B.G. Kyle

Chemical and Process Thermodynamics
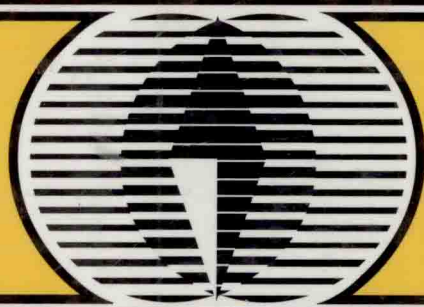
Third Edition

Chemical and Process

Thermodynamics

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This edition represents an attempt to produce a thermodynamics text suitable for the age of the personal computer. Steps toward this goal include providing a variety of computing resources on the companion CD-ROM, rewriting several sections, supplying many worked examples and student problems requiring the use of these resources, and adding Chapter 17 dealing with modeling of thermodynamic systems. The CD-ROM contains (a) spreadsheets and executable programs for specific applications, (b) POLYMATH, a general purpose numerical analysis program, (c) EQUATIONS OF STATE, a graphics program with tutorials illustrating various concepts with three-dimensional PVT plots, and (d) spreadsheet solutions to several worked examples in the text. A complete listing and brief description of these resources can be found in Appendix E.

Chapter 9, Principles of Phase Equilibrium, has been reorganized to include calculation of phase equilibrium via an equation of state as this topic is now an integral part of the thermodynamics of phase equilibrium. This change carries over into Chapter 10, Applied Phase Equilibrium, where the determination of the Peng-Robinson interaction parameter from VLE data parallels the determination of Wilson parameters from VLE data and both processes are viewed from the perspective of information processing. Executable programs are provided for these tasks.

Chapter 11, Additional Topics in Phase Equilibrium, has been augmented by the inclusion of executable programs for the determination the Peng-Robinson interaction parameter from solid-gas equilibrium data and for the calculation of solid-gas equilibrium from the Peng-Robinson equation. There is also an executable program using the UNIFAC method for estimating activity coefficients.

Chapter 13, Complex Chemical Equilibrium, has been rewritten in an attempt to clarify the phase rule as applied to chemically reacting systems and to accommodate the use of POLYMATH for solving the non-linear equations arising from free energy minimization.

Chapter 17, Thermodynamics and Models, presents the philosophy of modeling engineering systems and illustrates this with several realistic examples. Also, the technique of combining the UNIFAC model with the Peng-Robinson model for the prediction of phase equilibria is presented and illustrated with an example.

While there is an increased emphasis on computing, the major objective of this edition, as well as that of the two previous editions, is to expose and explain the rationale of thermodynamics. My philosophical stance toward computing in the curriculum is that it should never be an end in itself but should free students of burdensome and tedious calculations so that they can use this savings in time and attention to focus on fundamentals and be able to tackle larger and more complex problems. I also believe that students should understand what a particular program does and not regard it simply as a magic black box. Accordingly, while I have attempted to make the executable programs user-friendly, they are not written for a passive user but require the student's input and decisions.

The companion CD-ROM also contains auxiliary text: a multichaptered essay on entropy which presents the microscopic view of entropy, examines the connection between entropy and information, and discusses some of the paradoxes associated with entropy.

When applied to a thermodynamics course, the term *advanced* usually has the connotation of increased breadth or complexity of application and greater depth of understanding rather than a higher level of required mathematical skills. Consistent with this view, the book should also be suitable for a graduate level course. Many of the chapters contain topics that could be omitted in an undergraduate course but included in a graduate course. These topics are placed toward the end of the chapters and are marked with an asterisk in the Contents. It is intended that the omission of these topics not affect the orderly development of topics in subsequent chapters. Actually, few if any of these topics are beyond the reach of an undergraduate, and perhaps it is more appropriate to regard them as optional material, allowing flexibility in course design.

The underlying theme that permits the unification of what otherwise would be disparate topics resides in the following definition. *Thermodynamics is an approach to processing, evaluating, and extending experimentally gained information about systems capable of existing in equilibrium states.* While acknowledging the inadequacy of this definition, I believe that it has pedagogical value because it suggests that the subject should be presented and viewed from an experimental perspective. Indeed, this is especially true when it is recognized that the application of thermodynamics often involves the use of variables which are inherently abstract and therefore difficult to conceptualize. Students can hardly be expected to understand these applications if they lack the basic understanding of the phenomenon or system under study. This understanding should include how, and with what difficulty, the experimentally measured variables are determined. Equally, one can be comfortable with abstract thermodynamic variables only after their evaluation has been tied to experimentally determined quantities. A distinguishing feature of this book is the development of this experimental perspective.

