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Chapter 3

The Liquid State

Although plasma is the most common state of matter in the universe (because it exists at the high temperatures in all the stars), the other three states of matter—liquid, gas, and solid—are the most abundant on our planet. It would be impossible to say which state is most important to life because all three are essential for our survival: as creatures with material bodies, we must breathe gases, drink liquids, and eat solids. We need to ingest water constantly because it constitutes about 65% of our bodily mass. To make certain that plenty of water is available to us, God has surrounded the land areas of earth with vast oceans covering about 70% of the earth's surface. He has also designed a water cycle (also called a *hydrologic system*) to assure the constant movement of water from the sea to the land and then back to the sea. Though the study of water was an early interest of modern



science, the principles presented here relate not only to water but also to other liquids.

Key symbols and abbreviations

P	pressure
Pa	pascals
atm	atmospheres

3.1 Characteristics of a Liquid

● Surface tension

If you carefully lay a small sewing needle sideways on the water in a bowl, the needle will float even though it is made of steel, having a density much greater than that of water. The needle is kept from breaking through the surface and sinking by surface tension. **Surface tension** is a liquid's resistance to increase its surface area. It is due to intermolecular (between molecules) attractive forces that seem to bind together the surface molecules of a liquid into a thin skin that is resistant to penetration by any small object, regardless of its density. The skin is actually an illusion, however, as you will see later. On a perfectly calm surface of water, you can float not only needles, but also staples, wire, iron filings, corn starch, and other pow-

ders, even razor blades. Certain insects (such as the water strider) can walk on water because their tiny feet do not break through the surface tension.

To see the skin that appears to form on water, position a clear glass of water at eye level and lightly touch the surface of the water with one finger. Then raise your finger barely above the surface. There appears to be a skin of water clinging momentarily to your finger. The skin stretches upward until its weight causes it to snap back into place.

Adhesion and cohesion. Neighboring molecules in a solid or a liquid are strongly attracted to each other by a force that is electrical in origin. The positively charged nucleus in one molecule attracts the negatively charged electrons in

another molecule nearby. If the attraction is between different kinds of molecules, the attraction is called **adhesion**. For instance, an adhesive tape such as duct tape works because the tape's glue molecules have a strong attraction to many different molecules. On the other hand, if the two molecules are of the same kind, the attraction is called **cohesion**. Using the example of adhesive tape, the glue molecules have a great attraction to each other.

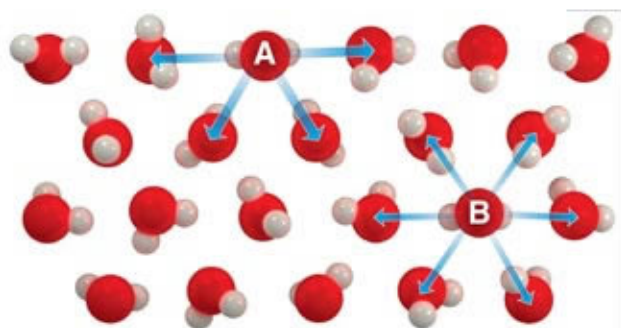


Figure 3.1 Cohesive forces at the surface of water

In Figure 3.1, consider the cohesive forces acting upon a single molecule situated in the surface of water (molecule A) versus the cohesive forces acting on a single molecule residing lower in the water (molecule B). The cohesive force that molecule A exerts on its surrounding molecules is equal to the cohesive force that molecule B exerts on its surrounding molecules. However, according to the

simple model in Figure 3.1, molecule A exerts this force over *four* molecules while molecule B exerts the same amount of force over *six* molecules. Thus, while the total force exerted by molecule B is equal to the total force exerted by molecule A, the force of molecule B exerted on each surrounding molecule is *less* than the force of molecule A on its surrounding molecules. Since molecule A has a greater individual attraction to each surrounding molecule, more external force is required to separate these surface molecules from molecule A. This same principle is applied to every molecule in the surface of the water.

The same thinking can be applied to the *adhesive* forces between the surface molecules and an object touching the surface. If the surface molecules have a strong attraction to this object, they will cling to the object when it is lifted out or pushed downward (Figure 3.2). Since the surface molecules cling to the object and at the same time resist an increase in surface area, the surface appears to be covered with a thin skin.

The resistance of a liquid surface to being stretched explains why a small quantity of water contracts inward, forming a spherical droplet. Once the water achieves a spherical shape, contraction can proceed no farther because a sphere has the least surface area of any other shape with equivalent volume. To see this, try making a piece of wax as small as possible. All your squeezing merely succeeds in making a round ball of wax. The contractile force, called surface tension, is therefore responsible for the spherical shape of raindrops, air bubbles in water, soap bubbles, and the balls spontaneously formed by mercury or any liquid when dropped onto a nonwetting surface.

