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Introduction to Chemical Engineering Thermodynamics

J.M. Smith • H.C. Van Ness • M.M. Abbott • M.T. Swihart



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Ninth Edition

INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS

NINTH EDITION

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Preface

Thermodynamics, a key component of many fields of science and engineering, is based on laws of universal applicability. However, the most important applications of those laws, and the materials and processes of greatest concern, differ from one branch of science or engineering to another. Thus, we believe there is value in presenting this material from a chemical engineering perspective, focusing on the application of thermodynamic principles to materials and processes most likely to be encountered by chemical engineers.

Although *introductory* in nature, the material of this text should not be considered simple. Indeed, there is no way to make it simple. A student new to the subject will find that a demanding task of discovery lies ahead. New concepts, words, and symbols appear at a bewildering rate, and a degree of memorization and mental organization is required. A far greater challenge is to develop the capacity to reason in the context of thermodynamics so that one can apply thermodynamic principles in the solution of practical problems. While maintaining the rigor characteristic of sound thermodynamic analysis, we have made every effort to avoid unnecessary mathematical complexity. Moreover, we aim to encourage understanding by writing in simple active-voice, present-tense prose. We can hardly supply the required motivation, but our objective, as it has been for all previous editions, is a treatment that may be understood by any student willing to put forth the required effort.

The text is structured to alternate between the development of thermodynamic principles and the correlation and use of thermodynamic properties as well as between theory and applications. The first two chapters of the book present basic definitions and a development of the first law of thermodynamics. Chapters 3 and 4 then treat the pressure/volume/temperature behavior of fluids and heat effects associated with temperature change, phase change, and chemical reaction, allowing early application of the first law to realistic problems. The second law is developed in Chapter 5, where its most basic applications are also introduced. A full treatment of the thermodynamic properties of pure fluids in Chapter 6 allows general application of the first and second laws, and provides for an expanded treatment of flow processes in Chapter 7. Chapters 8 and 9 deal with power production and refrigeration processes. The

remainder of the book, concerned with fluid mixtures, treats topics in the unique domain of chemical engineering thermodynamics. Chapter 10 introduces the framework of solution thermodynamics, which underlies the applications in the following chapters. Chapter 11 applies this to mixing processes. Chapter 12 then describes the analysis of phase equilibria, in a mostly qualitative manner. Chapter 13 provides full treatment of vapor/liquid equilibrium. Chemical-reaction equilibrium is covered at length in Chapter 14. Chapter 15 deals with topics in phase equilibria, including liquid/liquid, solid/liquid, solid/vapor, gas adsorption, and osmotic equilibria. Chapter 16 treats the thermodynamic analysis of real processes, affording a review of much of the practical subject matter of thermodynamics.

The material of these 16 chapters is more than adequate for an academic-year undergraduate course, and discretion, conditioned by the content of other courses, is required in the choice of what is covered. The first 14 chapters include material considered necessary to any chemical engineer's education. Where only a single-semester course in chemical engineering thermodynamics is provided, these chapters may represent sufficient content.

The book is comprehensive enough to make it a useful reference both in graduate courses and for professional practice. However, length considerations have required a prudent selectivity. Thus, we do not include certain topics that are worthy of attention but are of a specialized nature. These include applications to polymers, electrolytes, and biomaterials.

We are indebted to many people—students, professors, reviewers—who have contributed in various ways to the quality of this ninth edition, directly and indirectly, through question and comment, praise and criticism, through eight previous editions spanning more than 70 years.

We would like to thank McGraw Hill Education and all of the teams that contributed to the development and support of this project. In particular, we would like to thank the following editorial and production staff for their essential contributions to this ninth edition: Beth Bettcher, Mary Hurley, and Jane Mohr.

To all we extend our thanks.

J. M. Smith
H. C. Van Ness
M. M. Abbott
M. T. Swihart

A brief explanation of the authorship of the eighth and ninth editions

In December 2003, I received an unexpected e-mail from Hank Van Ness that began as follows: “I’m sure this message comes as a surprise to you; so let me state immediately its purpose. We would like to invite you to discuss the possibility that you join us as the fourth author . . . of *Introduction to Chemical Engineering Thermodynamics*.” I met with Hank and with Mike Abbott in summer 2004, and began working with them on the eighth edition in earnest almost immediately after the seventh edition was published in 2005. Unfortunately, the following years witnessed the deaths of Michael Abbott (2006), Hank Van Ness (2008), and Joe Smith (2009) in close succession. In the months preceding his death, Hank Van Ness worked diligently on revisions to this textbook. The reordering of content and overall structure of the eighth edition reflected his vision for the book.

