1

Introduction

1.1 Definition

Welcome to a new world, one without time! This is the world of *thermodynamics*, and it is the world we shall study in this course. Thermodynamics is an engineering/science field of study that is an exceptionally powerful tool for solving difficult problems with relatively little effort. For example, consider a glass of water that over the course of a day is heated, cooled, stirred, boiled, and frozen. How could we find the final condition of the water as represented by its characteristics knowing only the initial condition? It would be necessary to know the position and momentum of each molecule of water as a function of time and integrate from the initial time to the final time. Given that the water may contain 10^{25} molecules, this problem poses a prohibitively difficult task. However, with thermodynamics, we can translate this problem from a time domain to a timeless domain. In that new domain, we can solve the problem by knowing only a few things (less than five) about the water. Surely, you would rather tackle the latter problem than the former one. The translational procedure to move between the real world and the thermodynamic world is the application of the laws of thermodynamics. These are observations for which we have found no contradictions. The means for translation is mathematics. This process/procedure will become obvious as we progress through the course.

What is thermodynamics? The original Greek words from which we derive the name are *thermos* = heat and *dynamos* = power. This analysis would imply that thermodynamics is a study of heat power. Indeed, early thermodynamisists studied extracting energy transferred as work from energy transferred as heat. However, thermodynamics is a much richer and broader topic than that. The topic has very few concepts combined with formal elegance. Therefore, thermodynamics in a broader sense is a mathematical description of the real world using its physical properties.

Thermodynamics comes in two "flavors": classical and statistical. Classical thermodynamics derives from macroscopic observations. Statistical thermodynamics derives from microscopic models. A modern bridge between the two is computer simulation that uses numerical techniques to apply principles of statistical thermodynamics to macroscopic problems to increase understanding. This course considers classical thermodynamics, but, when appropriate, introduces the concepts of statistical thermodynamics to provide deeper understanding.

Thermodynamics for Chemical Engineers, First Edition. Kenneth R. Hall and Gustavo A. Iglesias-Silva.

1.2 Dimensions, Fundamental Quantities, and Units

Thermodynamics has simple mathematics, but the concepts are usually more demanding for students. It is important to recall several important definitions before beginning a course in thermodynamics to emphasize the importance of concepts. Therefore, let us define some common concepts that are useful in thermodynamics.

The numbers are meaningless without the correct specification of what they represent. For example, it does not make sense to say *I reduced my weight by three* or *the distance that I walk every day is five*. We must state that we have reduced our weight by 3 lb or 3 kg, and we traveled 5 mi or 5 km. These specifications are *units*. The product of a number and a unit can express any physical quantity. The number multiplying the unit is the *numerical value* of the quantity expressed in that unit, that is

$$A = \{A\}[A] \tag{1.1}$$

where $\{A\}$ is the numerical value or magnitude of A when expressing the value of A with units $[A]$. For example, if you weigh 60 kg, then $\{A\} = 60$ and $[A]$ is kilograms. Generally, in figures and tables, we see the labels $A/[A]$, which indicate numerical values according to Eq. (1.1). Thus, the axis of a graph or the heading of a column in a table should be "m kg^{-1}," denoting the mass measured in kilograms instead of "m (kg)" or "Mass (kg)."

Many units exist for different physical quantities, so it is convenient to introduce a general designation for a single class of units. Then, all the units employed for a particular physical property have the same **dimension** and use a separate symbol for it. The concept dimension is the name of a class of units, and a particular unit is an individual member of this class. The use of dimensions requires establishing a scale of measure with specific units. The International System of Units (SI: Systeme International) sets these units by international agreement. The SI establishes seven base units for seven base physical quantities that do not depend upon any other physical property (such as the length of the King's foot, the mass of a 90% platinum and 10% iridium bar, or suchlike).

The SI is a system of units for which

- the unperturbed ground-state hyperfine transition frequency of the cesium atom, $\Delta\nu_{Cs}$, is 9 192 631 770 Hz
- the speed of light under vacuum, c, is 299 792 458 m/s
- the Planck constant, h, is $6.62607015 \times 10^{-34}$ J s
- the elementary charge, e, is $1.602176634 \times 10^{-19}$ C
- the Boltzmann constant, k, is 1.380649×10^{-23} J/K
- the Avogadro constant, N_A, is $6.02214076 \times 10^{23}$ mol^{-1}
- the luminous efficacy of monochromatic radiation of frequency 540×10^{12} Hz and K_{cd} is 683 lm/W

in which Hz (hertz), J (joule), C (coulomb), lm (lumen), and W (watt) have relationships to the following units: s (second), m (meter), kg (kilogram), A (ampere), K

Table 1.1 Units of the base units in the English Engineering System.

Physical property	Unit	Symbol
Length	Foot	ft
Mass	Pound-mass	lbm, #m
Time	Second	sec
Electric current	Ampere	amp
Temperature	Rankine	°R
Amount of substance	Pound-mole	lbmol, # mole
Luminous intensity	Foot-candles	ft Cd

(kelvin), mol (mole), and cd (candela): $Hz = s^{-1}$, $J = kg\,m^2/s^2$, $C = A\,s$, $lm = cd\,m^2$, $m^{-2} = cd\,sr$, and $W = kg\,m^2/s^3$.

The base units of the SI are as follows:

- Time (t) is a measure of the separation of events. The SI unit of time is second (s), and it comes directly from $\Delta\nu_{Cs}$ defined above in terms of Hz, which is s^{-1}.
- Length (l) is a measure of the separation of points in space. Meter, m, is the fundamental unit of length defined as the length of the path traveled by light under vacuum during a time interval of 1/299 792 458 of a second.
- Mass (m) is a measure of the amount of an object. Kilogram, kg, comes from Planck's constant expressed in J s, which equals $kg\,m^2/s$ with m and s defined under time and length.
- Ampere (A) is the SI unit for electric current, and it comes from the elementary charge, e, expressed in C (=A s) with s defined under time.
- Thermodynamic temperature (T) measures the "hotness" of an object and reflects the motion of its molecules. The unit of thermodynamic temperature is kelvin (K), and it comes from the Boltzmann constant expressed in J/K or $kg\,m^2/(s^2\,K)$ (kg, m, and s already have definitions).
- The amount of substance is mole (n) in SI. It comes directly from N_A (Avogadro's number).
- The SI unit for luminous intensity in a given direction is candela (cd) defined by the luminous efficacy of monochromatic radiation of frequency expressed in lm/W.