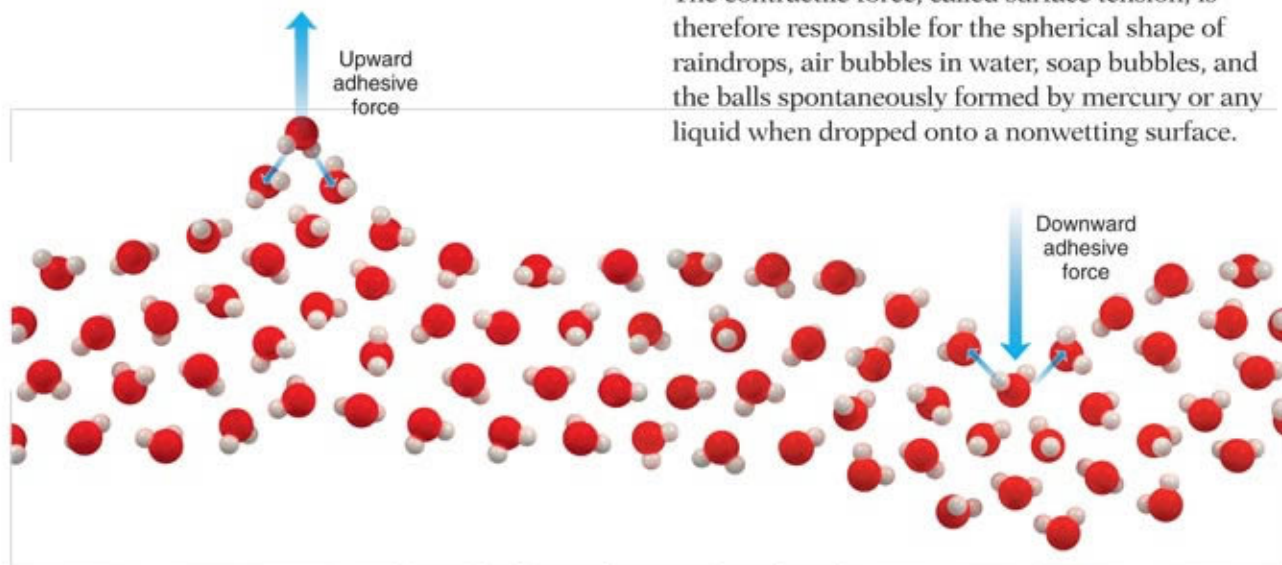


Figure 3.2 Adhesive forces at the surface of water

● Capillarity

If a thin glass tube is positioned vertically with its lower end below the surface of water, water rises in the tube (Figure 3.3A). The thinner the tube is, the higher the final level of the water. Tubes thin enough to show this effect are called **capillary tubes**, and the tendency of a liquid to rise in a narrow tube is called **capillarity** or *capillary action*.

The explanation can be framed again in terms of intermolecular forces. Adhesion between the glass molecules and the water molecules is greater than cohesion among the water molecules. As a result, the water inside the tube forms a curved surface called a **meniscus**; since the edges of the water reach outward in the glass tube, the meniscus is *concave* (Figure 3.3B). As adhesion pulls the edges of the surface upward, cohesion holds the surface together (surface tension) so that the entire surface rises to a higher level. The space below the rising surface is filled with water that has been pushed upward by atmospheric pressure—that is, by the weight of air on the water outside the tube. Adhesion, cohesion, and atmospheric pressure continue working jointly to raise the column of water until finally the downward weight of the water in the column is as great as the upward forces. At this point, the water rises no higher.

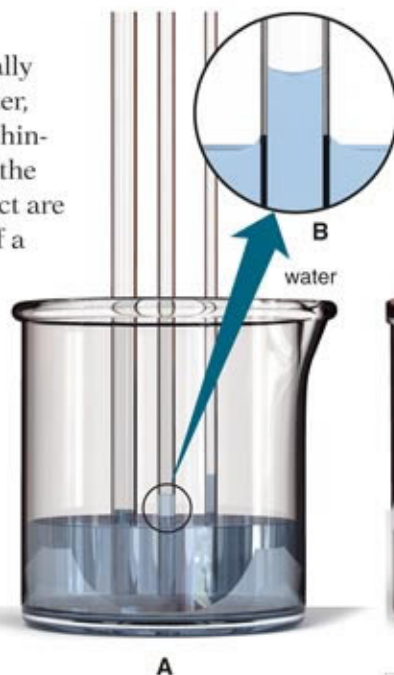


Figure 3.3 Water rising in a tube produces a concave meniscus.

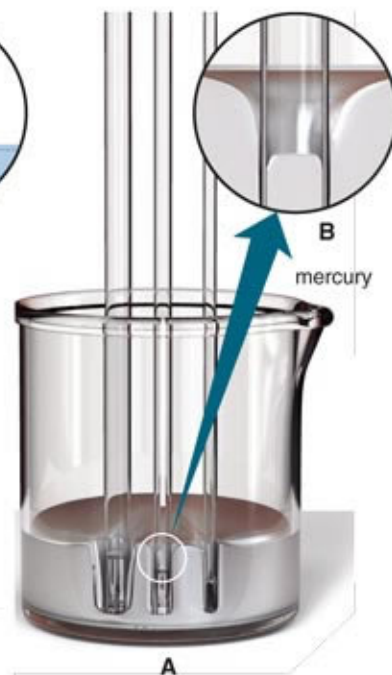


Figure 3.4 Mercury sinking in a tube produces a convex meniscus.

The opposite effect may be seen by lowering a thin tube into mercury (Figure 3.4A). Since in this case the adhesion between mercury and glass is much less than the cohesion among mercury molecules, the mercury molecules at the edge of the surface within the tube pull away from the wall into the liquid and form a *convex* (domelike) meniscus (Figure 3.4B). The column of mercury then sinks downward. In fact, the thinner the tube, the farther the mercury will depress.

3.2 Hydrostatics

The study of liquids at rest is called **hydrostatics** (*hydro* means “water,” and *static* means “causing to stand”). Hydrostatics is based on three important principles: the law of liquid pressure, Pascal’s principle, and Archimedes’ principle.

