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Fundamentals

As many of the terms of thermal physics are also used in everyday speech, it is important to understand their more restricted technical meanings. It is especially important to understand the fundamental distinction between heat and work, which describe the interaction of systems with each other, and the intrinsic property of individual systems called internal energy. Other important concepts are equilibrium, state, state function, process, and temperature.

1.1 *PVT* Systems

Pressure P, volume V, and temperature T are essential properties of solids, liquids, and gases. In scientific usage both liquids and gases are fluids, *i.e.*, substances that flow to conform to the shape of their container. Before introducing two relatively simple mathematical models of *PVT* systems, we review the units used in the description of thermodynamic behavior.

Units

The SI units for pressure, volume, and temperature are the pascal (Pa) named after Blaise Pascal, the cubic meter (m^3), and the kelvin (K) named after Lord Kelvin, who is also known as William Thompson. Other commonly used units for volume are the cubic centimeter (cm^3), the liter (L), and the cubic foot (ft^3).

$$1\,\mathrm{m}^3 = 10^3\,\mathrm{L} = 10^6\,\mathrm{cm}^3 = 35.31\,\mathrm{ft}^3. \tag{1.1}$$

One pascal equals one newton per square meter ($1\ \mathrm{Pa} = 1\,\mathrm{N\,m}^{-2}$). In many applications the convenient SI unit for pressure is the kilopascal (kPa). An important reference pressure is the *standard atmosphere* (1 atm), which is approximately 100 kPa.

$$1\ \text{standard atmosphere} = 101.325\,\mathrm{kPa}. \tag{1.2}$$

Thermodynamics and Statistical Mechanics: An Integrated Approach, First Edition.
Robert J Hardy and Christian Binek.

Other units for pressure are the bar (1 bar = 100 kPa), the pound per square inch (lb in^{-2}), the millimeter of mercury (mmHg), and the torr (1 torr = 1 mmHg) named after Evangelista Torricelli. The unit “mmHg” is based on the height of the mercury column in a barometer. These units are related by

$$1\,\text{atm} = 101.3\,\text{kPa} = 760\,\text{mmHg} = 760\,\text{torr} = 14.70\,\text{lb}\ \ \text{in}^{-2}. \tag{1.3}$$

The unit "atm" is sometimes called an atmosphere. The unit specifies a specific force per unit area and must not be confused with the less precise "atmospheric pressure," which is the pressure of the atmosphere and is only *approximately* equal to 1 atm at elevations not too far above sea level.

The commonly used temperature scales are the Kelvin, Celsius, and Fahrenheit scales. The relationship between a Celsius temperature Θ^{C} and a Kelvin temperature T^{K} is

$$\Theta^{\text{C}} = T^{\text{K}} - 273.15. \tag{1.4}$$

The relationship between a Fahrenheit temperature Θ^{F} (in units of °F) and a Celsius temperature Θ^{C} (in units of °C) is

$$\Theta^{\text{F}} = \frac{9}{5}\Theta^{\text{C}} + 32. \tag{1.5}$$

The symbol T is reserved for temperatures measured on an absolute temperature scale, a concept made precise in Chapters 7 and 8. The symbol Θ is used with other temperature scales. The Kelvin scale is an absolute temperature scale. (The symbol for the unit is K, not °K). The Celsius and Fahrenheit scales are not absolute scales. Although the numerical values of temperatures are different in units of K and °C, the values of the *temperature differences* are the same,

$$\Delta T^{\text{K}} = \Delta\Theta^{\text{C}}. \tag{1.6}$$

As indicated in (1.5), a temperature difference of five Celsius degrees is equivalent to a difference of nine Fahrenheit degrees.

Standard temperature and pressure (STP) refers to 273.15 K (0 °C) and 1 standard atmosphere. Room temperature and atmospheric pressure are not precisely defined. This book considers "room temperature" to be 300 K and "atmospheric pressure" to be 100 kPa.

Internal energy U is the thermodynamic property of a system that represents the sum of the kinetic and potential energies of its microscopic constituents. The SI unit for energy is the joule (J) named after James Prescott Joule. In thermal physics the calorie (cal) and kilocalorie (kcal) are convenient units for energy. The food Calorie (written with a capital C) is actually a kilocalorie. The British thermal unit (Btu) is used in engineering. The units of energy are related by

$$4184\,\text{J} = 1\,\text{kcal} = 1000\,\text{cal} = 3.968\,\text{Btu}. \tag{1.7}$$

The internal energy and pressure of PVT systems can be expressed as functions of temperature and volume.[1]

$$U = U(T, V) \qquad \text{and} \qquad P = P(T, V). \tag{1.8}$$

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[1] Equations like $V = V(T, P)$ and $U = U(T, P)$ are *constitutive relations*. The relationship $V = V(T, P)$ is sometimes called the *thermal equation of state* and $U = U(T, P)$ is called the *caloric equation of state*. In this book the phrase "equation of state" is used without modifier and refers to a relationship between P, V, and T.

