Chapter 15

Thermodynamics I: Temperature and Heat

15.1 MACROSCOPIC SYSTEMS

In this chapter and the following three chapters we deal with the properties of *large systems,* also known as *macroscopic systems.* Such systems are characterized by their having myriad atoms and/or molecules. Some examples of macroscopic systems are (1) The earth and all its contents; (2) a pebble on the beach; (3) an elephant; (4) an ant; (5) the ant's brain; (6) the earth's atmosphere; (7) a cloud; (8) a mixture of gases confined in a container; (9) a single gas confined in a container; (10) a combination of solid, liquid, and vapor of a single substance; (11) a carbon electrical resistor; and (12) a bar magnet.

From these examples we see that a macroscopic system can vary from huge to relatively small and from extremely complex to relatively simple. The main requirement for a macroscopic system is that it contain large numbers of the various types of atoms and molecules of which it is composed. The typical linear dimension of an atom or molecule is less than 1 nanometer (1.0×10^{-9} m). Even a tiny cube 0.01 mm on a side would hold a trillion atoms or molecules.

In our previous work we dealt with large systems in the form of rigid bodies and fluids at rest and in motion. In those cases, however, we were concerned with the collective organized motion of the system as a whole (e.g., the translation or rotation of the entire rigid body; the organized flow of the liquid as a whole). What we turn to now are the large-scale measurable properties of a system that depend on the myriad random motions and interactions of the component atoms and molecules, rather than their lockstep behavior. The study of such properties constitutes the subject of **thermodynamics**.

Quasistatic Systems

The thermodynamics of most systems is extremely complex—particularly if the system is filled with fiery explosions due to chemical reactions, wildly turbulent flow of material, or pressures that vary from location to location and moment to moment. To allow some kind of simple description, we have recourse to the notion of a *simple system,* such as a gas in a container, a liquid in a tube, or a magnet made of a homogeneous material. Moreover, we generally confine ourselves to simple systems that are **quasistatic**. This means either that they are in mechanical, chemical, and thermal equilibrium (see Sec. 15.2), or that their properties vary so slowly that they can be described at any instant as if in equilibrium.

Thermodynamic Variables

For all systems (quasistatic or not) with well-defined boundaries, there are two quantities that can always be used to characterize the system as a whole. One is the volume V of the system. The other is the total energy associated with the system or, as it is called, the **internal energy** of the system U. Such physical properties as U and V, which describe the system as a whole, are called **macroscopic variables** or **thermodynamic variables**.

Most other thermodynamic variables can be defined only if the system is quasistatic. Thus, in a quasistatic system consisting of a gas, liquid, and/or solid confined to a container, the pressure—that of the gas on the walls of the container and on the liquid and solid surfaces—is a characteristic of the system as a whole. Another thermodynamic variable, important in all quasistatic systems, is the temperature T of the system (see Sec. 15.2).

While P, V, T, and U are among the most common and important thermodynamic variables, we should note that there are many others associated with systems with special properties. For example, the resistance R, the voltage drop $\mathscr{E}$, and the current I are additional thermodynamic variables for a quasistatic simple system in which electricity is flowing. Our discussion of thermodynamics will be restricted to systems for which P, V, T, and U provide the primary description; these are called **chemical systems**.

15.2 THERMAL EQUILIBRIUM AND TEMPERATURE

Types of Equilibrium

Consider a simple system that is in **mechanical equilibrium**. This will be understood to mean not only that the system as a whole does not accelerate, but that within the system the different parts are in mechanical equilibrium with one another—no churning of fluids and no pressure imbalances.

A system in mechanical equilibrium may still undergo change through a chemical reaction. Even if the reaction is so slow that the mechanical equilibrium is not disturbed, the chemical composition is changing, and chemical energy is being released. If we assume that there is no change in chemical composition taking place, we say the system is in **chemical equilibrium**.

If we have a system in both mechanical and chemical equilibrium, we notice that the system can still be changing! Consider a cold block of copper brought into close contact with a hot block of aluminum. After awhile the copper will feel hotter to the touch, even though it has remained in mechanical and chemical equilibrium. A careful examination will also show that its volume has gotten somewhat larger. Similarly, the aluminum block will soon feel cooler to the touch, and its volume will have gotten somewhat smaller. Eventually, the volume changes will stop, and the two blocks will feel equally cool (or hot) to the touch. The two blocks are then said to be in **thermal equilibrium** with each other, or in the same thermal equilibrium state. Two objects in thermal equilibrium with each other are also said to be at the same *temperature*.

A system that is in mechanical, chemical, and thermal equilibrium with its surroundings, as well as internally (one part of the system with another), is said to be in **thermodynamic equilibrium**. Thermodynamic equilibrium means that there is no change on the macroscopic level.

Temperature and The Zeroth Law of Thermodynamics

Experiments involving thermal equilibrium of systems show that all systems have a continuous range of possible thermal equilibrium states, which we qualitatively associate with the degree of "hotness" or "coldness" of the system. For a given system, a change in the thermal equilibrium state is characterized by changes in one or more of the physical properties of the system (such as the change in volume for the blocks discussed in the previous section).

With each thermal equilibrium state of a system we assign a numerical value called the **temperature**, as determined by some agreed-upon procedure. Once we have set up such a numerical temperature scale for one "standard" system (say our copper block), then we can assign temperature values to the thermal equilibrium states of any other system. To do this, we prepare our standard system in a particular thermal equilibrium state with a particular temperature value. Then we assign the same temperature value to any other system that is prepared so that it is in thermal equilibrium with the standard system. The concept of the temperature, or thermal equilibrium state of a system, has great importance as a consequence of the following fundamental law:

> *If two systems A and B are each found to be in thermal equilibrium with a third system C, then when the two systems A and B are brought into contact with each other, they are themselves found to be in thermal equilibrium.*

In other words, the concept of temperature has a universal meaning. All systems at the same temperature T are in fact in thermal equilibrium with each other. This result was so taken for granted by scientists that it was not assigned a name until after the famous first and second laws of thermodynamics were established. Since its truth lies at the very foundation of thermodynamics, it is now often called the **zeroth law of thermodynamics**.

Problem 15.1.

(*a*) After the copper and aluminum blocks (referred to earlier in this section) came to thermal equilibrium, the copper block was quickly placed next to an iron block, and no changes in either block were observed. The iron block was then quickly moved into contact with the aluminum block. What changes do you expect in these two blocks?

(*b*) If the temperature of the iron block is 30° on some scale, what were the temperatures of the copper and aluminum blocks after they came to equilibrium?

Solution

(*a*) There would again be no changes, since, according to the zeroth law, the iron and aluminum are in the same equilibrium state.

(*b*) Each was at 30°, since they both were in thermal equilibrium with the iron block.

Temperature Measurement—Temperature Scales and Thermometers

The procedures for setting up a temperature scale and measuring temperature were outlined in the previous section. We will now actually set up a temperature scale.

First we single out a physical property of our standard system that varies with the thermal equilibrium states in a well-defined and reproducible way. Such a physical property of a system is called a **thermometric property**. Examples of thermometric properties are (1) the volume of a solid or liquid held under constant external pressure, (2) the length of a rod under constant pressure, (3) the resistance of a wire under constant pressure, (4) the pressure exerted by a constant volume of a confined gas, and (5) the volume of a container of gas held at constant pressure.

For concreteness, let the standard system be a sample of mercury in a sealed glass container with gas at nearly zero pressure (as in the mercury barometer), and choose volume as the thermometric property. To make the change in volume easily visible, our glass container will consist of a hollow bulb attached to a long, thin, hollow glass stem. When the mercury expands, it is forced up the thin stem so that even small changes in volume are observable (Fig. 15-1).

Now we are ready to develop the most widely used temperature scale, the **Celsius** (t_C) **scale**. We wish to assign the number $t_C = 0\,°\text{C}$ to the thermal equilibrium state (of our standard system) for which ice and water are in equilibrium at atmospheric pressure (the **ice point**). Thus, we dip the glass bulb into a large vat of ice and water in equilibrium, and when the mercury level stops changing, we make an etch mark on the glass tube and label it 0 °C. Similarly, we want $t_C = 100\,°\text{C}$ to represent the state in which the liquid and vapor phases of water are in equilibrium at atmospheric pressure (the

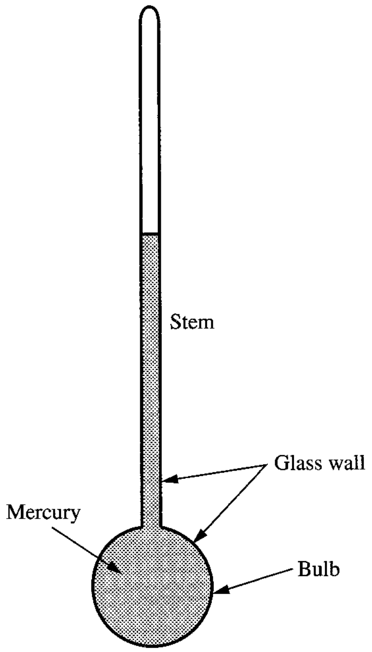


Fig. 15-1

steam point or boiling point), so we take the glass bulb and dip it into a large vat of boiling water. When the mercury level stops changing, we make another etch mark in the tube and label it 100 °C. We then divide the distance between the two etch marks into 100 equal marked intervals labeled in 1 °C steps. We can also mark off intervals of the same size above 100° and below 0°. Fig. 15-2(*a*) shows a schematic of system *A* with the Celsius scale.

The **Fahrenheit** (t_F) **scale** is defined in precisely the same way, except that the ice point and steam point are defined (for historical reasons) as $t_F = 32\,°\mathrm{F}$ and $t_F = 212\,°\mathrm{F}$, respectively, and the distance between the two etch marks is divided into 180 equal marked intervals labeled in 1 °F steps. [Fig. 15-2(*b*)].

Problem 15.2. Find the conversion formula between the Fahrenheit and Celsius temperature scales.

