

THERMO LOOP APPLICATIONS IN MATERIALS SYSTEMS DYNAMIC

FIRST EDITION:

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PREFACE

This book is intended for use in an initial one-semester course in "materials" thermodynamics, although it could be used for self-study or as a supplement to a text selected for a two-semester undergraduate-graduate sequence. Each chapter is designed so that the student can learn to use thermodynamics as a problem solving tool for a broad range of materials applications. The book is written from notes developed in a course entitled "Thermodynamics of Alloys." Although this course was originally designed as an elective in mechanical engineering at the University of Nebraska-Lincoln, the broader perspective of thermodynamics of materials has emerged as a result of student contacts in earth science, mechanical, chemical, and corrosion engineering, and electrical materials.

For many scientists and engineers, thermodynamics may be most useful for applications where quickly obtained numerical estimates are all that is needed. Such a situation may prevail for those working in materials-related areas where the generation of thermodynamic data is not an objective in itself. The earth scientist, for example, may need to interpret the stability of mineral assemblages in a rock by using thermodynamic data available in the literature. On the other hand, metallurgists and chemists as well as mechanical, electrical, and materials engineers may be concerned with elevated temperature phase equilibria, phase transformations, and environmental reactions. For the corrosion and chemical engineer, the concept of potential (EMF) is very important in corrosion control as it relates to the Nernst Equation and associated "Pourbaix" diagrams.

Fundamentals of classical thermodynamics are briefly reviewed and systematically introduced into problem solving using "thermodynamic loop" or TL analysis. This concept, derived from Kirchhoff's law, is analogous to cyclic analysis used to evaluate engine performance in mechanical systems. Virtually all material thermodynamic applications can be analyzed by TL analysis. TL analysis is a method of organization whereby the known state of a system is combined with thermodynamic properties of materials obtainable from the literature to calculate system properties in another state. TL analysis is a powerful analytical tool because it divides a problem into parts and graphically structures it in such a manner as to provide the student with a clearly depicted solution path. In addition, TL analysis eliminates some of the need for memorizing detailed formulas because it can be used to derive them. Extensive use of TL analysis is a unique feature of this book.

The first chapter introduces thermodynamics as a science and defines important terms. The thermodynamic loop is introduced in the second chapter. Example applications in the second chapter include constant and variable temperature enthalpy calculations and supercooling. The Second and Third Laws of Thermodynamics are introduced in the third chapter and the concept of entropy as a stability criterion is discussed. Example applications include constant and variable temperature calculations and supercooling. Finally, thermodynamic efficiency is defined graphically from a temperature-entropy (T-S) diagram. The fourth chapter is devoted to Gibbs free energy, stability criteria, and introduction of the Ellingham diagram. Example TL applications include variable temperature and pressure equilibrium calculations for closed

systems. The chapter includes the application of free energy stability criteria to the same supercooling problems presented in Chapters 2 and 3. A comparison with entropy stability criteria illustrates the simplicity of Gibbs free energy calculations in analyzing reactions at equilibrium. Chapter 4 concludes with numerous thermodynamic relations that are used later in the book. The fifth and sixth chapters further develop the analysis of systems at equilibrium. Chapter 5 covers systems open with respect to gaseous phases (variable gas composition), applications of the Ellingham diagram, and illustrations of techniques for calculating gas phase equilibria over pure condensed phases. These techniques are expanded in Chapter 6 to include variable condensed phase compositions. Chapter 6 begins by defining fugacity, thermodynamic activity, and partial properties in terms of volume and then builds upon these concepts to define other common mixing properties. Discussion is limited to two-component systems. Partial properties are the basis upon which ideal, dilute, and regular solution models are subsequently derived. The chapter concludes with several problems including alloy oxidation, application of the Gibbs-Duhem equation, and development of Sievert's law. Chapter 7 is devoted to the analysis of binary phase diagrams. There is a wealth of untapped information in phase diagrams and the intent of this chapter is to illustrate the utility of the TL concept in extracting, at the very least, useful estimates of partial molar properties from liquidus, solidus, and solvus equilibria. These estimates are incorporated into such applications as prediction of purity, carburizing potential, and analysis of reactions. In addition, techniques are developed for estimating the effect of pressure on phase boundaries. Finally, phase rule concepts are introduced. Chapter 8 introduces the concept of the equilibrium constant and illustrates its utility in more complex three component systems. The equilibrium constant, K_{eq} , is generally not required to solve any of the problems presented in this book. Experience has shown that the student or casual user often employs it improperly. In this connection, reliance upon computer programs to solve thermodynamic problems is left to the reader who has mastered basic concepts. The chapter concludes with a discussion of corrosion cell polarity.