Other systems of units exist, such as the English Engineering System (used sparingly throughout the world primarily in the United States and a few small political entities). The primary dimensions are force, mass, length, time, and temperature. The units for force and mass are independent. Table 1.1 contains the base units in this system.

A prefix added to any unit can produce an integer multiple of the base unit. For example, a kilometer denotes one thousand meters, and a millimeter denotes one thousandth of a meter: For example, $1\,km = 1\times10^3\,m$ and $1\,mm = 1\times10^{-3}\,m$. Table 1.2 contains the accepted prefixes for use with SI units.

Table 1.2 SI prefixes.

Name	Symbol	Factor	Name	Symbol	Factor
yotta	Y	10^{24}	deci	d	10^{-1}
zetta	Z	10^{21}	centi	c	10^{-2}
exa	E	10^{18}	milli	m	10^{-3}
peta	P	10^{15}	micro	μ	10^{-6}
tera	T	10^{12}	nano	n	10^{-9}
giga	G	10^{9}	pico	p	10^{-12}
mega	M	10^{6}	femto	f	10^{-15}
kilo	k	10^{3}	atto	a	10^{-18}
hecto	h	10^{2}	zepto	z	10^{-21}
deka	da	10^{1}	yocto	y	10^{-24}

1.3 Secondary or Derived Physical Quantities

All other quantities derive from base quantities by multiplication and division. These quantities have units that are a combination of the base units according to the algebraic relations of the corresponding physical quantities. Some derived physical properties are area, volume, force, pressure, etc.

Area is a measure of the surface of an object. It is two dimensional and in terms of dimensional symbols is L^2. The units employed to represent the area are square meters in the SI system or square feet in the English system.

Volume is the space occupied by an object and in terms of dimensions is the product of the lengths associated with the object: $L \times L \times L = L^3$. The SI unit for volume is the cubic meter. The volume of a substance depends upon the amount of the material, but a specific volume and molar volume (m^3/kg or m^3/mol) are independent of the amount of the material. The reciprocal of the specific volume is the density. Obviously, an object can have a total volume (the amount of space it occupies) and a specific or molar volume that applies to any sized object. **In this text, we use capital letters to denote the molar properties of a substance, so a total property would be the molar property multiplied by the number of moles.** For example, the total volume is

$$(nV) \equiv n \cdot V \tag{1.2}$$

The specific volume (volume per mass) is $(nV)/m = V/M$, where M is the molar mass (or molecular weight) and the molar volume is V (volume per mole).

Force induces motion or change. Newton's laws describe the action of forces in causing motion. Newton's second law states that force is the product of mass m and its acceleration a,

$$F = ma \tag{1.3}$$

Thus, force = (mass)(length)/(time)^2. The SI unit for force is newton (N), and according to the above equation, it is the force required to accelerate a mass of 1 kg at a rate of 1 m/s^2. Therefore,

$$1 \text{ N} = 1 \text{ kg m/s}^2 \tag{1.4}$$

In the English Engineering System, the unit of force is pound force (lb_f), and 1 lb force imparts an acceleration of 32.1740 ft/s^2 to a mass of 1 lb. In this system, force is an independent dimension that requires a proportionality constant to be consistent with the definition Eq. (1.3)

$$F = \frac{ma}{g_c} \tag{1.5}$$

Thus,

$$1 \text{ lb}_\text{f} = (1/g_c) \times 1 \text{ lb}_\text{m} \times 32.1740 \text{ ft/s}^2 \rightarrow g_c = 32.1740 \text{ lb}_\text{m} \text{ ft } /(\text{lb}_\text{f} \text{ s}^2)$$

and 1 lb_f = 4.4482216 N. In this system of units, confusion exists between the terms mass and weight, and often, they are used synonymously. For example, when we buy meat by weight, we are interested in the amount of meat. Likewise, when we measure our body weight, we want to know the amount of fat or muscle present. Scales measure force. Weight refers to the force exerted upon an object by virtue of its position in a gravitational field. In most circumstances, this ambiguity is not a problem because the weight of an object is directly proportional to its mass (see Eq. (1.3)), and on Earth, the proportionality constant is the gravitational acceleration, which is essentially constant. We conclude that the mass of an object does not change, but its weight does depend on the gravitational field surrounding the object.

Example 1.1

An alien weighs 102 N on his planet and 700 N on Earth. The gravitational acceleration on Earth is approximately 9.802 m/s^2. What is the gravitational acceleration of the alien's planet? From the following table (moons are in italics), can you infer from which planet or moon this alien comes?

Planet/moons	Approximate gravitational acceleration (m/s^2)	Planets/moons	Approximate gravitational acceleration (m/s^2)
Mercury	3.70	Saturn	11.19
Venus	8.87	*Titan*	1.36
Moon	1.63	Uranus	9.01
Mars	3.73	*Titania*	0.38
Jupiter	25.93	*Oberon*	0.35
Io	1.79	Neptune	11.28
Europa	1.31	*Triton*	0.78
Ganymede	1.43	Pluto	0.61
Callisto	1.24		

Solution

First, we calculate the mass of the alien using the information from Earth:

$$m = \frac{F}{a} = \frac{700\ \text{N}}{9.802\ \text{m/s}^2} = \frac{700\ \text{kg m/s}^2}{9.802\ \text{m/s}^2} = 71.414\ \text{kg}$$

Because the mass is independent of the location, on its native planet or moon

$$a = \frac{F}{m} = \frac{102\ \text{N}}{71.414\ \text{kg}} = \frac{102\ \text{kg m/s}^2}{71.414\ \text{kg}} = 1.428\ \text{m/s}^2$$

Most likely, the alien comes from the moon of Jupiter: *Ganymede*.