Solution

From the definition of the two scales it is clear that a Celsius degree is larger than a Fahrenheit degree, and that, in fact, a 1 °C interval corresponds to a 1.8 °F interval. Consider any Fahrenheit temperature t_F and corresponding Celsius temperature t_C. A quick calculation shows that we must have

$$t_F - 32 = 1.8(t_C - 0) = 1.8t_C \qquad (i)$$

Noting that $1.8 = \frac{9}{5}$, we get

$$t_C = \tfrac{5}{9}(t_F - 32) \qquad (ii)$$

$$t_F = \tfrac{9}{5}t_C + 32 \qquad (iii)$$

Problem 15.3. Find the temperature at which both Celsius and Fahrenheit have the same numerical value.

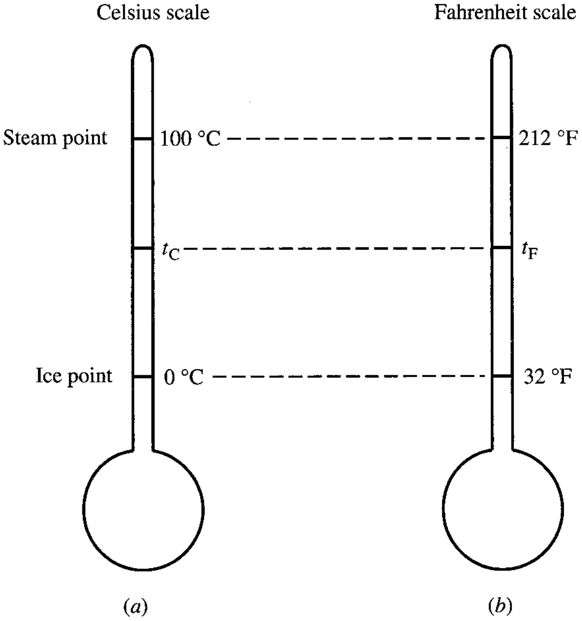


Fig. 15-2

Solution

Set $t_F = t_C$ in Eq. (*iii*) of Problem 15.2. Then

$$t_C = \tfrac{9}{5}t_C + 32 \Rightarrow -\tfrac{4}{5}t_C = 32 \Rightarrow t_C = -40°\text{C} = t_F = -40°\text{F}$$

Problem 15.4. Change the following temperatures to Celsius: (*a*) 128°F; (*b*) 60°F; (*c*) 0°F; (*d*) −459°F.

Solution

We substitute each value into Eq. (*ii*) of Problem 15.2 to get

(*a*) $t_C = \tfrac{5}{9}(128 - 32) = 53.3°\text{C}$.   (*b*) $t_C = \tfrac{5}{9}(60 - 32) = 15.6°\text{C}$.

(*c*) $t_C = \tfrac{5}{9}(0 - 32) = -17.8°\text{C}$.   (*d*) $t_C = \tfrac{5}{9}(-459 - 32) = -273°\text{C}$.

Our temperature-calibrated mercury system is called a **thermometer** because it can be used to measure the temperature of any other object. The procedure is simple: Let the object and thermometer, in contact, come to thermal equilibrium. Then, read their common temperature from the scale.

Problem 15.5. How can a thermometer measure the correct temperature of a system, since the thermal equilibrium of the system itself will change as a consequence of contact with the thermometer?

Solution

It is true that the thermometer records the temperature that corresponds to the final equilibrium state of the system, which is not the state it was in before contact with the thermometer. Nonetheless, if the thermometer is very small (in mass) compared to the system whose temperature is being measured, the change in the system will be negligible. Thus, for example, in using a mercury thermometer to measure the temperature of a child, the drop in the child's temperature due to contact with the cooler thermometer is negligible.

Problem 15.6. Suppose that a Celsius thermometer was created with alcohol (instead of mercury) as the liquid.

(*a*) Would the alcohol and mercury thermometers read exactly the same at every temperature being measured? Assume both thermometers are small in comparison with the objects whose temperatures are being measured.

(*b*) What does your answer to (*a*) imply about measurements of temperature?

Solution

(*a*) No. Only the two reference temperatures, 0 °C (the ice point) and 100 °C (the steam point), will definitely read the same. Only if the expansions of both liquids were perfectly linear with temperature would the readings at values in between be identical.

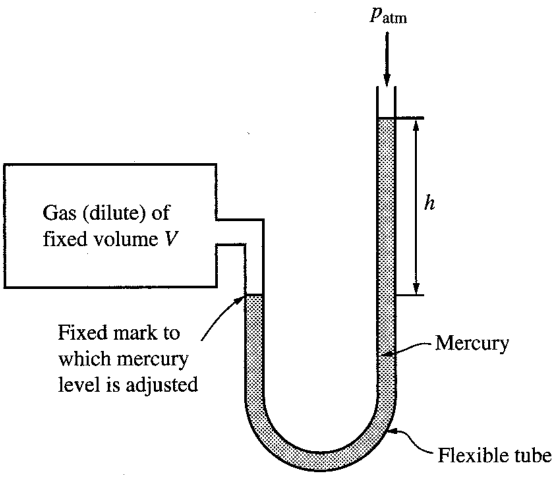
(*b*) The definition of temperature depends on the particular physical properties of the "official" thermometer. If the official thermometer were taken to be the mercury one, we could still use an alcohol thermometer, but on it the etch marks for the 1 ° intervals would not be equally spaced but would be calibrated against the readings of the official thermometer. As it turns out, the volumes of most liquids and solids vary nearly linearly with temperature (far from their melting or boiling points), so they do all give the same readings to a good approximation.

Problem 15.7. Develop a Celsius gas thermometer, choosing as the thermometric property the pressure of the confined gas.

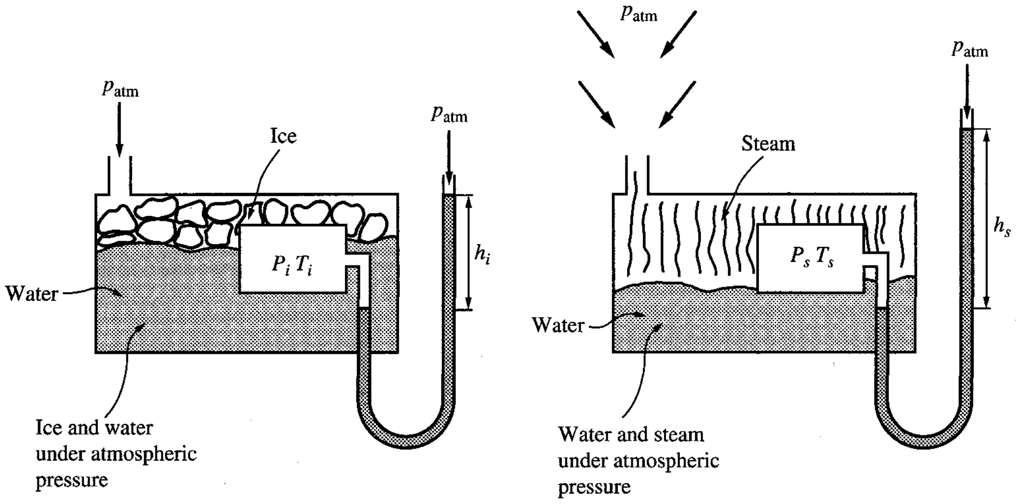
Solution

Figure 15-3(*a*) shows a gas confined to a fixed volume, with an open-tube manometer used to measure the pressure of the gas inside. We can set up the Celsius scale by noting the pressures corresponding to the ice point and the steam point, P_i and P_s [Fig. 15-3 (*b*) and (*c*)], respectively. Then we can take the temperature of any system by noting the equilibrium pressure of the gas when our gas thermometer is brought into close contact with that system. If the pressure is 40% of the way from P_i to P_s, we define the temperature as being 40% of the way from 0 °C to 100 °C, or $t_C = 40\,°\mathrm{C}$. We thus have a way of measuring Celsuis temperature with our gas thermometer. As in the cases of the alcohol thermometer there is no guarantee that this thermometer will read the same values as the mercury thermometer except at 0 °C and 100 °C.

As we have seen, our temperature scale is dependent on the particular material being used to define it. It would be nice to be able to set up our scale in a way that is completely independent of the nature of the substance of which the thermometer is made—a "universal" temperature scale. This turns out to be possible for materials in the gaseous state. It was experimentally shown that for all gases confined to fixed volumes and at very low density (dilute), the pressure varies linearly with the temperature, with great precision, over a much wider range of temperatures than for typical liquids. This means that very-low-density gas thermometers, of the type described in the last problem, all read the exact same temperature not only at 0 °C and at 100 °C but at all other temperatures as well. (For that reason the constant-volume gas thermometer is often considered the "standard" against which other thermometers are calibrated.) The graphs of pressure vs. temperature for all very-low-density gases at fixed volume are thus straight lines, as long as temperature is not so low that the gas is near the point of condensation to liquid or solid.



(*a*) Schematic of constant-volume gas thermometer



(*b*) (*c*)

Fig. 15-3

If one extrapolates these straight lines until they intersect the temperature axis, a remarkable result is observed. All the lines cut the axis at the same point, $-273.15\,^\circ\text{C}$, no matter what gas is involved [Fig. 15-4(*a*)]. On the basis of this result, one defines a new temperature scale T, known as the **absolute** or **Kelvin temperature scale**. A 1° interval—denoted 1 K—on this scale is the same size as a 1° interval on the Celsius scale (1 °C), but the zero point is shifted to $-273.15\,^\circ\text{C}$. Thus

$$T = t_C + 273.15 \tag{15.1}$$

Figure 15-4(*b*) shows that the pressure P of a low-density gas at constant volume is directly proportional to its Kelvin temperature T. Since pressure cannot be negative, one might surmise that $T = 0$ K was the lowest possible temperature in the universe—"absolute zero." In fact, this is the case.