● Law of liquid pressure

Force. If you immerse your hand in a tub full of water, you can feel the water gently pushing against your hand on all sides. In physics, a **force** is any push or pull on an object. Thus, the water exerts a force—a mild force, to be sure—on your immersed hand. In the U.S. customary system of units, force is measured in pounds (lb), which you have also

encountered as a unit for weight. A force of one pound is equal to the downward push felt by a one-pound weight. In SI units, the unit of force is the newton (N), which is approximately equal to 0.225 lb. The newton is derived from three fundamental units: the meter, kilogram, and second. Because of this, a newton can be simplified as follows: $1 \text{ N} = \frac{\text{kg}\cdot\text{m}}{\text{s}^2}$. How the newton is derived will be explained in chapter 8. For now, simply be familiar with this alternate form.

The force exerted by a liquid on a surface is always **normal**, or perpendicular, to the surface. If you hold your hand in a horizontal position under water, the push you feel from underneath is directed

straight upward, perpendicular to the lower surface of your hand. Moreover, the force you feel above your hand is directed straight downward. If you move your hand to a vertical position, the forces exerted by the water on the palm and back of your hand now push sideways against your hand. In general, we may say that a liquid exerts a normal force at each point on any surface exposed to the liquid (Figure 3.5). This surface may be the surface of any object inserted into the liquid.

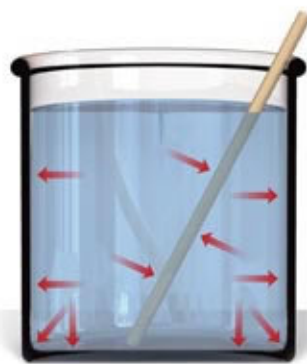


Figure 3.5 Liquids exert forces normal to any surface.

captured inside the inverted jar, we can determine the downward force of water (its weight) on the lid while it was submerged in the tank. The principle illustrated by this procedure is that the weight of the liquid above a submerged object determines how much downward force is exerted upon the object.

Pressure. The amount of force brought to bear on a unit area of surface is called **pressure**:

$$P = \frac{F}{A} \quad \text{1}$$

Pressure is commonly measured in N/m^2 . In SI units, one newton per meter squared is the same as one pascal (Pa). Since a pascal contains the derived unit of newtons, the pascal can also be equal to one kilogram per meter second squared ($\frac{\text{kg}}{\text{m}\cdot\text{s}^2}$).

In Figure 3.6, the screw-on cap of a plastic jar is securely held upside down by a clamp in a tank full of water. To determine exactly how much downward force is exerted on the cap, we take the empty jar and drill a hole through the bottom. Next, we lower the jar neck-down into the water and screw the neck into the lid, allowing air to escape through the hole. We adjust the clamp so that the entire jar is completely submerged just below water level. The water that was directly above the lid has flowed into the jar. We then plug the hole, release the lid, and remove the inverted jar. If we weigh the water

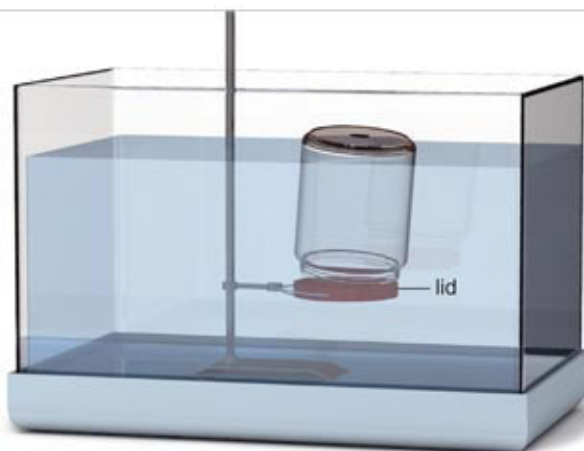


Figure 3.6 Measuring the weight of water on a submerged lid

The force of weight is due to the earth's gravitational attraction to an object's mass. The numerical value of that relationship is called **g** , the acceleration due to gravity. Though the value of g varies among locations, its average value is 9.80 m/s^2 . Thus, the weight of water in the jar can be found by multiplying the kilogram mass of the water by the acceleration due to gravity:

$$F_w = mg \quad \text{2}$$

Weight can also be found by applying another relationship about mass. From chapter 2, recall that density is the ratio of mass to volume:

$$\rho = \frac{m}{V} \quad \text{3}$$

One of the important items to notice in this equation is that, since force and weight are measured in newtons, the density value is kg/m^3 , not g/cm^3 as in chapter 2. For instance, the density of water is typically listed as 1 g/cm^3 ; however, as shown below, 1 g/cm^3 is not the same as 1 kg/m^3 .

$$\frac{1 \text{ g}}{1 \text{ cm}^3} \cdot \frac{1 \text{ kg}}{1000 \text{ g}} \cdot \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3 = 1000 \frac{\text{kg}}{\text{m}^3}$$

The conversion from g/cm^3 to kg/m^3 simply requires multiplication by 1000 and a change of units.