It is helpful when explaining the concepts of thermodynamics to have explicit expressions for these functions. Ideal gases and simple solids are useful for this purpose.

Ideal Gases

A gas is a collection of molecules that move about in random directions with occasional collisions with each other and with the walls of their container. In many applications real gases are accurately modeled as ideal gases, which are also called *perfect gases*. In the ideal gas model the relationship between pressure, volume, and temperature is

$$PV = nRT. \tag{1.9}$$

where the function $P(T, V)$ is nRT/V. This is the *ideal gas equation of state*, and R is the *universal gas constant*.

$$R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}} = 1.987\,\mathrm{cal\,mol^{-1}\,K^{-1}} \tag{1.10}$$

and n is the number of moles.

One *mole* is the quantity of material that has a mass in grams equal to its *molecular weight*. The mass m of one molecule of a pure substance is

$$m = (\text{molecular weight}) \cdot m_u = \frac{(\text{molecular weight in grams})}{N_A}, \tag{1.11}$$

where the *atomic mass constant* is

$$m_u = 1.661 \times 10^{-27}\,\mathrm{kg}$$

and the number of molecules per mole is given by *Avogadro's number* named after Amadeo Avogadro.

$$N_A = 6.022 \times 10^{23}\,\mathrm{mol^{-1}}. \tag{1.12}$$

The internal energy of an ideal gas depends on temperature only, which is a special case of the relationship indicated in (1.8). As there is no dependence on volume, it is expressed by

$$U = U(T). \tag{1.13}$$

It is shown in Chapter 10 that this special case is a consequence of $PV = nRT$. Until then, equations (1.9) and (1.13) are considered the defining characteristics of an ideal gas.

Simple Solids

More than one type of model system is needed to illustrate the generality of thermodynamics. The functions for the internal energy and pressure of another type of system are

$$U = M\,c_o T + b_o V\left[\ln\left(\frac{V}{V_o}\right) - 1\right] \tag{1.14}$$

and

$$P = a_o T - b_o \ln\left(\frac{V}{V_o}\right), \tag{1.15}$$

where a_o, b_o, c_o, and V_o are constants and M is the mass of the system. Although less significant that the ideal gas model, the above equations give a useful description of the behavior of solids over the limited ranges of temperatures and pressures of interest in many applications. For this reason a system described by (1.14) and (1.15) will be referred to as a *simple solid*.

It is shown in Chapter 3 that the above equations describe the internal energy and pressure of a system whose coefficient of thermal expansion α_V, bulk modulus B_T, and specific heat c_V^M are constant. Their values for a few solids are given in Table 1.2 on page 15. The equations that relate the a_o, b_o, and c_o to α_V, B_T, and c_V^M are $a_o = \alpha_V B_T$, $b_o = B_T$, and $c_o = c_V^M$ (see (3.28)). The constant V_o is chosen so that (1.15) gives the pressure at some specific temperatures, such as $P = 100\,\text{kPa}$ and $T = 300\,\text{K}$.

The significant differences in the functions for internal energy and pressure for ideal gases and simple solids reflect differences in their microscopic structures. The behavior of solids is dominated by the forces that bind the atoms into a rigid structure. These forces can be obtained from a potential energy function. An approximate expression for the internal energy function is

$$U(T, V) = Mc_oT + \Phi(V). \tag{1.16}$$

The term $M\,c_oT$ describes the kinetic and potential energies associated with the vibrational motion of the atoms. The *static energy* $\Phi(V)$ is the energy or the system when the atoms are stationary. The volume of a solid is changed by subjecting it to high pressure. The contribution to pressure resulting from the changes to $\Phi(V)$ is $-d\Phi/dV$. An approximate expression for the pressure is

$$P = a_oT - \frac{d\Phi}{dV}. \tag{1.17}$$

The term a_oT accounts for the tendency of solids to expand as temperature increases. The static energy $\Phi(V)$ is represented in the simple solid model by the term $b_oV[\ln(V/V_o) - 1]$ in (1.14), which implies that $d\Phi/dV = b_o\ln(V/V_o)$. Combining this with (1.17) yields the expression for pressure in (1.15).

1.2 Equilibrium States

System

Many of the systems that will be studied are homogeneous (uniform composition) and isotropic (same in all directions), such as the gas or liquid in a container or a sample of dielectric or magnetic material. Nevertheless, the concepts of thermal physics are applicable to much more complex systems, sometimes referred to as *devices*, such as engines, refrigerators, and electrical generating plants.