New to the ninth edition

The ninth edition maintains the order of presentation and structure of the eighth edition with minor changes in wording throughout the book to improve readability for today's students. Where points of confusion were identified, we have expanded and modified the explanations. Example problems have been expanded, or new examples added in Chapters 3, 5, 6, 10, 13, and 14. Several new end-of-chapter problems have also been added, even as the expanded use of algorithmic problems in Connect improves the effectiveness of many of the existing end-of-chapter problems by providing a unique set of parameters and solutions for each attempt of a problem.

I am both humbled and honored to have been entrusted with the task of revising this classic textbook, which by the time I was born had already been used by a generation of chemical engineering students. I hope that the changes we have made, from content revision and reordering to the addition of more structured chapter introductions and a concise synopsis at the end of each chapter, will improve the experience of using this text for the next generation of students, while maintaining the essential character of the text, which has made it the most-used chemical engineering textbook of all time. I look forward to receiving your feedback on the changes that have been made and those that you would like to see in the future, as well as what additional resources would be of most value in supporting your use of the text.

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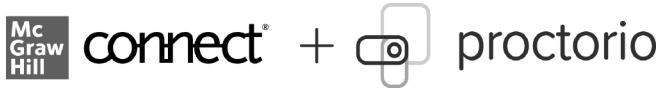
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I am sure Joe, Hank, and Michael would all be delighted to see this ninth edition in print and in a fully electronic version including Connect and SmartBook.

Mark T. Swihart, January 2021

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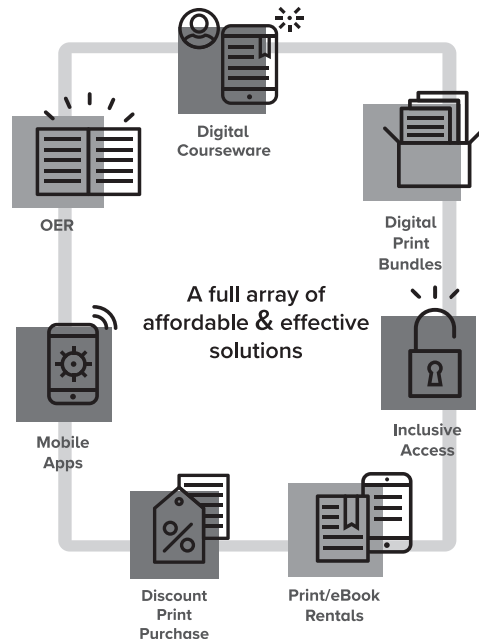
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List of Symbols

A	Area
A	Molar or specific Helmholtz energy $\equiv U - TS$
A	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.89), Eq. (13.29)
a	Acceleration
a	Molar area, adsorbed phase
a	Parameter, cubic equations of state
\bar{a}_i	Partial parameter, cubic equations of state
B	Second virial coefficient, density expansion
B	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.89)
\hat{B}	Reduced second-virial coefficient, defined by Eq. (3.58)
B'	Second virial coefficient, pressure expansion
B^0, B^1	Functions, generalized second-virial-coefficient correlation
B_{ij}	Interaction second virial coefficient
b	Parameter, cubic equations of state
\bar{b}_i	Partial parameter, cubic equations of state
C	Third virial coefficient, density expansion
C	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.90)
\hat{C}	Reduced third-virial coefficient, defined by Eq. (3.64)
C'	Third virial coefficient, pressure expansion
C^0, C^1	Functions, generalized third-virial-coefficient correlation
C_P	Molar or specific heat capacity, constant pressure
C_V	Molar or specific heat capacity, constant volume
C_P°	Standard-state heat capacity, constant pressure
ΔC_P°	Standard heat-capacity change of reaction
$\langle C_P \rangle_H$	Mean heat capacity, enthalpy calculations
$\langle C_P \rangle_S$	Mean heat capacity, entropy calculations
$\langle C_P^\circ \rangle_H$	Mean standard heat capacity, enthalpy calculations
$\langle C_P^\circ \rangle_S$	Mean standard heat capacity, entropy calculations
c	Speed of sound
D	Fourth virial coefficient, density expansion
D	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.91)
D'	Fourth virial coefficient, pressure expansion
E_K	Kinetic energy
E_P	Gravitational potential energy
F	Degrees of freedom, phase rule
F	Force
\mathcal{F}	Faraday's constant