Using this relationship in equation 2 requires solving equation 3 for mass.

$$m = \rho V$$

Substituting ρV for m into equation 2 gives

$$F_w = \rho V g \quad \text{4}$$

The volume of water in the jar is cylindrical. Since the volume of a cylinder is equal to the area of the base times the height, then

$$V = Ah \quad \text{5}$$

where A is the area of the lid and h is the height of water above the lid (or the *depth* of the surface

supporting the liquid). Substituting Ah in equation 5 for V in equation 4,

$$F_w = \rho Ahg$$

or, more commonly,

$$F_w = A\rho gh \quad 6$$

Since the weight of the water provides the downward force on the lid, then $F_w = F$. Thus,

$$F = A\rho gh \quad 7$$

Suppose you know the downward force on the lid. You may then also find the downward pressure by dividing both sides of equation 7 by A to obtain

$$\frac{F}{A} = \rho gh \quad 8$$

Since pressure was defined above as force per unit area, the left side of equation 8 is replaced with P :

$$P = \rho gh \quad 9$$

This equation, giving the downward pressure on a surface at constant depth h , is known as the **law of liquid pressure**. A useful equation for finding the total force on a surface is obtained by solving equation 1 for force:

$$F = AP \quad 10$$

Examination of equation 9 reveals that the pressure exerted on a surface by a given liquid is directly proportional to the depth of submersion. Being *directly proportional*, if depth increases by a certain factor, pressure must also increase by the same factor. Thus, if depth is doubled, so is pressure; if depth is increased fourfold, so is pressure. This dependence of pressure upon depth is evident when a person dives to the bottom of a lake or pool. As he lingers momentarily at the point of farthest descent, he can feel a pronounced heaviness of water against his body, especially against his ears. In fact, while a few scuba divers have descended to nearly 300 meters, many divers have trouble breathing at relatively shallow depths (near 200 meters), even with the pressurized air from their tanks, because their muscles are not strong enough to push back against the weight of the water resting on their rib cages.

Equation 9 also states that pressure is directly proportional to the density of the liquid. If you could lower your hand deep into a vat of thick molasses, you would sense a greater push against your hand than you would sense at the same depth in a vat of water.

Example 3.1

- (a) If the density of water is 1000 kg/m^3 , what is the pressure at the bottom of a pool filled to a depth of 2.40 m?
 (b) What is the total force in newtons on the bottom if it is 5.50 m wide and 10.0 m long?

Solution

- (a) Substitute directly into equation 9, where ρ is 1000 kg/m^3 and h is 2.40 m.

$$P = \rho gh$$

$$P = (1000 \frac{\text{kg}}{\text{m}^3})(9.80 \frac{\text{m}}{\text{s}^2})(2.40 \text{ m})$$

$$P = 2.352 \times 10^4 \text{ N/m}^2 = 2.35 \times 10^4 \text{ N/m}^2$$

- (b) Use equation 10, where P is $2.352 \times 10^4 \text{ N/m}^2$ (unrounded) and A is the area of the bottom. Substitute to obtain

$$F = AP$$

$$F = [(5.50 \text{ m})(10.0 \text{ m})](2.352 \times 10^4 \frac{\text{N}}{\text{m}^2})$$

$$F = 1.2936 \times 10^6 \text{ N} = 1.29 \times 10^6 \text{ N}$$

Pascal's vases. Equation 9 implies that, at a given depth of liquid within a single container, the downward pressure is everywhere the same. This means that the pressure at a given depth of liquid is the same for all containers, regardless of their shape. This fact may be proved experimentally with the help of Pascal's vases (Figure 3.7), named after the French Christian philosopher and genius Blaise Pascal (1623–1662). Each is closed at the bottom by a flexible diaphragm. When the vases are filled with liquid

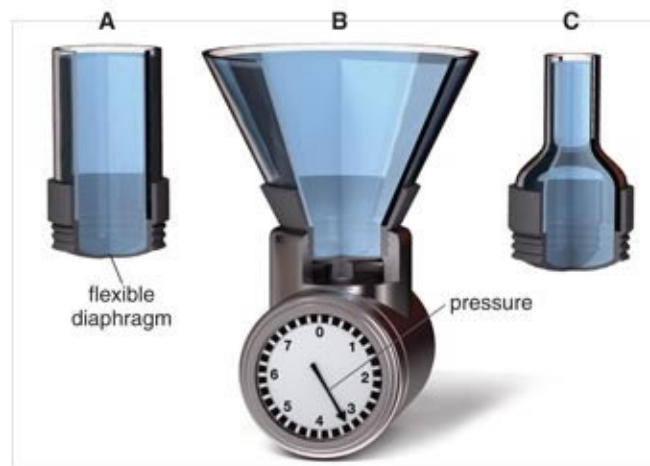


Figure 3.7 Pascal's vases

Chapter 15

The Laws of Thermodynamics

The laws of thermodynamics deal with the movement of heat between two bodies. Since heat is the transfer of energy and since heat spontaneously moves from a warmer body to a cooler body, we can determine several relationships, the laws of thermodynamics.

The first law of thermodynamics states that the sum of the universe's energy has always been constant, but no scientific law states the origin of the universe's energy. This implies that only some entity outside the universe—and not bounded by the universe's scientific laws—could have provided the universe with the energy it now contains.

The second law of thermodynamics implies that the universe is growing old and wearing out. Because it inescapably follows that the universe must have had a beginning, the second law is often used as an effective argument for creation.



All scientific truth agrees with Scripture. This chapter will present thermodynamic principles that can help you address evolutionary arguments against the biblical account of creation.

Key symbols and abbreviations

E_{int}	internal energy
Q	heat
S	entropy

15.1 First Law of Thermodynamics

● Internal energy

Systems and surroundings. A **system** is any body or collection of bodies that can exchange energy with the surroundings. The system's **surroundings** are anything outside the system. It is important to note that, just because a system *can* exchange energy, a system is not *required* to exchange energy. A system can be closed or open. A **closed system** is sealed off from any mass (or volume) exchange with its surroundings, but work or energy can be exchanged. An **open system** can exchange both mass and energy with its surroundings. To have a clear understanding of the following discussion, you must define the system's contents and its interaction with the surroundings.