Pressure is the force applied over an area. In the SI system, the unit of force is newton and that for area is square meters, so the unit of pressure is N/m^2. This unit is called pascal, and its symbol is Pa. In the English Engineering System, the usual pressure unit is pound force per square inch (psi). If an object rests on a surface, the force pressing on the surface is its weight. However, in different positions, the area in contact can be different, and it can exert different pressures. **Pressure is an observable and it is not a function of mass.**

$$P = \frac{F}{A} \tag{1.6}$$

We use various terms for pressure:

- Atmospheric pressure, P_{atm}, is the pressure caused by the weight of the Earth's atmosphere on an object. We might find this pressure called "barometric" pressure. The standard atmosphere (atm) is a unit of pressure equal to 101.325 kPa.
- Absolute pressure, P_{abs}, is the total pressure. An absolute pressure of 0 is perfect vacuum. All thermodynamic calculations must use absolute pressure.
- Gauge or manometric pressure, P_{man}, is the pressure relative to atmospheric pressure, $P_{man} = P_{abs} - P_{atm}$.
- Vacuum is a gauge pressure that is below the atmospheric pressure. It reports a positive number for vacuum.

We calculate the absolute pressure by adding the atmospheric pressure to the gauge pressure:

$$P_{abs} = P_{atm} + P_{man} \tag{1.7}$$

Many pressure measurement techniques are available. First, we must define primary and secondary measurement standards. A primary standard is a measurement device for which the theoretical relation between the measured physical property and the desired quantity (pressure in this case) is known exactly. A secondary standard is a measurement device for which the theoretical relation between the measured physical property and the desired quantity (pressure, temperature, etc.) is not known exactly. Secondary measurement devices must have calibrations against the primary standards.

First, let us consider manometers and dead-weight gauges. These are primary pressure devices commonly used in engineering. Figure 1.1 shows a manometer and

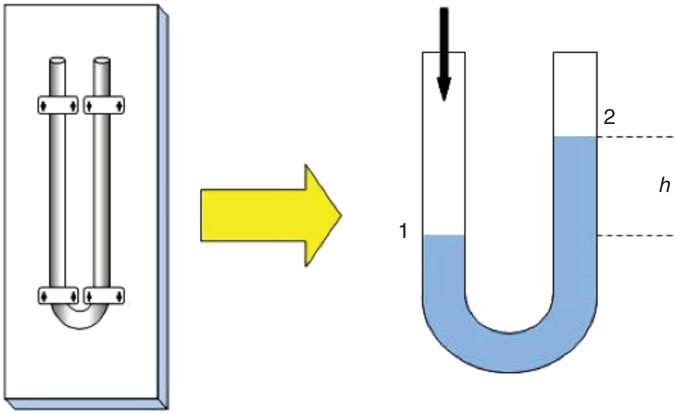


Figure 1.1 A U-tube glass manometer and its schematic diagram.

its schematic diagram. Manometers measure differential pressures. The differential equation that expresses pressure is

$$\frac{\partial P}{\partial z} = -\rho g \tag{1.8}$$

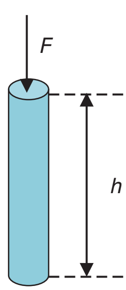
where ρ is the density of the fluid and g is the local acceleration of gravity. If the density is constant, the integration of the Eq. (1.8) is

$$P_2 - P_1 = -\rho g \Delta z = -\rho g(z_2 - z_1) = -\rho g h \tag{1.9}$$

In Figure 1.1, a force pushes on the fluid in position 1 and the atmospheric pressure acts against the fluid in position 2, then

$$P_1 = P_2 + \rho g h \tag{1.10}$$

This equation indicates that the hydraulic pressure (gauge pressure) is $\rho g h$. This effect also is the pressure that a vertical column of fluid exerts at its base caused by gravity



Applying Newton's law and the definition of pressure,

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{\rho V^t g}{A} = \frac{\rho A h g}{A} = \rho h g \tag{1.11}$$

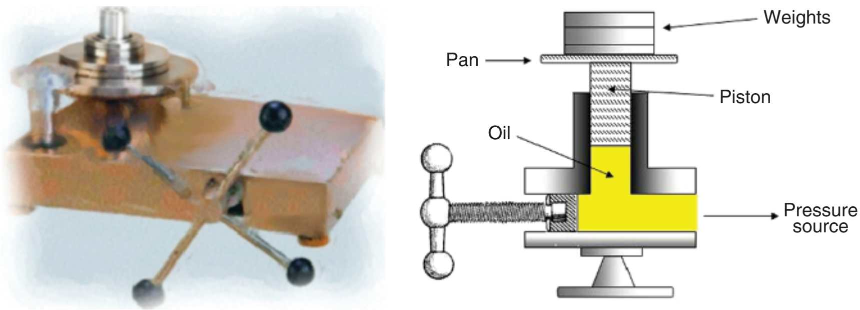


Figure 1.2 Dead-weight gauge.

in which ρ is the mass density (mass per volume). Equation (1.11) is the theoretical relation for pressure as a function of height and density of a fluid in a manometer. For very precise measurement of pressure with a manometer, the density of the measuring fluid must be corrected for its thermal expansion and for the height measuring device in a gravitational field.

Calibration of commercial mercury manometers uses the density at 0 °C, and the measuring scale (usually brass) has zero correction at either 70 or 77 °F. Because these devices measure distances, units of pressure exist such as mm Hg, in of H_2O, etc. Torr is the pressure equal to 1 mm of mercury at 0 °C in a standard gravitational field. One torr equals 133.322 Pa. The overall uncertainty in a manometer is approximately 8.1×10^{-5} Pa. Manometers are useful and practical for measurements from 10^{-3} to 2 atm.

