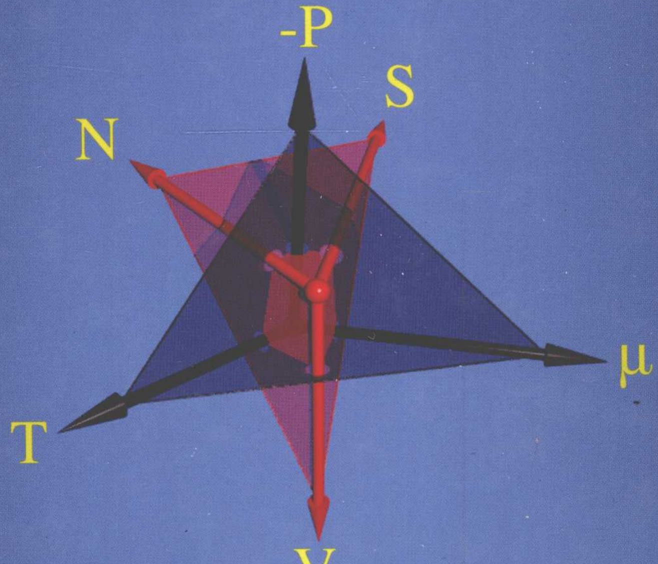
Classical and Geometrical Theory of

CHEMICAL AND PHASE THERMODYNAMICS



Frank Weinhold

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It was an act of desperation. For six years I had struggled with the blackbody theory. I knew the problem was fundamental, and I knew the answer. I had to find a theoretical explanation at any cost, except for the inviolability of the two laws of thermodynamics.

Max Planck (letter to R. W. Wood, 1931)

If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much the worse for Maxwell's equations. If it is found to be contradicted by observation—well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can offer you no hope; there is nothing for it but to collapse in deepest humiliation.

Sir Arthur Eddington (*The Nature of the Physical World*, 1929)

PREFACE

This book has two primary aims. The first is to provide an accurate but accessible introduction to the theory of chemical and phase thermodynamics as first enunciated by J. Willard Gibbs. The second is to exhibit the transcendent beauty of the Gibbsian theory as expressed in the mathematical framework of Euclidean and Riemannian geometry.

Both aims may seem unrealistic within the pedagogical constraints of a textbook for undergraduates or beginning graduate students. However, the author believes that accurate and thorough grounding in the Gibbsian viewpoint is not only the best introduction to research-level thermodynamic applications, but also the low-barrier entryway to a remarkably simple and effective set of geometrical tools that make accurate thermodynamic reasoning accessible to students with only modest mathematical training.

In attempting this amalgamation of Gibbsian and geometric concepts, I have adhered closely in Parts I (Chapters 1–4) and II (Chapters 5–8) to the actual content of the first-semester physical chemistry course at the University of Wisconsin (Chem 561) for more than two decades. This includes the usual topics pertaining to the pre-Gibbsian historical development (Part I) and the final Gibbs synthesis of chemical and phase thermodynamics (Part II), expressed in the traditional language of partial differential calculus. Aside from certain subtle points of rigor and emphasis, the content of Chapters 1–8 can be closely mapped onto other introductory thermodynamics expositions, such as the venerable "Wisconsin" series of physical chemistry textbooks (as authored by Getman and Daniels in 1931, Daniels and Alberty in the author's student days, and Silbey, Alberty, and Bawendi at present).

Part III (Chapters 9–13), in contrast, is quite novel, representing the first full textbook exposition of the metric geometry of equilibrium thermodynamics as originally formulated in a series of papers (1975–1978) by the author. Although this "thermodynamic geometry" has seen extensive research applications in such diverse areas as optimal process control and black hole thermodynamics, its many pedagogical and practical advantages have not been sufficiently exhibited for beginning students of physical chemistry.

In a sense, the material of Part III is far the easiest to master, even though it is logically equivalent to the traditional Gibbsian-based formalism outlined in Parts I and II. Indeed, it is conceivable that a motivated high school student with only basic skills in Euclidean geometry could reasonably begin with Part III, proceeding immediately to derive complex thermodynamic relationships with confidence and accuracy! (The only "trick" is to learn how to associate the geometrical distances or angles with measurable thermodynamic properties or equivalent partial differential expressions of Parts I and II, as illustrated in Fig. 11.2.) However, thoughtful students would undoubtedly find this short cut to be excessively "magical" if insufficiently supported by the historical and physical background of Parts I and II. Hence, Part III does not attempt to revisit all the topics of Parts I and II, as though this background were unfamiliar to the reader. Instead, the basic geometrical isomorphism is established with traditional thermodynamic concepts of assumed familiarity, allowing students to carry out desired geometrical re-derivations of thermodynamic identities at their leisure (in analogy to the many examples provided in sidebars) while focusing primarily on novel extensions of the thermodynamic geometry, including many described here for the first time. Part III therefore assumes some familiarity with Parts I and II, but students with alternative physical chemistry backgrounds (e.g., the textbooks of Atkins, Engel–Ried, Levine, or Silbey–Alberty–Bawendi) should encounter little difficulty in picking up the thread.