f_i	Fugacity, pure species i
f_i°	Standard-state fugacity
\hat{f}_i	Fugacity, species i in solution
G	Molar or specific Gibbs energy $\equiv H - TS$
G_i°	Standard-state Gibbs energy, species i
\bar{G}_i	Partial Gibbs energy, species i in solution
G^E	Excess Gibbs energy $\equiv G - G^{id}$
G^R	Residual Gibbs energy $\equiv G - G^{ig}$
ΔG	Gibbs-energy change of mixing
ΔG°	Standard Gibbs-energy change of reaction
ΔG_f°	Standard Gibbs-energy change of formation
g	Local acceleration of gravity
g_c	Dimensional constant = $32.1740(\text{lb}_m)(\text{ft})(\text{lb}_f)^{-1}(\text{s})^{-2}$
H	Molar or specific enthalpy $\equiv U + PV$
\mathcal{H}_i	Henry's constant, species i in solution
H_i°	Standard-state enthalpy, pure species i
\bar{H}_i	Partial enthalpy, species i in solution
H^E	Excess enthalpy $\equiv H - H^{id}$
H^R	Residual enthalpy $\equiv H - H^{ig}$
$(H^R)^0, (H^R)^1$	Functions, generalized residual-enthalpy correlation
ΔH	Enthalpy change ("heat") of mixing; also, latent heat of phase transition
$\widetilde{\Delta H}$	Heat of solution
ΔH°	Standard enthalpy change ("heat") of reaction
ΔH_0°	Standard heat of reaction at reference temperature T_0
ΔH_f°	Standard enthalpy change of formation
I	Represents an integral, defined, e.g., by Eq. (13.71)
K	Equilibrium constant
K_0, K_1, K_2	Factors comprising equilibrium constant, Eq. (14.20)
K_j	Equilibrium constant, chemical reaction j
K_i	Vapor/liquid equilibrium ratio, species $i \equiv y_i / x_i$
k	Boltzmann's constant
k_{ij}	Empirical interaction parameter, Eq. (10.71)
\mathcal{L}	Molar fraction of system that is liquid
l	Length
l_{ij}	Equation-of-state interaction parameter, Eq. (15.31)
\mathbf{M}	Mach number
\mathcal{M}	Molar mass (molecular weight)
M	Molar or specific value, extensive thermodynamic property
\bar{M}_i	Partial property, species i in solution
M^E	Excess property $\equiv M - M^{id}$
M^R	Residual property $\equiv M - M^{ig}$
ΔM	Property change of mixing
ΔM°	Standard property change of reaction
ΔM_f°	Standard property change of formation
m	Mass
\dot{m}	Mass flow rate
N	Number of chemical species, phase rule

N_A	Avogadro's number
n	Number of moles
\dot{n}	Molar flow rate
\bar{n}	Moles of solvent per mole of solute
n_i	Number of moles, species i
P	Absolute pressure
P°	Standard-state pressure
P_c	Critical pressure
P_r	Reduced pressure
P_r^0, P_r^1	Functions, generalized vapor-pressure correlation, Eq. (6.92)
P_0	Reference pressure
p_i	Partial pressure, species i
P_i^{sat}	Saturation vapor pressure, species i
Q	Heat
\dot{Q}	Rate of heat transfer
q	Volumetric flow rate
q	Parameter, cubic equations of state
q	Electric charge
\bar{q}_i	Partial parameter, cubic equations of state
R	Universal gas constant (Table A.2)
r	Compression ratio
r	Number of independent chemical reactions, phase rule
S	Molar or specific entropy
\bar{S}_i	Partial entropy, species i in solution
S^E	Excess entropy $\equiv S - S^{id}$
S^R	Residual entropy $\equiv S - S^{ig}$
$(S^R)^0, (S^R)^1$	Functions, generalized residual-entropy correlation
\dot{S}_G	Entropy generation per unit amount of fluid
\dot{S}_G	Rate of entropy generation
ΔS	Entropy change of mixing
ΔS°	Standard entropy change of reaction
ΔS_f°	Standard entropy change of formation
T	Absolute temperature, kelvins or rankines
T_c	Critical temperature
T_n	Normal-boiling-point temperature
T_r	Reduced temperature
T_0	Reference temperature
T_σ	Absolute temperature of surroundings
T_i^{sat}	Saturation temperature, species i
t	Temperature, °C or (°F)
t	Time
U	Molar or specific internal energy
u	Velocity
V	Molar or specific volume
\mathcal{V}	Molar fraction of system that is vapor
\bar{V}_i	Partial volume, species i in solution
V_c	Critical volume

V_r	Reduced volume
V^E	Excess volume $\equiv V - V^{id}$
V^R	Residual volume $\equiv V - V^{ig}$
ΔV	Volume change of mixing; also, volume change of phase transition
W	Work
\dot{W}	Work rate (power)
W_{ideal}	Ideal work
\dot{W}_{ideal}	Ideal-work rate
W_{lost}	Lost work
\dot{W}_{lost}	Lost-work rate
W_s	Shaft work for flow process
\dot{W}_s	Shaft power for flow process
x_i	Mole fraction, species i , liquid phase or general
x^v	Quality, i.e., vapor fraction
y_i	Mole fraction, species i , vapor phase
Z	Compressibility factor $\equiv PV/RT$
Z_c	Critical compressibility factor $\equiv P_c V_c / RT_c$
Z^0, Z^1	Functions, generalized compressibility-factor correlation
z	Adsorbed phase compressibility factor, defined by Eq. (15.38)
z	Elevation above a datum level
z_i	Overall mole fraction or mole fraction in a solid phase