Numerous people helped the authors during the development and preparation of the final draft and its accompanying solutions manual. Sincere appreciation goes to Dr. Russell C. Nelson, Department of Mechanical Engineering, University of Nebraska-Lincoln, for his review and critique of manuscript drafts. Thanks also goes to Dr. Dana J. Medlin, Department of Metallurgical and Materials Engineering, Colorado School of Mines, for helpful comments on the initial draft. The authors are especially grateful to Janet L. Stracher for valuable and untiring assistance with the preliminary preparation of figures and graphs and for final editing of the solutions manual.

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SYSTEMS AND UNITS

The standardization of physical quantities is necessary so that measurements based on these quantities or combinations of them mean the same thing in various disciplines. Quantities chosen as *standards* represent the *basic units* of measurement. Basic units are selected so as to represent the smallest number of physical quantities from which all others may be derived. *Derived units* then, are simply combinations of the basic units. Because of the variety of units used, conversions are presented in this section.

The Fourteenth Conference on Weights and Measures in 1971 adopted three classes of units internationally accepted today: (1) base units in Table SI-1, (2) derived units in Table SI-2, and (3) supplementary units (NBS Publication 330, 1972). The symbols for derived units are obtained by expressing the base and/or supplementary units with the mathematical symbols for division and multiplication. For example, the derived SI unit for force is $\text{kg}\cdot\text{m}/\text{s}^2$ (to which is assigned the name Newton, symbolized by a capital N). Likewise, the derived SI unit for power is $[(\text{kg}\cdot\text{m}/\text{s}^2)\cdot\text{m}]/\text{s} = (\text{Newton}\cdot\text{m})/\text{s} = \text{joule}/\text{s}$ (where joule is symbolized by a capital J).

The SI system excludes using units such as the dyne ($1 \text{ dyne} = 10^{-5} \text{ N}$) and the erg ($1 \text{ erg} = 10^{-7} \text{ J}$), disapproves of using the torr [$1 \text{ torr} = 1 \text{ mm Hg} = (101.325/760) \text{ kPa}$] and the calorie ($1 \text{ thermochemical calorie} = 4.184 \text{ J}$), and tolerates using the bar ($1 \text{ bar} = 10^5 \text{ Pa}$) and the standard atmosphere ($1 \text{ atm} = 101.325 \text{ kPa}$). Because of past and currently widespread use of the calorie, bar, and standard atmosphere by engineers and scientists, these units will be used on occasion throughout this book.

U.S. Customary Units

In addition to the SI system of units, the U.S. customary or British system of units is commonly used today in the United States, Great Britain, and elsewhere. Conversion factors between SI and U.S. customary units, given in Table CF-1, may be useful.

Table SI-1: SI (Système International) Base Units

Quantity	Name	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	I

Table SI-2: Derived SI Units

Quantity	SI Formula	Special Symbol	Special Name
Area	m ²	A	—
Volume (solids)	m ³	V	—
Volume (liquids)	10 ⁻³ m ³	L	liter
Density	kg/m ³	—	—
Force	kg·m/s ²	N	Newton
Pressure, stress	N/m ²	Pa	pascal
Pressure	101.325 kPa	atm	atmosphere
Pressure	10 ⁵ Pa	—	bar
Work, energy	N·m	J	joule
Power	J/s	W	watt
Linear velocity	m/s	—	—
Linear acceleration	m/s ²	—	—
Electric charge	I·s	C	coulomb
Electromotive force	W/I	V	volt

Table CF-1: SI and U.S. Customary Equivalents

Quantity	SI Unit	U.S. Customary Equivalent
Length	25.40 mm	in
Length	0.3048 m	ft
Area	645.2 mm ²	in ²
Area	0.0929 m ²	ft ²
Volume	16.39 cm ³	in ³
Volume	0.02832 m ³	ft ³
Volume liquid	0.9464 L	qt (quart)
Volume liquid	3.785 L	gal (gallon)
Mass	0.4536 kg	lb mass
Mass	14.59 kg	slug
Mass	907.2 kg	ton
Force	4.448 N	lb _f
Force	4.448 kN	kip
Pressure, stress	47.88 Pa	lb _f /ft ²
Pressure, stress	6.895 kPa	lb _f /in ² (psi)
Pressure, stress	6.895 MPa	1000 lb _f /in ² (ksi)
Pressure	101,325 Pa = 1 atm	—
Pressure	10 ⁵ Pa = 1 bar	—
Work, energy	1.356 J	ft·lb _f
Heat, energy	1054.8 J	BTU (British thermal unit)
Power	1.356 watts	ft·lb _f /s
Power	745.7 watts	hp