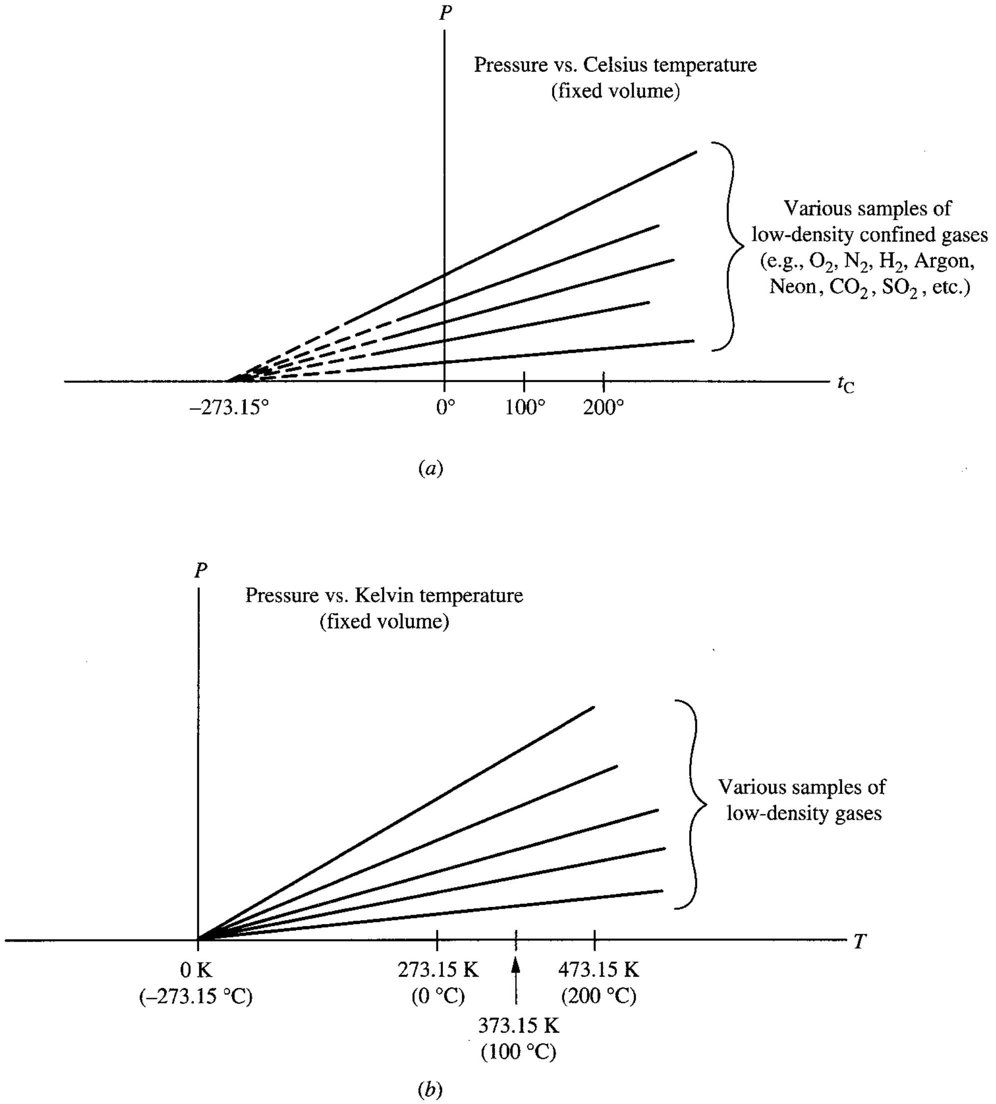


Fig. 15-4

Problem 15.8. Find the Kelvin temperature corresponding to (*a*) $t_C = 0\,^\circ\text{C}$; (*b*) $t_C = 100\,^\circ\text{C}$; (*c*) $t_F = 100\,^\circ\text{F}$.

Solution

(*a*) Using Eq. (*15.1*), we get $T = 0 + 273 = 273\text{ K}$. (To three significant figures.)

(*b*) $T = 100 + 273 = 373\text{ K}$.

(*c*) We first convert from Fahrenheit to Celsius:

$$t_C = \tfrac{5}{9}(t_F - 32) = \tfrac{5}{9}(100 - 32) = 37.8\,^\circ\text{C}$$

Next we convert to Kelvin: $T = 37.8 + 273.2 = 311\text{ K}$.

Problem 15.9. The entire development of the Kelvin scale can be redone using the Fahrenheit scale rather than the Celsius scale as the starting point. The resulting scale is called the Rankine scale, T_R.

(*a*) Find the Fahrenheit temperature that corresponds to zero on the Rankine scale.

(*b*) Find the formula that relates the Rankine and Fahrenheit scales.

Solution

(*a*) This Fahrenheit temperature must correspond to $t_C = -273.15\,°\text{C}$. Then

$$t_F = \tfrac{9}{5}t_C + 32 = -459.67\,°\text{F}$$

(*b*) Since the zero of the Rankine scale corresponds to $t_F = -459.67\,°\text{F}$ and the degree size is the same as the Fahrenheit degree, we must have $T_R = t_F + 459.67$.

Problem 15.10. In setting up the Celsius and Fahrenheit temperature scales, we needed two reference points, which we took to be the ice point and the steam point. Show that the Kelvin scale can be completely defined with only one reference point.

Solution

We use a constant-volume gas thermometer to establish the scale, and we recall that P is proportional to T for such a thermometer. Let P^* be the pressure reading of the thermometer at some reference temperature T^*, and let P be the reading at any other temperature T. We must have

$$\frac{P}{T} = \frac{P^*}{T^*} \quad \text{or} \quad T = \frac{T^*}{P^*}P \tag{15.2}$$

Thus one reference temperature T^* allows us to use the thermometer to determine any temperature T.

The reference temperature in Problem 15.10, in principle, could be chosen as either the ice point or the steam point, but in fact it is not. Instead, it is chosen as the unique equilibrium state of water, called the **triple point**, the temperature at which all three phases of water—solid, liquid, and vapor—coexist. The temperature of the triple point is just slightly above the temperature of the ice point and corresponds on the Celsius scale to $t_C = 0.01\,°\text{C}$. For this reason the value of T^* (Problem 15.10) is defined to be 273.16 K, assuring that the newly defined scale will be essentially identical to the earlier version. Then

$$T = \frac{P}{P^*}\,(273.16\ \text{K}) \tag{15.3}$$

where P^* is the pressure reading of our gas thermometer at the triple point of water, and P is the pressure reading at the temperature T.

Problem 15.11.

(*a*) A constant-volume gas thermometer is immersed in water at the triple point, and the pressure is measured as $P^* = 2.5 \times 10^3$ Pa. The thermometer is next placed in an oven cavity, where its pressure is found to be 3.0×10^4 Pa. What is the Kelvin temperature of the oven?

(*b*) What would be the pressure reading in the same oven for a gas thermometer whose pressure at the triple point was 1.0 kPa?

Solution

(*a*) By (*15.3*),

$$T = \frac{30}{2.5}(273\ \text{K}) = 3280\ \text{K}$$

(*b*) By Problem 15.10, the pressures of both thermometers must increase by the factor 30/2.5 = 12. The pressure of the new thermometer must then be 12(1.0 kPa) = 12 kPa.

Linear and Volume Expansivity

Among the most common thermometric properties of matter are the linear dimensions, surface area, and volume of solids, and the volume of liquids, all under constant pressure. If we have a rod of length L at a given absolute temperature and we increase the temperature by a small amount ΔT, we find that the length of the rod increases by an amount ΔL that is proportional to the original length L and to the temperature increase ΔT:

$$\Delta L = \alpha L\,\Delta T \tag{15.4}$$

The proportionality constant α is called the **coefficient of linear expansion**; it depends on the material of which the rod is made. The units of α are those of reciprocal temperature, as can be seen from (*15.4*). Note that $\Delta T = \Delta t_C$, since the degree sizes are the same; it is common to give α in $°\mathrm{C}^{-1}$. For most solids α will vary only slightly with temperature and pressure, so long as the solid is not close to the melting temperature. Equation (*15.4*) holds reasonably well, even when ΔT is substantial, as long as $\Delta L/L \ll 1$. Values of α for selected solids are given in Table 15.1.

Table 15.1. Linear Expansion

Solid	$10^5 \times \alpha$, $°\mathrm{C}^{-1}$
Aluminum	2.55
Brass	1.93
Copper	1.67
Glass (Pyrex)	0.33
Iron (steel)	1.20
Platinum	0.90
Silver	1.90
Zinc	3.20

Problem 15.12. An aluminum rod 3.0 m long is heated uniformly until its temperature rises by 20 °C. Find the fractional change in the length of the rod.

Solution

By (*15.4*) and Table 15.1,

$$\frac{\Delta L}{L} = \alpha\,\Delta T = (2.55 \times 10^{-5}\,°\mathrm{C}^{-1})(20\,°\mathrm{C}) = 0.00051$$

Problem 15.13. A railroad track is made of steel rails which are each 30 m long. If each rail can expand freely, how much space should be left between successive rails to avoid buckling? Assume that the maximum increase in temperature due to heating from the sun is 60 °C.

Solution

The space should be sufficient to accommodate the maximum ΔL of each rail due to heating.

$$\Delta L = (1.2 \times 10^{-5}\,°\mathrm{C}^{-1})(30\ \mathrm{m})(60°\mathrm{C}) = 21.6\ \mathrm{mm}$$

Problem 15.14. A homogeneous material will have the same expansivity properties in every direction. Hence such an object changes its overall size upon heating, but not its shape.

(*a*) Given this fact, find the new diameter of a solid brass sphere of radius 0.9535 m when its temperature rises 200 °C.

(*b*) If the sphere of (*a*) were hollow instead, with inner diameter 0.8535 m, what would be the new inside and outside diameters for the same temperature rise?

(*c*) In (*b*), by how much does the thickness of the spherical shell increase?

Solution

(*a*) Equation (15.4) applies to any diameter:

$$\Delta d = (1.93 \times 10^{-5}\,°\mathrm{C}^{-1})(0.9535\ \mathrm{m})(200°\mathrm{C}) = 0.0037\ \mathrm{m}$$

For a new diameter of 0.9572 m.