Superscripts

E	Denotes excess thermodynamic property
av	Denotes phase transition from adsorbed phase to vapor
id	Denotes value for an ideal solution
ig	Denotes value for an ideal gas
l	Denotes liquid phase
lv	Denotes phase transition from liquid to vapor
R	Denotes residual thermodynamic property
s	Denotes solid phase
sl	Denotes phase transition from solid to liquid
t	Denotes a total value of an extensive thermodynamic property
v	Denotes vapor phase
∞	Denotes a value at infinite dilution

Greek letters

α	Function, cubic equations of state (Table 3.1)
α, β	As superscripts, identify phases
$\alpha\beta$	As superscript, denotes phase transition from phase α to phase β
β	Volume expansivity
β	Parameter, cubic equations of state
Γ_i	Integration constant
γ	Ratio of heat capacities C_p/C_v
γ_i	Activity coefficient, species i in solution
δ	Polytropic exponent

ε	Constant, cubic equations of state
ε	Reaction coordinate
η	Efficiency
κ	Isothermal compressibility
Π	Spreading pressure, adsorbed phase
Π	Osmotic pressure
π	Number of phases, phase rule
μ	Joule/Thomson coefficient
μ_i	Chemical potential, species i
ν_i	Stoichiometric number, species i
ρ	Molar or specific density $\equiv 1/V$
ρ_c	Critical density
ρ_r	Reduced density
σ	Constant, cubic equations of state
Φ_i	Ratio of fugacity coefficients, defined by Eq. (13.14)
ϕ_i	Fugacity coefficient, pure species i
$\hat{\phi}_i$	Fugacity coefficient, species i in solution
ϕ^0, ϕ^1	Functions, generalized fugacity-coefficient correlation, Eq. 10.66
Ψ, Ω	Constants, cubic equations of state
ω	Acentric factor

Notes

cv	As a subscript, denotes a control volume
fs	As a subscript, denotes flowing streams
°	As a superscript, denotes the standard state
-	Overbar denotes a partial property
·	Overdot denotes a time rate
^	Circumflex denotes a property in solution
Δ	Difference operator

Chapter 1

Introduction

By way of introduction, in this chapter we outline the origin of thermodynamics and its present scope. We also review a number of familiar, but basic, scientific concepts essential to the subject:

- Dimensions and units of measure
- Force and pressure
- Temperature
- Work and heat
- Mechanical energy and its conservation

1.1 THE SCOPE OF THERMODYNAMICS

The science of thermodynamics was developed in the nineteenth century as a result of the need to describe the basic operating principles of the newly invented steam engine and to provide a basis for relating the work produced to the heat supplied. Thus the name itself denotes power generated from heat. From the study of steam engines, there emerged two of the primary generalizations of science: *the First and Second Laws of Thermodynamics*. All of classical thermodynamics is implicit in these laws. Their statements are very simple, but their implications are profound.

The First Law simply says that *energy* is conserved, meaning that it is neither created nor destroyed. It provides no definition of energy that is both general and precise. No help comes from its common informal use where the word has imprecise meanings. However, in scientific and engineering contexts, energy is recognized as appearing in various forms, useful because each form has mathematical definition as a *function* of some recognizable and measurable characteristics of the real world. Thus kinetic energy is defined as a function of velocity and mass, and gravitational potential energy as a function of elevation and mass.

Conservation implies the transformation of one form of energy into another. Windmills were historically used to transform the kinetic energy of the wind into work used to raise water

from land lying below sea level. The overall effect was to convert the kinetic energy of the wind into potential energy of water. Wind energy is now more widely converted to electrical energy. Similarly, the potential energy of water was historically transformed into work used to grind grain or saw lumber. Hydroelectric plants are now a significant source of electrical power.

The Second Law is more difficult to comprehend because it depends on *entropy*, a word and concept not in everyday use. Its consequences in daily life are significant with respect to environmental conservation and efficient use of energy. Formal treatment is postponed until we have laid the necessary foundation.

The two laws of thermodynamics have no proof in a mathematical sense. However, they are universally observed to be obeyed. An enormous volume of experimental evidence demonstrates their validity. Thus, thermodynamics shares with mechanics and electromagnetism a basis in primitive laws.

These laws lead, through mathematical deduction, to a network of equations that are applied across all branches of science and engineering. Included are calculation of heat and work requirements for physical, chemical, and biological processes and the determination of equilibrium conditions for chemical reactions and for the transfer of chemical species between phases. Practical application of these equations almost always requires information on the properties of materials. Thus, the study and application of thermodynamics is inextricably linked with the tabulation, correlation, and prediction of properties of substances. Figure 1.1 illustrates schematically how the two laws of thermodynamics are combined with information on material properties to yield useful analyses of, and predictions about, physical, chemical, and biological systems. It also notes the chapters of this text that treat each component.