I wish to express sincere gratitude to many teachers and colleagues, present and past, who have aided my understanding of thermodynamics and phase equilibria. These include Steve Berry, Bob Bird, Phil Certain, Dan Cornwell, Chuck Curtiss, Tom Farrar, John Ferry, Joop de Heer, Michael Fisher, Stan Gill, Joe Hirschfelder, Ed Jaynes, Fred Koenig, Arthur Lodge, Ralf Ludwig, Mike McBride, Gil Nathanson, John Perepezko, Tom Record, Peter Salamon, Jim Skinner, Laszlo Tisza, Worth Vaughan, Hyuk Yu, and John Wheeler.

I also wish to express my appreciation to David Strasfeld, Gil Nathanson, John Harriman, and (particularly) Bob Bird, who suggested helpful improvements to an early draft; to Mark Wendt, who prepared the rendered graphics for the cover and Figure 11.1; and to John Herbert, Phillip Thomas, and David Strasfeld (all former teaching assistants in Chem 561), who assembled problems and exercises to accompany the book.

Neither the writing of this book nor the original research on which it is based could have come about without the loving support of my family, for which I am deeply grateful.

Frank Weinhold

Madison, Wisconsin

CONTENTS

PART I

INDUCTIVE FOUNDATIONS OF CLASSICAL THERMODYNAMICS

CHAPTER 1

Mathematical Preliminaries: Functions and Differentials

1.1 PHYSICAL CONCEPTION OF MATHEMATICAL FUNCTIONS AND DIFFERENTIALS

Science consists of interrogating nature by experimental means and expressing the underlying patterns and relationships between measured properties by theoretical means. Thermodynamics is the science of heat, work, and other energy-related phenomena.

An experiment may generally be represented by a set of stipulated control conditions, denoted $x_1, x_2, \ldots, x_n$, that lead to a unique and reproducible experimental result, denoted z. Symbolically, the experiment may be represented as an input–output relationship,

$$\underset{\text{(input)}}{x_1, x_2, \ldots, x_n,} \xrightarrow{\text{experiment}} \underset{\text{(output)}}{z} \tag{1.1}$$

Mathematically, such relationships between independent $(x_1, x_2, \ldots, x_n)$ and dependent (z) variables are represented by *functions*

$$z = z(x_1, x_2, \ldots, x_n) \tag{1.2}$$

We first wish to review some general mathematical aspects of functional relationships, prior to their specific application to experimental thermodynamic phenomena.

Two important aspects of any experimentally based functional relationship are (1) its *differential* dz, i.e., the *smallest sensible increment of change* that can arise from corresponding differential changes $(dx_1, dx_2, \ldots, dx_n)$ in the independent variables; and (2) its *degrees of freedom* n, i.e., the number of "control" variables needed to determine z uniquely. How "small" is the magnitude of dz (or any of the dx_i) is related to specifics of the experimental protocol, particularly the inherent experimental uncertainty that accompanies each variable in question.

For $n = 1$ ("ordinary" differential calculus), the dependent differential dz may be taken proportional to the differential dx of the independent variable,

$$dz = z'\,dx \tag{1.3}$$

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where z' (the total *derivative* of z with respect to x) is evidently related to the differentials dz, dx by the ratio formula

$$z' = \frac{dz}{dx} \tag{1.4}$$

The validity of (1.3), i.e., the existence of the derivative dz/dx in (1.4), is an essential requisite for application of the formalism of differential calculus. It is therefore important that the magnitudes of differentials dz, dx be taken "sufficiently small" (but not "zero," a meaningless and unphysical extrapolation in this context!) for the limiting ratio in (1.4) to have an experimentally well-defined value, within usual limits of experimental precision.