Another primary standard is the dead-weight gauge. Figure 1.2 depicts such a gauge along with a schematic. In this case, masses impose the downward force on the plate and piston (with a known cross-sectional area).

The theoretical relationship for this device comes from a force balance between the working fluid (oil or air) and the weights:

$$Upward\ \ force = downward\ \ force \rightarrow PA = mg \tag{1.12}$$

in which P is the pressure; A is the cross-sectional area of the piston; m is the mass of the piston, pan, and load; and g is the local gravitational acceleration. Therefore,

$$P = \frac{mg}{A} \tag{1.13}$$

The ultimate accuracy for the best dead-weight gauges is about 1 part in 30 000 with a precision of 1 part in 20 000. Dead-weight gauges are the instrument of choice for the measurement of highest accuracy or for calibrating other pressure gauges. The secondary pressure devices are pressure transducers, bourdon tubes, and differential pressure indicators (DPIs) (Figure 1.3).

Example 1.2

Calculate the pressure that the atmosphere exerts on the head of a man who is 1.75 m tall and who is on top of a mountain that is 1000 m high. The temperature is 10 °C.

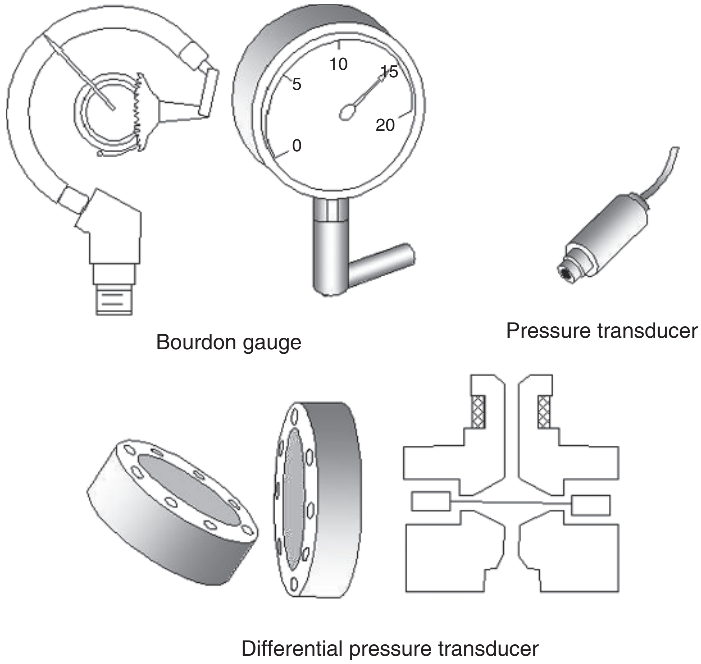


Figure 1.3 Secondary pressure measurement devices.

Assume that the pressure at the sea level is 101 kPa, $g = 9.80665\ \text{m/s}^2$, and the density of air in kg/m^3 is a function of temperature (but not pressure) given by

$$\rho_{air} = 1.29235 - 4.76457 \times 10^{-3} t + 1.66653 \times 10^{-5} t^2$$

Solution

Using Eq. (1.9).

$$P_{top} - P_{sea} = -\rho_{air} g \Delta z = -\rho_{air} g (z_{top} - z_{sea}) = -\rho_{air} g h_{mountain+man\ height}$$

$$\rho_{air} = 1.29235 - 4.76457 \times 10^{-3}(10) + 1.66653 \times 10^{-5}(10)^2 = 1.246371\ \ \text{kg/m}^3$$

$$\rho_{air} g h_{mountain+man\ height} = 1.246371\ \ \text{kg/m}^3 \times 9.89665\ \ \text{m/s}^2 \times (1000 + 1.75)\ \ \text{m}$$

$$\rho_{air} g h_{mountain+man\ height} = 12244.11\ \ \text{kg/(m s}^2) = 12244.11\ \ \text{Pa} = 12.244\ \ \text{kPa}$$

$$P_{top} = P_{sea} - \rho_{air} g h_{mountain+man\ height} = 101 - 12.244 = 88.766\ \ \text{kPa}$$

Example 1.3

A dead-weight gauge has the following specifications:

Piston diameter = 2.5 cm
Pan mass = 415 g
Cylinder mass = 500 g
Masses: #1: 100 g, #2: 500 g, #3: 1 kg, #4: 3 kg, and #5: 5 kg

An experimenter uses two #1, one #2, one #4, and 1 #5 masses to balance the gauge with the pressure of the system. What is the gauge pressure if the local acceleration of gravity is 9.805 m/s^2?

Solution

The total mass (pan plus weights) is

$$m = 500\ \text{g}\frac{1\ \text{kg}}{1000\ \text{g}} + 2\times 100\ \text{g}\frac{1\ \text{kg}}{1000\ \text{g}} + 500\ \text{g}\frac{1\ \text{kg}}{1000\ \text{g}} + 3\ \text{kg}$$
$$+ 5\ \text{kg} + 415\ \text{g}\frac{1\ \text{kg}}{1000\ \text{g}} = 9.615\ \text{kg}$$

$$A = \pi r^2 = 3.1416\times\left(\frac{2.5\ \text{cm}}{2}\times\frac{1\ \text{m}}{100\ \text{cm}}\right)^2 = 3.1416\times(0.0125)^2\ \text{m}^2$$
$$= 4.90875\times 10^{-4}\ \text{m}^2$$

Using Eq. (1.13)

$$P = \frac{mg}{A} = \frac{9.615\ \text{kg}\times 9.805\ \text{m/s}^2}{4.90875\times 10^{-4}\ \text{m}^2} = 193753\ \text{kg/(m s}^2) = 193753$$
$$\text{Pa} = 193.75\ \text{kPa} = 0.19375\ \text{MPa}$$