NOTATION

P	Pressure
P_i	Partial Pressure of Gas Component i
V	Molar Volume
v	Specific Volume (mass basis)
l	Length
L	Liter
ρ	Density
T	Temperature
T^{Tr}	Transformation Temperature
T^f	Fusion Temperature, Pure Component
$^{\circ}\text{C}$	Degrees Centigrade
$^{\circ}\text{F}$	Degrees Fahrenheit
K	Degrees Kelvin
R	Degrees Rankine or Ideal Gas
J	Joules
kJ	Kilojoules
θ	General State Function
m	Mass
gm	Gram
kg	Kilogram
lb _m	Pound Mass
lb _f	Pound Force
W	Work/Mol or Work/Unit Volume
Q	Heat (Transfer)/Mol
q	Heat (Transfer)/Unit Mass
E_P	Molar Potential Energy
E_K	Molar Kinetic Energy
E_T	Total Energy/Mol
U	Molar Internal Energy
u	Internal Energy (mass basis)
H	Molar Enthalpy
ΔH	Molar Enthalpy Change
ΔH^0	Standard State Molar Enthalpy Change
ΔH^{0f}	Standard State Molar Enthalpy of Formation
ΔH^{Tr}	Molar Heat of Transformation
ΔH^f	Molar Heat of Fusion, Pure Component
ΔH^v	Molar Heat of Vaporization
ΔH^s	Molar Heat of Sublimation
$\Delta H_s, \Delta H_s^0$	Molar or Standard Molar Heat of Solution (Alternately, \bar{H}_i^m)
h	Enthalpy (mass basis)
S	Molar Entropy
ΔS	Molar Entropy Change

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ΔS^0	Standard State Molar Entropy Change
ΔS^{0f}	Standard State Molar Entropy of Formation
ΔS^f	Molar Entropy of Fusion, Pure Component
$\Delta S_s, \Delta S_s^0$	Molar or Standard Molar Entropy of Solution (Alternately, \bar{S}_i^m)
s	Entropy (mass basis)
G	Molar Gibbs Free Energy
ΔG	Molar Gibbs Free Energy Change
ΔG^0	Standard State Molar Gibbs Free Energy Change
ΔG^{0f}	Standard State Molar Gibbs Free Energy of Formation
ΔG^f	Molar Gibbs Free Energy of Fusion
$\Delta G_s, \Delta G_s^0$	Molar or Standard Molar Gibbs Free Energy of Solution (Alternately, \bar{G}_i^m)
g	Gibbs Free Energy (mass basis)
A	Molar Helmholtz Free Energy or area
C_p	Constant Pressure Molar Heat Capacity
C_v	Constant Volume Molar Heat Capacity
c_p	Constant Pressure Specific Heat Capacity (mass basis)
c_v	Constant Volume Specific Heat Capacity (mass basis)
a_i	Activity of Component i
γ_i	Activity Coefficient of Component i
Π	Product of Activities
J_a	Activity Quotient
C_i	Concentration of Component i
K_{eq}	Equilibrium Constant
f_i	Fugacity of Component i
μ_i	Chemical Potential of Component i
σ	Uniaxial Stress
ϵ	Uniaxial Strain
$(s), < >$	Solid: e.g., PbS(s) or <PbS>
$(l), []$	Liquid: e.g., H ₂ O(l) or [H ₂ O]
$(g), ()$	Gas: e.g., N ₂ (g) or (N ₂)
'	Superscript Prime: Used for extensive thermodynamic variables. For example, $\Delta H'$ is the <i>total</i> enthalpy change of a substance or a reaction.
$f_{w,i}$	Weight Fraction of Component i
$f_{v,i}$	Volume Fraction of Component i
mole (mol)	Gram Mole, or Gram Atom
pct	Percent
ppm	Parts Per Million (mass basis)
ppb	Parts Per Billion (mass basis)
N_i	Number of Atoms of Component i
N_T	Total Number of Atoms
N_{AV}	Avogadro's Number