A system may be made up of smaller systems, called *subsystems*. We may refer to something as a subsystem at one time and as a system at another time. Sometimes we concentrate on one system and refer to everything it interacts with as its *surroundings*, or the *environment*. Since the focus of a discussion often changes, it is important to clearly identify the system to which the principles of thermodynamics are being applied.

A system with a fixed quantity of matter is a *closed* system, and one that can exchange matter with its surrounding is an *open* system. An automobile engine, which takes in fuel and air and exhausts combustion products, is an open system. The mass of a closed system is constant, and in the absence of chemical reactions the numbers of moles of its different constituents are constant.

Equilibrium

A system is in equilibrium if it does not spontaneously change. A glass of warm water with a cube of ice in it is *not* in equilibrium, as the ice will spontaneously melt until either the water cools to 0.0 °C or all of the ice melts. The tendency of systems to spontaneously change until their temperatures are uniform throughout is a widely observed phenomenon. Systems in *thermal equilibrium* have a uniform temperature.

A system can be in equilibrium even when it is changing, provided the change is caused by a change in the *constraints* on it. Consider the gas confined in a cylinder with a piston at one end, as diagrammed in **Figure 1.1**. The temperature and pressure of the gas will change when the piston is moved. The gas is considered to be in equilibrium as it changes, because it is not changing spontaneously. However, this is only true if the piston is not moved too rapidly. If moved fast enough, the motion will create sound waves that move back and forth within the cylinder, so that the gas will not be in equilibrium until the sound waves die out.

A system may not be changing and yet *not* be in equilibrium. This is the case when its condition is maintained by a continuous exchange of energy with its surroundings. For example, the pane of glass that separates the warm interior of a building from the cold exterior is in a *steady state*, provided the inside and outside temperatures are steady, but the glass is *not* in equilibrium. To maintain the temperature distribution in the glass, heat must be continuously transferred to it from the room and removed by the air outside. If the pane of glass is removed from the wall and isolated, the temperature distribution in it will spontaneously change until it is uniform.

The concept of equilibrium is also important in mechanics. An object is in *mechanical equilibrium* when its translational and rotational velocities do not spontaneously change,

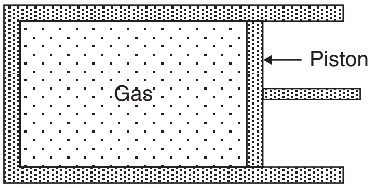

Figure 1.1 *Gas Confined in a Cylinder*

i.e., when its linear acceleration and its angular acceleration are zero. The conditions that must be satisfied for an object to be in mechanical equilibrium are

$$\sum_i \boldsymbol{F}_i = 0 \quad \text{and} \quad \sum_i \boldsymbol{\tau}_i = 0, \tag{1.18}$$

where $\boldsymbol{F}_i$ and $\boldsymbol{\tau}_i$ are the external forces and torques on the object.

State

The concept of state is fundamental but not easy to define. The different *states* of a system refer to different conditions or configurations. For example, a ball could be resting on a table or moving across the room. These mechanical states are described by giving its position, velocity, and angular momentum. The state of a system in quantum mechanics is described by its wave function, which is also called a state function. In thermodynamics we are interested in the *thermodynamic states* of systems, which are also called *equilibrium states*.

The number of properties needed to specify the equilibrium state of a system is the number of *thermodynamic degrees of freedom*. The number depends on the system involved and the type of behavior being investigated. A simple *PVT* system has two degrees of freedom, which can be specified by giving its temperature and volume (T, V) or its temperature and pressure (T, P). Other choices such as internal energy and volume are also used. A homogeneous fluid whose dielectric properties are being investigated has three thermodynamic degrees of freedom: In addition to temperature and pressure, we need to specify the strength of the electric field $\mathcal{E}$.

State Function

Properties whose values are determined by the system's state are called *state functions*. Temperature T, volume V, pressure P, internal energy U, entropy S, enthalpy H, etc. are state functions. When the state of a system is specified by T and V, the values of P, U, S, and H are given by functions $P(T, V)$, $U(T, V)$, $S(T, V)$, and $H(T, V)$. The independent variables T and V are the *thermodynamic coordinates* of the system. The number of thermodynamic coordinates, *i.e.*, the number of independent variables, equals the number of thermodynamic degrees of freedom. State functions are also called state variables. It should be noted that heat Q and work W are *not* state functions. They are process dependent quantities.