Temperature from statistical thermodynamics is a variable that describes how atoms or molecules distribute among the quantum energy levels available to them. In classical thermodynamics, the definition of temperature comes from the second law of thermodynamics, while its measurement comes from the zeroth law. **Temperature is an observable and not a function of mass.**

Now, imagine that you are a Neanderthal, and you have many hot stones. How can you tell a person of your tribe which stone is the hottest and then the next hottest? Probably, you can use different tones and sounds to solve the problem, but if you come upon a different tribe, and you want to explain the hotness, these sounds may not mean anything to them. Therefore, it is necessary to create a system for measuring the temperature that is the same for everyone. Temperature scales are the solution. We define these scales by using a primary thermometer to determine temperatures corresponding to the observed physical behavior, i.e. triple points, boiling points, and melting points. Like the primary pressure device, a primary thermometer is one for which a known relationship exists between some physical property and the absolute temperature. The examples of primary thermometers are gas thermometer, acoustic thermometer, noise thermometer, and total radiation thermometer. The relationship for the gas thermometer is

$$T = \lim_{P\to 0}\frac{PV}{R} \tag{1.14}$$

where V is the molar volume, P is the pressure, and R = 8.3144621 J/(mol K) is the universal gas constant (the gas constant is not actually a constant, rather it is an experimental number subject to change, but “constant” at any given time). It is convenient to use a reference point temperature

$$\frac{T}{T_{ref}} = \lim_{P\to 0}\frac{(PV)}{(PV)_{ref}} \tag{1.15}$$

The common reference temperature is the triple point of water (273.16 K). Primary thermometers are difficult to use and expensive, so their use is primarily to establish temperature scales and to calibrate secondary thermometers. The Kelvin and Celsius scales are by international agreement defined numerically by two points: absolute zero (0 K) and the triple point of water. At absolute zero, all kinetic motion of particles ceases, and the molecules and atoms are in their ground states. Gas thermometry establishes the Kelvin scale.

In the Celsius scale, the freezing point of water is 0 °C, and the boiling point of water at atmospheric pressure is 100 °C. Every unit is a degree Celsius. The name of this temperature scale comes from the Swedish astronomer Anders Celsius (1701–1744), who developed the temperature scale two years before his death. The mathematical relationship between the Kelvin and Celsius scales is

$$t/^{\circ}\mathrm{C} = T/K - 273.15 \tag{1.16}$$

In addition to the Kelvin and Celsius scales, two other scales exist in the English Engineering System: Rankine and Fahrenheit. The Rankine scale is an absolute temperature scale like the Kelvin scale. The relationship between them is

$$T/^{\circ}\mathrm{R} = 1.8T/K \tag{1.17}$$

A direct relation exists between the Fahrenheit and Rankine temperatures

$$t/^{\circ}\mathrm{F} = T/^{\circ}\mathrm{R} - 459.67 \tag{1.18}$$

and between the Fahrenheit and Celsius scales

$$t/^{\circ}\mathrm{F} = 1.8t/^{\circ}\mathrm{C} + 32 \tag{1.19}$$

Because primary thermometers are not useful for practical purposes, we use secondary thermometers for such applications. Examples of secondary thermometers are glass thermometers, thermistors, platinum resistance thermometers (PLTs), bimetallic strips, and thermocouples. These devices require calibration using an internationally recognized temperature scale based on primary thermometers and fixed points. PLTs also find use as transfer standards. Their calibration uses a primary thermometer to calibrate other temperature-measuring devices. The primary scale is the International Temperature Scale of 1990 (ITS-90) with its addendum the Provisional Low Temperature Scale of 2000 (PLTS-2000). ITS-90 contains seventeen fixed points and four temperature instruments. The temperatures range from 0.65 to 10000 K using a gas thermometer and a PRT. Below 0.65 K, the PLTS-2000 scale uses Johnson noise and nuclear orientation thermometers. Figure 1.4 depicts secondary thermometers.

Example 1.4

An experimentalist has problems with a PLT giving incorrect temperatures. He knows that the electrical resistance of a wire is a function of temperature

$$R = R_0[1 + \alpha(T - T_0)]$$

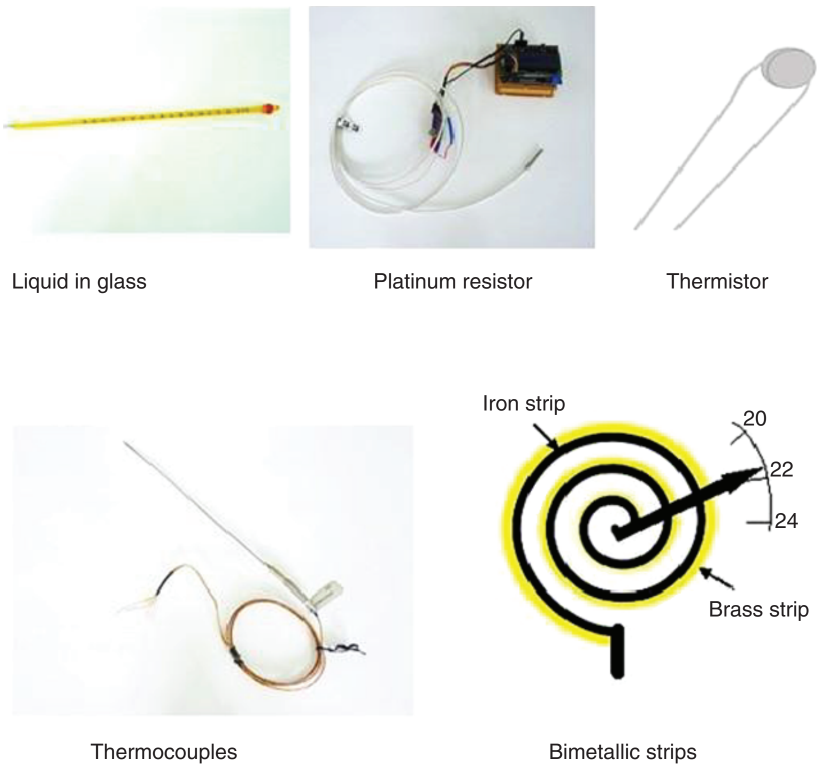


Figure 1.4 Secondary thermometers.