For instance, suppose you are discussing the heat exchange between a warm can of soda and a cold refrigerator. If you are discussing the heat that leaves the soda, the soda is a *closed system* exchanging only energy with the “surrounding” refrigerator. On the other hand, if you discuss the heat that enters the refrigerator, the *refrigerator* is the closed system exchanging energy with the “surrounding” can of soda. Finally, since the refrigerator is insulated from the atmosphere, the refrigerator and the soda are two bodies exchanging heat within an *isolated system*. An **isolated system** is a special case of a closed system where not only can no mass cross the boundary, but also no energy can cross the boundary between a system and its surroundings.

Surroundings

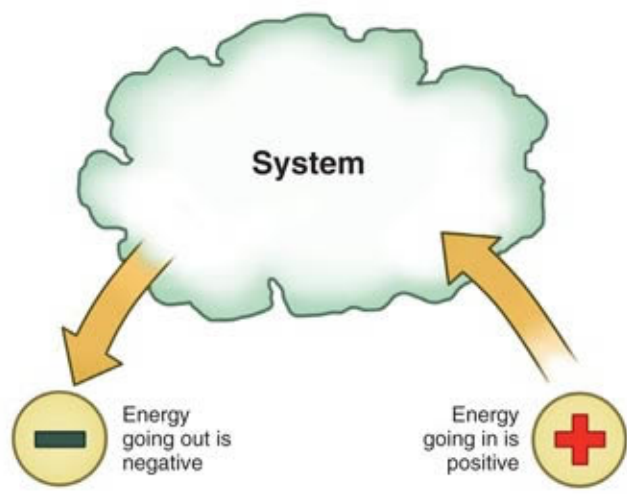


Figure 15.1 Heat exchange between system and surroundings

Defining one's system determines the sign of the energy exchange. Energy entering a system is positive, and energy leaving a system is negative (Figure 15.1). Suppose the can of soda cools by transferring 20 J of heat to the refrigerator. If the soda is the system, then $Q = -20$ J because it is losing heat. However, if the refrigerator is the system, then $Q = 20$ J because it is gaining heat. If the system is both the soda and refrigerator together, then $Q = 0$ J because the isolated system does not exchange energy with the surroundings.

Heat and work. Recall from the work-energy theorem that, under certain conditions, work is equal to a change in kinetic energy. Now that the concept of energy has been expanded to include heat, both work and heat should be defined more precisely. Heat and work are ways of describing the transfer of energy from one body to another. If the transfer is caused by a difference between the initial temperatures of the two bodies, the energy that passes from one to the other is called **heat**. If the transfer is caused by a force operating over a distance, the transfer is called **work**. If no energy transfer (either in the form of heat or work) is occurring among them, the system of bodies is at **equilibrium**.

If you start pushing a shopping cart down the aisle of a supermarket, stored energy in your body is changed by a chain of energy conversions into kinetic energy in the cart. In effect, a trans-

fer of energy occurs. This transfer is work rather than heat since it is accomplished by the force you apply over a distance—the cart's movement does not depend upon the initial temperature of either the cart or your body. If, however, the cart sits in the hot sun, the transfer of energy that causes the cart to become warm and then hot to the touch is heat rather than work because the cart's temperature change is the result of the vast temperature difference between the sun and the cart.

Although heat is caused by the unequal temperatures of two bodies, it does not necessarily change the temperature of either one. Imagine holding an ice cube in the palm of your hand. Even as the ice is absorbing heat and melting into a puddle, your body stays at normal body temperature (though your hand does cool somewhat), and the mixture of solid and liquid water stays at 0°C . This is further evident if you recall that water freezes at 0°C and ice melts at 0°C . The total energy in both the liquid and solid is obviously different, but their temperatures are still the same.

The heat transferred to a body and the work done by that body affect that body's total internal energy. **Internal energy** (E_{int}) may be defined as the total molecular energy content of a physical system. Internal energy includes the particles' kinetic energy and potential energy. The particles' kinetic energy as they vibrate or rush about is often referred to as **thermal energy**, and this thermal energy is measured as temperature. The potential energy possessed by a system is due to the interparticle forces (attraction among molecules or atoms) exerted upon them; this potential energy depends on whether the system is a solid, liquid, or gas.

For simplicity, discussion will include only the energies due to the particles' motions or forces. Also, assume that the total energy in these other various forms—such as the energy stored in chemical bonds, the mechanical energy of the system as a whole, or electrical energy—is constant for a given system.

The mechanical equivalent of heat. The work of the English scientist James Prescott Joule (1818–1889) was undoubtedly the most important development leading to the modern view of the



Figure 15.2 Apparatus for Joule's experiment on the mechanical equivalent of heat

relationship between heat and work. In one of the many experiments he performed, falling weights turned a shaft set vertically into a water-filled container (Figure 15.2). As a result, paddles mounted on the shaft were forced to move through circular paths against the resistance of water. Friction between the paddles and the water caused the temperature of the water to rise. Since the container was well insulated, none of the energy added to the water in this manner could escape.

The transfer of energy from the paddles to the water was ultimately caused by the downward motion of the weights. If their combined mass was m , the total gravitational force on the weights was mg ; and if the distance each fell was h , the total work done by the gravitational field upon the weights was

$$W = mgh \quad 1$$

Notice that this is equal to the gravitational potential energy lost by the weights in their descent. Since the descent of the weights was very slow, essentially none of their lost potential energy was converted to the weights' own kinetic energy. Instead, nearly all of the lost potential energy contributed to the rising temperature of the water. Thus, the work done by the gravitational field upon the weights and, consequently, upon the water caused the water to gain internal energy.