(*b*) The outer diameter still changes by 3.7 mm. Since all linear dimensions of the hollow sphere must expand in proportion, the inner diameter changes by

$$\Delta d_i = (1.93 \times 10^{-5}\,°\mathrm{C}^{-1})(0.8535\ \mathrm{m})(200°\mathrm{C}) = 0.0033\ \mathrm{m}$$

(*c*) We could reapply Eq. (*15.4*) to the 50-mm thickness of the brass shell. Instead we can just take the difference between the known expansions of the outer and inner *radii*, to obtain a

$$\tfrac{1}{2}(3.7\ \mathrm{mm} - 3.3\ \mathrm{mm}) = 0.2\ \mathrm{mm}$$

increase in shell thickness.

Note. The hole (any hole) expands upon heating just like the homogeneous material itself.

Problem 15.15. A steel hoop at $t_\mathrm{C} = 20°\mathrm{C}$ has inner diameter 100.005 cm. The hoop is to be placed over the rim of a wheel that is 100.044 cm in diameter. To what temperature t'_C should the hoop be heated to just fit over the wheel?

Solution

The inner diameter of the hoop must be increased by 0.039 cm. Then, from Eq. (*15.4*), $0.039\ \mathrm{cm} = (1.2 \times 10^{-5}\,°\mathrm{C}^{-1})\ (100.005\ \mathrm{cm})\ \Delta T$. Solving for ΔT, we have $\Delta T = 32.5°\mathrm{C}$, and $t'_\mathrm{C} = 52.5°\mathrm{C}$.

Problem 15.16. A steel sphere of diameter 4.0025 cm is to be passed through a brass loop of inner diameter 4.0012 cm. If the steel and brass are heated together, by how many degrees must they be heated for the sphere to just fit through the loop?

Solution

Since the sphere starts off with a diameter 0.0013 cm larger than the loops, we must have

$$\alpha_b d_\mathrm{loop}\,\Delta T = \alpha_s d_\mathrm{sph}\,\Delta T + 0.0013\ \mathrm{cm}$$

The diameters are given, and the expansion coefficients are available from Table 15.1.

$$(1.93 \times 10^{-5}\,{}^\circ\mathrm{C}^{-1})(4.00\ \mathrm{cm})\,\Delta T = (1.2 \times 10^{-5}\,{}^\circ\mathrm{C}^{-1})(4.00\ \mathrm{cm})\,\Delta T + 0.0013\ \mathrm{cm}$$

(Note that we approximated both diameters as 4.00 cm in the above expression, since these are to be multiplied by extremely small numbers, and the last decimal places of the diameters will contribute negligibly). Solving, we get $\Delta T = 44.5\,{}^\circ\mathrm{C}$.

Problem 15.17. Show that the change in volume of a homogeneous rectangular solid, due to a temperature rise ΔT, can be expressed as

$$\Delta V = \beta V\,\Delta T$$

where $\beta = 3\alpha$ is the coefficient of volume expansion of the solid.

Solution

If the dimensions of the solid are originally L_1, L_2, and L_3, then after heating, the new dimensions are

$$L_1' = L_1 + \alpha L_1\,\Delta \mathrm{T} = L_1(1 + \alpha\,\Delta \mathrm{T}) \qquad L_2' = L_2(1 + \alpha\,\Delta T) \qquad L_3' = L_3(1 + \alpha\,\Delta \mathrm{T})$$

The new volume is then

$$V' = L_1'L_2'L_3' = L_1L_2L_3(1 + \alpha\,\Delta T)^3 \tag{i}$$

We expand the term in parentheses, getting

$$(1 + \alpha\,\Delta T)^3 = 1 + 3\alpha\,\Delta T + 3(\alpha\,\Delta T)^2 + (\alpha\,\Delta T)^3 \tag{ii}$$

Recalling that $\alpha\,\Delta T$ is very small, even for reasonably large values of ΔT, we can ignore the last two terms to get $(1 + \alpha\,\Delta T)^3 \approx 1 + 3\alpha\,\Delta T$. Substituting into Eq. (i) we get

$$V' = V(1 + 3\alpha\,\Delta T) \qquad \text{or} \qquad \Delta V = V' - V = (3\alpha)V\,\Delta T = \beta V\,\Delta T \qquad \text{with} \qquad \beta = 3\alpha$$

Problem 15.18. Assume that the rectangular solid of the previous problem is made of aluminum and has dimensions $L_1 = 30$ cm, $L_2 = 20$ cm, and $L_3 = 50$ cm. Find (a) the volume expansivity of the rectangle; (b) the change in volume due to a ΔT of 40°C.

Solution

(a) The volume expansivity of aluminum can be obtained from Table 15.1: $\beta = 3\alpha = 7.65 \times 10^{-5}\,{}^\circ\mathrm{C}^{-1}$.

(b) $V = L_1L_2L_3 = 30{,}000\ \mathrm{cm}^3 \Rightarrow \Delta V = (7.65 \times 10^{-5}\,{}^\circ\mathrm{C}^{-1})\,(30{,}000\ \mathrm{cm}^3)\,(40\,{}^\circ\mathrm{C}) = 91.8\ \mathrm{cm}^3$.

The notion of linear expansion does not apply to liquids. Nevertheless, liquid volumes expand in accordance with the same law as for solids:

$$\Delta V = \beta V\,\Delta T \tag{15.5}$$

where β is now the volume expansivity of the liquid in question. Some values of β for liquids are shown in Table 15.2. Note that liquids generally have larger β values than solids.

Problem 15.19. The volume of the Pyrex glass bulb of a large mercury thermometer is $V = 0.30\ \mathrm{cm}^3$. The cross-sectional area of the inside of the stem is $A = 0.0020\ \mathrm{cm}^2$. If the temperature of the bulb increases by 30°C, what is the increase Δh in the height of mercury in the stem?

Table 15.2. Volume Expansion

Liquid	$10^5 \times \beta$, °C^{-1}
Alcohol	110
Glycerine	53
Mercury	18.2
Turpentine	94
Water	30

Solution

We note that as the temperature increases, the volume of mercury increases, forcing mercury up the tube. However, the volume of the glass bulb also increases, and this must be taken into account. We ignore the expansion of the tiny amount of mercury already in the stem, as well as the slight change in cross section of the stem itself. The net volume that is forced up the stem, $A\,\Delta h$, is then the difference between the increase in volume of the mercury and the glass bulb:

$$A\,\Delta h = \Delta V_{\text{merc}} - \Delta V_{\text{bulb}} = (\beta_{\text{merc}} - \beta_{\text{glass}})V\Delta T$$

From Tables 15.1 and 15.2, we get $(18.2 \times 10^{-5}\,°\text{C}^{-1} - 1.0 \times 10^{-5}\,°\text{C}^{-1})$ $(0.30\ \text{cm}^3)$ $(30\,°\text{C}) = 0.00155\ \text{cm}^3$. We must have $\Delta h A = \Delta V_{\text{net}} \Rightarrow \Delta h = \Delta V/A = 0.00155\ \text{cm}^3 / 0.0020\ \text{cm}^2 = 0.775$ cm.

It should be noted that for liquids near the melting point, *(15.5)* can be quite a poor approximation. In fact, in some cases, β changes rapidly near the melting point; it can even change sign. This occurs for those few liquids that expand upon freezing, such as water. With decreasing temperature, the volume of water decreases until about 4 °C, below which the volume increases until solidification at 0 °C. The fact that water expands upon freezing explains why ice floats, since the ice is less dense than the water.

15.3 THERMAL ENERGY; HEAT CONSTANTS

Thermal Energy and Heat

As we have seen, when two systems in mechanical and chemical equilibrium, but at different temperatures, are brought into contact, changes in both systems take place until they reach a common temperature. Early scientists believed that some invisible and weightless substance, which they called **caloric**, flows from a hotter to a cooler object until both objects reach thermal equilibrium. Thanks to the work of Joule and others in the first half of the nineteenth century, it became clear that it is not a substance but **thermal energy** that is transferred between two macroscopic systems in contact.

At the interface between the two systems, the more energetic atoms and molecules of the hotter system interact with their less energetic counterparts in the cooler system. The net result of these interactions is a transfer of energy to the atoms and molecules of the cooler system. Such transfer of energy is called **heat**.

Viewed macroscopically, heat is a *nonmechanical transfer of energy*, since the interacting systems are in mechanical equilibrium. Heat, then, is the counterpart of *work*, which (Sec. 6.6) is the *mechanical transfer of energy* from one system to another. Heat is actually the statistical "summing up" of the mechanical work done by the random interactions of the individual atoms and molecules of our two systems. Like work, heat is not something that resides in a system but is the thermal energy transfer from one system to another. The related quantity that resides in a system is "disorganized" internal energy, or thermal energy, which is due to the random motion and jiggling of the myriad atoms and molecules making up our macroscopic system.

Problem 15.20. The three common forms of internal energy are mechanical, chemical, and thermal. Figure 15-5 shows a system consisting of a container of hydrogen and oxygen gases and a long spiral spring. The container is slowly oscillating at the end of the spring. The entire system is at temperature *T*.

(*a*) Describe the various internal energies of the system.

(*b*) A spark causes the oxygen and hydrogen to explode, but the container doesn't burst. Is this process quasistatic? If not, explain why.

(*c*) If no energy can escape from the system, what changes in the internal energy distribution would you expect after the system comes to internal equilibrium?

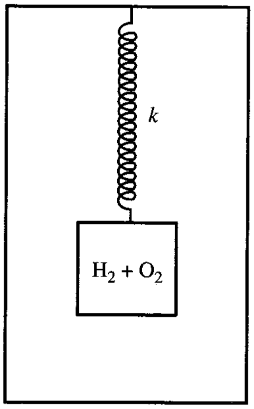


Fig. 15-5

Solution

(*a*) This system possesses all three forms of internal energy. The *mechanical energy* is the sum of the kinetic energy, the gravitational potential energy, and the spring potential energy associated with the oscillation. The *chemical energy* is the potential energy of forces within the oxygen and hydrogen molecules that is available to be released in their combination into water molecules. The *thermal energy* is that associated with the jiggling molecules making up the gas mixture, the container, and the spring, at their common temperature *T*.