k	Boltzmann's Constant (R/N_{AV})
n_i	Number of Moles of Component i
n_T	Total Number of Moles
M	Molar Mass
X_i	Atomic Fraction of Component i in Condensed Phase
Y_i	Atomic Fraction of Component i in Gas Phase
a/o	Atomic Percent
w/o	Weight Percent
h, s	Nonideal Solution Constants
Ω, ω, δ	Nonideal Solution Constants
z	Coordination Number
ϕ, F, Γ	Phases, Degrees of Freedom, and Components respectively: Gibbs Phase Rule
E	Electromotive Force (EMF)
F	Faraday's Constant: Coulomb/equivalent(eq)
n	Valence (eq/mol) or molar mass/equivalent mass where M/n is equivalent mass
α	Volume Thermal Expansion Coefficient or Polymorphic Phase
β	Isothermal Compressibility Coefficient or Polymorphic Phase
η	Thermodynamic Efficiency

SYMBOLS FOR MOLAR PROPERTIES: CHARACTERIZED BY VOLUME*

V_A^0, V_B^0	Molar volume of pure components A and B respectively
\bar{V}_A, \bar{V}_B	Partial molar volume of A and B respectively
n_A, n_B	Number of moles of A and B respectively
X_A, X_B	Mole fraction of A and B respectively, where $X_A = n_A/(n_A + n_B)$, $X_B = n_B/(n_A + n_B)$ and $X_A + X_B = 1.0$
\bar{V}_A^m, \bar{V}_B^m	Partial molar volume of mixing of A and B respectively, where $\bar{V}_A^m = \bar{V}_A - V_A^0$ and $\bar{V}_B^m = \bar{V}_B - V_B^0$
V^m	Molar volume of mixing where $V^m = X_A \bar{V}_A^m + X_B \bar{V}_B^m$
\bar{V}_A^{XS}	Partial molar excess volume of A
$V^{m'}$	Total Volume of Mixing where $V^{m'} = n_A \bar{V}_A^m + n_B \bar{V}_B^m$

- * (1) Identical expressions are used for thermodynamic properties other than volume.
 (2) Ideal properties are designated by "id". For example, $\bar{V}_A^{m,id}$ is the partial molar volume of mixing of A in liquid solution; reference is pure liquid A.
 (3) Phase identification is denoted with a superscript. For example, $\bar{V}_A^{m,l}$ is the partial molar volume of mixing of A in liquid solution; reference is pure liquid A.

TABLE OF PHYSICAL CONSTANTS AND CONVERSION FACTORS

Ideal Gas Constant	$R = 8.3144 \text{ joules}/(\text{mol}\cdot\text{K})$ $= 1.987 \text{ calories}/(\text{mol}\cdot\text{K})$ $= 82.057 \text{ cm}^3\cdot\text{atm}/(\text{mol}\cdot\text{K})$ $= 0.082057 \text{ liter}\cdot\text{atm}/(\text{mol}\cdot\text{K})$ $= 0.083144 \text{ liter}\cdot\text{bar}/(\text{mol}\cdot\text{K})$ $= 1.987 \text{ BTU}/(\text{lb mol}\cdot\text{R})$ $= 0.73 \text{ atm}\cdot\text{ft}^3/(\text{lb mol}\cdot\text{R})$
Pressure	1 atmosphere (atm) = 760 mm Hg = 760 torr = 14.696 lb_f/in^2 = 1.01325 bar = 101.325 kN/m^2 = 101.325 kPa
Temperature	$\text{K} = ^\circ\text{C} + 273.16 \text{ degrees}$ $^\circ\text{F} = (9/5)^\circ\text{C} + 32.00 \text{ degrees}$ $\text{R} = ^\circ\text{F} + 459.67 \text{ degrees}$
Energy Equivalents	1 calorie = 4.184 joules (J) = 4.184×10^7 ergs = 0.041293 liter·atm = 41.3223 $\text{cm}^3\cdot\text{atm}$ = 3.0855 ft· lb_f = 1.4580×10^{-3} atm·ft ³ = 3.9683×10^{-3} BTU
Avogadro's Number	$N_{AV} = 6.0232 \times 10^{23}/\text{mol}$
Boltzmann's Constant	$k = R/N_{AV}$
Faraday's Constant	= 95,000 coulomb/equivalent