in which α is the temperature coefficient of resistance and R_0 and T_0 are reference resistance and reference temperature (triple point of water), respectively. The manufacturer says that the thermometer has a calibrated standard resistance of 10.5 Ω at 0.01 °C. The experimentalist measures a resistance of 12.94 Ω at 75 °C. Is the manufacturer correct? Assume $\alpha = 3.92 \times 10^{-3}\ °\mathrm{C}^{-1}$.

Solution

Find the R_0:

$$R_0 = \frac{R}{[1+\alpha(T-T_0)]} = \frac{12.94\ \Omega}{1+3.92\times10^{-3}\ °\mathrm{C}^{-1}\times(75-0.01)\ °\mathrm{C}} = 10.0003\ \ \Omega$$

Either the manufacturer is wrong, or the experimenter has a faulty resistance measurement.

It is possible to perform dimensional analysis in SI because any derived unit A can be expressed in terms of the SI base units by

$$A = l^{\alpha} m^{\beta} t^{\gamma} I^{\delta} T^{\epsilon} n^{\zeta} I_v^{\eta} \sum_{k=1} a_k$$

in which the exponents $\alpha, \beta, \gamma, \ldots$ and the factors a_k are numbers. The dimension of A is

$$\dim A = \mathrm{L}^{\alpha}\mathrm{M}^{\beta}\mathrm{T}^{\gamma}\mathrm{I}^{\delta}\theta^{\epsilon}\mathrm{N}^{\zeta}\mathrm{J}^{\eta}$$

where L, M, T, I, θ, N, and J are the *dimensions* of the SI base units and α, β, γ, … are the dimensional exponents. The general SI-derived unit of A is $\mathrm{m}^{\alpha}\ \mathrm{kg}^{\beta}\ \mathrm{s}^{\gamma}\ \mathrm{A}^{\delta}\ \mathrm{K}^{\epsilon}\ \mathrm{mol}^{\zeta}\ \mathrm{cd}^{\eta}$, which is obtained by replacing the dimensions of the SI base quantities with the symbols for the corresponding base units. For dimensionless quantities, the exponents are zero and $\dim A = 1$. This quantity does not have units (symbols) because its unit is 1 (the exponents are zero).

Example 1.5
Consider an object of mass m that moves uniformly a distance l in a time t. If the total kinetic energy is $(nE_k) = m\dot{z}^2/2$, express the velocity and the energy in terms of their symbols and express their dimensions.

Solution
Symbols mass = m, length = l, and time = t.
For the velocity: $\dot{z} = lt^{-1}$ and the kinetic energy is $(nE_k) = ml^2t^{-2}/2$.
For the dimensions:

$\dim \dot{z} = \mathrm{LT}^{-1}$ and the dimensional exponents are 1 and −1.
$\dim(nE_k) = \mathrm{ML}^2\mathrm{T}^{-2}$ and the dimensional exponents are 1, 2, and −2.

The SI-derived unit of the kinetic energy is then $\mathrm{kg\,m^2/s^2}$ named joule with the symbol J.

1.4 SI Usage of Units and Symbols

Several rules exist for using SI units and symbols. The most important are:

- Roman type (not italics or bold) denotes unit symbols regardless of the type used in the surrounding text.
- The unit symbols are lowercase except when the name of the symbol derives from a proper name. The unit name is in lowercase, but the symbol may be upper case, e.g. meter (m), kelvin (K), pascal (Pa), and second (s).
- Plurals used if indicated by normal grammar rules are henries and seconds. Lux, hertz, and siemens are the same for plural and singular. Unit symbols do not change when plural.
- A space appears between the numerical value and the unit or symbol, e.g. 10 Hz and 15 MPa. A period does not follow unit symbols unless at the end of a sentence.
- Raised dots or a space indicate products of symbols. Slashes, a horizontal line, or negative exponents denote quotients of symbols. No more than one slash should appear in any expression. For example,

$$1\ \text{newton} = 1\ \mathrm{N} = 1\ \mathrm{kg\ m/s^2} = 1\ \mathrm{kg\ m\ s^{-2}}$$

$$1\ \text{pascal} = 1\ \mathrm{Pa} = 1\ \mathrm{N/m^2} = 1\ \mathrm{kg\ m/(m^2\ s^2)} = 1\ \mathrm{kg/(m\ s^2)} = 1\ \mathrm{kg\ m^{-1}\ s^{-2}}$$

- Unit symbols and unit names do not appear together, e.g. meter per second, m/s, and $\mathrm{m\,s^{-1}}$ are correct while meter/s, meter per s, and meter $\mathrm{s^{-1}}$ are incorrect.

