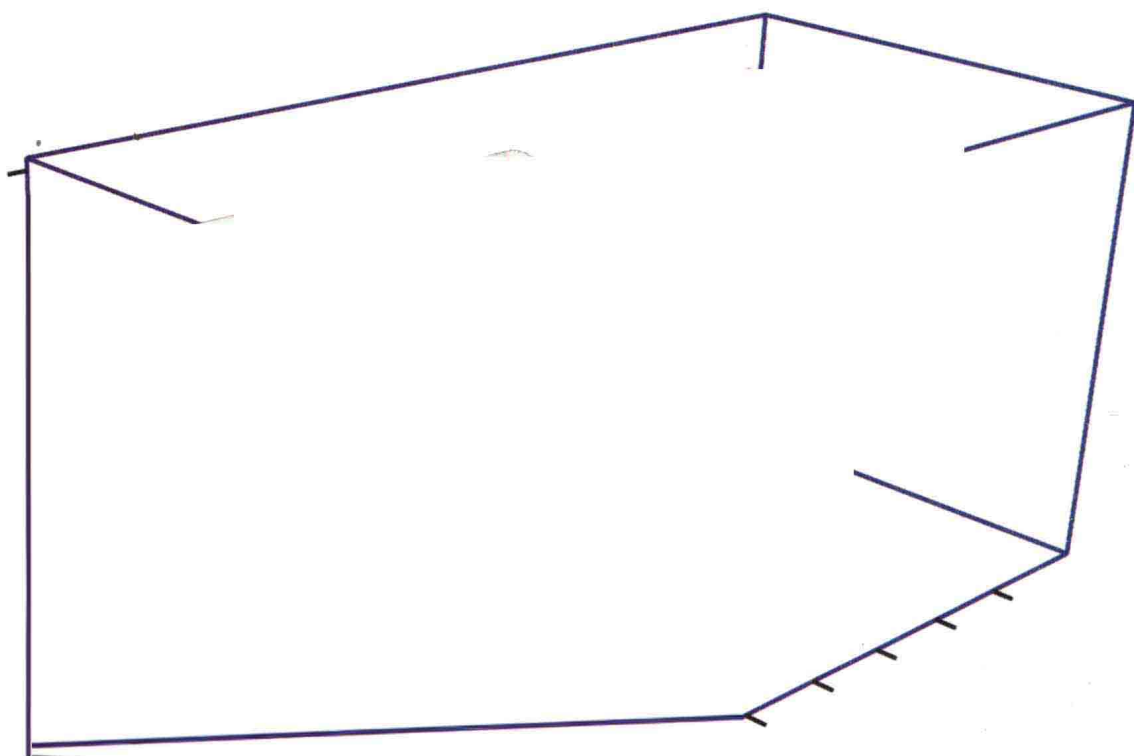


Introduction to

CHEMICAL ENGINEERING THERMODYNAMICS

Sixth Edition



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

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SIXTH EDITION

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This book is printed on acid-free paper.

3 4 5 6 7 8 9 0 DOC/DOC 0 9 8 7 6 5 4 3

ISBN 0-07-240296-2

Publisher: Thomas: Casson

Executive editor: Eric M. Munson

Developmental editor: Maja Lorkovic

Senior marketing manager: John T. Wannemacher

Project manager: Christine A. Vaughan

Lead production supervisor: Heather D. Burbridge

Coordinator freelance design: Mary L. Christianson

Supplement producer: Carol A. Bielski

Senior Media technology producer/developer: Phil Meek

Compositor: Interactive Composition Corporation

Typeface: 10/12 Times Roman

Printer: R. R. Donnelley & Sons Company

Cover illustration taken from "Phase," an interactive tutorial for showing fluid-phase equilibria through computer graphics.

Software design by Kenneth R. Jolls and Walter G. Chapman, graphics programming by Perry Miller, image preparation by Chad Sanborn.

Library of Congress Cataloging-in-Publication Data

Smith, J. M. (Joe Mauk)

Introduction to chemical engineering thermodynamics / J.M. Smith,

H.C. Van Ness, M.M. Abbott. — 6th ed.

p. cm. (McGraw-Hill chemical engineering series)

Includes bibliographical references and indexes.