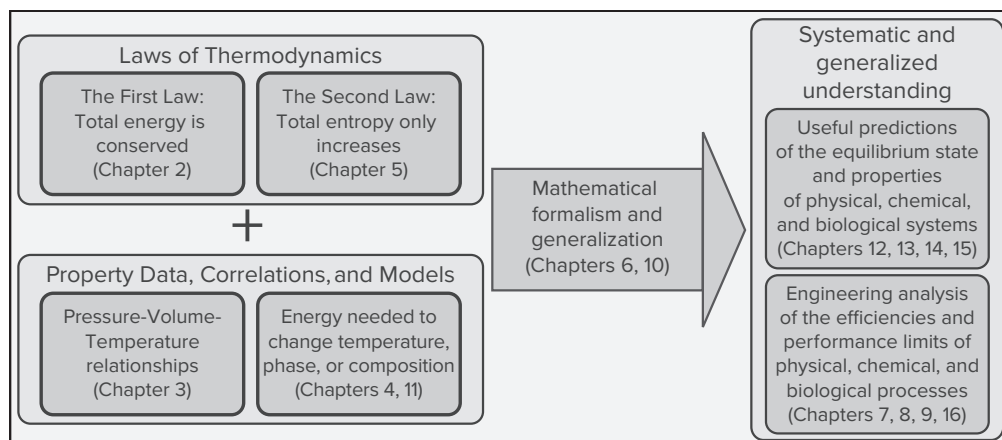


Figure 1.1: Schematic illustrating the combination of the laws of thermodynamics with data on material properties to produce useful predictions and analyses.

Examples of questions that can be answered on the basis of the laws of thermodynamics combined with property information include the following:

- How much energy is released when a liter of ethanol is burned (or metabolized) by reaction with oxygen in air to produce water and carbon dioxide?
- What maximum flame temperature can be reached when ethanol is burned in air?

- What maximum fraction of the heat released in an ethanol flame can be converted to electrical energy or work?
- How do the answers to the preceding two questions change if the ethanol is burned with pure oxygen, rather than air?
- What is the maximum amount of electrical energy that can be produced when a liter of ethanol is reacted with O_2 to produce CO_2 and water in a fuel cell?
- In the distillation of an ethanol/water mixture, how are the vapor and liquid compositions related?
- How much energy must be removed from (or added to) a fermenter in which yeast converts glucose to ethanol and carbon dioxide?
- When water and ethylene react at high pressure and temperature to produce ethanol, what are the compositions of the phases that result?
- How much ethylene is contained in a high-pressure gas cylinder for given temperature, pressure, and volume?
- When ethanol is added to a two-phase system comprising toluene and water, how much ethanol goes into each phase?
- If a water/ethanol mixture is partially frozen, what are the compositions of the liquid and solid phases?
- What volume of solution results from mixing one liter of ethanol with one liter of water? (It is *not* exactly 2 liters!)

The application of thermodynamics to any real problem starts with the specification of a particular region of space or body of matter designated as the *system*. Everything outside the system is called the *surroundings*. The system and surroundings interact through transfer of material and energy across the system boundaries, but the system is the focus of attention. Many different thermodynamic systems are of interest. A pure vapor such as steam is the working medium of a power plant. A reacting mixture of fuel and air powers an internal-combustion engine. A vaporizing liquid provides refrigeration. Expanding gases in a nozzle propel a rocket. The metabolism of food provides the nourishment for life. Photosynthesis in plants converts solar energy into stored chemical energy.

Once a system has been selected, we must describe its *state*. There are two possible points of view, the *macroscopic* and the *microscopic*. The former relates to quantities such as composition, density, temperature, and pressure. These *macroscopic coordinates* require no assumptions regarding the structure of matter. They are few in number, are suggested by our sense perceptions, and are measured with relative ease. A macroscopic description thus requires specification of a *few fundamental measurable properties*. The macroscopic point of view, as adopted in classical thermodynamics, reveals nothing of the microscopic (molecular) mechanisms of physical, chemical, or biological processes.

A microscopic description depends on the existence and behavior of molecules, is not directly related to our sense perceptions, and treats quantities that cannot routinely be directly measured. Nevertheless, it offers insight into material behavior and contributes to evaluation of thermodynamic properties. Bridging the length and time scales between the microscopic behavior of molecules and the macroscopic world is the subject of *statistical mechanics* or *statistical*

thermodynamics, which applies the laws of quantum mechanics and classical mechanics to large ensembles of atoms, molecules, or other elementary objects to predict and interpret macroscopic behavior. Although we make occasional reference to the molecular basis for observed material properties, the subject of statistical thermodynamics is not treated in this book.¹

1.2 INTERNATIONAL SYSTEM OF UNITS

Descriptions of thermodynamic states depend on the fundamental *dimensions* of science, of which length, time, mass, temperature, and amount of substance are of greatest interest here. These dimensions are *primitives*, recognized through our sensory perceptions, and are not definable in terms of anything simpler. Their use, however, requires the definition of arbitrary scales of measure, divided into specific *units* of size. Primary units have been set by international agreement, and are codified as the International System of Units (abbreviated SI, for *Système International*).² This is the primary system of units used throughout this book.