- Unit symbols or names do not have abbreviations, e.g. sec for s or seconds, sq mm for mm^2 or square millimeter, and cc for cm^3 or cubic centimeter. If the name of a unit appears, it must be written out in full.
- Conventions also exist for the use of the prefixes in Table 1.2. The following rules apply to prefix names, and symbols follow the first rule of the unit symbols (roman type not italics or bold) regardless of the type used in the surrounding text, the prefix name can be attached to a unit name without a space, which also applies to a prefix symbol attached to the unit symbol, e.g. mm (millimeter), TΩ (teraohm), and GHz (gigahertz).
- The union of a prefix and a unit symbol is a new, inseparable symbol that indicates a multiple or sub-multiple of the unit that follows all the rules for SI units. The prefix name is also inseparable from the unit name forming a single word when attached to each other, e.g. cm^3, μs^{-1}, megapascal, and microliter.
- Prefix names and symbols cannot appear more than once, e.g. nm (nanometer) is correct but not mμm ("millimicrometer").
- It is not desirable to use multiple prefixes in a derived unit formed by a division. It is preferable to reduce the prefixes to a minimum, e.g. it is correct to write 10 kW/ms, but it is preferable to write 10 MW/s because it contains only one prefix. This rule also applies to the product of units with prefixes, e.g. 10 kV s is preferable to 10 MV ms. When working with units that involve the kilogram, it is always preferable to use kg rather than g.
- Prefix symbols or names cannot appear alone, for example, 5 M.
- The kilogram is the only SI unit with a prefix as part of its name and symbol. The prefixes in Table 1.2 are applicable to the unit gram and the unit symbol g. For instance, 10^{-6} kg = 1 μg is acceptable but not 10^{-6} kg = 1 μkg (1 microkilogram).
- The prefix symbols and names are acceptable for use with the unit symbol °C and the unit name degree Celsius. The examples are 12 m °C (12 millidegrees Celsius).
- SI prefix symbols and prefix names may be used with the unit symbols and names: L (liter), t (metric ton), eV (electronvolt), u (unified atomic mass unit), and Da (dalton). However, although submultiples of liter, such as mL (milliliter) and dL (deciliter), are common, multiples of liter, such as kL (kiloliter) and ML (megaliter), are not. Similarly, although multiples of metric tonne such as kt (kilometric ton) are common, submultiples such as mt (millimetric ton) are not. The examples of the use of prefix symbols with eV and u are 80 MeV (80 megaelectronvolts) and 15 nu (15 nanounified atomic mass units), respectively.

1.5 Thermodynamic Systems and Variables

A system is a volume of space set aside to study. A boundary is a physical or imaginary surface (mathematical sense) that separates the system from the remainder of the universe. Everything outside the system is its surroundings. Three classes of systems exist depending on mass and energy transfer:

- *Isolated system* is one that has no mass or energy crossing its boundary
- *Closed system* is one that permits energy, but not mass, to cross its boundaries
- *Open system* is one that permits energy and mass to cross its boundaries

The state is the condition of the system. Its physical properties determine the state of a system. A property is a characteristic. An open system is in **steady state** if its properties vary with position but not with time. When the properties of any system vary with neither position nor time, the system is in **equilibrium**.

Application of thermodynamics is possible when the system consists of one or more parts with spatially uniform properties. Each of these parts is a phase. Many events can happen in a system. This sequence of events is a process. In thermodynamics, the process is **reversible** if the system can return from its final state to its initial state without finite changes in the surroundings. If the system requires finite changes in the surroundings to return from its final state to its initial state, the process is **irreversible**.

In classical thermodynamics, we utilize the physical properties mentioned in Sections 1.2 and 1.3. They fall into two groups:

Intensive properties do not depend on the amount of the material in the object. They are point functions, so they exist at each point within the system and can vary from point to point (if the system is not at equilibrium). They are not additive. The examples of these properties are pressure, temperature, density, and specific volume. Consider a pure component in a closed system that contains a single phase at equilibrium. For such a system, any intensive variable depends upon two other intensive variables,

$$I_j = f(I_1, I_2) \quad \text{for } j = 3, 4, \cdots n \tag{1.20}$$

For example, if we know the density and temperature of a pure substance, then we know other properties such as pressure and surface tension. In the case of mixtures, the intensive property depends upon the two intensive variables and the composition of the mixture. A pure component is a special case of a mixture with a composition of 100% of the component.

Extensive properties are those that depend upon the amount of the material in the object. They are additive; that is, the value of the property for the object is the sum of the values of all its constituent parts. The examples are total volume, mass, length, and area. Again, for a pure component in a closed system with a single equilibrium phase, any extensive property is a function of two intensive properties plus the amount of the material

$$E_j = mf(I_1, I_2) \quad \text{for } j = 1, 2, \cdots n \tag{1.21}$$

in which m is the mass of the system. Equation (1.21) enables the definition of a specific property

$$\frac{E_j}{m} = f(I_1, I_2) \quad \text{for } j = 1, 2, \cdots n \tag{1.22}$$

All specific properties are intensive properties.

1.6 Zeroth Law

The statement of the law is: The initial law of thermodynamics we shall investigate is the zeroth law (discovered after the first and second laws, hence the zeroth law). It has but one function: it enables construction of thermometers. The statement of the law is as follows:

Two systems separately in thermal equilibrium with a third system are in thermal equilibrium with each other.

Mathematically, this statement is

$$F_1(P_A, V_A, P_B, V_B) = 0 \quad A \text{ and } B \text{ are in thermal equilibrium}$$

$$F_2(P_C, V_C, P_B, V_B) = 0 \quad C \text{ and } B \text{ are in thermal equilibrium}$$

We can solve each equation for one variable, e.g. P_B

$$P_B = f_1(P_A, V_A, V_B)$$

$$P_B = f_2(P_C, V_C, V_B)$$

Thus, $f_1 = f_2$ and A and C are in equilibrium with B. If A and C are in equilibrium with B, then by the zeroth law, they are in equilibrium with each other and

$$F_3(P_A, V_A, P_C, V_C) = 0$$

This implies that f_1 and f_2 contain V_B in such a manner that it cancels exactly, e.g.

$$f_1 = \Theta_1(P_A, V_A)\xi(V_B) + \zeta(V_B)$$

$$f_2 = \Theta_2(P_C, V_C)\xi(V_B) + \zeta(V_B)$$

If this is the case, then

$$\Theta_1(P_A, V_A) = \Theta_2(P_C, V_C) = \Theta_3(P_B, V_B)$$

or

$$\theta = \Theta(P, V)$$

When we study the second law of thermodynamics, this final equation establishes the empirical temperature and the definition of the absolute temperature. Absolute thermodynamic temperature is a mathematical function that depends upon two variables, commonly pressure and molar volume.