State Space

The thermodynamic coordinates that specify a system's state define a space called *thermodynamic state space* or *equilibrium state space*. If no ambiguity results, it is simply called *state space*. As the state space of a homogeneous *PVT* system has two coordinates, we can represent its states by points on a two dimensional graph. More coordinates are required for more complex systems. For example, in a system of ice and water, a third coordinate is required to specify the fraction of the system that is ice (or water).

Internal Energy

When viewed microscopically, thermodynamic systems are collections of electrons, atoms, and molecules. The energy associated with these microscopic constituents is determined by the velocities and positions of the huge number of constituent particles, which is typically of the order of Avogadro's number. In contrast, when in thermal equilibrium, the system's internal energy is determined by its thermodynamic coordinates which are few in number. The existence of the internal energy state function is fundamental to thermodynamics.

Equation of State

The relationship between pressure, volume, and temperature in a *PVT* system is called the *equation of state* and can be expressed as $P = P(T, V)$, $V = V(T, P)$, or $T = T(P, V)$. A general form that treats the properties symmetrically is

$$F(P, V, T) = 0. \tag{1.19}$$

For ideal gases the explicit expressions for the functions $P(T, V)$, $V(T, P)$, and $T(P, V)$ are nRT/V, nRT/P, PV/nR, and PV/nR, respectively. The expression for $F(P, V, T)$ is $(PV - nRT)$, and the equation of state is usually written as $(PV = nRT)$.

Example 1.1 $V(T, P)$ and $U(T, P)$ for simple solids

Find the functions that give the dependence of the volume and internal energy of a simple solid on its temperature and pressure.

Solution. According to (1.14) and (1.15), the functions for the pressure and internal energy of a simple solid are

$$P(T, V) = a_o T - b_o \ln(V/V_o)$$

and

$$U(T, V) = M c_o T + b_o V[\ln(V/V_o) - 1].$$

To find the dependence V and U on the system's state when the thermodynamic coordinates are (T, P), instead of (T, V), we rewrite the above expression for pressure as $\ln(V/V_o) = (a_o T - P)/b_o$. It then follows that the function for the dependence of volume on temperature and pressure is

$$V(T, P) = V_o \, e^{(a_o T - P)/b_o}. \tag{1.20}$$

The function that gives the dependence of the internal energy on temperature and pressure is $U(T, P) = U(T, V(T, P))$. Substituting the expression for $V(T, P)$ into the expression for $U(T, V)$ gives

$$U(T, P) = M c_o T + (a_o T - P - b_o) V_o \, e^{(a_o T - P)/b_o}. \tag{1.21}$$

The significant difference in the appearance of the expressions for $U(T, V)$ and $U(T, P)$ illustrates the extent to which the functional form of state functions depend on the choice of thermodynamic coordinates.

1.3 Processes and Heat

A process starts at an initial time t_0 and ends at some final time t_f ($t_0 < t_f$) and brings about a change in the state of the system. Thermodynamics is concerned with the direction in which processes evolve but not in its rate of evolution. Although the system is often not in equilibrium at all times throughout a process, it is usually assumed to be in thermal equilibrium at the start and end.

Equilibrium and Quasi-Static Processes

A process in which the system is in equilibrium at all times between time t_0 and time t_f is an *equilibrium process*. If at any time during the process the system is not in equilibrium, it is a *nonequilibrium process*. In equilibrium processes, a system changes in response to changes in the constraints and stops changing when the constraints stop changing. Many processes can be idealized as equilibrium processes, provided they proceed sufficiently slowly, where the meaning of slowly depends on the process. For example, the compression of the air-fuel mixture in the cylinders of an automobile engine, which occurs in a time of the order of a hundredth of a second, is often idealized as an equilibrium process. In contrast, the melting of an ice cube placed in a glass of water, which may take several minutes, is not an equilibrium process.

Equilibrium processes are sometimes called quasi-static processes. A *quasi-static* (almost-unchanging) process is one that is performed slowly enough that the system is effectively in equilibrium at all times. The term "equilibrium process" is preferred to "quasi-static process," because it suggests the useful characteristic of being representable by a line in state space.