(*b*) Prior to the explosion the system is quasistatic: the slow oscillations do not cause turbulence in the gas, which has a definite pressure associated with it. During and immediately after the explosion the system is, of course, not quasistatic. There is no common pressure in all parts of the container during the explosion, and the same is true for temperature. After the explosion, the contents of the container (water and any leftover gases) quickly reach a common pressure and temperature, but it takes a certain amount of time for thermal energy to travel from the gas and container to the spring, thereby bringing the entire system into equilibrium.

(*c*) The chemical potential energy will have been largely converted to thermal energy, as evidenced by the new higher temperature of the container and the spring. If the explosion occurred symmetrically within the container, no net force was exerted by the exploding gases on the container and the mechanical energy will remain unchanged. In an asymmetric explosion, however, some of the energy of the explosion could appear as increased mechanical energy of the system.

Heat Units

The historical unit of heat in the metric system is the **calorie** (cal), which originally was defined as the "amount of heat"—i.e., the amount of thermal energy in transit—necessary (at atmospheric pressure and a particular starting temperature) to raise the temperature of 1 gram of water 1 °C. In the English system the corresponding unit is the **British thermal unit** (Btu), which is the amount of heat necessary to raise 1 lb of water 1 °F. The conversion is 1 Btu = 252 cal. The fact that several definitions of the calorie have been in use, differing one from another in the fourth decimal place, may lead to some confusion. These calories are given separate labels and are now all defined in terms of the SI unit of energy, the joule. In this book we will employ only the "thermochemical" calorie, where 1 cal $\equiv$ 4.184 J.

Note. The common food calorie is really 1000 heat calories, as defined above: 1 food calorie = 1 kcal or 4184 J.

Problem 15.21.

(*a*) A bunsen burner flame has been adjusted so that it generates 30 cal/s. Assuming that all this heat enters a container of water, what is the change, in J, of the internal energy of the container and water after 3.0 min?

(*b*) If instead the same change in internal energy were to take place through the work done on the water by a rotating paddle driven by a falling 100-kg mass (Fig. 15-6), through what distance would the mass have to fall? Assume that the mass falls at constant speed and that the pulley systems are frictionless.

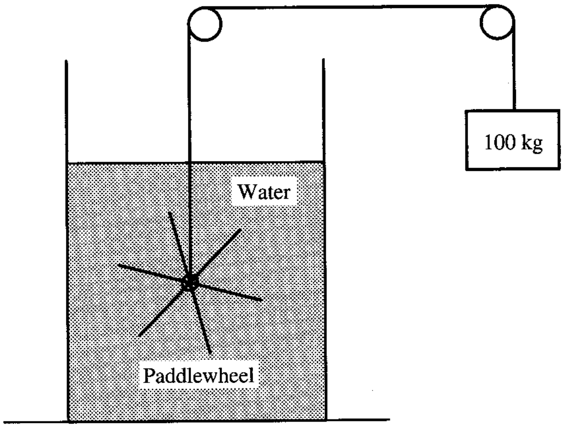


Fig. 15-6

Solution

(*a*) The increase in the internal energy of the system is just (30 cal/s) (180 s) = 5400 cal. Multiplying by 4.184 J/cal, we get 22,600 J.

(*b*) The falling mass must lose 22,600 J of gravitational potential energy. Thus, $mgh = 22{,}600\ \text{J} \Rightarrow (100\ \text{kg})\ (9.8\ \text{m/s}^2)h = 22{,}600\ \text{J} \Rightarrow h = 23\ \text{m}$.

Specific Heats and Heat Capacities

The relationship between temperature and heat was already a major topic of investigation in the time of the caloric hypothesis. It was noted that for each different substance a characteristic amount of heat had to flow into a unit mass of the substance to produce a 1° rise in temperature. This characteristic property was quantified in the concept of **specific heat**. If ΔQ is the amount of heat entering a mass m of a pure substance and if the consequent temperature rise is ΔT, the specific heat c of the substance is given by

$$c = \frac{\Delta Q}{m\,\Delta T} \qquad \text{or} \qquad \Delta Q = mc\,\Delta T \tag{15.6}$$

The working SI unit of specific heat is the kJ/(kg · K), in which °C may be substituted for K. Other commonly used metric units are cal/(g · °C) = kcal/(kg · °C), J/(g · °C) = kJ/(kg · °C), and J/(kg · °C) = 10^{-3} kJ/(kg · °C).

Clearly a substance with a high specific heat requires more heat energy to raise its temperature by a given amount than one with a low specific heat. The **heat capacity** C of our sample of material is the total amount of heat needed to produce a degree rise in temperature: $C = \Delta Q/\Delta T$. From Eq. (*15.6*),

$$C = mc \tag{15.7}$$

Unlike heat capacity, which depends on the mass of the sample, specific heat is an intrinsic property. Nonetheless, it does depend to a slight degree on two other intrinsic properties, the material's temperature and pressure. For many substances the specific heat stays constant over moderate ranges of these variables. For water at atmospheric pressure, for example, the specific heat varies from about 4210 J/(kg · K) at $t_C = 0°\text{C}$ down to about 4180 J/(kg · K) at $t_C = 30°\text{C}$ and back up to about 4210 J/(kg · K) at $t_C = 100°\text{C}$. It thus varies by less than 1% over the full 100°C temperature range of water.

The specific heat also depends on the manner in which thermal energy is transferred to the substance. For example, the specific heat will be different depending on whether pressure or volume is held fixed during the heating process. As a practical matter, it is much easier to heat liquids and solids at constant pressure than at constant volume. Table 15.3 gives the specific heats of some solids and liquids under constant atmospheric pressure: the values are valid over a fairly wide range of temperatures. For specific heats of gases, see the next chapter.

Calorimetry is the experimental measurement of specific heats and other heat constants. It is based on the fact that, for systems in mechanical and chemical equilibrium, the thermal energy lost by one system must, by conservation of energy, equal the thermal energy gained by the other systems it is in contact with. Consider an isolated system that is composed of two subsystems in close "thermal" contact, meaning that heat can easily transfer from one subsystem to the other. If Q_{out} is the magnitude of heat transferring out of the first subsystem and Q_{in} is the magnitude of heat entering the second subsystem, then $Q_{\text{out}} = Q_{\text{in}}$. In a typical experimental situation, an insulated container holding water makes up the second subsystem, or **calorimeter**, while a sample of the substance whose specific heat is to be measured composes the first subsystem. The sample is inserted into the calorimeter and the two come to thermal equilibrium.

Table 15.3. Specific Heats at Atmospheric Pressure

	Specific Heat	
Substance	kcal/(kg · °C)	kJ/(kg · °C)
Solids:		
Aluminum	0.22	0.92
Brass	0.090	0.377
Copper	0.093	0.389
Gold	0.031	0.130
Ice (near 0 °C)	0.50	2.09
Iron (steel)	0.11	0.46
Lead	0.031	0.130
Platinum	0.032	0.134
Zinc	0.092	0.385
Liquids:		
Alcohol	0.55	2.30
Glycerine	0.58	2.43
Mercury	0.33	1.38
Turpentine	0.42	1.76
Water	1.00	4.184

Problem 15.22. A lead brick, of mass $m_l = 3.0$ kg and at a temperature of $t_l = 300°\text{C}$, is dropped into an insulated copper vessel of mass $m_c = 1.5$ kg that contains $m_w = 2.0$ kg of water; the calorimeter temperature is $t_0 = 20°\text{C}$. If the final temperature at equilibrium is $t = 31.7°\text{C}$, find the specific heat of lead.

Solution

For the lead,

$$Q_{\text{out}} = m_l c_l (t_l - t) = (3.0\ \text{kg})c_l(300°\text{C} - 31.7°\text{C})$$

For the calorimeter,

$$\begin{aligned} Q_{\text{in}} &= m_w c_w (t - t_0) + m_c c_c (t - t_0) \\ &= (2.0\ \text{kg})[4.184\ \text{kJ}/(\text{kg} \cdot °\text{C})](31.7°\text{C} - 20°\text{C}) + (1.5\ \text{kg})[0.389\ \text{kJ}/(\text{kg} \cdot °\text{C})](31.7°\text{C} - 20°\text{C}) \end{aligned}$$

Equating Q_{out} and Q_{in}, and solving for c_l, we get $c_l = 0.130\ \text{kJ}/(\text{kg} \cdot °\text{C})$, which checks with Table 15.3.

Note. In Q_{out} we subtract the final temperature from the hot temperature, while in Q_{in} we subtract the cold temperature from the final temperature, since both Q's are defined to be positive.

Problem 15.23. An aluminum block, of mass 200 g and a temperature of 400 °C, is dropped into an aluminum calorimeter of mass 1.0 kg filled with 100 g of water at a temperature of 5.0 °C. Find the temperature when equilibrium is reached.

Solution

Using the specific heats from Table 15.3, we have

$$Q_{\text{out}} = Q_{\text{in}} \Rightarrow (0.200\ \text{kg})[0.22\ \text{kcal}/(\text{kg}\cdot{}^\circ\text{C})](400^\circ\text{C} - t_\text{F})$$
$$= (0.100\ \text{kg})[1.00\ \text{kcal}/(\text{kg}\cdot{}^\circ\text{C})](t_\text{F} - 5.0^\circ\text{C}) + (1.00\ \text{kg})[0.22\ \text{kcal}/(\text{kg}\cdot{}^\circ\text{C})](t_\text{F} - 5.0^\circ\text{C})$$

We bring all terms involving t_F to the right and all numerical terms to the left, obtaining $19.2 = 0.364t_\text{F} \Rightarrow t_\text{F} = 52.7^\circ\text{C}$.