Problems for Chapter 1

1.1 What thermodynamic variable results from the zeroth law of thermodynamics?

1.2 A European data sheet provides a pressure specification of $350\,\text{kg}_\text{f}/\text{cm}^2$. Convert this pressure to units of atmospheres. (This pressure unit was widely used in both research and practical applications for many years and persists today even though it is not an accepted SI unit.) The kg_f unit is defined analogously to the lb_f unit using the same value for the acceleration due to gravity but in appropriate SI units.

1.3 If the density of the gasoline fluctuates between 650 and 870 kg/m^3, what is the minimum and maximum volume that 10000 kg occupies in a cylindrical steel tank? What is the mass of gasoline? What is the minimum and maximum height of the tank if its diameter is 1 m. Calculate the mass of the two tanks if the density of steel is 7850 kg/m^3.

1.4 A black and white cat that weighs 5 kg kneads the stomach of its owner with its two front paws. What is the pressure that it exerts upon his owner's stomach? Consider that the paws are circular with a diameter of 1.8 cm.

1.5 A diver plunges vertically into the sea until reaching a depth of 100 m. To decompress, he must reduce his pressure by 122.625 kPa and rest for one minute; to do so, he must climb a certain distance. What pressure does the diver endure at the end? How many minutes should he rest? The density of water is 1 g/cm^3, $g = 9.81$ m/s^2.

1.6 Calculate the force caused by pressure acting on a horizontal hatch of 1 m diameter for a submarine submerged 600 m from the surface. What is the force if the submarine is on the surface of water?

1.7 The municipal water service fills a house cistern with a mass flow rate of 10 kg/s. The dimensions of the cistern are 7 m long by 1.2 m wide and 1.5 m high. Convert the mass flow rate to volumetric flow rate in l/min. How long does it take to fill the cistern? Consider the density of water equal to 1000 kg/m^3.

1.8 At which temperature is the Celsius scale three times the Kelvin scale? Also, at which temperature is the Celsius scale three times the Fahrenheit scale?

1.9 A pressurized tank filled with gas has a leak through a hole with a 0.4 mm diameter. An engineer finds a quick temporary solution to put a weight on the hole, so the gas does not escape. What is the mass of the weight that the engineer must put on the hole if the pressure inside of the tank is 2750 kPa?

1.10 An American travels by car to México. Suddenly, he notices that the speed limit signs say 90 km/h in the country and is 60 km/h in the city. Unfortunately, his car speedometer shows the speed in miles per hour. He is driving the car at 70 the speed limit in most highways in America and at 40 in the city. Is he violating the law? A mile is 1609 m.

1.11 What is the total mass and weight of an oak barrel containing 59 gal of Cabernet Sauvignon wine? The mass of the barrel is 110 kg. The density of the wine is 0.985 g/cm^3.

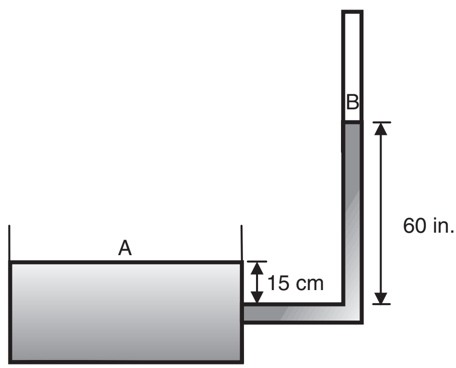
1.12 Shock-compression experiments on diamond have reported the melting temperature of carbon at a pressures of up to 1.1 TPa (6^{11} Mbar). Convert the pressure into atm, psia, MPa, and inches of Hg.

1.13 An equation of state presents the pressure as a function of temperature and molar volume. A simple equation is

$$P = \frac{RT}{V - b} - \frac{a}{V}$$

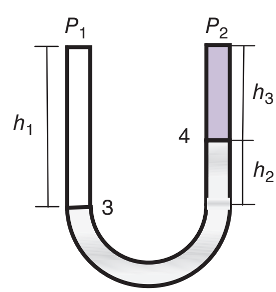
The unit of P is MPa, and the value of R is 8.314. What units should R, a, and b have if the volume is cm^3/mol and T is in kelvins?

1.14 What is the pressure in atm at point B in the following diagram if an open container contains oil with a density of 0.845 g/cm^3?



1.15 If a mercury barometer reads 27 in. of mercury, what is the pressure in atm? Is this device measuring absolute pressure? The density of mercury is 13 590 kg/m^3.

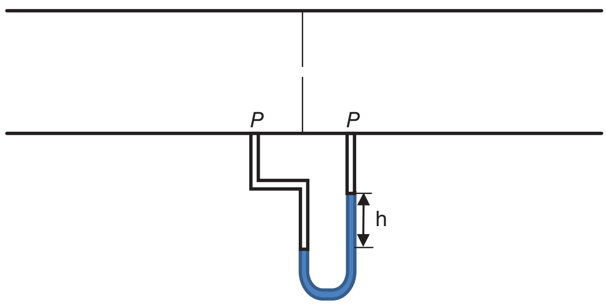
1.16 Find the expression for the difference pressure between P_2 and P_1 for a manometer containing three different fluids:



1.17 A manometer can measure pressure differences of a fluid flowing through an orifice as shown in the figure below. The expression for measuring the pressure differences is

$$P_2 - P_1 = (\rho_{fluid} - \rho_l)gh$$

Find the expression for the difference in pressure between P_2 and P_1. The density of the liquid in the manometer is ρ_l



1.18 A pressure gauge is connected in the same tank as a lamp oil manometer. If the display of the gauge reads 5 kPa, what is the height of oil in the manometer? Consider the density of the oil to be 0.81 g/cm^3.