ISBN 0-07-240296-2 (alk. paper)

1. Thermodynamics. 2. Chemical engineering. I. Van Ness, H.C. (Hendrick C.)

II. Abbott, Michael M. III. Title. IV. Series.

TP149.S582 2001

660'.2969 dc—21

00-051546

Preface

The purpose of this text is to present thermodynamics from a chemical-engineering viewpoint. Although the laws of thermodynamics are universal, the subject is most effectively taught in the context of the discipline of student commitment. This is the justification for a separate text for chemical engineers, just as it has been for the previous five editions, which have been in print for more than 50 years.

In writing this text, we have sought to maintain the rigor characteristic of sound thermodynamic analysis, while at the same time providing a treatment that may be understood by the average undergraduate. Much is included of an introductory nature, but development is carried far enough to allow application to significant problems in chemical-engineering practice.

For a student new to this subject a demanding task of discovery lies ahead. New ideas, terms, and symbols appear at a bewildering rate. The challenge, ever present, is to think topics through to the point of understanding, to acquire the capacity to reason, and to apply this fundamental body of knowledge to the solution of practical problems.

The first two chapters of the book present basic definitions and a development of the first law. Chapters 3 and 4 treat the pressure/volume/temperature behavior of fluids and certain heat effects, allowing early application of the first law to realistic problems. The second law and some of its applications are considered in Chap. 5. A treatment of the thermodynamic properties of pure fluids in Chap. 6 allows general application of the first and second laws, and provides for an expanded treatment of flow processes in Chap. 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. Chapters 11 and 12 provide a comprehensive exposition of the theory and application of solution thermodynamics. Chemical-reaction equilibrium is covered at length in Chap. 13. Chapter 14 deals with topics in phase equilibria, including an extended treatment of vapor/liquid equilibrium, and adsorption and osmotic equilibria. Chapter 15 treats the thermodynamic analysis of real processes, affording a review of much of the practical subject matter of thermodynamics. Finally, Chap. 16 presents an introduction to molecular 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 13 chapters include material thought necessary as part of any chemical engineer's education. Where only a single-semester course in chemical-engineering thermodynamics is provided, these 13 chapters 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 make necessary a prudent selectivity. Thus, we have not been able to include certain topics worthy of attention, but of a specialized nature. These include applications to polymers, electrolytes, and biomaterials.

We cannot begin to mention the many persons to whom we are indebted for contributions of various kinds, direct and indirect, over the years during which this text has evolved, edition to edition, into its present form. To all we extend our thanks.

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

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Chapter 1

Introduction

1.1 THE SCOPE OF THERMODYNAMICS

The science of thermodynamics was born in the nineteenth century of the need to describe the operation of steam engines and to set forth the limits of what they can accomplish. Thus the name itself denotes power developed from heat, with obvious application to heat engines, of which the steam engine was the initial example. However, the principles observed to be valid for engines are readily generalized, and are known as the first and second laws of thermodynamics. These laws have no proof in the mathematical sense; their validity lies in the absence of contrary experience. Thus thermodynamics shares with mechanics and electromagnetism a basis in primitive laws.

These laws lead through mathematical deduction to a network of equations which find application in all branches of science and engineering. The chemical engineer copes with a particularly wide variety of problems. Among them are calculation of heat and work requirements for physical and chemical processes, and the determination of equilibrium conditions for chemical reactions and for the transfer of chemical species between phases.

Thermodynamic considerations do not establish the *rates* of chemical or physical processes. Rates depend on driving force and resistance. Although driving forces are thermodynamic variables, resistances are not. Neither can thermodynamics, a macroscopic-property formulation, reveal the microscopic (molecular) mechanisms of physical or chemical processes. On the other hand, knowledge of the microscopic behavior of matter can be useful in the calculation of thermodynamic properties.¹ Property values are essential to the practical application of thermodynamics. The chemical engineer deals with many chemical species, and experimental data are often lacking. This has led to development of “generalized correlations” that provide property estimates in the absence of data.

The application of thermodynamics to any real problem starts with the identification of a particular body of matter as the focus of attention. This body of matter is called the *system*, and its thermodynamic state is defined by a few measurable macroscopic properties. These depend on the fundamental *dimensions* of science, of which length, time, mass, temperature, and amount of substance are of interest here.

¹ An elementary treatment is presented in Chap. 16.

1.2 DIMENSIONS AND UNITS

The *fundamental* dimensions are *primitives*, recognized through our sensory perceptions and 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*).