To be precise, work does not produce heat. Yet it is proper to determine how much heat would have produced the same increase in water temperature. If Q is that equivalent amount of heat, by setting $W = Q$, Joule found equivalent values of heat and work. That amount of heat (from the previous chapter) is

$$W = Q = m_w c_w (T_f - T_i) \quad 2$$

Presently, both work and heat are commonly measured in joules (named after Joule) or calories. It has been well established by Joule's experiments that

$$1 \text{ cal} = 4.184 \text{ J} \quad 3$$

One virtue of this approximation is that it is consistent with both the traditional and modern definitions of a calorie. The traditional definition equates one calorie to the heat required at one atmosphere to raise one gram of water from 14.5°C to 15.5°C . The modern definition avoids the uncertainty of measurement by simply equating one calorie to a certain quantity of joules.

The amount of work equal to a unit of heat is called the **mechanical equivalent of heat**. The interchangeability of heat units and work units is fundamental to the study of the relationship between heat and work. This study is called **thermodynamics**.

Example 15.1

If you wanted to use the apparatus of Figure 15.2 to increase the temperature of 1.0 kg of water by 0.10°C , what total mass should you use? Assume each weight falls a distance of 1.0 m.

Solution

To find the mass needed, set $W = Q$, taking Q from equation 2 and W from equation 1; then solve for m .

$$mgh = m_w c_w (T_f - T_i)$$

$$m = \frac{m_w c_w (T_f - T_i)}{gh}$$

It is given that m_w is $1.0 \times 10^3 \text{ g}$, the change in temperature is 0.10°C , and h is 1.0 m. Knowing that c_w is $4.184 \text{ J/g}\cdot^\circ\text{C}$ and g is 9.80 m/s^2 , substitute known quantities into the foregoing equation to find

$$m = \frac{(1.0 \times 10^3 \text{ g})(4.184 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}})(0.10^\circ\text{C})}{(9.80 \frac{\text{m}}{\text{s}^2})(1.0 \text{ m})}$$

$$m = 43 \frac{\text{J}\cdot\text{s}^2}{\text{m}^2}$$

Remember that $1 \text{ J} = 1 \text{ N}\cdot\text{m} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$. Thus,

$$m = 43 \frac{\text{J}\cdot\text{s}^2}{\text{m}^2} \left(\frac{1 \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2}}{1 \text{ J}} \right) = 43 \text{ kg}$$

Internal energy equation. In Joule's experiment, the gravitational potential energy lost by the falling weights did not simply disappear; instead, it was converted into the internal energy of the water. This result was a landmark in the history of physics, because it helped to prepare the way for general acceptance of the law of conservation of energy. One of the most important and most general formulations of this law is called the **first law of thermodynamics**, which specifies the energy budget that must be observed by any physical system. *The change in internal energy of a system equals the heat added to the system minus the work that the system does on the surroundings.* Stated mathematically, the law says

$$\Delta E_{\text{int}} = Q - W \quad 4$$

where Q is the heat added to the system, W is the work the system does on the surroundings, and ΔE_{int} is the change in the internal energy of the

system. The first law of thermodynamics is based on conservation of energy as applied to the system. Apart from Q and W , *the system is assumed to be closed.*

Illustrative cases. Suppose that heat is exchanged with a closed system (a can of soda) that does no work on its surroundings. On the one hand, if 1 J of heat is added to this system, then $Q = 1 \text{ J}$, $W = 0$, and

$$\Delta E_{\text{int}} = 1 \text{ J} - 0 = 1 \text{ J}$$

ΔE_{int} is positive because the individual soda molecules gain energy to move faster.

On the other hand, suppose the heat leaves this closed system: $Q = -1 \text{ J}$, $W = 0$, and

$$\Delta E_{\text{int}} = -1 \text{ J} - 0 = -1 \text{ J}$$

ΔE_{int} is negative because the molecules lose energy. As soon as soda in a rigid container (a can) is placed in the refrigerator, the container and its enclosed soda begin to lose heat. The diminishing internal energy of the system is shown by its decreasing temperature. Here, no work is done by the system on the surroundings since the sides of the container are rigid.

Now suppose a closed system does 1 J of work on its surroundings without exchanging heat. On the one hand, if the system does 1 J of work on the surroundings, then $Q = 0$, $W = 1 \text{ J}$, and

$$\Delta E_{\text{int}} = 0 - 1 \text{ J} = -1 \text{ J}$$

The reason positive work leads to a decrease in internal energy can be explained when you mow your lawn. As you lose energy, and since energy is the ability to do work, you are less able to do work after mowing the lawn than you were before mowing.

On the other hand, if the surroundings do work on the system, then $Q = 0$, $W = -1 \text{ J}$, and

$$\Delta E_{\text{int}} = 0 - (-1 \text{ J}) = 1 \text{ J}$$

In the case of a bicycle pump, work is done on the system of gases inside the pump and the tire when the plunger is thrust downward. The effect is a rise in the internal energy and the temperature of these gases, giving them a greater ability to push back against the plunger or the walls of the tire.

Example 15.2

The air inside a balloon placed in a refrigerator loses 11.8 J of heat. At the same time, the shrinking rubber does 0.302 J of work in compressing the air. What is the change in the internal energy of the air inside the balloon?