Heat Constants

All substances have a solid, a liquid, and a vapor phase. For a solid substance under a fixed pressure, there is a definite temperature at which it will become liquid (melt) called the **melting point**. At the melting point one must add a definite amount of heat, called the **heat of fusion** L_f, to melt each unit mass of the substance. This process is reversible: if one extracts a like amount of heat from the liquid at the melting point (now renamed the **fusion point**), the liquid will become solid again.

Likewise, for a liquid under fixed pressure, there is a definite temperature, called the **boiling point**, at which the liquid will convert to vapor. Again, one must add a definite amount of heat, called the **heat of vaporization** L_v, to vaporize each unit mass of the substance at the boiling point. This process, too, is reversible, with the boiling point becoming the **liquefaction point**.

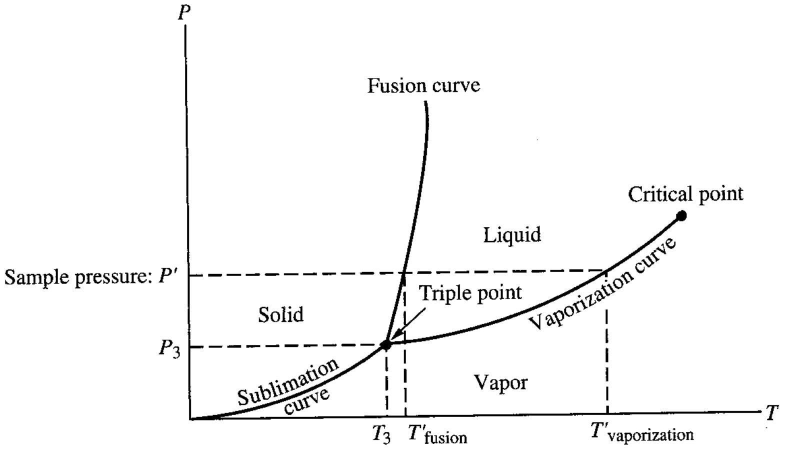
Melting and boiling points, and their associated heat constants, vary with pressure. The values given in Table 15.4 reflect normal atmospheric pressure.

Table 15.4. Heat Constants at Normal Atmospheric Pressure

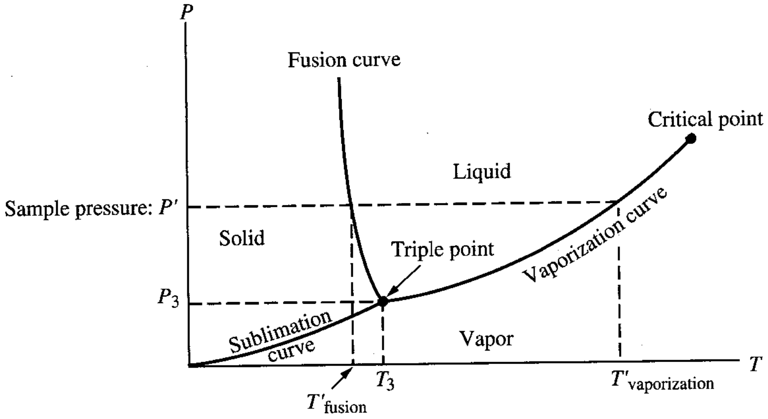
Substance	Melting Point, °C	L_f, kJ/kg	Boiling Point, °C	L_v, kJ/kg
Hydrogen	−259	58.6	−253	452
Oxygen	−219	13.8	−183	213
Alcohol	−114	104.	78	854
Mercury	−39	11.8	357	272
Water	0	335.	100	2256
Lead	327	24.6	1750	871
Zinc	420	118.		
Gold	1064	64.5	2660	1578

A third phase transition—solid to vapor, or **sublimation**—must also be considered. For each substance there is a pressure below which there can be no liquid phase. Below that pressure, adding heat to a solid will lead directly to the vapor state. Again, for each fixed pressure, there is a definite temperature, or **sublimation point**, at which sublimation occurs, and a definite amount of heat, called the **heat of sublimation** L_s must be added to each unit mass of solid at that temperature to convert it to vapor. Again, the process is reversible.

A helpful means of keeping track of phase changes is a **pressure vs. temperature**, or *P-T*, **diagram**. For a pure substance (e.g., carbon dioxide, methane, mercury, water, or aluminum) the diagram will resemble Fig. 15-7(*a*) or (*b*). The three smooth curves separate the solid, liquid, and vapor domains. At any pressure and temperature to the left of the sublimation and fusion curves the



(*a*) Substance contracts on freezing



(*b*) Substance expands on freezing

Fig. 15-7

substance is in the solid phase. Similarly, any point below the sublimation and vaporization curves lies in the vapor domain. The liquid phase corresponds to the region between the fusion and vaporization curves above the triple point. For any given pressure P there is a corresponding temperature on the fusion curve, which is the melting point or fusion point for that pressure. For the same pressure there is also a corresponding (higher) temperature on the vaporization curve, and this is the boiling point or liquefaction point for that pressure. The graph clearly shows how the values of the melting and boiling points vary with pressure. Below the **triple point**, which is clearly the single point at which vapor, liquid, and solid coexist, we have only sublimation.

The P-T diagram (Fig. 15-7) also allows us to visualize the effects of heating. If we start at a given pressure, say P', and at $T = 0\,\text{K}$, and we slowly add heat to the substance while holding the pressure constant, the solid's temperature will rise until it reaches the melting point on the fusion curve. The temperature will stay constant throughout the melting process. After all the solid has been converted to liquid, the temperature begins to rise again, and we slowly move along the dashed line until the vaporization curve is reached. At this point the liquid starts turning into vapor; the temperature remains at the boiling point until the vaporization is complete. After that the temperature continues to rise.

It should be noted that while the entire melting or vaporization process seems to take place at a single point on the P vs. T graph, in fact the volume of the system is changing during the process. The volume of the liquid at a given P and T on the fusion curve is different than the corresponding volume of the solid. This is even more dramatic for liquid and vapor on the vaporization curve.

Thus, for example, during the vaporization process, the volume changes from that of 100% liquid until it becomes that of 100% vapor. We must keep adding heat until all the liquid has become completely vapor. The same analysis is true of solid and liquid at a point on the fusion curve.

As shown above, crossing from one side of the vaporization curve to the other corresponds to a major change in the volume of the substance. As we repeat this process at higher and higher constant pressures, however, the difference in the volume between 100% liquid and 100% vapor decreases. At the pressure of the critical point (see Fig. 15-7) this difference in volume completely disappears, and the difference between liquid and vapor loses its meaning. Figure 15-8 illustrates the crossing of the vaporization curve at different fixed pressures (and corresponding temperatures) ranging from the triple-point pressure P_3 to the critical pressure P_c in a graph of P vs. V (pressure vs. volume). The dotted line on the left, called the **liquid saturation curve**, corresponds to points of 100% liquid, on the verge of starting to vaporize, while the dotted line on the right, called the **vapor saturation curve**, corresponds to points where the substance has just become 100% vapor. The horizontal dashed lines represent the changing volume for changing relative composition of the liquid-vapor mixtures at the given sample pressures and temperatures. Note how the volume differences between 100% liquid and 100% vapor decreases toward the critical point.

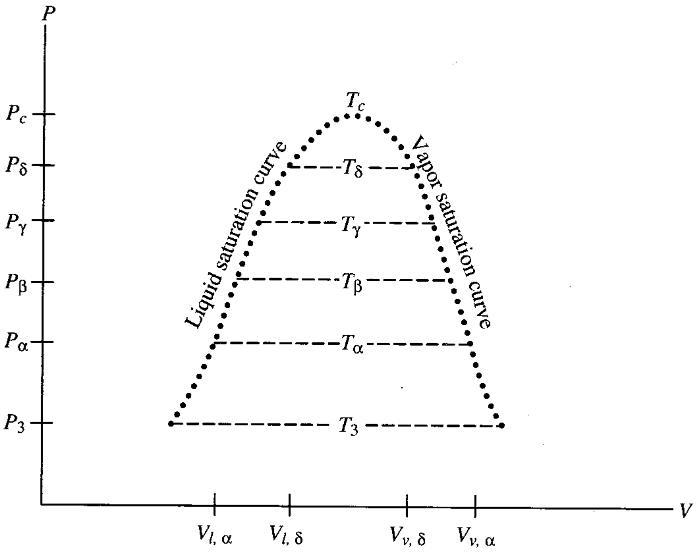


Fig. 15-8

Problem 15.24. The triple-point pressure of water is $P_3 = 0.006P_{\text{atm}}$, while the critical pressure is $P = 221P_{\text{atm}}$.

(*a*) What is the requirement for the sublimation of water?

(*b*) What is the difference between the densities of liquid and vapor water at the critical point?

(*c*) Are these phenomena observable in everyday life?

Solution

(*a*) One must reduce the pressure to below $0.006P_{\text{atm}}$; otherwise ice first melts into a liquid phase and then vaporizes.

(*b*) Zero (compare the volumes of a unit mass of liquid and a unit mass of vapor).

(*c*) Ice must be present in a highly evacuated chamber to reproduce the conditions for the triple point or for sublimation. Similarly, one would have to have water under extreme pressure to reproduce the conditions at the critical point or above. Thus these phenomena are not part of our normal experience.

Problem 15.25.

(*a*) Suppose the volume $V_{l,\delta}$ in Fig. 15-7 is 30.0 mL, while that of $V_{v,\delta}$ is 200 mL. What fraction, x, of the mass of the liquid has vaporized (at pressure P_δ) when the volume is $V'_\delta = 100$ mL?

(*b*) If the heat of vaporization of this fictitious substance is 600 kJ/kg and the mass is 80 g, how much heat must be added to the 30.0 mL of liquid to reach the volume 100 mL?