For the general case of n variables, the expression for dz must include corresponding "partial" contributions from each possible differential change dx_i. This is expressed by the important equation

$$\boxed{dz = \sum_{i=1}^{n} \left(\frac{\partial z}{\partial x_i}\right)_{\underline{x}} dx_i = \sum_{i=1}^{n} z_i' \, dx_i} \tag{1.5}$$

where

$$z_i' = \left(\frac{\partial z}{\partial x_i}\right)_{\underline{x}} \tag{1.6}$$

and where the subscript $\underline{x}$ denotes the list of all control variables held constant (i.e., all but the "active" variable dx_i). In general, each "partial" derivative $(\partial z/\partial x_i)_{\underline{x}}$ in (1.5) [like each ordinary derivative z' in (1.3)] is itself a function of all variables on which z depends. Equation (1.5) is referred to as the "chain rule" of partial differential calculus. It represents the most fundamental relationship between differential changes for a system with n degrees of freedom, and often forms the starting point for thermodynamic reasoning.

SIDEBAR 1.1: RECTANGLE EXERCISE

Exercise For a rectangle of sides x, y, find the function for area $A = A(x, y)$, its partial derivatives with respect to x and y, and its differential dA.

Solution The area function is $A(x, y) = xy$, so the partial derivatives are $(\partial A/\partial x)_y = y$ and $(\partial A/\partial y)_x = x$, and the differential is $dA = y\, dx + x\, dy$.

SIDEBAR 1.2: CIRCUMFERENCE EXERCISE

Exercise Suppose that the circumference of the Earth is snugly encircled with a band of 25,000-mile length. If the band is slightly *lengthened* by 10 ft, how high above the surface does it rise? (Does the Earth's precise circumference matter?)

Solution Circumference C and radius R are related by $R = C/2\pi$. To determine the small radial change dR accompanying a change of circumference dC, we need $R' = dR/dC = 1/2\pi$. We can therefore approximate the radial increase ΔR as $\Delta R = R'\Delta C = (1/2\pi)(10\text{ ft}) \cong 1.59$ ft (independent of C).

The important functional relationships of thermodynamic systems also permit second derivatives to be evaluated. For example, the derivative function $z_i' = z_i'(x_1, x_2, \ldots, x_n)$ of (1.6) can be differentiated with respect to a second variable x_j to give the mixed second derivative of z with respect to x_i and x_j,

$$z_{ij}'' = \left(\frac{\partial z_i'}{\partial x_j}\right)_{\underline{x}} = \frac{\partial^2 z}{\partial x_i \partial x_j} \tag{1.7}$$

As first shown by J. W. Gibbs, the analytical characterization of thermodynamic equilibrium states can be expressed completely in terms of such first and second derivatives of a certain "fundamental equation" (as described in Section 5.1).

Note that differentials (dz) have fundamentally different mathematical character than do functions (such as z, z', z''). The former are inherently "infinitesimal" (microscopic) in scale and carry multivariate dependence on all possible "directions" of change, whereas the latter carry only macroscopic numerical values. Thus, it is mathematically inconsistent to write equations of the form "differential = function" (or "differential = derivative"), just as it would be inconsistent to write equations of the form "vector = scalar" or "apples = oranges." Careful attention to proper balance of thermodynamic equations with respect to differential or functional character will avert many logical errors.

The student of thermodynamics must learn to cope with the functional, differential, and derivative relationships in (1.2)–(1.7) from a variety of formulaic, graphical, and experimental aspects. Let us briefly discuss each in turn.

Formulaic Aspect The student should be familiar with analytical formulas for derivatives z' of common algebraic and transcendental functions z, such as

$$z = x^n, \; z' = nx^{n-1}; \qquad \text{or} \qquad z = u^n, \; z' = nu^{n-1}u' \tag{1.8a}$$

$$z = e^x, \; z' = e^x; \qquad \text{or} \qquad z = e^u, \; z' = e^u u' \tag{1.8b}$$

$$z = \ln x, \; z' = \frac{1}{x}; \qquad \text{or} \qquad z = \ln u, \; z' = \frac{u'}{u} \tag{1.8c}$$

These formulas are also generally sufficient for partial derivatives (because holding some terms *constant* in z can only simplify its differentiation!). Although such formulas may prove useful in certain contexts (such as homework problems based on assumed functional forms of forgiving mathematical simplicity), they are less useful than, for example, graphical or numerical techniques for dealing with realistic experimental data.

Graphical Aspect Functional relationships such as (1.1) and (1.2) can often be most effectively depicted in graphical (or geometric model) form. Innovative graphical methods were developed by Gibbs and others to display the complex thermodynamic relationships of single- and multicomponent chemical systems, as illustrated in Fig. 1.1. For thermodynamic purposes, the ability to "read" equations such as (1.2)–(1.5) through graphical visualization is more important than facility with analytical formulas such as (1.8a–c).

Graphical visualization of a function z or its derivative(s) is similar in the case of ordinary ($n = 1$) and multivariate systems, except that the latter necessarily requires additional dimensions. In a standard 2-dimensional graph, the *height* of the curve at given x_0