In keeping with the experimental perspective, thermodynamic functions are not introduced until the need for them has been established or at least suggested. Hopefully, this allows the functions to be viewed as tools needed to accomplish a specific objective and not simply meaningless, abstract, and arbitrarily defined functions. This approach has led to an unorthodox development of phase equilibrium wherein partial molar properties are not introduced until the fourth of a four-chapter sequence. Thus the treatment of many common topics and a delineation of the rationale for the thermodynamic approach can occur before the student is encumbered with yet another type of function.

S.I. units are used extensively but not exclusively. For some time to come, engineers will find pressure gauges calibrated in psi, thermometers in °F, and physical property data reported in various units. They therefore should be able to work in any system of units. Additionally, in the major applications of thermodynamics—phase equilibrium and chemical equilibrium—S.I. units offer little computational advantage. In fact, because the standard state remains one atmosphere, their use in the treatment of chemical equilibrium can often cause confusion or error. For this reason, fugacities are always expressed in atmospheres in Chapters 12 and 13.

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Notation

Latin Symbols

A	Area	E	Total energy, extensive
A	Helmholtz free energy, extensive	e	Total energy, intensive
		$\mathbf{E}$	Work equivalent, extensive
A, B, C	Empirical constants	$\mathbf{e}$	Work equivalent, intensive
$\mathbf{A}$	Surface Area	E_K	Kinetic energy, extensive
a, b, c	Empirical constants	E_P	Potential energy, extensive
A_i	A chemical specie	F	Feed rate
a_i	Activity of component i	$\mathbf{F}$	Force
a_{12}, a_{21}	Parameters in Wilson equation		Generalized force
B	Second virial coefficient		Degrees of freedom
B	Availability, extensive	f	Friction factor
b	Availability, intensive	f	Fugacity
b_l	Number of atomic weights of element l in the system		Fraction liquefied
		f_i	Fugacity of component i
C	Number of components	G	Gibbs free energy, extensive
$\mathbf{c}$	Sonic velocity	$\mathbf{G}$	Mass flux
C_P	Constant-pressure heat capacity, extensive	g	Gibbs free energy, intensive
		$\mathbf{g}$	Acceleration of gravity
c_P	Constant-pressure heat capacity, intensive	G_{12}, G_{21}	Parameters in Wilson equation
		ΔG^f	Free energy of formation
C_V	Constant-volume heat capacity, extensive	H	Enthalpy, extensive
		h	Enthalpy, intensive
		$\mathbf{H}$	Magnetic field strength
C_v	Constant-volume heat capacity, intensive	ΔH^f	Heat of formation
		Δh^*	Enthalpy of departure
		Δh_s	Integral heat of solution
$\bar{c}_P$	Mean heat capacity	I	Magnetization intensity
D	Diameter	I	Ionic strength

K	Equilibrium constant
K_i	Equilibrium ratio
k_i	Henry's law constant
k_i'	Henry's law constant based on molality
L	Liquid rate
L	Length
l	Displacement or distance
L_m	Latent heat of melting
M	Any extensive property
m	Any intensive property
m	Mass
m	Molality
$\mathbf{M}$	Mach number
m	Mass flow rate
m_i	Molality of component i
N	Number of chemical species
n	Number of mols
P	Pressure
P°	Vapor pressure
p_i	Partial pressure of component i in a mixture
Q	Heat flow
$\mathbf{Q}$	Thermodynamic function for a mixture
q	Heat flow per unit of flowing fluid
R	Gas law constant
R	Number of independent chemical reactions
$\mathbf{R}$	Reaction matrix
r	Generalized displacement
S	Number of stoichiometric constraints
S	Entropy, extensive
s	Entropy, intensive
Δs^*	Entropy departure
T	Absolute temperature
t	Empirical temperature
T_m	Melting temperature
T_0	Temperature of the medium
U	Internal energy, extensive
u	Internal energy, intensive

V	Vapor rate
V	Volume, extensive
v	Volume, intensive
$\mathbf{v}$	Velocity
W	Work
$\mathbf{W}$	Total work (work + equivalent work of heat exchanges) in an open system
$\mathbf{w}$	Total work in a closed system
W_e	Electrical work
W_f	Fluid work
W_s	Shaft work
w_s	Shaft work per unit of flowing fluid
W'	Net, or useful, work
W^E	Equivalent work of heat
X^l	The lth element
X_i	Solid mol fraction of component i
x_i	Liquid mol fraction of component i
y_i	Vapor mol fraction of component i
Z	Compressibility factor
z	Elevation
z	Electrical charge
z_i	Mol fraction of compound i in feed stream

Greek Symbols

α	Relative volatility
α	Extent of reaction
β	Formula coefficient matrix
β_{ij}	Specie formula coefficient
γ	Heat capacity ratio
γ_i	Activity coefficient of component i
Γ_i	Activity coefficient of component i in a solid solution
δ	Solubility parameter
η	Efficiency, general, but always based on second law