Solution

(*a*) $$V'_\delta = 100\ \text{mL} = (1-x)(30.0\ \text{mL}) + x(200\ \text{mL}) \qquad \text{or} \qquad x = 0.41$$

(*b*) From part (*a*), the amount of liquid vaporized is (0.41) (80 g) = 32.8 g. Then,

$$\text{Heat} = (600\ \text{kJ/kg})(0.0328\ \text{kg}) = 19.7\ \text{kJ}$$

We now apply the techniques of calorimetry to heats of fusion, vaporization, and sublimation.

Problem 15.26. A 0.500-kg block of ice, initially at −50 °C, is placed in a large pot that is open to the atmosphere. The pot is heated at a constant rate of 20 W; all the heat enters the ice.

(*a*) Describe qualitatively the processes that occur as the ice is heated, from the start until it has turned into water vapor.

(*b*) How long does it take to raise the temperature of the ice to 0 °C?

(*c*) How long does it take to completely melt the block at 0 °C?

(*d*) How long does it take to raise the temperature of the liquid water from 0 °C to 100 °C?

(*e*) How long does it take to vaporize the water at 100 °C?

Solution

(*a*) The ice will first warm up until it reaches 0 °C, the melting point at atmospheric pressure. At that point the ice will start to melt, and the temperature will remain at 0 °C all through the melting process. After all the ice has melted, we have water at 0 °C, which will now absorb the incoming heat and rise steadily in temperature until it reaches the boiling point at 100 °C. At that point it will start to boil while it stays at 100 °C, until all the liquid has turned to vapor.

(*b*) From Table 15.3 we see that the specific heat of ice is 2090 J/(kg · °C). Then, the heat necessary to raise the temperature of the ice to 0 °C is $Q = (0.50\ \text{kg})\,[2090\ \text{J/(kg}\cdot{}^\circ\text{C)}]\,(50\,^\circ\text{C}) = 52.3$ kJ. At a rate of 20 J/s this will take 2615 s = 43.6 min.

(*c*) The heat of fusion of ice is 335 kJ/kg, so the heat necessary to melt the ice is $Q = (0.50\ \text{kg})\,(335\ \text{kJ/kg}) = 167.5$ kJ. The time is then 8375 s = 140 min.

(*d*) The specific heat of water is 4.184 kJ/(kg · °C), so the heat to raise the water from 0 °C to 100 °C is

$$(0.50\ \text{kg})[4.184\ \text{kJ}/(\text{kg}\cdot{}^\circ\text{C})](100\,^\circ\text{C}) = 209\ \text{kJ}$$

and the time it takes is 10,500 s = 174 min.

(*e*) The heat of vaporization of water is 2256 kJ/kg, so the heat to vaporize all the water is

$$(0.50\ \text{kg})(2256\ \text{kJ/kg}) = 1128\ \text{kJ}$$

and the time taken is 56,400 s = 940 min.

Problem 15.27. A calorimeter has a shell of negligible heat capacity and contains 0.5 kg of ice and 0.5 kg of water in equilibrium. A 2.0-kg block of steel at 500 °C is placed in the calorimeter, and the system is allowed to come to equilibrium.

(*a*) What is the final equilibrium temperature t_0?

(*b*) What would have happened if the mass of the steel block were 0.50 kg, all else being the same?

Solution

(*a*) For the steel,

$$Q_{\text{out}} = m_s c_s(t_s - t_0) = (2.0\ \text{kg})[0.46\ \text{kJ}/(\text{kg}\cdot{}^\circ\text{C})]\,(500\,^\circ\text{C} - t_0)$$

For the calorimeter,

$$Q_{\text{in}} = m_{\text{ice}}L_i + (m_{\text{ice}} + m_w)c_w(t_0 - 0\,^\circ\text{C}) = (0.50\ \text{kg})(335\ \text{kJ/kg}) + (1.0\ \text{kg})(4.184\ \text{kJ/kg}\cdot{}^\circ\text{C})t_0$$

Setting $Q_{\text{out}} = Q_{\text{in}}$ and solving for t_0, we get $t_0 = 57.3\,^\circ\text{C}$.

[In equating Q_{out} and Q_{in} we assume that Q_{out} is sufficient to melt all the ice. If that had not been the case, we would have found that $t_0 < 0\,^\circ\text{C}$—which is absurd, because the equilibrium temperature has to lie between the highest and lowest initial temperature in the system. There is a more direct way to check whether all the ice melts or not; see (*b*).]

(*b*) Let us first check to see if all the ice melts. The maximum value of Q_{out} is the heat necessary to drop the temperature to $t_0 = 0\,^\circ\text{C}$. Thus,

$$Q_{\text{out}} \le (0.50\ \text{kg})[0.46\ \text{kJ}/(\text{kg}\cdot{}^\circ\text{C})]\,(500\,^\circ\text{C} - 0\,^\circ\text{C}) = 115\ \text{kJ}$$

The amount of heat needed to melt all the ice is $Q_{\text{melt}} = (0.50\ \text{kg})\ (335\ \text{kJ/kg}) = 164\ \text{kJ}$. Clearly, not all the ice melts. We can easily find the amount of ice that does melt, since we now know that the final temperature is indeed 0 °C and that $Q_{\text{out}} = 115$ kJ. Thus,

$$(335\ \text{kJ/kg})x = 115\ \text{kJ} \qquad \text{or} \qquad x = 0.34\ \text{kg}$$

Problem 15.28. How many grams of live steam at atmospheric pressure must be injected into a calorimeter initially containing 100 g of ice and 200 g of water in equilibrium if the final temperature is to be 50 °C? Ignore the heat capacity of the vessel.

Solution

$$\begin{aligned}
Q_{\text{out}} &= m_s L_v + m_s c_w(t_s - t_0)\\
&= m_s(2256\ \text{kJ/kg}) + m_s[4.184\ \text{kJ}/(\text{kg}\cdot{}^\circ\text{C})]\,(100\,^\circ\text{C} - 50\,^\circ\text{C}) = m_s(2465\ \text{kJ/kg})\\
Q_{\text{in}} &= m_i L_f + (m_i + m_w)c_w(t_0 - 0\,^\circ\text{C})\\
&= (0.10\ \text{kg})(335\ \text{kJ/kg}) + (0.30\ \text{kg})[4.184\ \text{kJ}/(\text{kg}\cdot{}^\circ\text{C})]\,(50\,^\circ\text{C} - 0\,^\circ\text{C}) = 96.3\ \text{kJ}
\end{aligned}$$

Equating Q_{out} and Q_{in}, we get $m_s = 0.039\ \text{kg} = 39$ g.

Evaporation and Cooling

It has been seen that, for a given pressure, boiling will take place at a definite temperature. Boiling, which occurs within the bulk of the liquid, is a different phenomenon from **evaporation**, which takes place only at the *surface* of a liquid in contact with a gas at a given pressure. At temperatures well below the boiling point, molecules from the liquid that are particularly energetic can break free and rise above the liquid to form a vapor. If this vapor is trapped above the liquid surface, then eventually equilibrium is established, with as many vapor molecules reentering the liquid as leaving. But if the liquid is open to the atmosphere, the evaporation process continues unabated. The evaporating molecules carry off thermal energy with them—on average the amount of energy per unit mass is the same order of magnitude as the heat of vaporization for boiling. Thus the evaporation process removes heat from the liquid, cooling it and anything in contact with it.

Problems for Review and Mind Stretching

Problem 15.29.

(*a*) Find the relationship between the Kelvin and Rankine temperature scales, and find the triple-point temperature of water in the Rankine scale.

(*b*) Convert all the values of specific heats in Table 15.3 to units of Btu/(lb ·°F).

Solution

(*a*) The two absolute temperatures are each directly proportional to pressure and hence directly proportional to each other. We know that the kelvin (or Celsius degree) is nine-fifths as large as the Rankine (or Fahrenheit) degree. It follows that $T_R = \frac{9}{5}T$. From this for the triple point of water, we get $T_{R,3} = \frac{9}{5}(273.16) = 491.69$ R.

(*b*) Recalling that the definition of the Btu is the amount of heat necessary to raise 1 lb of water 1 °F, we have $c_w = 1.0$ Btu/(lb · °F). This is numerically identical to the specific heat of water in kcal/(kg · °C) [or cal/(g · °C)]: $c_w = 1.0$ kcal/(kg · °C). This implies that all other specific heats must also have the same numerical values in both systems, and the first column of Table 15.3 already gives the correct values of the specific heats in Btu/(lb · °F).

Problem 15.30. A flat plate of brass has area $A = 0.4500\ \text{m}^2$. The temperature is raised by 100°C. Find the new area of the plate.

Solution

Just as for volume, the area expansion is related simply to the linear expansion. If we repeat the analysis found in Problem 15.17 for a flat rectangle of sides L_1 and L_2, we can quickly conclude that the area expansivity is just 2α. Then, for our brass plate,

$$\Delta A = 2\alpha A\,\Delta T = 2(1.93 \times 10^{-5}\,{}^\circ\text{C}^{-1})(100\,{}^\circ\text{C}) = 0.0039\ \text{m}^2$$

The new area is $A' = A + \Delta A = 0.4500 + 0.0039 = 0.4539\ \text{m}^2$.

Problem 15.31. An aluminum pot of volume 600 cm^3 is filled to the top with water at 20°C. The pot and contents are heated up to 60°C. What volume of water spills over the top of the pot during the heating?

Solution

The volume of the pot increases, but the volume of the water increases faster. The difference in the two volume increases, ΔV, is the volume of water that overflows. Recalling that the water and pot occupy the same initial volume V, we have

$$\begin{aligned}\Delta V &= \beta_w V \Delta t - \beta_{\mathrm{Al}} V \Delta t \\ &= (30 \times 10^{-5}\,{}^\circ\mathrm{C}^{-1})(600\ \mathrm{cm}^3)(40^\circ\mathrm{C}) - (7.65 \times 10^{-5}\,{}^\circ\mathrm{C}^{-1})(600\ \mathrm{cm}^3)(40^\circ\mathrm{C}) = 5.36\ \mathrm{cm}^3\end{aligned}$$

Problem 15.32. The **heat of combustion** of a fuel is defined as the amount of chemical potential energy converted to thermal energy for each kilogram of the fuel that burns up (completely combines with oxygen). To find the heat of combustion of gasoline, 2.0 g of gasoline is completely burned in an under-chamber of a 1.0-kg copper calorimeter containing 500 g of water initially at 20°C. The setup is such that all the energy from the combustion enters the calorimeter and contents as thermal energy. The final equilibrium temperature of the calorimeter is found to be 57°C.