As the state space of a *PVT* system is two dimensional, an equilibrium process can be represented by a line on a two dimensional graph. When the thermodynamic coordinates are pressure and volume, the graph is called a *PV*-diagram. Some important equilibrium processes in ideal gases are shown in **Figure 1.2**. The point "0" represents the initial state of the gas. The points labeled “*f*” represent the final states. An *isothermal process* is a

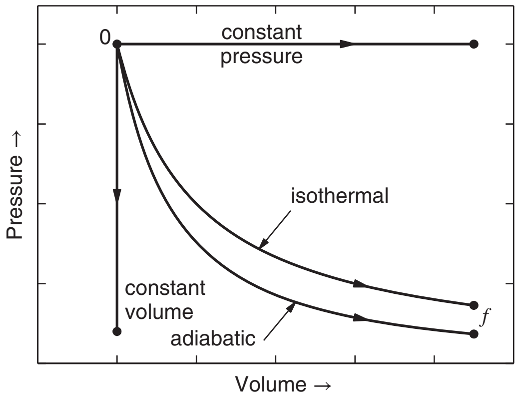

Figure 1.2 *PV-Diagram of Equilibrium Processes*

constant-temperature process, and a line at constant temperature is an *isotherm*. An *isobaric process* is a constant-pressure process, and a line at constant pressure is an *isobar*. A constant-volume process in a *PVT* system is sometimes called an *isochoric process*, which indicates that no work is done. Adiabatic processes are discussed below. As the points on lines represent equilibrium states, nonequilibrium processes are not representable by lines in state space.

Reversible Processes

A *reversible process* is one whose direction in time can be reversed. A process that starts in state "0" and proceeds along a line in state space to state "*f*" is reversed by starting in state "*f*" and traversing the same line in the opposite direction. Processes that can be idealized as reversible are especially important in thermodynamics. In practice, a reversible process is made to evolve in the reversed direction by a small change in the constraints on the system. Although equilibrium, quasi-static, and reversible processes have different defining characteristics, processes with the characteristics of one type also have the characteristics of the other types.

Heat

The word "heat" is familiar to us from everyday life. Although its technical meaning is consistent with colloquial usage, it is much more restricted. Unlike temperature and internal energy, heat does not describe the condition of a system, but instead describes what is happening during a process. The heat transferred to a system is represented by Q. By convention, Q is positive when the energy is transferred *to* the system and negative when energy is transferred *from* it. The heat transferred *to* one system *from* another is the negative of the heat transferred *to* the second system *from* the first.

We can increase the temperature of water by putting it in a container over a flame or on a hot plate. We can cool a hot object by putting it in cold water. When doing these things, something appears to pass between the water and its surroundings. That something is heat: *Heat is the energy transferred from one system to another because of a temperature difference*.

Adiabatic Processes

Adiabatic processes are important both in applications and in establishing the foundations of thermodynamics. *An adiabatic process is one in which no heat is accepted or rejected by the system at any time during the process*. An *adiabatically isolated* system is one that cannot exchange heat with its surroundings. In everyday speech we would say the system is perfectly insulated. The contents of a high quality Dewar flask, named after its inventor Sir James Dewar, is an example of an adiabatically isolated system. Dewar flasks are double-walled containers with the space between the walls evacuated to prevent the transfer of heat by conduction, and the inside surfaces of the walls are silvered to minimize heat transfer by radiation.

Adiabatic processes can be either reversible or irreversible. When a gas is compressed with no exchange of heat with its container, the process in the gas is both reversible and adiabatic. In contrast, when some ice is added to the hot water in a Dewar flask, the process in the contents of the flask is adiabatic but *not* reversible. Interfaces across which heat *cannot* be exchanged are *adiabatic boundaries*. Interfaces across which heat *can* be exchanged are sometimes called *diathermic boundaries*.

1.4 Temperature

Thermally Interacting Systems

Systems that can exchange heat with each other are in *thermal contact*, and a system with no adiabatically isolated parts is a *thermally interacting system*. When in thermal equilibrium, a thermally interacting system possesses a single temperature. In contrast, systems made up of two or more adiabatically isolated subsystems can have more than one temperature. For example, the contents of a Dewar flask and the space outside can be thought of as a single system. Although the system may be in equilibrium, *i.e.*, not spontaneously changing, it will possesses two temperatures, *i.e.* the temperature of the contents and the temperature of the space outside.

Temperature

The concepts of heat and temperature are closely related. Temperature is a state function that describes the tendency of a system (or subsystem) to exchange heat with other systems: (i) All systems in thermal contact have the same temperature when in thermal equilibrium and no heat is exchanged between them. (ii) Systems with different initial temperatures spontaneously exchange heat when brought into thermal contact. The direction of the exchange is described by saying that heat is transferred from the *hotter* system to the *colder* system. On the Kelvin, Celsius, and Fahrenheit temperature scales the hotter system has the higher temperature. The data in Table 1.1 illustrates the wide range of temperatures possessed by various systems.