θ	Tentative absolute temperature
θ	Ideal-gas temperature
θ	Freezing point depression
λ	Lagrangian multiplier
μ_i	Chemical potential of component i
v_i	Stoichiometric coefficient
π	Number of phases
π	Lagrangian multiplier
ρ	Density
ρ	Rank of formula coefficient matrix
ρ	Lagrangian multiplier
σ	Created entropy
σ	Surface tension
ϕ_i	Fugacity coefficient of component i
φ_i	Volume fraction
ω	Acentric factor

Operators

δ	Denotes a virtual variation
Δ	Finite change in a state property
d	Infinitesimal change or total differential operator
∂	Partial differential operator
$\int$	Integral operator
$\oint$	Integral operator for closed path
$\ln$	Natural logarithm operator (base e)
$\log$	Common logarithm operator (base 10)
$\prod$	Cumulative product operator
Σ	Cumulative summation operator

Special Notation

$\wedge$ (as in $\hat{f}_i$)	Denotes property of a component in a mixture
$^{-}$ (as in $\overline{H}_i$)	Denotes partial molar property

Subscripts

$A, B, C, \ldots,$	Denotes system states or species in a mixture
c	Critical property
P	Constant pressure
r	Reduced property
s	Saturated phase
V	Constant volume
0	Reference state, initial state or dead state
$1, 2, 3, \ldots,$	Denotes system states or species in a mixture
$\pm$	Denotes a mean ion property

Superscripts

e	With operator Δ denotes excess property change upon mixing
i	With operator Δ denotes property change on forming an ideal solution
L, S, V, α, β	Phase identification
$'$	The prime designates the ideal-gas state or a liquid phase
$''$	The double prime designates a liquid phase
$\circ$	Standard state. With operator Δ denotes a standard property change
$*$ or $\square$	Hypothetical pure component state extrapolated from infinite dilution behavior

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Introduction

1-1 THE ANATOMY OF THERMODYNAMICS

Before committing a great deal of time and effort to the study of a subject, it is reasonable to ask the following two questions: What is it? What is it good for? Regarding thermodynamics, the second question is more easily answered, but an answer to the first is essential to an understanding of the subject. Although it is doubtful that many experts or scholars would agree on a simple and precise definition of thermodynamics, necessity demands that a definition be attempted. However, this is best accomplished after the applications of thermodynamics have been discussed.

Applications of Thermodynamics.   There are two major applications of thermodynamics, both of which are important to chemical engineers:

1. The calculation of heat and work effects associated with processes, as well as the calculation of the maximum work obtainable from a process or the minimum work required to drive a process

2. The establishment of relationships among the variables describing systems at equilibrium

The first application is suggested by the name *thermodynamics*, which implies heat in motion. Most of these calculations can be made by the direct implementation of the first and second laws. Examples are calculating the work of compressing a gas, performing an energy balance on an entire process or a process unit, determining the minimum work of separating a mixture of ethanol and water, or evaluating the efficiency of an ammonia synthesis plant.

The application of thermodynamics to a particular system results in the definition of useful properties and the establishment of a network of relationships among the properties and other variables such as pressure, temperature, volume, and mol fraction. Actually, application 1 would not be possible unless a means existed for evaluating the necessary thermodynamic property changes required in implementing the first and second laws. These property changes are calculated from experimentally determined data via the established network of relationships. Additionally, the network of relationships among the variables of a system allows the calculation of values of variables that are either unknown or difficult to determine experimentally from variables that are either available or easier to measure. For example, the heat of vaporizing a liquid can be calculated from measurements of the vapor pressure at several temperatures and the densities of the liquid and vapor phases, the heat of mixing two liquids can be determined by measuring the equilibrium pressure and compositions of coexisting liquid and vapor phases at several temperatures, and the maximum conversion obtainable in a chemical reaction at any temperature can be calculated from calorimetric measurements performed on the individual substances participating in the reaction.

The Nature of Thermodynamics.   The laws of thermodynamics have an empirical or experimental basis, and in the delineation of its applications the reliance upon experimental measurement stands out. Thus, thermodynamics might be broadly defined as a means of extending our experimentally gained knowledge of a system or as a framework for viewing and correlating the behavior of the system. To understand thermodynamics, it is essential to keep an experimental perspective, for if we do not have a physical appreciation for the system or phenomenon studied, the methods of thermodynamics will have little meaning. We should always ask the following questions: How is this particular variable measured? How, and from what type of data, is a particular property calculated?

Often it is easy to miss the intimate experimental dependence of thermodynamics if we are concerned only with the direct applications of the first and second laws. Here the required thermodynamic property changes are usually obtained from a convenient tabulation (e.g., steam tables), or we calculate property changes for a simple substance such as an ideal, monatomic gas with $c_p = 5/2R$. In any event we seldom question the origin of our data and thereby remove thermodynamics from its experimental context, rendering it a lifeless and meaningless set of equations.