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 mass of a platinum/iridium cylinder kept at the International Bureau of Weights and Measures at Sèvres, France. The unit of temperature is the *kelvin*, symbol K, equal to $1/273.16$ of the thermodynamic temperature of the triple point of water. A detailed discussion of temperature, the characteristic dimension of thermodynamics, is given in Sec. 1.5. The *mole*, symbol mol, is defined as the amount of substance represented by as many elementary entities (e.g., molecules) as there are atoms in 0.012 kg of carbon-12. This is equivalent to the “gram mole” commonly used by chemists.

Multiples and decimal fractions of SI units are designated by prefixes. Those in common use are listed in Table 1.1. Thus, the centimeter is given as $1\text{ cm} = 10^{-2}\text{ m}$ and $10^3\text{ g} = 1\text{ kg}$.

Table 1.1: Prefixes for SI Units

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

Other systems of units, such as the English engineering system, use units that are related to SI units by fixed conversion factors. Thus, the foot (ft) is defined as 0.3048 m, the pound mass (lb_m) as 0.45359237 kg, and the pound mole (lb mol) as 453.59237 mol.

1.3 MEASURES OF AMOUNT OR SIZE

Three measures of amount or size 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, a *primitive* without definition, may be divided by the molar mass M , commonly called the molecular

weight, to yield number of moles:

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

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

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

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. They are functions of the temperature, pressure, and composition of a system, additional quantities that are independent of system size.

1.4 FORCE

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 :

$$F = ma$$

The newton is defined as the force which when applied to a mass of 1 kg produces an acceleration of 1 m s^{-2} ; thus the newton is a *derived* unit representing 1 kg m s^{-2} .

In the English engineering system of units, force is treated as an additional independent dimension along with length, time, and mass. The pound *force* (lb_f) is defined as that force which accelerates 1 pound *mass* 32.1740 feet per second per second. Newton's law must here include a dimensional proportionality constant for consistency with this definition:

$$F = \frac{1}{g_c} ma$$

Whence,²

$$1(\text{lb}_f) = \frac{1}{g_c} \times 1(\text{lb}_m) \times 32.1740(\text{ft})(\text{s})^{-2}$$

and

$$g_c = 32.1740(\text{lb}_m)(\text{ft})(\text{lb}_f)^{-1}(\text{s})^{-2}$$

The pound *force* is equivalent to 4.4482216 N.

Since force and mass are different concepts, a pound *force* and a pound *mass* are different quantities, and their units do not cancel one another. When an equation contains both

²Where non-SI units (e.g., English units) are employed, parentheses enclose the abbreviations of all units.

units, (lb_f) and (lb_m), the dimensional constant g_c must also appear in the equation to make it dimensionally correct.

Weight properly refers to the force of gravity on a body, and is correctly expressed in newtons or in pounds *force*. Unfortunately, standards of mass are often called “weights,” and use of a balance to compare masses is called “weighing.” Thus, one must discern from the context whether force or mass is meant when “weight” is used in a casual or informal way.

Example 1.1

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

Solution 1.1

With $a = g$, Newton's law is: $F = mg$. Whence,

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

Since the newton N has the units kg m 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:

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

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

Use of the English engineering system of units requires conversion of the astronaut's weight to (lb_f) and the values of g to $(\text{ft})(\text{s})^{-2}$. With 1 N equivalent to 0.224809(lb_f) and 1 m to 3.28084(ft):

$$\text{Weight of astronaut in Houston} = 164.1(\text{lb}_f)$$

$$g(\text{Houston}) = 32.13 \quad \text{and} \quad g(\text{moon}) = 5.48(\text{ft})(\text{s})^{-2}$$

Newton's law then gives:

$$m = \frac{F g_c}{g} = \frac{164.1(\text{lb}_f) \times 32.1740(\text{lb}_m)(\text{ft})(\text{lb}_f)^{-1}(\text{s})^{-2}}{32.13(\text{ft})(\text{s})^{-2}}$$

$$\text{or} \quad m = 164.3(\text{lb}_m)$$

Thus the astronaut's mass in (lb_m) and weight in (lb_f) in Houston are *numerically* almost the same, but on the moon this is not the case:

$$F(\text{moon}) = \frac{mg(\text{moon})}{g_c} = \frac{(164.3)(5.48)}{32.1740} = 28.0(\text{lb}_f)$$

1.5 TEMPERATURE

Temperature is commonly measured with liquid-in-glass thermometers, wherein the liquid expands when heated. Thus a uniform tube, partially filled with mercury, alcohol, or some other fluid, can indicate degree of “hotness” simply by the length of the fluid column. However, numerical values are assigned to the various degrees of hotness by arbitrary definition.