The *second*, symbol s, the SI unit of time, is the duration of 9,192,631,770 cycles of radiation associated with a specified transition of the cesium atom. The *meter*, symbol m, is the fundamental unit of length, defined as the distance light travels in a vacuum during $1/299,792,458$ of a second. The *kilogram*, symbol kg, is the basic unit of mass, previously defined as the mass of a platinum/iridium cylinder kept at the International Bureau of Weights and Measures at Sèvres, France. (The *gram*, symbol g, is 0.001 kg.) In 2018, the SI was revised to define the kilogram in terms of fundamental constants of nature, by setting an exact value for the Planck constant, $h = 6.62607015 \times 10^{-34} \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-1}$. Temperature is a characteristic dimension of thermodynamics, and is measured on the Kelvin scale, as described in Sec. 1.4. The *mole*, symbol mol, is defined as the amount of a substance represented by as many elementary entities (e.g., molecules) as there are atoms in 0.012 kg of carbon-12.

The SI unit of force is the *newton*, symbol N, *derived* from Newton's second law, which expresses force F as the product of mass m and acceleration a : $F = ma$. Thus, a newton is the force that, when applied to a mass of 1 kg, produces an acceleration of $1 \text{ m}\cdot\text{s}^{-2}$, and is therefore a unit representing $1 \text{ kg}\cdot\text{m}\cdot\text{s}^{-2}$. This illustrates a key feature of the SI system, namely, that derived units always reduce to combinations of primary units. Pressure P (Sec. 1.5), defined as the normal force exerted by a fluid on a unit area of surface, is expressed in pascals, symbol Pa. With force in newtons and area in square meters, 1 Pa is equivalent to $1 \text{ N}\cdot\text{m}^{-2}$ or $1 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2}$. Essential to thermodynamics is the derived unit for energy, the joule, symbol J, defined as $1 \text{ N}\cdot\text{m}$ or $1 \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2}$.

Multiples and decimal fractions of SI units are designated by prefixes, with symbol abbreviations, as listed in Table 1.1. Common examples of their use are the centimeter, $1 \text{ cm} = 10^{-2} \text{ m}$, the kilopascal, $1 \text{ kPa} = 10^3 \text{ Pa}$, and the kilojoule, $1 \text{ kJ} = 10^3 \text{ J}$.

¹Many introductory texts on statistical thermodynamics are available. The interested reader is referred to *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*, 2nd ed. by K. A. Dill and S. Bromberg, Garland Science, 2010, and many books referenced therein.

²In-depth information on the SI is provided by the National Institute of Standards and Technology (NIST) online at <http://physics.nist.gov/cuu/Units/index.html>.

Table 1.1: Prefixes for SI Units

Multiple	Prefix	Symbol
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m
10^{-2}	centi	c
10^2	hecto	h
10^3	kilo	k
10^6	mega	M
10^9	giga	G
10^{12}	tera	T
10^{15}	peta	P

Two widely used units in engineering that are not part of SI, but are acceptable for use with it, are the bar, a pressure unit equal to 10^2 kPa, and the liter, a volume unit equal to 10^3 cm³. The bar closely approximates atmospheric pressure. Other acceptable units are the minute, symbol min; hour, symbol h; day, symbol d; and the metric ton, symbol t, equal to 10^3 kg.

Weight properly refers to the force of gravity on a body, expressed in newtons, and not to its mass, expressed in kilograms. Force and mass are, of course, directly related through Newton's law, with a body's weight defined as its mass times the local acceleration of gravity. The comparison of masses by a balance is called "weighing" because it also compares gravitational forces. A spring scale (or a digital scale based on a strain gauge) provides correct mass readings only when used in the gravitational field of its calibration.

Although the SI is well established throughout most of the world, use of the U.S. Customary system of units persists in daily commerce in the United States. Even in science and engineering, conversion to SI is incomplete, though globalization is a major incentive. U.S. Customary units are related to SI units by fixed conversion factors. Those units most likely to be useful are defined in Appendix A. Conversion factors are listed in Table A.1.

Example 1.1

An astronaut weighs 730 N in Houston, Texas, where the local acceleration of gravity is $g = 9.792$ m·s⁻². What are the astronaut's mass and weight on the moon, where $g = 1.67$ m·s⁻²?