Thermometers

A thermometer is a device that possesses an equilibrium property that is easily observed and depends on the tendency of the device to exchange heat. The significant property of a

Table 1.1 *Miscellaneous temperatures*

1.5×10^7 K	Estimated temperature at the center of sun
5800 K	Approximate temperature of the surface of sun
1809 K	Iron melts (1536 °C)
273.15 K	Ice point (0 °C)
234 K	Mercury freezes (−39 °C)
195 K	Solid carbon dioxide (dry ice) sublimes at 1 atm (−78 °C)
77 K	Nitrogen liquefies at 1 atm (−196 °C)
4.2 K	Helium liquefies at 1 atm
10^{-8} K	Bose–Einstein condensation of Rb gas (first observed in 1996)

liquid-in-glass thermometer is the length of the column of liquid. The significant property in many laboratory thermometers is an electrical resistance or a voltage. To measure the temperature of a system, we bring it into thermal contact with the thermometer and let the combined system come into thermal equilibrium. As the system and thermometer have the same temperature, the system is assigned the temperature of the thermometer.

Local Temperature

We sometimes need to distinguish between the fundamental concept of temperature and the reading on a thermometer. The distinction is made by calling the equilibrium state function an *equilibrium temperature* and the reading on a thermometer a *local temperature*. Systems that are not in equilibrium do not have an equilibrium temperature but may have local temperatures, which in general are different at different locations. The local temperature at a particular location is the temperature a thermometer would indicate if placed in thermal contact at that point. A system in thermal equilibrium has the same local temperature throughout, and its value is the same as the equilibrium temperature. When a system is rapidly changing, very small, or far from equilibrium, it may not be possible to assign values to the local temperature.

Zeroth Law

Two systems in thermal equilibrium with a third will be in thermal equilibrium with each other when brought into contact. This statement is often called the *zeroth law of thermodynamics*. Essentially, it is an assertion that the concept of thermal equilibrium is transitive. Transitive relationships are important in science, but are usually not called laws. For example, an equal arm balance can be used to compare the weights of objects, but it is assumed without calling it a law that two objects that individually balance a third can balance each other. As its unusual numbering suggests, the zeroth law does not have the significance of the first and second laws of thermodynamics.

Heat Reservoirs

A heat reservoir is an idealization of a system that can transfer significant amounts of heat to or from a system with no change in its temperature. It is a source or sink of heat with a fixed tendency to exchange heat. They are also called *heat baths*. For example, to maintain an object at a constant temperature of 0 °C, we can use a mixture of ice and water as a heat reservoir.

1.5 Size Dependence

Intensive Versus Extensive

Thermodynamic properties can be either intensive or extensive. *Intensive properties are independent of the size of the system. Extensive properties are proportional to size*. Temperature T and pressure P are intensive, while mass M, number of moles n, volume V, and internal energy U are extensive. *Extensive properties are additive*. For example, the values of the mass, volume, and internal energy of systems consisting of several subsystems are the sums of the masses, volumes, and internal energies of the subsystems.

When a system is made up of N identical subsystems, the values of its extensive variables (properties) are N times their values in the subsystems, while the values of its intensive variables are the same as the values in the subsystems. The sizes of homogeneous systems can be varied continuously. *When the size of a homogeneous system is scaled by a factor of* λ, *the values of its extensive properties are multiplied by* λ, *while its intensive properties remain unchanged*. For example, if a system whose mass, volume, internal energy, temperature, and pressure are M_0, V_0, U_0, T_0, and P_0 has its size increased by 20%, so that $\lambda = 1.20$, its mass, volume, and internal energy will become $M = 1.2M_0$, $V = 1.2\,V_0$, and $U = 1.2\,U_0$, while its temperature and pressure remain unchanged.

Intensive variables can be formed by dividing one extensive variable by another. For example,

$$\rho = \frac{M}{V}, \tag{1.22}$$

where the *mass density* ρ is intensive while mass M and volume V are extensive. An intensive property, obtained by dividing by the mass M or the number of moles n, is called a *specific* property. For example, depending on the divisor, the *specific volume* of a system is

$$v_M = \frac{V}{M} \qquad \text{or} \qquad v = \frac{V}{n}. \tag{1.23}$$

The subscript on v_M identifies it as a "per unit mass" property. A "per mole" value is also called a molar value. When expressed in terms of the specific volume V/n, the ideal gas equation of state simplifies to

$$Pv = RT. \tag{1.24}$$

When an extensive property is represented by a capital letter, it is convenient (but not always practical) to represent the associated intensive property by the same letter in lower case. The characteristics of the material that makes up a homogeneous system are specific values that can be listed in tables of material properties, like those in Table 1.2. The intensive property M/n obtained by dividing the mass of a pure substance in grams by the number of moles is the *molecular weight* of the substance.

In beginning physics courses, we learn that terms that are added or subtracted in an equation must all have the same units. Similarly, terms with thermodynamic significance that are added or subtracted in an equation must have the same size dependence, *i.e.*, the same intensive or extensive character. Also, except for functions that are powers, such as $f(x) = cx^n$, the arguments of the functions used should be dimensionless and intensive. Logarithms are a special case.