Solution

Use equation 4. The system in this case is the air inside the balloon. Since work is done on the system and since heat leaves the system, the work is -0.302 J and the heat is -11.8 J.

$$\Delta E_{\text{int}} = Q - W$$

$$\Delta E_{\text{int}} = (-11.8 \text{ J}) - (-0.302 \text{ J})$$

$$\Delta E_{\text{int}} \approx -11.5 \text{ J}$$

An adiabatic process. Consider the hot gases that form behind a bullet in a rifle after the rifle is fired. In the brief moment while the gases are pushing the bullet out of the barrel, essentially no heat enters or leaves the system of gases; since the gases (our system) are doing positive work on the bullet, the system loses internal energy. If no heat enters or leaves a system while its internal energy is changing, the process is **adiabatic** (Greek *adiabatos* denotes “unable to cross”). In an adiabatic process, $Q = 0$; therefore, from equation 4,

$$\Delta E_{\text{int}} = 0 - W$$

$$\Delta E_{\text{int}} = -W \quad \text{5}$$

This equation implies that the adiabatically expanding gases in a rifle must undergo a negative change in internal energy as they do work on the bullet; it follows that the temperature of the gases must sharply decrease.

When the piston in the cylinder of an internal combustion engine rises during the compression stroke, little heat enters or leaves the confined gases; that is, the compression of the system of gases is essentially adiabatic. Since the piston does work on the system of confined gases, the work in equation 5 is negative, implying that the system must undergo a positive change in internal energy:

$$\Delta E_{\text{int}} = -(-W) = W$$

In this case, the temperature of the system must sharply increase.

Scientists achieve extremely low temperatures in the laboratory by a sequence of operations. First, a

gas is compressed nonadiabatically so that the energy added to the gas is conveyed, in the form of heat, from the gas to the environment. Here, the temperature of the gas is unchanged by the compression, and the compression is said to be **isothermal**. The temperature of the gas is then lowered by allowing the gas to expand adiabatically to its original volume. If a further reduction of temperature is desirable, the cycle of compression and expansion is repeated.

Some texts reverse the sign of the work in equation 4, stating that work done *by* the system is negative and the work done *on* the system is positive. This changes equation 4 to $\Delta E_{\text{int}} = Q + W$. If you apply this convention to the illustrative cases mentioned previously, you arrive at the same conclusions. However, since our stated sign convention agrees with the positive work (for instance, when a gas expands in a cylinder), we will use the signs mandated by equation 4.

Ideal gas law

Reversible and irreversible processes. Figure 15.3 illustrates a system consisting of a movable piston in a gas-filled cylinder. Initially, the system is at equilibrium; that is, the pressure, volume, and temperature of the gas are constant over time. Let the initial pressure be defined as P_i , the initial volume as V_i , and the initial temperature as T_i . Then suppose the system is brought to another equilibrium state, having a volume V_f equal to $\frac{1}{2}V_i$ and a temperature T_f equal to T_i . This process must be selected from either of two kinds.

The first kind of process is caused by suddenly pushing the piston halfway down the cylinder and then waiting for equilibrium to be established. Until it is established—that is, until P , V , and T become constant—the values of these thermodynamic quantities are not well defined. An equation cannot be written to describe how each varies over



Figure 15.3 Movable piston in a gas-filled cylinder

time. Nor, after equilibrium is established, can the system go through the same changes in reverse to restore each quantity to its original value. A process of this kind is called an **irreversible process**. We know the initial and final equilibrium states, but we do not know by what path the system went from the former to the latter.

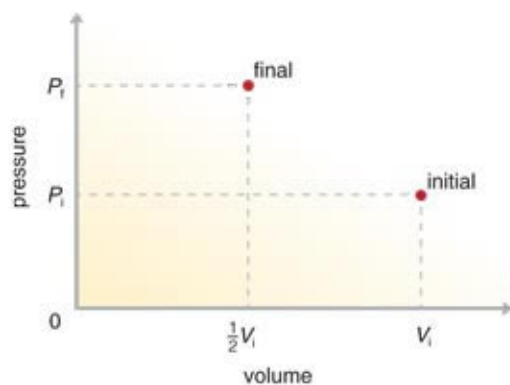


Figure 15.4 P - V diagram of an irreversible process

The relationship between the final and initial values is shown graphically by means of the P - V diagram in Figure 15.4. The initial and final states of the gas in the cylinder are at the same temperature, but since the final volume is equal to one half the initial volume, the pressure must change according to Boyle's law. This law, first presented in chapter 4, says that the pressure and the volume of a gas at constant temperature are inversely proportional:

$$P = \frac{k_B}{V} \quad \text{6}$$

In other words, the product of pressure and volume is a constant:

$$PV = k_B \quad \text{7}$$

It follows that the product of initial pressure and volume must equal the product of final pressure and volume:

$$P_i V_i = P_f V_f \quad \text{8}$$

This equation clearly implies that if the final volume is half of the initial volume ($V_f = \frac{1}{2} V_i$), then the final pressure must be doubled:

$$P_f V_i = P_f \left(\frac{1}{2} V_i\right)$$

$$P_f = \frac{P_i V_i}{\frac{1}{2} V_i}$$

$$P_f = 2P_i$$

Thus, enough information is given to plot the points shown in Figure 15.4. However, more information as to the path of the process is needed before a line is drawn to connect these points.

To implement the second kind of process, the piston is moved very slowly. The movement is so slow that the values of pressure, temperature, and volume are always well defined. The system is always close to an equilibrium state. This kind of process can be thought of as moving from one equilibrium state directly to another, each equilibrium state being nearly identical to the previous one. Since the process can be reversed to regain the original volume, V_i , it is called a **reversible process**. Although a reversible process cannot be perfectly achieved in the real world, the concept is a useful one, because it helps explain important thermodynamic principles.