Solution 1.1

By Newton's law, with acceleration equal to the acceleration of gravity, g ,

$$m = \frac{F}{g} = \frac{730 \text{ N}}{9.792 \text{ m}\cdot\text{s}^{-2}} = 74.55 \text{ N}\cdot\text{m}^{-1}\cdot\text{s}^2$$

Because $1 \text{ N} = 1 \text{ kg}\cdot\text{m}\cdot\text{s}^{-2}$,

$$m = 74.55 \text{ kg}$$

This *mass* of the astronaut is independent of location, but *weight* depends on the local acceleration of gravity. Thus on the moon the astronaut's weight is:

$$F(\text{moon}) = m \times g(\text{moon}) = 74.55 \text{ kg} \times 1.67 \text{ m}\cdot\text{s}^{-2}$$

or

$$F(\text{moon}) = 124.5 \text{ kg}\cdot\text{m}\cdot\text{s}^{-2} = 124.5 \text{ N}$$

1.3 MEASURES OF AMOUNT OR SIZE

Three measures of amount or size of a homogeneous material are in common use:

- Mass, m
- Number of moles, n
- Total volume, V^t

These measures for a specific system are in direct proportion to one another. Mass can be divided by the *molar mass* \mathcal{M} (formerly called molecular weight) to yield number of moles:

$$n = \frac{m}{\mathcal{M}} \quad \text{or} \quad m = \mathcal{M}n$$

Total volume, representing the size of a system, is a defined quantity given as the product of three lengths. It can be divided by the mass or number of moles of the system to yield *specific* or *molar* volume:

- Specific volume: $V \equiv \frac{V^t}{m}$ or $V^t = mV$
- Molar volume: $V \equiv \frac{V^t}{n}$ or $V^t = nV$

Specific or molar density is defined as the reciprocal of specific or molar volume: $\rho \equiv V^{-1}$.

These quantities (V and ρ) are independent of the size of a system, and are examples of *intensive* thermodynamic variables. For a given state of matter (solid, liquid, or gas) they are functions of temperature, pressure, and composition, additional quantities independent of system size. Throughout this text, the same symbols will generally be used for both molar and specific quantities. Most equations of thermodynamics apply to both, and when distinction is necessary, it can be made based on the context. The alternative of introducing separate notation for each leads to an even greater proliferation of variables than is already inherent in the study of chemical thermodynamics.

1.4 TEMPERATURE

The notion of temperature, based on sensory perception of heat and cold, needs no explanation. It is a matter of common experience. However, giving temperature a scientific role requires a scale that affixes numbers to the perception of hot and cold. This scale must also extend far beyond the range of temperatures of everyday experience and perception. Establishing such a scale and devising measuring instruments based on this scale has a long and intriguing history. A simple instrument is the common liquid-in-glass thermometer, wherein the liquid expands when heated. Thus a uniform tube, partially filled with mercury, alcohol, or some other fluid, and connected to a bulb containing a larger amount of fluid, indicates degree of hotness by the length of the fluid column.

The scale requires definition and the instrument requires calibration. The Celsius³ scale was established early and remains in common use throughout most of the world. Its scale is defined by fixing zero as the *ice point* (freezing point of water saturated with air at standard atmospheric pressure) and 100 as the *steam point* (boiling point of pure water at standard atmospheric pressure). Thus a thermometer when immersed in an ice bath is marked zero and when immersed in boiling water is marked 100. Dividing the length between these marks into 100 equal spaces, called *degrees*, provides a scale, which may be extended with equal spaces below zero and above 100.

Scientific and industrial practice depends on the *International Temperature Scale of 1990* (ITS-90).⁴ This is the Kelvin scale, based on assigned values of temperature for a number of reproducible *fixed points*, that is, states of pure substances like the ice and steam points, and on *standard instruments* calibrated at these temperatures. Interpolation between the fixed-point temperatures is provided by formulas that establish the relation between readings of the standard instruments and values on ITS-90. The platinum-resistance thermometer is an example of a standard instrument; it is used for temperatures from -259.35°C (the triple point of hydrogen) to 961.78°C (the freezing point of silver).

The Kelvin scale, which we indicate with the symbol T , provides SI temperatures. An *absolute* scale, it is based on the concept of a lower limit of temperature, called absolute zero. Its unit is the *kelvin*, symbol K. Celsius temperatures, indicated in this text by the symbol t , are defined in relation to Kelvin temperatures:

$$t^{\circ}\text{C} = T \text{ K} - 273.15$$

The unit of Celsius temperature is the degree Celsius, $^{\circ}\text{C}$, which is equal in size to the kelvin.⁵ However, temperatures on the Celsius scale are 273.15 degrees lower than on the Kelvin scale. Thus absolute zero on the Celsius scale occurs at -273.15°C . Kelvin

³Anders Celsius, Swedish astronomer (1701–1744). See: http://en.wikipedia.org/wiki/Anders_Celsius.

⁴The English-language text describing ITS-90 is given by H. Preston-Thomas, *Metrologia*, vol. 27, pp. 3–10, 1990. It is also available at <http://www.its-90.com/its-90.html>.