1.6 Heat Capacity and Specific Heat

Heat capacities describe the change in the temperature of a system that results from a transfer of heat. More heat is required to raise the temperature by (say) 10° when the system is a kilogram of water than when it is a kilogram of aluminum. Heat capacities are found by measuring an initial temperature T_0, transferring a small amount of heat Q to a system, and

Table 1.2 *Material properties. The data are for room temperature and atmospheric pressure, except for ice. The coefficients of thermal expansion* α_L *and* α_V *and the bulk modulus* B_T *are defined in Section 3.2*

	Aluminum	Copper	Iron	Lead	Ice (0 °C)	Water
ρ (kg m^{-3})	2700.	8960.	7880.	11340.	917.	1000.
c_P^M (kcal kg^{-1} K^{-1})	0.216	0.092	0.106	0.0306	0.502	1.000
c_P^M (kJ kg^{-1} K^{-1})	0.904	0.385	0.444	0.128	2.10	4.184
c_V^M (kJ kg^{-1} K^{-1})	0.863	0.374	0.436	0.120	2.03	
α_L (10^{-6} K^{-1})	23.2	16.6	11.9	29.0	55.	
α_V (10^{-6} K^{-1})	69.6	49.8	35.7	87.0	165.	
B_T (10^9 Pa)	75.	135.	160.	41.	7.7	

then measuring the final temperature T_f. Its heat capacity is $Q/\Delta T$, where $\Delta T = T_f - T_0$. Heat capacities can be associated with a single temperature by introducing successively smaller amounts of heat, which yield successively smaller temperature changes, and extrapolating the values of $Q/\Delta T$ to $Q = 0$. The extrapolated quantity is a state function. The value of the heat capacity depends on the process involved. The *constant-volume* and *constant-pressure heat capacities* are

$$C_V = \lim_{Q\to 0} \frac{Q}{\Delta T}\bigg|_{V=\text{const}} \qquad \text{and} \qquad C_P = \lim_{Q\to 0} \frac{Q}{\Delta T}\bigg|_{P=\text{const}}, \tag{1.25}$$

where “lim” refers to an extrapolation of experimental measurements.

Heat capacities are extensive. The intensive property formed by dividing them by the number of moles n or the mass M are called *specific heats*. The constant-pressure specific heats are

$$c_P = \frac{C_P}{n} \qquad \text{and} \qquad c_P^M = \frac{C_P}{M}. \tag{1.26}$$

Specific heats based on moles are commonly used for gases, while those based on mass are used for solids. As the units given indicate whether the specific heat was obtained by dividing by n or by M, the superscript M is often omitted. Specific heats are convenient because their values are independent of the size of the system and thus can be listed in tables of material properties. A few values are given in Table 1.2.

Constant Specific Heats

Although specific heats depend on the state of the system, they often change sufficiently slowly that they can be treated as constants. When constant, the heat transferred in a constant-pressure process is $Q = C_P\Delta T$, which in terms of the specific heats is

$$Q = n\,c_P\Delta T \qquad \text{or} \qquad Q = M\,c_P^M\Delta T. \tag{1.27}$$

Similarly, for a constant-volume process $Q = n\,c_V\Delta T = M\,c_V^M\Delta T$. The temperature dependence of the constant-pressure specific heat c_P^M of water at a pressure of 1 atm is shown in **Figure 1.3**. In units of J kg^{-1} K^{-1} the values range from 4178 to 4218. The range is small

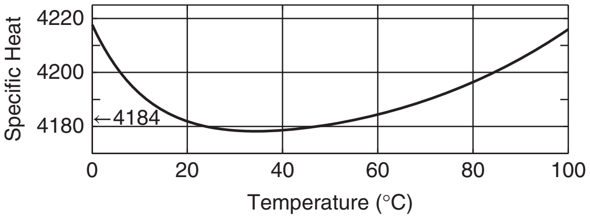

Figure 1.3 *Specific Heat of Water.* c_P^M *at 1.0 atm in Units of* J kg^{-1}K^{-1}

enough that the specific heat of water is often treated as a constant. The commonly used value for c_P^M is 4184 J kg^{-1} K^{-1}, which in terms of kilocalories is 1.00 kcal kg^{-1} K^{-1}.

Specific heats are measured with a *calorimeter*. Simple calorimeters use an insulated cup of known heat capacity, a thermometer, and a stirring device. A measured quantity of water is placed in the cup, the cup and water are allowed to come to equilibrium, and the temperature T_0 is measured. The mass and initial temperature of a heated sample is measured, the sample is placed in the cup of water, the combined system is allowed to come to equilibrium (with the aid of the stirrer), and the final temperature T_f is measured. The following example illustrates the procedure.