For the Celsius scale, the ice point (freezing point of water saturated with air at standard atmospheric pressure) is zero, and the steam point (boiling point of pure water at standard atmospheric pressure) is 100. A thermometer may be given a numerical scale by immersing it in an ice bath and making a mark for zero at the fluid level, and then immersing it in boiling water and making a mark for 100 at this greater fluid level. The distance between the two marks is divided into 100 equal spaces called *degrees*. Other spaces of equal size may be marked off below zero and above 100 to extend the range of the thermometer.

All thermometers, regardless of fluid, provide the same reading at zero and at 100 if they are calibrated by the method described, but at other points the readings do not usually correspond, because fluids vary in their expansion characteristics. Thus an arbitrary choice of fluid is required, and the temperature scale of the SI system, with its kelvin unit, symbol K, is based on the ideal gas as thermometric fluid. Since the definition of the Kelvin scale depends on the properties of gases, its detailed discussion is delayed until Chap. 3. We note, however, that as an absolute scale, it depends on the concept of a lower limit of temperature.

Kelvin temperatures are given the symbol T ; Celsius temperatures, given 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, $^{\circ}\text{C}$, equal in size to the kelvin. However, temperatures on the Celsius scale are 273.15 degrees lower than on the Kelvin scale. Thus the lower limit of temperature, called absolute zero on the Kelvin scale, occurs at -273.15°C .

In practice the *International Temperature Scale of 1990* (ITS-90) is used for calibration of scientific and industrial instruments.³ The ITS-90 scale is defined so that its values differ from ideal-gas temperatures by no more than the present accuracy of measurement. It is based on assigned values of temperature for a number of reproducible phase-equilibrium states of pure substances (*fixed 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).

In addition to the Kelvin and Celsius scales two others are still used by engineers in the United States: the Rankine scale and the Fahrenheit scale. The Rankine scale is an absolute scale directly related to the Kelvin scale by:

$$T(\text{R}) = 1.8 T \text{ K}$$

³The English-language text of the definition of ITS-90 is given by H. Preston-Thomas, *Metrologia*, vol. 27, pp. 3–10, 1990.

The Fahrenheit scale is related to the Rankine scale by an equation analogous to the relation between the Celsius and Kelvin scales:

$$t(^{\circ}\text{F}) = T(\text{R}) - 459.67$$

Thus the lower limit of temperature on the Fahrenheit scale is $-459.67(^{\circ}\text{F})$. The relation between the Fahrenheit and Celsius scales is:

$$t(^{\circ}\text{F}) = 1.8 t(^{\circ}\text{C}) + 32$$

The ice point is therefore $32(^{\circ}\text{F})$ and the normal boiling point of water is $212(^{\circ}\text{F})$.

The Celsius degree and the kelvin represent the same temperature *interval*, as do the Fahrenheit degree and the rankine. The relationships among the four temperature scales are shown in Fig. 1.1. In thermodynamics, absolute temperature is implied by an unqualified reference to temperature.

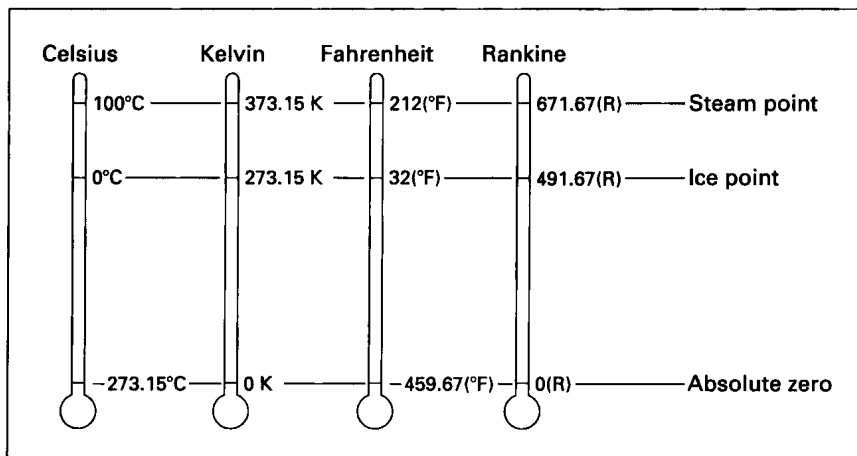


Figure 1.1: Relations among temperature scales.