(*a*) What is the heat of combustion h_g of the gasoline?

(*b*) If the energy content of 1.0 g of peanut butter is 12 kcal = 12 food calories, how does this compare to the combustion energy of gasoline?

Solution

(*a*) The amount of heat entering the calorimeter is

$$\begin{aligned}Q_{\mathrm{in}} &= m_w c_w \Delta t + m_c c_c \Delta t \\ &= (0.500\ \mathrm{kg})[4184\ \mathrm{J}/(\mathrm{kg}\cdot{}^\circ\mathrm{C})]\,(37^\circ\mathrm{C}) + (1.00\ \mathrm{kg})[389\ \mathrm{J}/(\mathrm{kg}\cdot{}^\circ\mathrm{C})]\,(37^\circ\mathrm{C}) = 91{,}800\ \mathrm{J}\end{aligned}$$

Then $m_g h_g = 91{,}800\ \mathrm{J} \Rightarrow (0.0020\ \mathrm{kg})h_g = 91{,}800\ \mathrm{J} \Rightarrow h_g = 45{,}900\ \mathrm{kJ/kg}$.

(*b*) We recall that 1 food calorie = 1 kcal = 4184 J. Dividing h_g by 4184 J/food calorie yields 10,970 food calories/kg, or approximately 11 food calories/g. The peanut butter, upon digestion, yields more energy per gram than the gasoline!

Problem 15.33. If a weighted wire rests on a block of ice, as shown in Fig. 15-9, the wire will slowly descend through the ice. When the wire has sliced completely through the ice, however, the block is still in one piece. Explain this example of **regelation** (refreezing).

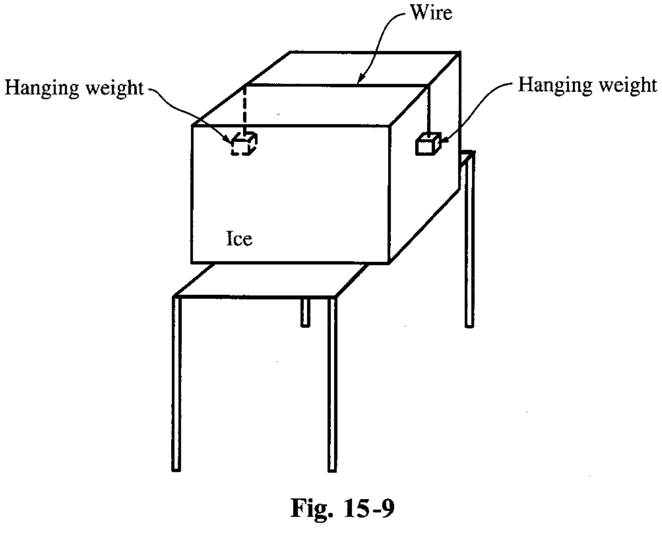


Fig. 15-9

Solution

The wire exerts great pressure on the ice immediately beneath it. Since the temperature of the ice is relatively constant, we can visualize what happens by following a vertical path in Fig. 15-7(*b*). As the pressure increases we move vertically upward on the graph from the solid region until we reach the fusion curve. If the pressure increases further, we are forced into the liquid region, which means that the ice melts. As the ice in the high-pressure region just below the wire melts, the wire displaces the liquid which rises above the wire. The liquid is now at lower pressure and resolidifies. The heat removed from the liquid then contributes to melting the next layer of ice under the wire, and the process repeats as the wire slices downward. At the end we are left with a solid block of ice.

Supplementary Problems

Problem 15.34. ~~Using~~ Table 15.4, calculate the melting and boiling points of oxygen and mercury on (*a*) the Kelvin scale, (*b*) the Fahrenheit scale.

Ans. (*a*) oxygen: 54 K and 90 K, mercury: 234 K and 630 K; (*b*) oxygen: −362 °F, −297 °F, mercury: −38.2 °F, 675 °F

Problem 15.35. A metal rod of length 3.000 m is uniformly heated so that its temperature rises 300 °C. The new length is found to be 3.015 m. Find the coefficient of linear expansion. What is a likely candidate for the metal of which the rod is made?

Ans. $1.67 \times 10^{-5}\,°\mathrm{C}^{-1}$; copper

Problem 15.36. A steel rod of length $L = 2.0$ m and cross-sectional area $A = 200\ \mathrm{mm}^2$ is held rigidly between two walls. Heating raises the rod's temperature by $\Delta t = 300\,°\mathrm{C}$.

(*a*) What would be the increase in length of the steel if it were free to expand?

(*b*) If the walls hold the steel rigidly to its original length, find an expression for the force that must be exerted by each wall on the rod. [*Hint*: Recall the definition of Young's modulus (Sec. 11.1).]

(*c*) Find the numerical value for the force of part (*b*). (The Young's modulus for steel is $Y = 1.98 \times 10^{11}$ Pa.)

Ans. (*a*) 7.2 mm; (*b*) $F = \alpha Y A\,\Delta t$; (*c*) 143 kN

Problem 15.37. An aluminum hoop of inner diameter 1.0024 m is to be fitted over a steel disk of diameter 1.0045 m. Both the disk and the hoop are originally at 20 °C. If they are uniformly heated, at what temperature will the hoop just fit over the disk?

Ans. 176 °C

Problem 15.38.

(*a*) Find the change in volume of a zinc sphere of radius $r = 20$ cm when the temperature increases by 250 °C.

(*b*) What percentage change in volume does this correspond to?

(*c*) What percentage change in density does this correspond to?

Ans. (*a*) 804 cm^3; (*b*) 2.4%; (*c*) −2.4%

Problem 15.39. A steel block weighing 10 lb and at a temperature of 450 °F is dropped into a copper vessel weighing 1.0 lb filled with 3.0 lb of water; the calorimeter temperature is 40 °F. Find the final temperature.

Ans. 148 °F

Problem 15.40. 100 g of steam at 100 °C is fed into a calorimeter; the vessel has negligible heat capacity and is filled with 0.200 kg of ice and 0.500 kg of water in equilibrium. Find the final temperature of the system.

Ans. 60 °C

Problem 15.41. A lead brick of mass 20 kg and temperature 300 °C is placed on a 10-kg block of ice at 0 °C. The system is well insulated from the environment. Describe the situation at equilibrium.

Ans. Final temperature is 0 °C, 2.33 kg of ice having melted.

Problem 15.42. A sealed 20-kg steel chamber contains 0.200 kg of gasoline [see Problem 15.32(*a*)] and enough air to completely burn it. This chamber is suspended in a larger, 40-kg steel chamber filled with 50 kg of water. The entire system, consisting of both chambers and their contents, is originally at 27 °C and is well insulated from the outside environment. The gasoline is ignited and completely burns. Calculate the changes in the system's (*a*) chemical internal energy, (*b*) mechanical internal energy, (*c*) thermal internal energy, (*d*) total internal energy.

Ans. (*a*) −9.18 MJ; (*b*) 0 MJ; (*c*) +9.18 MJ; (*d*) 0 MJ

Problem 15.43. Find the final temperature of the system of Problem 15.42. (Ignore the heat capacity of the products of combustion in the inner chamber.)

Ans. 65.8 °C

Problem 15.44. 1.0 kg of molten zinc at 420 °C is poured onto a 2.5-kg lead brick initially at 27 °C, resting in a calorimeter.

(*a*) If the heat capacity of the calorimeter is negligible, find the final temperature of the mixture.

(*b*) What fraction of each mass is liquid and what fraction is solid?

Ans. (*a*) 327 °C; (*b*) zinc is 100% solid, while lead is 8.45% solid and 91.55% liquid.

Problem 15.45. A solid steel cylinder, of radius $R = 20$ cm and mass $M = 5.0$ kg, rotates about its symmetry axis without friction at an angular velocity of 30.00 rad/s. The cylinder is then uniformly heated so that its temperature is raised by 100 °C. What is the new angular velocity?

Ans. 29.93 rad/s

Problem 15.46. The density of mercury at 0 °C is 13.6×10^3 kg/m^3. Find its density at 200 °C.

Ans. 13.1×10^3 kg/m^3

Problem 15.47. An electric hot water heater takes in cool water at 10 °C and heats it to 70 °C. If the hot water is drawn off at 20 kg/min, what must be the minimum power rating of the heater?

Ans. 83.7 kW

Problem 15.48. A lead bullet is fired into a very heavy block of wood in which it becomes embedded. Assume that all the heat generated goes into the bullet and that the bullet's temperature when it hits the wood is 127 °C. What is the minimum velocity of the bullet that will cause it to completely melt in the wood?

Ans. 318 m/s

Problem 15.49.

(*a*) Referring to Problem 15.48, what would the actual kinetic energy of the bullet be if the mass of the bullet was 20 g?

(*b*) How much gasoline (h_g = 4.6 MJ/kg) would have to burn to generate an equivalent amount of thermal energy?

Ans. (*a*) 1.011 kJ; (*b*) 22 mg

Problem 15.50. How much heat must be removed from 4.0 kg of water at 27 °C to convert it to ice at (*a*) 0 °C? (*b*) −15 °C?

Ans. (*a*) 1.792 MJ; (*b*) 1.917 MJ

Problem 15.51. A 15-kg child is running a fever of 3 °C above her normal temperature of 37 °C. Her father rinses her with water at 40 °C, knowing that the water will evaporate, drawing heat from the girl. If the heat of vaporization of water at 40 °C is 580 kcal/kg and the effective specific heat of the child is 0.85 kcal/(kg · °C) how much water must evaporate to restore her to normal temperature?

Ans. 66 g