⁵Note that neither the word *degree* nor the *degree sign* is used for temperatures in kelvins, and that the word *kelvin* as a unit is not capitalized.

temperatures are used in thermodynamic calculations. Celsius temperatures can only be used in thermodynamic calculations involving *temperature differences*, which are of course the same in both degrees Celsius and kelvins.

1.5 PRESSURE

The primary standard for pressure measurement is the dead-weight gauge in which a known force is balanced by fluid pressure acting on a piston of known area: $P \equiv F/A$. The basic design is shown in Fig. 1.2. Objects of known mass (“weights”) are placed on the pan until the pressure of the oil, which tends to make the piston rise, is just balanced by the force of gravity on the piston and all that it supports. With this force given by Newton’s law, the pressure exerted by the oil is:

$$P = \frac{F}{A} = \frac{mg}{A}$$

where m is the mass of the piston, pan, and “weights”; g is the local acceleration of gravity; and A is the cross-sectional area of the piston. This formula yields *gauge pressures*, the difference between the pressure of interest and the pressure of the surrounding atmosphere. They are converted to *absolute pressures* by addition of the local barometric pressure. Gauges in common use, such as Bourdon gauges, are calibrated by comparison with dead-weight gauges. Absolute pressures are used in thermodynamic calculations.

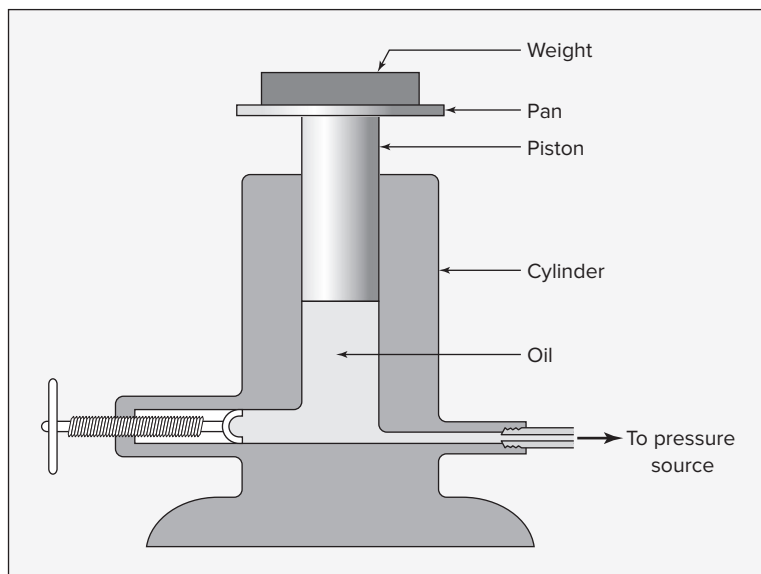


Figure 1.2:
Dead-weight gauge.

Because a vertical column of fluid under the influence of gravity exerts a pressure at its base in direct proportion to its height, pressure can be expressed as the equivalent height of a fluid column. This is the basis for the use of manometers for pressure measurement. Conversion of height to force per unit area follows from Newton’s law applied to the force of gravity

acting on the mass of fluid in the column. The mass is given by: $m = Ah\rho$, where A is the cross-sectional area of the column, h is its height, and ρ is the fluid density. Therefore,

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{Ah\rho g}{A}$$

Thus,

$$P = h\rho g \quad (1.1)$$

The pressure to which a fluid height corresponds is determined by the density of the fluid (which depends on its identity and temperature) and the local acceleration of gravity.

A unit of pressure in common use (but not an SI unit) is the *standard atmosphere*, representing the average pressure exerted by the earth's atmosphere at sea level, and defined as 101.325 kPa.

Example 1.2

A dead-weight gauge with a piston diameter of 1 cm is used for the accurate measurement of pressure. If a mass of 6.14 kg (including piston and pan) brings it into balance, and if $g = 9.82 \text{ m}\cdot\text{s}^{-2}$, what is the *gauge* pressure being measured? For a barometric pressure of 0.997 bar, what is the *absolute* pressure?

Solution 1.2

The force exerted by gravity on the piston, pan, and “weights” is:

$$F = mg = 6.14 \text{ kg} \times 9.82 \text{ m}\cdot\text{s}^{-2} = 60.295 \text{ N}$$

$$\text{Gauge pressure} = \frac{F}{A} = \frac{60.295}{(\frac{1}{4})(\pi)(0.01)^2} = 7.677 \times 10^5 \text{ N}\cdot\text{m}^{-2} = 767.7 \text{ kPa}$$

The absolute pressure is therefore:

$$P = 7.677 \times 10^5 + 0.997 \times 10^5 = 8.674 \times 10^5 \text{ N}\cdot\text{m}^{-2}$$

or

$$P = 867.4 \text{ kPa}$$

Example 1.3

At 27°C the reading on a manometer filled with mercury is 60.5 cm. The local acceleration of gravity is 9.784 m·s⁻². To what pressure does this height of mercury correspond?