1.6 PRESSURE

The pressure P exerted by a fluid on a surface is defined as the normal force exerted by the fluid per unit area of the surface. If force is measured in N and area in m^2 , the unit is the newton per square meter or N m^{-2} , called the pascal, symbol Pa, the basic SI unit of pressure. In the English engineering system a common unit is the pound *force* per square inch (psi).

The primary standard for pressure measurement is the dead-weight gauge in which a known force is balanced by a fluid pressure acting on a known area; whence $P \equiv F/A$. A simple design is shown in Fig. 1.2. The piston is carefully fitted to the cylinder making the clearance small. 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 of 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. Gauges in common use, such as Bourdon gauges, are calibrated by comparison with dead-weight gauges.

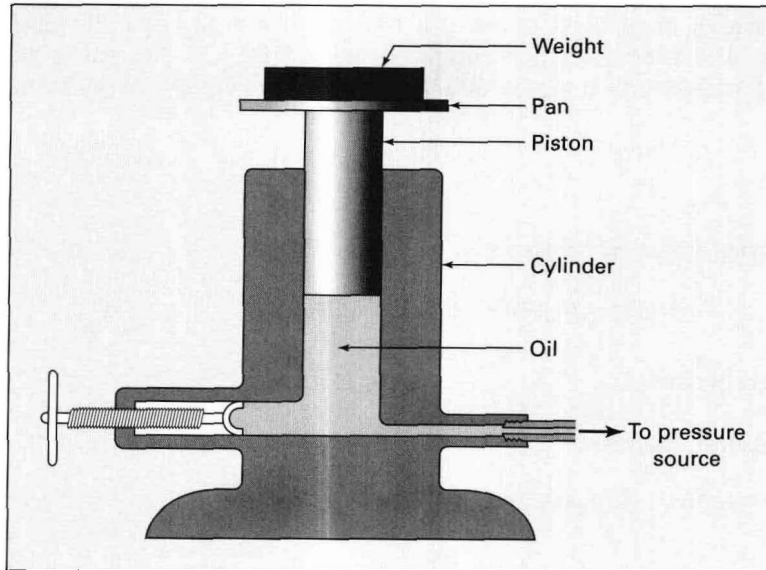


Figure 1.2:
Dead-weight
gauge.

Since a vertical column of a given fluid under the influence of gravity exerts a pressure at its base in direct proportion to its height, pressure is also 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,

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

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. Thus the (torr) is the pressure equivalent of 1 millimeter of mercury at 0°C in a standard gravitational field, and is equal to 133.322 Pa.

Another unit of pressure is the standard atmosphere (atm), the approximate average pressure exerted by the earth's atmosphere at sea level, defined as 101,325 Pa, 101.325 kPa, or 0.101325 MPa. The bar, an SI unit defined as 10^5 Pa, is equal to 0.986923(atm).

Most pressure gauges give readings which are the difference between the pressure of interest and the pressure of the surrounding atmosphere. These readings are known as *gauge* pressures, and can be converted to *absolute* pressures by addition of the barometric pressure. Absolute pressures must be used in thermodynamic calculations.

Example 1.2

A dead-weight gauge with a 1-cm-diameter piston is used to measure pressures very accurately. In a particular instance a mass of 6.14 kg (including piston and pan) brings it into balance. If the local acceleration of gravity is 9.82 m s^{-2} , what is the *gauge* pressure being measured? If the barometric pressure is 748(torr), what is the *absolute* pressure?

Solution 1.2

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

$$F = mg = (6.14)(9.82) = 60.295 \text{ N}$$

$$\text{Gauge pressure} = \frac{F}{A} = \frac{60.295}{(1/4)(\pi)(1)^2} = 76.77 \text{ N cm}^{-2}$$

The absolute pressure is therefore:

$$P = 76.77 + (748)(0.013332) = 86.74 \text{ N cm}^{-2}$$

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?

Solution 1.3

Recall the equation in the preceding text, $P = h\rho g$. At 27°C the density of mercury is 13.53 g cm^{-3} . Then,

$$P = 60.5 \text{ cm} \times 13.53 \text{ g cm}^{-3} \times 9.784 \text{ m s}^{-2} = 8,009 \text{ g m s}^{-2} \text{ cm}^{-2}$$

or

$$P = 8.009 \text{ kg m s}^{-2} \text{ cm}^{-2} = 8.009 \text{ N cm}^{-2} = 80.09 \text{ kPa} = 0.8009 \text{ bar}$$