Example 1.2 Calorimetry

A 150 g piece of glass at 85 °C is placed in a calorimeter cup containing 500 g of water at 20 °C. The combined system comes to equilibrium at 22.1 °C. Find the specific heat of the glass. The heat capacity of the calorimeter cup is 0.026 kcal K^{-1}. See **Figure 1.4**.

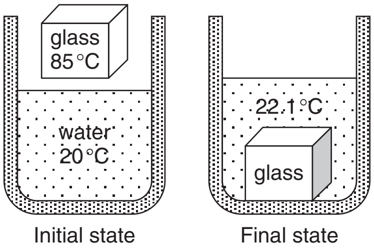

Figure 1.4 *Calorimetry Experiment*

Solution. The system consists of two subsystems: One is the glass (g), the other is the water and calorimeter cup (w + c). In principle, the states of the subsystems depend on T and P. As the experiment is presumably carried out at atmospheric pressure, P is constant, so that temperature is the important variable. In the initial state the subsystems are in equilibrium at different temperatures, while in the final state they are in equilibrium at a single temperature. Assume that no heat is exchanged between the combined system (glass, water, and cup) and the environment. As no heat is exchanged with the surroundings, the heat transferred *to* one subsystem equals the heat transferred *from* the other

(heat *to* water and cup) = (heat *from* glass).

According to the sign convention for Q, this implies that

$$Q^{\mathrm{w+c}} = -Q^{\mathrm{g}},$$

where the superscripts identify the subsystems. With $Q = C_P \Delta T$, $\Delta T = \Theta_f - \Theta_0$, and $C_P = M c_P$ this becomes

$$(M^{\mathrm{w}} c_P^{\mathrm{w}} + C_P^{\mathrm{c}})(\Theta_f - \Theta_0^{\mathrm{c+w}}) = -M^{\mathrm{g}} c_P^{\mathrm{g}}(\Theta_f - \Theta_0^{\mathrm{g}}).$$

As both subsystems have the same final temperature, a superscript identifying the subsystem is not needed on Θ_f. Solving for the specific heat of the glass gives

$$c_P^{\mathrm{g}} = \frac{(M^{\mathrm{w}} c_P^{\mathrm{w}} + C_P^{\mathrm{c}})(\Theta_f - \Theta_0^{\mathrm{c+w}})}{M^{g}(\Theta_0^{g} - \Theta_f)}.$$

or

$$c_P^{\mathrm{g}} = \frac{[(0.5\,\mathrm{kg})(1.0\,\mathrm{kcal\,kg^{-1}K^{-1}}) + 0.026\,\mathrm{kcal\,K^{-1}}](22.1 - 20\,°\mathrm{C})}{(0.15\,\mathrm{kg})(85 - 22.1\,°\mathrm{C})}.$$

Thus, the constant-pressure specific heat of the glass is

$$c_P^{\mathrm{g}} = 0.117\,\mathrm{kcal\,kg^{-1}K^{-1}}.$$

Problems

1.1 Express common room temperature (68 °F) and normal body temperature (98.6 °F) in kelvins and degrees Celsius.

1.2 The gauge pressure in the tires of your car is 210 kPa (30.5 psi) when the temperature is 25 °C (77 °F). Several days later it is much colder. Use the ideal gas equation of state to estimate the gauge pressure in your tires, when the temperature is 0 °C. Give you answer both in kilopascal and pounds per square inch (Gauge pressure is the difference between absolute pressure and atmospheric pressure, which is approximately 100 kPa.)

1.3 When expressed as a function of temperature and volume, the entropy of an ideal gas is given by the function $S(T, V) = nR\ln(T/T_o) + nc_o\ln(V/V_o)$, where n, R, c_o, T_o, V_o, and P_o are constants. Find the entropy $S(T, P)$ of the gas expressed as a function of temperature and pressure. (Remember: $\ln(xy) = \ln x + \ln y$, $\ln(1/z) = -\ln z$, and $\ln 1 = 0$.)

1.4 300 g of aluminum at 90 °C is placed in a calorimeter cup containing 400 g of water. The mass of the copper calorimeter cup 80 g. The initial temperature of the water and cup is 22.0 °C. What is the final temperature?

1.5 A 250 g sample at 80 °C is placed in a calorimeter containing 300 g of water. The mass of the aluminum calorimeter cup is 100 g. The initial temperature of the water and cup is 20.0 °C, and the final temperature is 21.8 °C. What is the specific heat of the sample?