ \left(\frac{\partial S}{\partial P}\right)_T$ |
| Addition of variable | Anything | $\left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial X}{\partial W}\right)_Z \Big/ \left(\frac{\partial Y}{\partial W}\right)_Z$ | $\left(\frac{\partial H}{\partial V}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial T}\right)_P$ |
| Non-natural derivative | Anything | $Z(X,Y) \rightarrow \left(\frac{\partial Z}{\partial Y}\right)_W = \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_W + \left(\frac{\partial Z}{\partial Y}\right)_X$ | $\left(\frac{\partial E}{\partial V}\right)_P = \left(\frac{\partial E}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_P + \left(\frac{\partial E}{\partial V}\right)_S = T\left(\frac{\partial S}{\partial V}\right)_P - P$ |
| Potential transformation | Potentials | $\frac{\partial}{\partial X}\left(\frac{F_1}{X}\right)_Y = -\frac{F_2}{X^2}$ | $\frac{\partial}{\partial T}\left(\frac{A}{T}\right)_V = -\frac{E}{T^2}$ |
| Maxwell relations | Potential second derivatives | $\left(\frac{\partial^2 F}{\partial X\, \partial Y}\right) = \left(\frac{\partial^2 F}{\partial Y\, \partial X}\right) \rightarrow \left(\frac{\partial \mathcal{A}}{\partial X}\right)_Y = \left(\frac{\partial \mathcal{B}}{\partial Y}\right)_X$ | $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ |

The term "anything" indicates any complete state function.

**Table F** Measurable quantities

| Name | Notation and definition |
|---|---|
| Pressure | $P$ |
| Temperature | $T$ |
| Volume | $V$ |
| Total mass of species $i$ | $m_i$ |
| Total moles of species $i$ | $n_i$ |
| Molecular weight of species $i$ | $\mathcal{M}_i$ |
| Molecules of species $i$ | $N_i = m_i/\mathcal{M}_i$ |
| Mole fraction of species $i$ | $x_i$, $y_i$, or $z_i$ |
| Enthalpy or latent heat of phase change | $\Delta H_{\text{latent}}$ |
| *per particle or per mole* | $\Delta h_{\text{latent}}$ |
| Constant-volume heat capacity | $C_V \equiv \left(\frac{\partial E}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$ |
| *per particle or per mole* | $c_V \equiv \left(\frac{\partial e}{\partial T}\right)_{v} = T\left(\frac{\partial s}{\partial T}\right)_{v}$ |
| Constant-pressure heat capacity | $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$ |
| *per particle or per mole* | $c_P \equiv \left(\frac{\partial h}{\partial T}\right)_{P} = T\left(\frac{\partial s}{\partial T}\right)_{P}$ |
| Isothermal compressibility | $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = -\left(\frac{\partial \ln V}{\partial P}\right)_{T,N} = -\left(\frac{\partial \ln v}{\partial P}\right)_{T}$ |
| Thermal expansivity or thermal expansion coefficient | $\alpha_P \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} = \left(\frac{\partial \ln V}{\partial T}\right)_{P,N} = \left(\frac{\partial \ln v}{\partial T}\right)_{P}$ |

**Table G** Common single-component statistical-mechanical ensembles

| Property | Microcanonical | Canonical | Grand canonical | Isothermal–isobaric |
|---|---|---|---|---|
| Constant conditions | $E, V, N$ | $T, V, N$ | $T, V, \mu$ | $T, P, N$ |
| Fluctuations | None | $E$ | $E, N$ | $E, V$ |
| Microstate probabilities | $\wp_m = \frac{\delta_{E_m,E}}{\Omega(E,V,N)}$ | $\wp_m = \frac{e^{-\beta E_m}}{Q(T,V,N)}$ | $\wp_m = \frac{e^{-\beta E_m+\beta\mu N_m}}{\Xi(T,V,\mu)}$ | $\wp_m = \frac{e^{-\beta E_m-\beta PV_m}}{\Delta(T,P,N)}$ |
| Partition function | $\Omega(E,V,N) = \sum_n \delta_{E_n,E}$ | $Q(T,V,N) = \sum_n e^{-\beta E_n}$ | $\Xi(T,V,\mu) = \sum_N \sum_n e^{-\beta E_n+\beta\mu N}$ | $\Delta(T,P,N) = \sum_V \sum_n e^{-\beta E_n-\beta PV}$ |
| Relations to other partition functions | None | $Q = \sum_E e^{-\beta E}\Omega(E,V,N)$ | $\Xi = \sum_N \lambda^N Q(T,V,N)$<br>$= \sum_N \sum_E \lambda^N e^{-\beta E}\Omega(E,V,N)$<br>where $\lambda \equiv \exp(\beta\mu)$ | $\Delta = \sum_V e^{-\beta PV} Q(T,V,N)$<br>$= \sum_V \sum_E e^{-\beta E-\beta PV}\Omega(E,V,N)$ |
| Potential | $S = k_B \ln \Omega(E,V,N)$ | $A = -k_B T \ln Q(T,V,N)$ | $PV = k_B T \ln \Xi(T,V,\mu)$ | $G = -k_B T \ln \Delta(T,P,N)$ |
| Classical partition function | $\Omega = \frac{1}{h^{3N}N!}\int \delta\left[H(\mathbf{p}^N,\mathbf{r}^N) - E\right] d\mathbf{p}^N\, d\mathbf{r}^N$ | $Q = \frac{Z(T,V,N)}{\Lambda^{3N}N!}$<br>$Z \equiv \int e^{-\beta U(\mathbf{r}^N)}\, d\mathbf{r}^N$<br>$\Lambda \equiv \left[h^2/(2\pi m k_B T)\right]^{1/2}$ | $\Xi = \sum_{N=0}^{\infty} \frac{\lambda^N Z(T,V,N)}{\Lambda^{3N}N!}$<br>where $\lambda \equiv \exp(\beta\mu)$ | $\Delta = \frac{1}{\Lambda^{3N}N!}\int_0^\infty e^{-\beta PV} Z(T,V,N) dV$ |

Sums over $n$ are sums over all microstates at a given $V$ and $N$.
Sums over $N$ are from 0 to $\infty$, sums over $V$ are from 0 to $\infty$, and sums over $E$ are from $-\infty$ to $\infty$.
Classical partition functions are given for a monatomic system of indistinguishable, structureless particles.

**Table H** Fundamental physical constants

| Name | Notation and definition |
|---|---|
| Boltzmann constant | $k_B = 1.38065 \times 10^{-23}$ J/K |
| Gas constant | $R = 8.31446$ J/mol · K |
| Avogadro constant | $\mathcal{N}_A = 6.02214 \times 10^{23}$ mol$^{-1}$ |
| Elementary unit of charge | $e = 1.60218 \times 10^{-19}$ C |
| Planck constant | $h = 6.62607 \times 10^{-34}$ J · s |
| Reduced Planck constant | $\hbar = h/(2\pi) = 1.05457 \times 10^{-34}$ J · s |
| Standard gravitational acceleration | $g = 9.80665$ m/s$^2$ |
| Vacuum permittivity | $\epsilon_0 = 8.8542 \times 10^{-12}$ C$^2$/J · m |