The P - V diagram for the same gas when it changes by a reversible process is shown in Figure 15.5. In this case, the temperature of the gas is constant throughout its compression. So, this process is not only reversible but also isothermal. Notice that the initial and final states are the same as for the irreversible process in Figure 15.4. For the reversible process in Figure 15.5, however, the curve between the points representing these states can be drawn since the values of pressure and volume along the entire path are known. If the constant temperature is known, the pressure corresponding to any volume may be found from the **ideal gas law**

$$PV = nRT \quad \text{9}$$

where n is the number of moles of the gas, T is the Kelvin temperature, and R is the universal gas constant, previously defined as $0.0821 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol}$. This is equivalent to $8.3145 \text{ J}/\text{K}\cdot\text{mol}$.

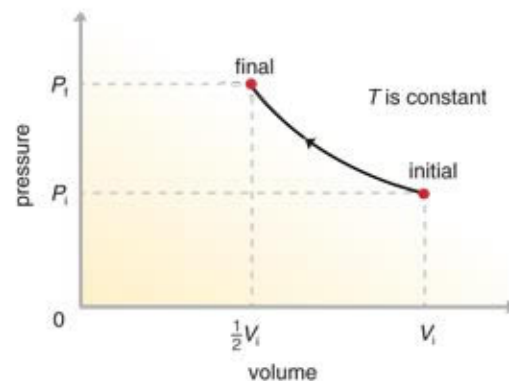


Figure 15.5 P - V diagram of a reversible process

Example 15.3

At a pressure of 1.00 atm, 1.00 L of gas is maintained at 300. K. Suddenly the gas is compressed to a volume of 0.333 L. The temperature of the gas is still 300. K. (a) Is this process reversible or irreversible? (b) Draw a P - V diagram for this process.

Solution

(a) The process is irreversible since the volume is changed suddenly.

(b) To find the final pressure, use equation 8. Solve for P_f and substitute known values to obtain

$$P_f = \frac{P_i V_i}{V_f}$$

$$P_f = \frac{(1.00 \text{ atm})(1.00 \text{ L})}{0.333 \text{ L}}$$

$$P_f \approx 3.00 \text{ atm}$$

Since the process is irreversible, the path from the initial to the final state is unknown. The appropriate P - V diagram is given in Figure 15.6.

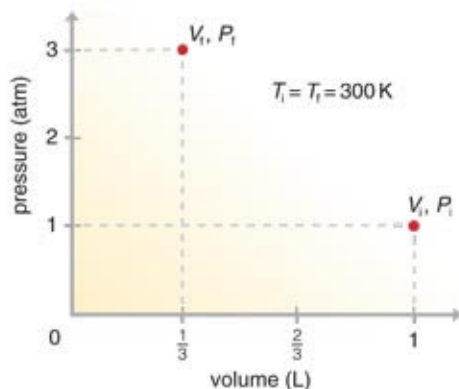


Figure 15.6 P - V diagram of a sudden gas expansion

Example 15.4

Suppose 1.00 mol of a gas undergoes a reversible, isothermal expansion from a volume of 1.00 L to a volume of 5.00 L. (a) Draw the P - V diagram for this process at 305 K. (b) On the same diagram show the reversible process at 200. K.

Solution

(a) To find the pressure at various stages of expansion, solve the ideal gas law for P and substitute known values to obtain

$$P = \frac{nRT}{V}$$

$$P = \frac{(1.00 \text{ mol})(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}})(305 \text{ K})}{V}$$

$$P = \frac{25.0405 \text{ L} \cdot \text{atm}}{V}$$

If V is expressed in liters, then P will be in units of atm. Use this equation to construct the following table, which gives P at five stages of expansion from V_i to V_f (1.00 L to 5.00 L).

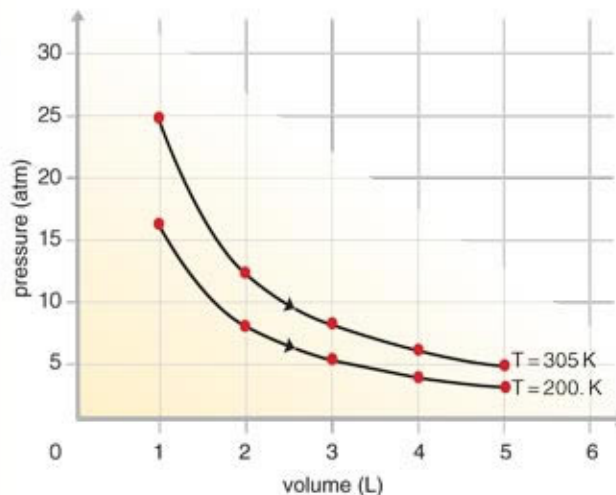


Figure 15.7 P - V diagram of a reversible gas expansion

The P - V points are plotted in Figure 15.7, and a smooth curve is drawn through them. This treats the process at $T = 305 \text{ K}$ as a series of equilibrium states.

V (L)	P (atm)
1.00	25.0
2.00	12.5
3.00	8.34
4.00	6.26
5.00	5.01

(b) Do the same at $T = 200. \text{ K}$; now

$$P = \frac{(1.00 \text{ mol})(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}})(200. \text{ K})}{V}$$

$$P = \frac{16.42 \text{ L} \cdot \text{atm}}{V}$$

The table of P - V points is as follows:

V (L)	P (atm)
1.00	16.4
2.00	8.21
3.00	5.47
4.00	4.10
5.00	3.28

These are plotted in Figure 15.7.